

Structural and Functional Evolution of Metallacrowns

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1. Introduction

In 1967 Pederson reported the synthesis of macrocyclic crown ethers and their ability to selectively bind alkali and alkaline earth ions,^{1,2} and since then supramolecular compounds have captivated chemists.^{3–5} Following Pederson's revolutionary discovery, a plethora of organic macrocyclic molecules were synthesized including thiacycrown ethers,⁶ azacycrown ethers,⁷ lariat ethers,⁸ chiral crown ethers,^{9,10} cryptands,^{11–13} spherands,^{14,15} cryptahemispherands,^{16,17} hemispherands,¹⁸ calixarenes,^{19–21} cavitands,^{22–24} hemicarcerands,²⁵ carcerands (molecular containers),^{26–28} and boron macrocycles.^{29–32} These complexes have the ability to bind cations and anions, function as ion transport agents, stabilize unstable molecules, and act as a host for chemical reactions. This work led to the 1987 Nobel Prize in chemistry being awarded to Charles Pederson,³³ Jean-Marie Lehn,³⁴ and Donald Cram³⁵ for their pioneering work in the field. Unfortunately, inorganic chemistry has lagged behind in synthesizing metal-containing supramolecules. However, recently there has been a surge in the number and type of metallasupramolecules.^{4,36} Some of these complexes resemble organic counterparts and are aptly named, whereas others present new structural types. Included in this family of metallamacrocycles are metallacryptands and metallacryptates,^{37–60} metallahelices and metallahelicates,^{61–82} metallacalixarenes,^{83–89} metallacoronates,⁹⁰ metal molecular wheels,⁹¹ metal molecular rings and polygons,^{92–132} metal-containing cages and polyhedra,^{133–160} metal-containing molecular machines,^{161–163} and metallacrowns.¹⁶⁴ Metallamacrocycles have been studied not only for their esthetic appeal but also for their potential functions. Metallamacrocycles have been used as cation, anion, and molecular recognition agents; catalysts; building blocks for extended solids; and sensors. This review will focus on the class of molecules known as metallacrowns. For excellent reviews of other metallamacrocyclic systems please see the noted references.

In 1989 Pecoraro and Lah reported the first metallacrown structure.^{165,166} Since then the field has expanded to research laboratories around the world. Chemists in the United States, Italy, Greece, Germany, Switzerland, South Korea, and China, to name but a few countries, are expanding the utility of metallacrown chemistry. A large variety of structures have been synthesized since the initial report, and metallacrowns have been used for an assortment of functions including antibacterial compounds, building two- and three-dimensional solids, stabilization of unstable molecules, single-molecule

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magnets, and molecular, cation, and anion recognition agents. This review will focus on two aspects of metallacrown chemistry. First, the expanse of metallacrown structures will be analyzed. Second, the numerous functions of metallacrowns will be explored. The literature is covered through February 1, 2007.

2. Metallacrown Structural Types

2.1. Introduction

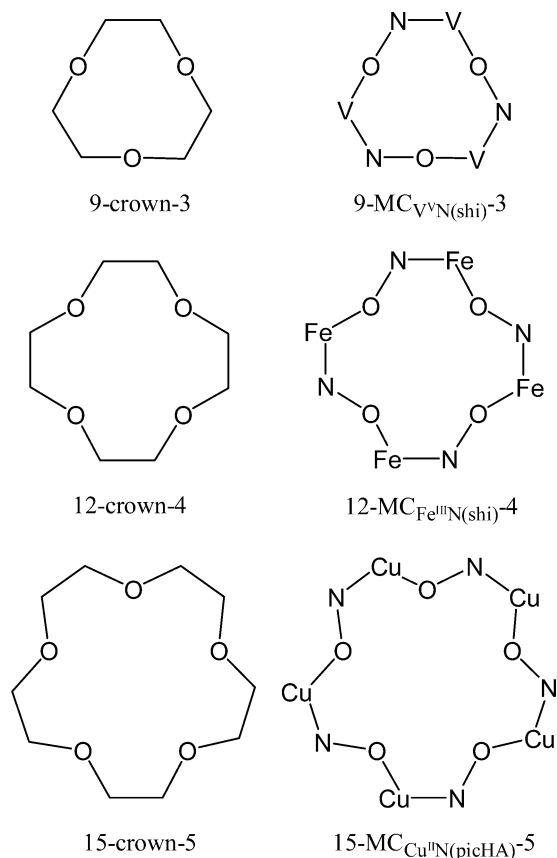
Metallacrowns draw on the crown ether analogy for its definition and nomenclature. The traditional definition of a metallacrown is a repeat unit of $-[M-N-O]_n-$ in a cyclic arrangement where the ring metal and nitrogen atom replace the methylene carbon atoms of a crown ether (Scheme 1). As in crown ethers, metallacrowns are named on the basis of the ring size and the number of donating oxygen atoms. For example, a 15-MC-5, where MC represents metallac-



Vincent L. Pecoraro received his B.S. degree in biochemistry at the University of California, Los Angeles, in 1977 and his Ph.D. in chemistry under the supervision of Prof. Kenneth N. Raymond in 1981 at the University of California, Berkeley. After completing an NIH postdoctoral fellowship with Prof. W. W. Cleland in the Department of Biochemistry at the University of Wisconsin, Madison, Dr. Pecoraro joined the chemistry faculty at the University of Michigan, Ann Arbor, in 1984. He was promoted to associate professor in 1989 and professor in 1992 and then appointed as the John T. Groves Collegiate Professor in 2005. Also in 2005, Prof. Pecoraro became a senior research scientist in the Biophysics Research Division at the University of Michigan, Ann Arbor. His research has focused on the role of metals in biology, in particular, defining the biological chemistry of manganese and vanadium. In recent years his research group has become deeply involved in de novo metalloprotein design and the elucidation of heavy metal complexation by cysteine-rich proteins. An area of Prof. Pecoraro's interest includes metallamacrocyclic chemistry, which was advanced significantly by his recognition of the metallacrown structural motif in 1989. Prof. Pecoraro has received numerous awards and honors including the G. D. Searle Biomedical Research Scholarship, an Alfred P. Sloan Fellowship, and an Alexander von Humboldt Award to Senior Research Scientists. He is a Fellow of the American Association for the Advancement of Science and has served as an Associate Editor of *Inorganic Chemistry* since 1994. Prof. Pecoraro is married to Prof. Peggy Carver of the College of Pharmacy at the University of Michigan, Ann Arbor. They enjoy traveling, eating well, fine art, and the company of their many good friends around the world.

rown, is a 15-membered ring comprising 5 repeating units of $-[M-N-O]-$ with 5 donating oxygen atoms. The preferred nomenclature also includes the bound central metal, the ligand, and any bound or unbound ions. The typical metallacrown nomenclature abides by the following scheme: $MX[\text{ring size-MC}_{M'(Z,L)}\text{-ring oxygens}]Y$, where M is the bound central metal and its oxidation state, X is any bound anions, M' is the ring metal and its oxidation state, Z is the third heteroatom of the ring, usually N, L is the organic ligand used in the complex, and Y is any unbound anions. On occasion there can be unbound cations, and these are placed before the bound central metal. An example of the above naming scheme would be $\{Gd^{III}(NO_3)_2[15-MC_{Cu^{II}N(S-pheHA)}-5]\}NO_3$, where S-pheHA is S-phenylalanine hydroxamic acid. This simplified naming scheme will be utilized in this review. For a very detailed naming scheme please see a previous review.^{164,167}

The first reported metallacrowns were 9-MC-3, 12-MC-4, and 15-MC-5 structures with a $-[M-N-O]_n-$ repeat unit. But just as crown ethers can be altered to make azacrown ethers¹⁶⁸ and thiocrown ethers,⁶ metallacrowns with different compositions and topologies have been synthesized and now include molecules known as expanded metallacrowns, metallacoronates, azametallacrowns, expanded azametallacrowns, and molecular wheels. Expanded metallacrowns are macrocyclic compounds in which the repeat unit now includes a carbon atom, $-[M-N-C-O]_n-$. Metallacoro-

Scheme 1. Examples of the Analogy between Organic Crown Ethers and Metallacrowns


nates replace both heteroatoms with oxygen atoms and include carbon atom extenders, $-[M-O-C_m-O]_n-$. Azametallacrown complexes have a repeat unit of $-[M-N-N]_n-$, and expanded azametallacrowns have a repeat unit of $-[M-N-C-N]_n-$. These additional metallacrowns follow the same nomenclature scheme with the number before the MC representing the ring size and the number after the MC signifying the number of the second heteroatom in the repeat unit. In addition, metallamacrocyclic complexes have been synthesized with a repeat unit of $[M-X]$, where X is a nonmetal atom. These complexes are commonly referred to as molecular wheels, but they have also been referred to as metallacrowns and metallacoronates. This extended family of metallacrowns has led to a diversity of metallacrown structures: 8-MC-4, 9-MC-3, 10-MC-5, 12-MC-3, 12-MC-4, 12-MC-6, 14-MC-7, 15-MC-3, 15-MC-5, 15-MC-6, 16-MC-4, 16-MC-8, 18-MC-6, 18-MC-9, 20-MC-10, 22-MC-11, 24-MC-6, 24-MC-8, 24-MC-12, 28-MC-14, 30-MC-10, 32-MC-8, 32-MC-16, 36-MC-12, 36-MC-18, 40-MC-10, 48-MC-24, and 60-MC-20. Some of the most commonly used ligands for the synthesis of these metallamacrocyclic complexes are depicted in Scheme 2.

2.2. 9-MC-3

The first recognized metallacrown was a $9-MC_{V^V N(shi)}-3 \cdot 3CH_3OH$ complex (where H_3shi is salicylhydroxamic acid), as a nine-membered metallamacrocyclic ring consisting of a repeat unit of $-[V^V-N-O]-$ (Figure 1).¹⁶⁵ Each ligand is bidentate, forming five- and six-membered chelate rings about adjacent vanadium ions. The hydroximate oxygen and nitrogen atoms (Scheme 3) provide the repeat unit within the metallacrown. The coordination about each vanadium ion consists of a phenolate oxygen and hydroximate nitrogen

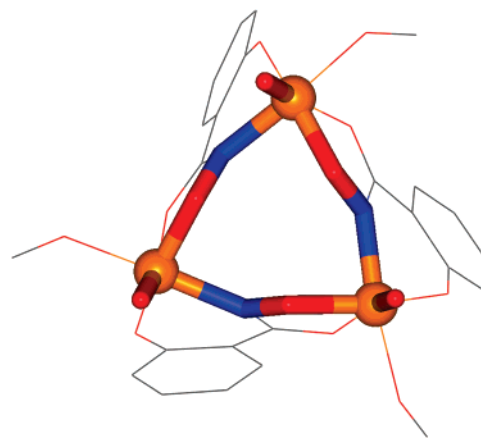


Figure 1. X-ray crystal structure of the first identified metallacrown (vacant): $9-MC_{V^V N(shi)}-3 \cdot 3CH_3OH$ with the MC ring highlighted. Color scheme: orange sphere, V^V ; red tube and line, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.¹⁶⁵

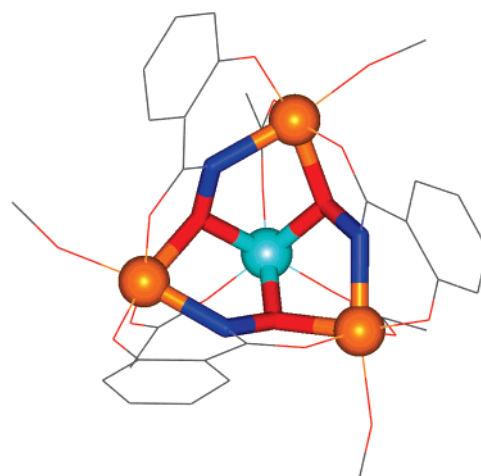
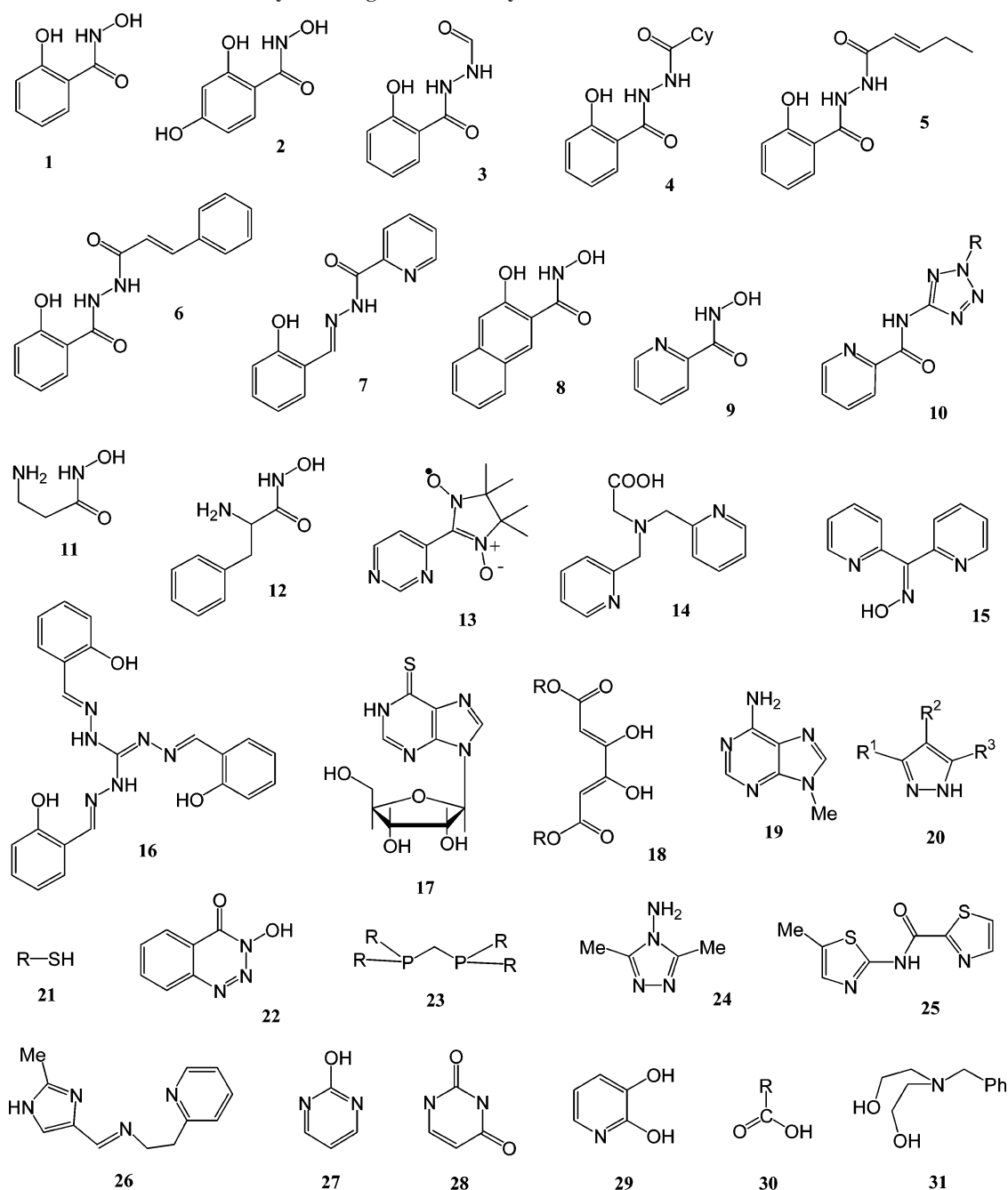


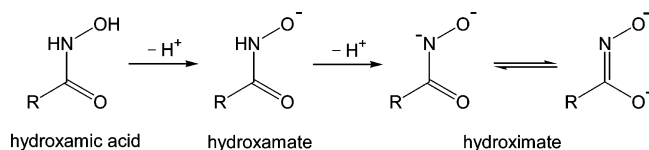
Figure 2. X-ray crystal structure of the first identified metallacrown with a central ion: $\{Fe(O_2CCH_3)_3\}_3[9-MC_{Fe^{III} N(shi)}-3] \cdot 3CH_3OH$. Color scheme: aqua sphere, central Fe^{III} ; orange sphere, ring Fe^{III} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.¹⁷⁰

in a six-membered ring, a carboxylate oxygen and hydroximate oxygen making a five-membered ring, and the remaining position occupied by a unidentate vanadyl oxygen atom and a methanol oxygen atom. The two chelate rings engender absolute stereochemical isomerism on each of the vanadium ions. The 9-MC-3 structure requires that all three vanadium ions adopt the same absolute configuration, which corresponds to the Δ propeller configuration. The shi^{3-} -based metallacrowns can form the MC structure only when all three metal centers are in a propeller configuration and each adopts the same absolute stereochemistry. This observation is contrasted with the pyrazole-based metallacrowns described below, which form only planar 9-MC-3 structures. Unlike the vast majority of subsequently prepared metallacrowns, the MC center is vacant. The most likely explanation for this observation is that the vanadyl oxygen atoms block the complexation of anions that could stabilize a captured central cation. The structure type has proven to be general with other hydroxamic acid ligands, 3-hydroxy-2-naphthohydroxamic acid and 2,4-dihydroxybenzohydroxamic acid, leading to nearly identical structures.¹⁶⁹ The first identified metallacrown with an encapsulated cation is $\{Fe(O_2CCH_3)_3\}_3[9-MC_{Fe^{III} N(shi)}-3] \cdot 3CH_3OH$ (Figure 2).¹⁷⁰ The MC topology is

Scheme 2. Some of the Most Commonly Used Ligands for the Synthesis of Metallacrowns^a

^a (1) Salicylhydroxamic acid; (2) 2,4-dihydroxybenzohydroxamic acid; (3) *N*-formylsalicylhydrazide; (4) *N*-cyclohexanoylsalicylhydrazide; (5) *N*-*trans*-2-pentenoylsalicylhydrazide; (6) *N*-3-phenyl-*trans*-2-propenoylsalicylhydrazide; (7) salicylaldehyde 2-pyridinecarboxylhydrazone; (8) 3-hydroxy-2-naphthohydroxamic acid; (9) picoline hydroxamic acid; (10) picoline-tetrazolylamide; (11) β -alanine hydroxamic acid; (12) phenylalanine hydroxamic acid; (13) 4-pyrimidinyl nitronyl nitroxide; (14) bis(2-pyridylmethyl)glycine; (15) di(2-pyridyl)ketone oxime; (16) tris(2-hydroxybenzylidene)triaminoguanidine; (17) 6-purinethione riboside; (18) dialkyl-3,4-dihydroxyhexa-2,4-diene-1,6-dioate; (19) 9-methyladenine; (20) 3,4,5- R^1, R^2, R^3 -pyrazole; (21) thiol; (22) 3-hydroxy-1,2,3-benzotriazine-4(3*H*)-one; (23) bis(R_2 -phosphino)methane; (24) 4-amino-3,5-dimethyl-1,2,4-triazole; (25) *N*-(5-methylthiazole-2-yl)thiazole-2-carboxamide; (26) *N*-(2-methylimidazol-4-ylmethylidene)-2-aminoethylpyridine; (27) 2-hydroxypyrimidine; (28) uracil; (29) 2,3-dihoxypyrimidine; (30) carboxylic acid; (31) *N*-benzyl-diethanolamine.

Scheme 3. Successive Deprotonation of Hydroxamic Acids Yielding Hydroxamate and Hydroximate Anions



very similar to that of 9-MC_V^{N(shi)}-3, but a Fe^{III} is encapsulated within the central cavity by the three ring hydroximate oxygens and three bridging acetate groups. The acetate

groups bridge between each ring Fe^{III} ion and the central Fe^{III}. The ring Fe^{III} ions have a similar coordination sphere as the ring V^V ions in 9-MC_V^{VN(shi)}-3. The bridging acetate anions are probably the key reason why {Fe(O₂CCH₃)₃[9-MC_{Fe}^{III}N(shi)-3]} encapsulates a central cation, whereas 9-MC_V^{VN(shi)}-3 does not.

Though not recognized as MCs at the time, several triangular trinuclear complexes with M–N–O connectivity made with oxime ligands have been known in the literature since the late 1960s. A common set of compounds is 9-MC-3

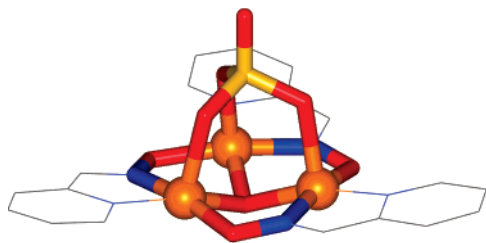


Figure 3. X-ray crystal structure of the inverse $(\mu_3\text{-OH})[9\text{-MC}_{\text{Cu}^{\text{II}}}\text{-3}]$ complex with the ligand pyridine-2-aldehyde. In addition, a SO_4^{2-} anion bridges the three ring Cu^{II} ions. Color scheme: orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; yellow tube, sulfur; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.¹⁷²

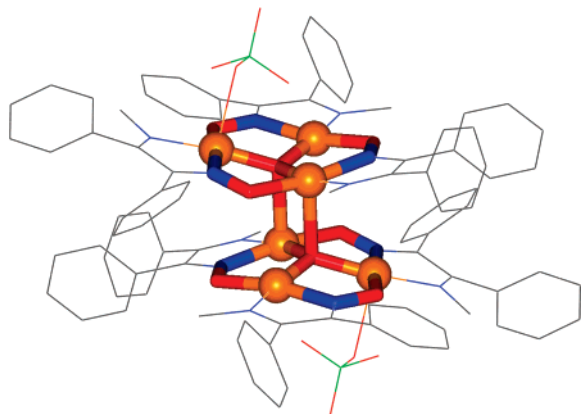


Figure 4. X-ray crystal structure of the inverse $(\mu_3\text{-O})[9\text{-MC}_{\text{Cu}^{\text{II}}}\text{-3}]$ complex with the ligand 1,2-diphenyl-2-(methylimino)ethanone 1-oxime. The metallacrowns dimerize by the central $\mu_3\text{-O}$ atoms binding to a ring Cu^{II} ion of the opposite MC. Two ClO_4^- anions bind to the faces of the MCs. Color scheme: orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; green line, chloride; gray line, carbon. Hydrogen atoms have been removed for clarity.¹⁷⁸

complexes made with a $-\text{[Cu}^{\text{II}}\text{-N-O]}-$ repeat unit. These structures are considered to be inverse metallacrowns (*inv*-MC) because they bind anions within the central cavity, usually a μ_3 -oxide oxygen or a μ_3 -hydroxide oxygen (Figure 3).^{171–177b} The N–O repeat unit is provided by the oxime ligands of the complex; a variety of different oxime ligands have been used to synthesize these structures. In some cases the *inv*9-MC-3 structures may dimerize via the central oxygen atom, which binds to a copper ion of the opposite MC (Figure 4).¹⁷⁸ In addition, a vacant 9-MC_{Cu^{II}}-3 has been prepared in which the 9-MC_{Cu^{II}}-3 is connected to a 6-MC_{Cu^{II}}-2 through an oxime oxygen atom of the 9-MC-3 ring.^{177b} Two vacant 9-MC_{Pd^{II}}-3 structures have been synthesized with oxime ligands. One consists of three Pd^{II} ions connected by double N–O bridges each,¹⁷⁹ and the other complex has only one N–O bridge between the Pd^{II} ions.¹⁸⁰ A doubly bridged *inv*9-MC_{Mn^{III}}-3 has been synthesized that encapsulates a $\mu_3\text{-O}$.¹⁸¹ Viewed down the three-fold axis, the upper connectivity has a N–O bridge repeating in a clockwise fashion. The lower bridge, though, has O–N clockwise connectivity. One interesting structure can be considered two *inv*9-MC_{Ni^{II}}-3 structures connected via a common Ni^{II} ion (Figure 5).¹⁸² The MC connectivity, though, is not made from an organic ligand, but from six nitrite anions. Within the center of each *inv*9-MC_{Ni^{II}}-3 is a $\mu_3\text{-OH}$ group. Related to the fused *inv*9-MC_{Ni^{II}}-3 structure is a Zn^{II} pentanuclear complex, in which two collapsed 9-MC_{Zn^{II}}-3 rings share a common Zn^{II} ion to create two 9-MC-3 rings within the same complex.¹⁸³ A

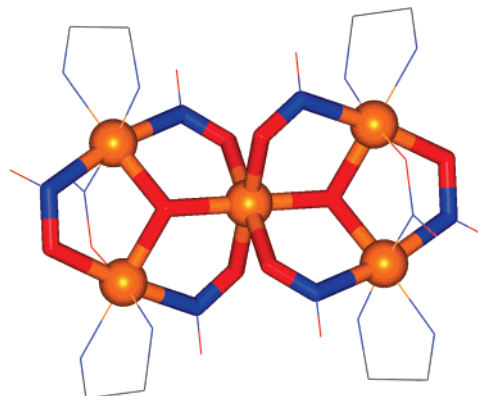


Figure 5. X-ray crystal structure of the inverse $(\mu_3\text{-OH})[9\text{-MC}_{\text{Ni}^{\text{II}}}\text{-3}]$ complex with the ligand ethane-1,2-diamine. Only the NO_2^- anions provide the bridging atoms for the metallacrown. Color scheme: orange sphere, ring Ni^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.¹⁸²

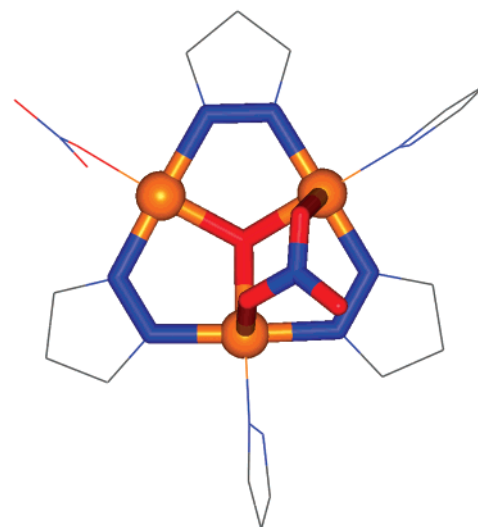


Figure 6. X-ray crystal structure of the inverse azametallacrown $(\mu_3\text{-OH})[9\text{-MC}_{\text{Cu}^{\text{II}}}\text{-3}]$ with the ligand pyrazole. The nitrate that bridges two of the ring Cu^{II} ions also binds to a Cu^{II} of an adjacent MC to form a one-dimensional chain of MCs. Color scheme: orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.¹⁸⁸

collapsed MC is a complex in which no central ion is bound but instead a ring metal binds to a ring heteroatom on the opposite side, thus collapsing the central cavity.

Triangular 9-MC-3 azametallacrowns (M–N–N) have been a much more common structure type. Most of the structures are based on the pyrazole ligand providing the N–N bridging unit. Excellent reviews exist on the coordination chemistry of pyrazole ligands.^{184–187} The most common structures rely on the group 11 elements copper, silver, and gold. The first aza9-MC_{Cu^{II}}-3 was synthesized with a simple pyrazolate anion (Figure 6).¹⁸⁸ The inverse MC binds a $\mu_3\text{-OH}$ group within the central cavity. In addition, a nitrate anion binds adjacent MCs to form a one-dimensional chain. From this initial structure, various inverse aza9-MC_{Cu^{II}}-3 structures have been synthesized with pyrazole derivatives and by capturing different anions such as $\mu_3\text{-O}$, $\mu_3\text{-Cl}$, and $\mu_3\text{-Br}$.^{189–194} By using Cu^I, vacant aza9-MC_{Cu^I}-3 structures are able to be synthesized with a variety of derivatized pyrazole ligands (Figure 7).^{195–201} These structures have the

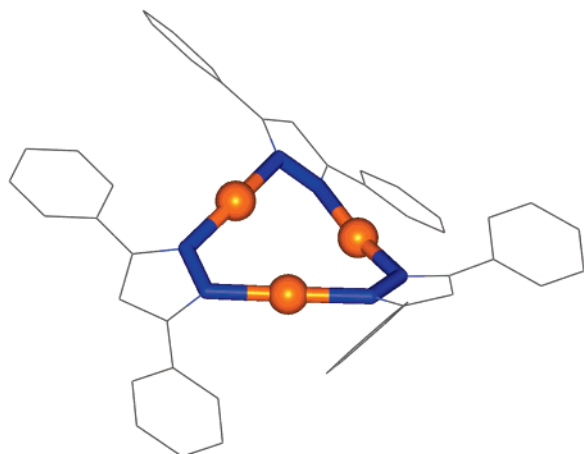


Figure 7. X-ray crystal structure of the vacant azametallacrown [9-MC_{Cu}^I-3] with the ligand 3,5-diphenylpyrazole. The complex is not as planar as the (μ_3 -OH)[9-MC_{Cu}^{II}-3] complex in Figure 6. Color scheme: orange sphere, ring Cu^I; blue tube, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.¹⁹⁵

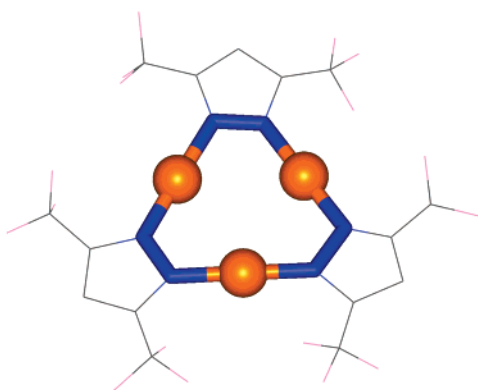


Figure 8. X-ray crystal structure of the vacant azametallacrown [9-MC_{Au}^I-3] with the ligand 3,5-bis(trifluoromethyl)pyrazole. The complex is much more planar than the corresponding Cu^I metallacrown in Figure 7. Color scheme: orange sphere, ring Au^I; blue tube, nitrogen; purple line, fluorine; gray line, carbon. Hydrogen atoms have been removed for clarity.²⁰⁵

same connectivity and display Cu–Cu distances similar to those of their aza9-MC_{Cu}^{II}-3 counterparts, but do not contain a μ_3 -guest within the central cavity. Several aza9-MC_{Ag}^I-3 and aza9-MC_{Au}^I-3 structures have been synthesized from pyrazole ligands and its derivatives (Figure 8).^{202–209} These structures also do not contain a μ_3 -guest within the central cavity just as the aza9-MC_{Cu}^I-3 complexes do not. In addition to the group 11 aza9-MC-3 complexes, an aza9-MC_{Pt}^{II}-3 and two aza9-MC_{Pd}^{II}-3 pyrazole vacant complexes have been synthesized with two pyrazolates bridging between each Pt^{II}²¹⁰ and each Pd^{II}.^{60,211} Also, an inverse aza9-MC_{Co}-3 has been synthesized that encapsulates a μ_3 -OH.²¹² The structure is mixed-valent with an oxidation state distribution of Co^{II}-Co^{III}₂. Each Co^{III} is bridged to the Co^{II} via one pyrazolate ligand, whereas the two Co^{III} ions are bridged by two pyrazolate ligands.

An interesting subset of these pyrazole aza9-MC-3 complexes has been synthesized in which two vacant aza9-MC-3 topologies can be observed within one complex. An aza9-MC_{Pd^{II}₂Ag^I-3} structure is built from three 3-*tert*-butylpyrazolate ligands.⁶⁰ Then a second Ag^I cation is bound to the two Pd^{II} ions via two 3-*tert*-butylpyrazolate ligands. A third 3-*tert*-butylpyrazolate bridges the two Pd^{II} ions to give the appear-

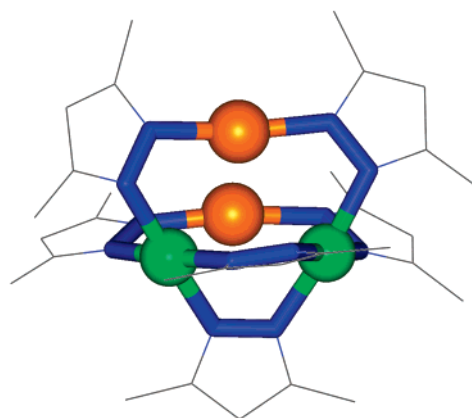


Figure 9. X-ray crystal structure of two vacant azametallacrowns within one structure. The structure may be considered as two vacant aza[9-MC_{Pd^{II}₂Ag^I-3}] built into each other with the ligand 3,5-dimethylpyrazole. Color scheme: green sphere, Pd^{II}; orange sphere, Ag^I; blue tube, nitrogen; gray line, carbon. Hydrogen atoms have been removed for clarity.²¹³

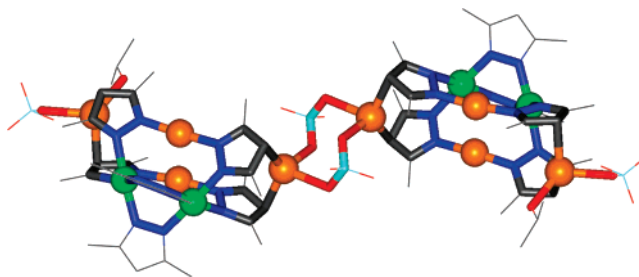


Figure 10. X-ray crystal structure of dimers of interconnected aza[9-MC_{Pd^{II}₂Ag^I-3}] complexes. The 9-MC-3 complexes are connected via a Ag^I₂(ClO₄)₂ bridge. The terminal Ag^I ions do not bridge to additional 9-MC-3 complexes. An analogous dimer can be synthesized with aza[9-MC_{Pd^{II}₂Au^I-3}] and Ag^I₂(ClO₄)₂. Color scheme: green sphere, Pd^{II}; orange sphere, Ag^I; blue tube, nitrogen; aqua tube, chlorine; gray line, carbon. Hydrogen atoms have been removed for clarity.²¹³

ance of two interconnected aza9-MC_{Pd^{II}₂Ag^I-3} complexes. A similar complex is observed with 3,5-dimethylpyrazolate with interlinking aza9-MC_{Pd^{II}₂Ag^I-3} complexes (Figure 9).²¹³ Two of these aza9-MC-3 complexes can then be connected via a Ag^I₂(ClO₄)₂ bridge to create a dimer (Figure 10). In addition, an aza9-MC_{Pd^{II}₂Au^I-3} complex may be dimerized with a Ag^I₂(ClO₄)₂ bridge.

Aza-9-MC-3 complexes have been synthesized without pyrazole ligands. Diazabutadiene provides a N–N bridge to form an aza9-MC-3 with a ring repeat unit of –[Al^{III}–N–N]– (Figure 11).²¹⁴ This metallamacrocycle encapsulates an Al^{III} ion. A vacant Ni^{II} aza9-MC-3 is formed by using an imine-based ligand.²¹⁵ Aza9-MC_{Pd}^{II}-3 and aza9-MC_{Zn}^{II}-3 complexes can be synthesized using the multidentate ligand tris(2-hydroxybenzylidene)triaminoguanidine (Figure 12).²¹⁶ The single ligand provides enough binding sites to allow for the formation of an aza9-MC-3 structure. A carbon atom resides in the middle of each aza9-MC-3 complex; however, the carbon atom is a part of the ligand and not bound to the ring metal ions as in the other inverse 9-MC-3 structures.

Related to these 9-MC-3 and aza9-MC-3 complexes, two 9-MC-3 complexes have been synthesized with a repeat unit of –[Pt^{II}–P–O]–.^{217,218} The structures are very similar to the other triangular inverse 9-MC-3 complexes. In both complexes a diphenylphosphinoyl ligand provides the P–O connectivity and a P(C₆H₅)₂(CH₃) group completes the

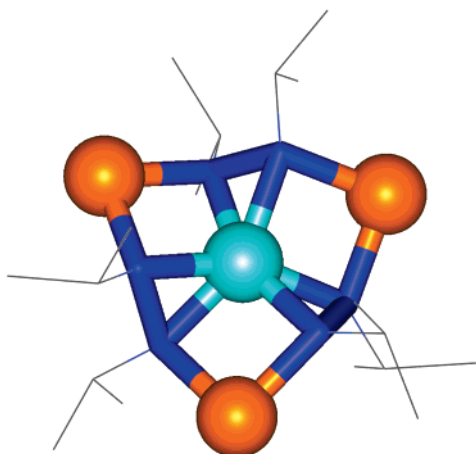


Figure 11. X-ray crystal structure of the azaAl^{III}[9-MC_{Al^{III}-3}] complex with the ligand 1,1,4,4-tetramethyl-2,3-diazabutadiene. Each nitrogen atom of the N–N bridge binds to the encapsulated Al^{III}. Color scheme: aqua sphere, central Al^{III}; orange sphere, ring Al^{III}; blue tube, nitrogen; gray line, carbon. Hydrogen atoms have been removed for clarity.²¹⁴

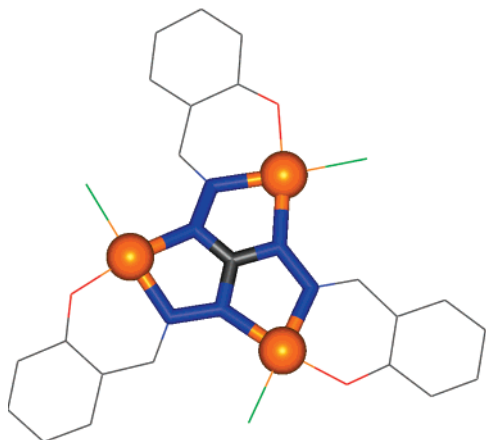


Figure 12. X-ray crystal structure of the aza[9-MC_{Pd^{II}-3}]²⁻ complex with the ligand tris(2-hydroxybenzylidene)triaminoguanidine. One ligand provides enough binding sites to generate the 9-MC-3 complex. Color scheme: orange sphere, Pd^{II}; blue tube, nitrogen; gray tube, carbon; red line, oxygen; green line, chloride. Hydrogen atoms, (C₂H₅)₄N⁺ counteranions, and lattice solvent have been removed for clarity.²¹⁶

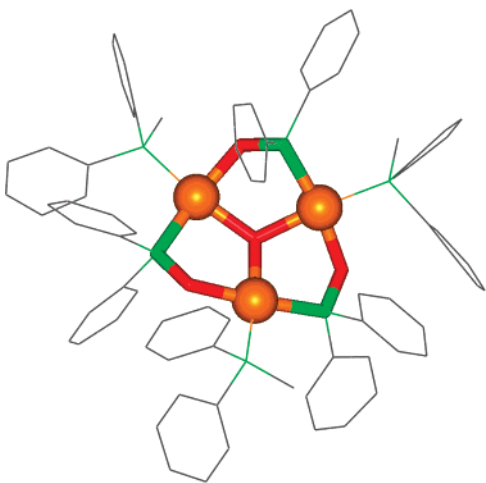


Figure 13. X-ray crystal structure of the inverse (μ_3 -OH)[9-MC_{Pd^{II}-3}] complex with the ligand diphenylphosphinoyl bridging between the Pd^{II} ions. Color scheme: orange sphere, Pd^{II}; green tube, phosphorus; red tube, oxygen; gray line, carbon. Hydrogen atoms, BF₄⁻ counteranions, and lattice solvent have been removed for clarity.²¹⁷

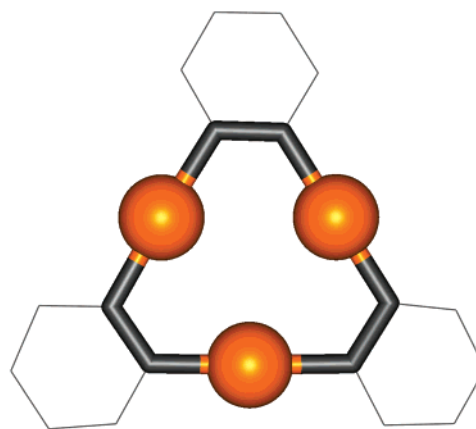


Figure 14. X-ray crystal structure of 9-MC_{Hg^{II}-3} with benzene rings providing the carbon atoms of the bridges. Color scheme: orange sphere, Hg^{II}; gray tube, carbon. Hydrogen atoms have been removed for clarity.²¹⁹

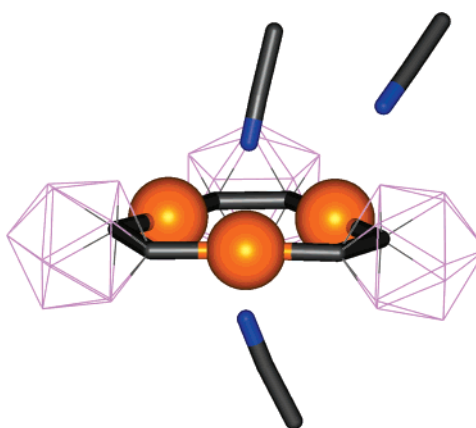


Figure 15. X-ray crystal structure of 9-MC_{Hg^{II}-3} with dicarbon boron cages providing the carbon atoms of the bridges. Two acetonitrile solvent molecules reside below and above the central cavity of the MC. A third acetonitrile approaches one of the ring Hg^{II} ions. Color scheme: orange sphere, Hg^{II}; gray tube, carbon; blue tube, nitrogen; purple line, boron. Hydrogen atoms and additional lattice solvent have been removed for clarity.²²¹

coordination of the Pt^{II}. The difference lies in the μ_3 -anion. In one complex the inverse 9-MC_{Pt^{II}-3} complex binds a μ_3 -OH²¹⁷ (Figure 13), and in the other complex, a μ_3 -O is encapsulated.²¹⁸

A number of 9-MC-3 complexes with a $-\text{[Hg}^{\text{II}}-\text{C}-\text{C]}-$ repeat unit have been synthesized. In the first 9-MC_{Hg^{II}-3} complex, the Hg^{II} ions are connected via three benzene groups (Figure 14).²¹⁹ The structure does not contain any guest species. An analogous complex can be made with 1,2,3,4-tetrafluorobenzene.²²⁰ This 9-MC_{Hg^{II}-3} is capable of binding chloride, bromide, or iodide anions between two 9-MC_{Hg^{II}-3} complexes and forming polymeric chains. In a second series of compounds, the source of the carbon atoms is dicarbon boron cages. The first 9-MC_{Hg^{II}-3} with dicarbon boron cages consisted of a vacant structure with the Hg^{II} ions connected via 1,2-C₂B₁₀H₁₀ cages (Figure 15).²²¹ However, two acetonitrile solvent molecules do approach the central cavity on opposite faces of the MC ring. Subsequent related structures have shown the ability to bind solvent molecules and halide anions in sandwich complexes with the guest trapped between two 9-MC_{Hg^{II}-3} complexes.^{222–225} In addition, a [Hg^{II}–B–B] 9-MC-3 complex has been synthesized with the boron atoms provided by boron cages.²²⁶

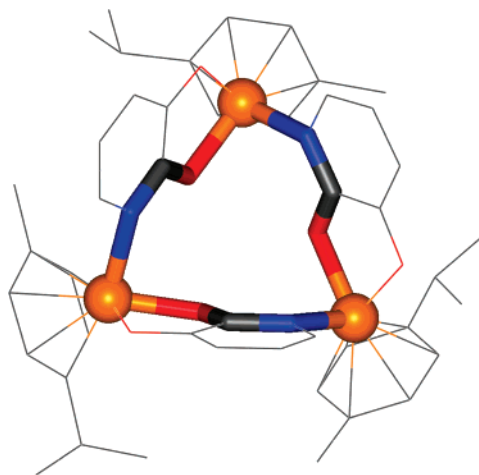


Figure 16. X-ray crystal structure of the vacant 12-MC_{Ru^{II}}-3 complex. Each Ru^{II} ion is capped by a cymene ligand and bridged to adjacent Ru^{II} ions by the ligand 3-hydroxy-2-pyridone. Color scheme: orange sphere, Ru^{II}; gray tube, carbon; blue tube, nitrogen; red tube, oxygen. Hydrogen atoms have been removed for clarity.²²⁸

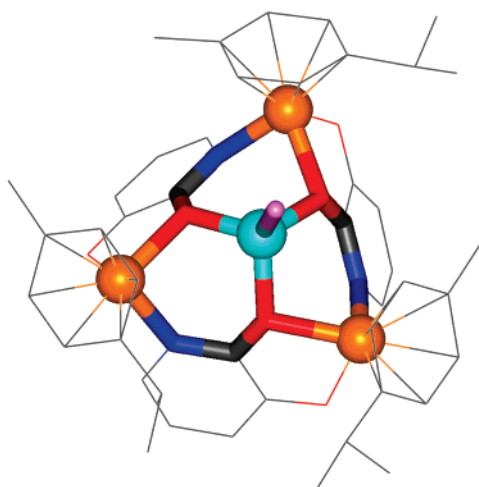


Figure 17. X-ray crystal structure of the LiCl[12-MC_{Ru^{II}}-3] complex with the ligand 3-hydroxy-2-pyridone. The ring oxygen atoms bind the Li⁺ within the central cavity, and the chloride anion binds to the Li⁺. This is the same MC as in Figure 16. Color scheme: orange sphere, Ru^{II}; gray tube, carbon; blue tube, nitrogen; red tube, oxygen; magenta tube, chloride. Hydrogen atoms have been removed for clarity.²²⁸

2.3. 12-MC-3

The class of 12-MC-3 complexes represents the smallest extended MCs with three metal centers connected by three atom bridges. Severin and co-workers began the investigation of the M–N–C–O series of 12-MC-3 complexes.²²⁷ The initial structure is a vacant 12-MC-3 structure dependent upon a [Ru^{II}–N–C–O]₃ metallamacrocycle (Figure 16). The MC connectivity is provided by three 3-hydroxy-2-pyridone ligands, and the coordination sphere of the Ru^{II} is completed by an aromatic ligand, in this case, cymene. This structure type has proven to be very general, with ring metals such as Ir^{III} and Rh^{III}, different derivatives of the 3-hydroxy-2-pyridone ligand, and different aromatic ligands attached to the ring metal used to create an array of 12-MC-3 complexes.^{228–239} The 12-MC-3 complexes, however, have been shown to bind a number of guests including LiCl^{228–230,236} (Figure 17), NaCl,^{228,229,236} NaBr,²²⁹ LiBF₄,²³¹ LiF,^{231,233} LiFHF²³¹ (Figure 18), NaBF₄,²³² Na₂SiF₆²³² (Figure 19), and

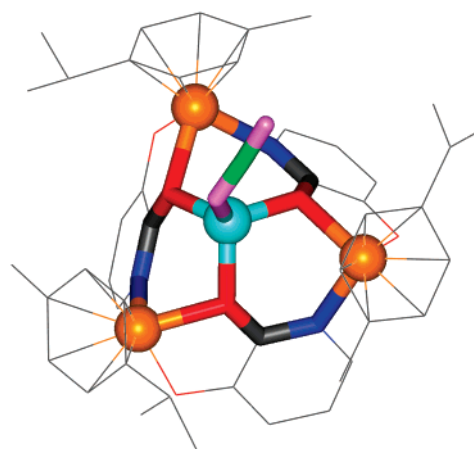


Figure 18. X-ray crystal structure of the LiFHF[12-MC_{Ru^{II}}-3] complex with the ligand 3-hydroxy-2-pyridone. The ring oxygen atoms bind the Li⁺ within the central cavity, and the anion hydrogen difluoride binds to the Li⁺ with a bent fashion. The F–F distance is 2.32 Å. This is the same MC as in Figure 16. Color scheme: orange sphere, Ru^{II}; gray tube, carbon; blue tube, nitrogen; red tube, oxygen; magenta tube, fluoride; green tube, hydrogen of FHF[–] anion. Additional hydrogen atoms have been removed for clarity.²³¹

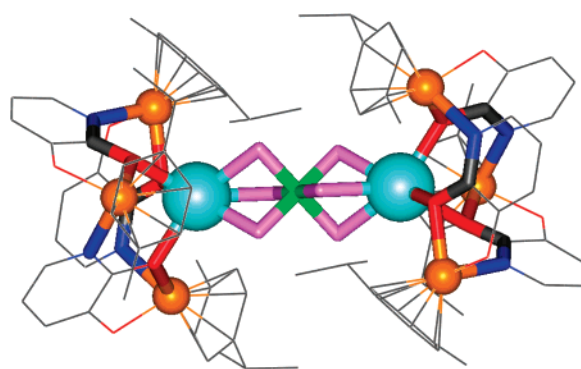


Figure 19. X-ray crystal structure of the (Na₂SiF₆)[12-MC_{Ru^{II}}-3]₂ complex with the ligand 3-hydroxy-2-pyridone. The ring oxygen atoms of each MC bind the Na⁺ within the central cavity. The Na⁺ ions are then connected by a SiF₆^{2–} anion. This is the same MC as in Figure 16. Color scheme: orange sphere, Ru^{II}; gray tube, carbon; blue tube, nitrogen; red tube, oxygen; magenta tube, fluoride; green tube, silicon. Hydrogen atoms and lattice solvent have been removed for clarity.²³²

H₂O.²³⁸ In all of the complexes, the alkali metal ion is bound to the oxygen atoms of the MC ring, and the halide anion is bound to the alkali metal. For the guest Na₂SiF₆, the molecule is encapsulated by two 12-MC_{Ru^{II}}-3 complexes with one Na^I bound to each 12-MC-3. A similar 12-MC-3 complex can be made with Rh^{III}. The 12-MC_{Rh^{III}}-3 complex has –[Rh^{III}–N–C–O]– repeat units, and the Rh^{III} is capped by η⁵-pentamethylcyclopentadiene. However, the ligand used to provide the bridge between the Rh^{III} ion is the nucleobase 9-ethylhypoxanthine.²⁴⁰

Analogous expanded aza12-MC-3 complexes have existed in the literature since the early 1990s with a [M–N–C–N]₃ metallamacrocycle. The N–C–N bridge is usually provided by a nucleobase, nucleotide, or nucleoside ligand.²⁴¹ In the first reported aza12-MC-3, a vacant complex was synthesized with Rh^{III} and the nucleobase 9-methyladenine (Figure 20).²⁴² The coordination of the Rh^{III} is completed by η⁵-pentamethylcyclopentadiene. This model has also been generalized as many different nucleobases, nucleotides, and nucleosides have been used as the bridging ligand, several different aromatic metal ligands have been used, and

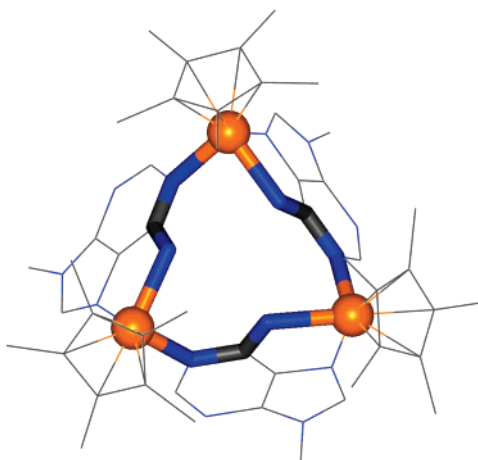


Figure 20. X-ray crystal structure of the vacant 12-MC_{Rh^{III}}-3 complex. Each Rh^{III} ion is capped by a η^5 -pentamethylcyclopentadiene ligand and bridged to adjacent Rh^{III} ions by the nucleobase 9-methyladenine. Color scheme: orange sphere, Rh^{III}; gray tube, carbon; blue tube, nitrogen. Hydrogen atoms and CF₃SO₃⁻ counteranions have been removed for clarity.²⁴²

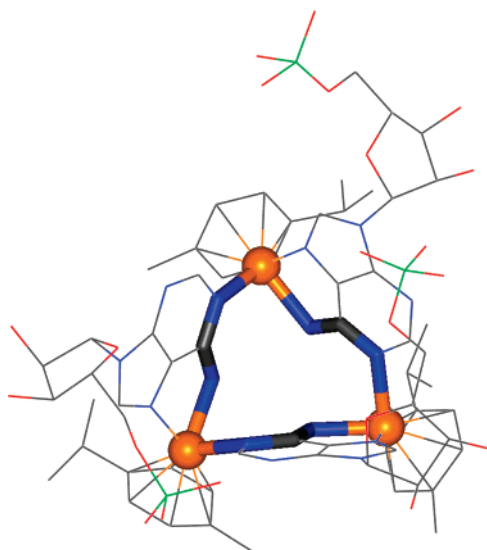


Figure 21. X-ray crystal structure of the vacant 12-MC_{Ru^{II}}-3 complex. Each Ru^{II} ion is capped by a cymene ligand and bridged to adjacent Ru^{II} ions by the nucleotide 5'-adenosine monophosphate. Color scheme: orange sphere, Ru^{II}; gray tube, carbon; blue tube, nitrogen; red line, oxygen; green line, phosphorus. Hydrogen atoms and CF₃SO₃⁻ counteranions have been removed for clarity.²⁴⁶

complexes with Ir^{III}, Ru^{II}, and Pd^{II} have been synthesized (Figure 21).^{243–250} Some of these complexes are able to recognize aromatic and aliphatic amino acid guests and aromatic and aliphatic carboxylic acid guests in aqueous solution.^{244,245}

Two other aza12-MC-3 structures have been identified. The first is based on a system in which three pentadentate 2,6-bis[(1-methyltetrazol-5-yl)amido]pyridine ligands provide N–C–N bridges between three iron centers with an oxidation state distribution of Fe^{II}Fe^{III}₂ (Figure 22).²⁵¹ This inverse metallacrown binds a μ_3 -O in the central cavity, and each metal ion is bridged to the adjacent metal ions via two N–C–N bridges. In addition, the analogous Cu^{II}Fe^{III}₂, Co^{II}-Fe^{III}₂, and Ni^{II}Fe^{III}₂ complexes have been made. In the other system, a macrocyclic ligand provides N–C–N bridges between three Cu^{II} ions to form a bowl-like aza12-MC_{Cu^{II}}-3 (Figure 23). This inverse aza12-MC-3 binds either a μ_3 -O

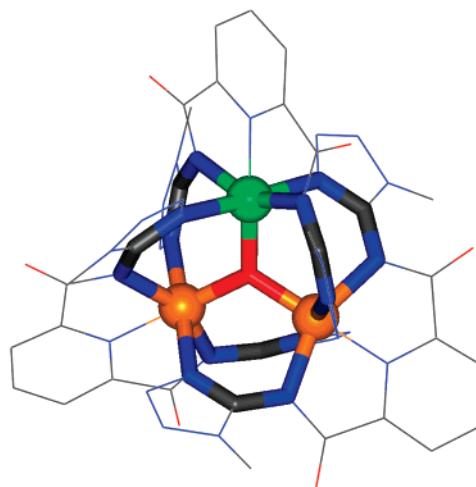


Figure 22. X-ray crystal structure of the inverse (μ_3 -O)[12-MC_{Fe^{III},Fe^{II}}-3] complex with three pentadentate 2,6-bis[(1-methyltetrazol-5-yl)amido]pyridine ligands. Each ring metal ion is connected to the adjacent metal ion by two N–C–N bridges. Color scheme: orange sphere, Fe^{III}; green sphere, Fe^{II}; gray tube, carbon; blue tube, nitrogen; red line, oxygen. Hydrogen atoms and lattice solvent have been removed for clarity.²⁵¹

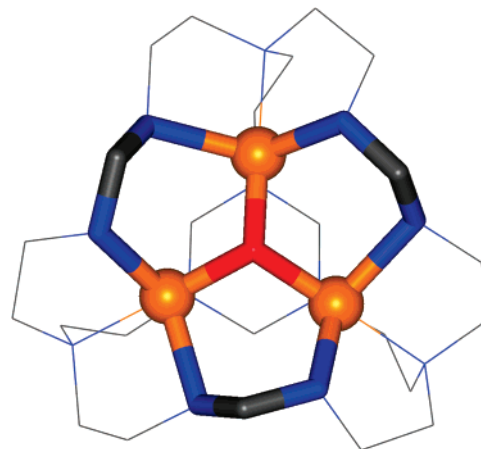


Figure 23. X-ray crystal structure of the inverse $\{(\mu_3\text{-O})[12\text{-MC}_{\text{Cu}^{\text{II}}}\text{-3}]\}^{4-}$ complex with a molecular bowl dodecaaza ligand. Each Cu^{II} ion is bridged to adjacent Cu^{II} ions via a N–C–N connectivity. Color scheme: orange sphere, Cu^{II}; gray tube, carbon; blue tube, nitrogen; red tube, oxygen. Hydrogen atoms, ClO₄⁻ counteranions, and lattice solvent have been removed for clarity.²⁵²

or a μ_3 -OH guest.²⁵² Furthermore, two μ_3 -O inverse aza12-MC_{Cu^{II}}-3 may be joined together by a Cu^I metal bridge to form a dumbbell-shaped structure²⁵³ (Figure 24), and two μ_3 -OH inverse aza12-MC_{Cu^{II}}-3 structures may be joined by a 1,3,5-benzenetricarboxylate bridge to form a bent structure.²⁵⁴

Bis(diphenylphosphino)methane (dppm) has been used to synthesize a number of 12-MC-3 structures with a wide variety of metals, although these complexes were not recognized as MCs at the time. Excellent reviews exist on the coordination chemistry of dppm, and only a few structures from the vast amount of literature will be highlighted here.^{255–258} One of the most common elements studied with dppm is platinum. In the 12-MC-3 complexes, a Pt₃ triangle is bridged by three dppm ligands, which provide a P–C–P connectivity. Typically the Pt₃ core consists of three Pt–Pt bonds, although numerous examples exist with two, one, or zero metal–metal bonds. The oxidation state of each Pt center in the core may range from 0 to 2+, and partial

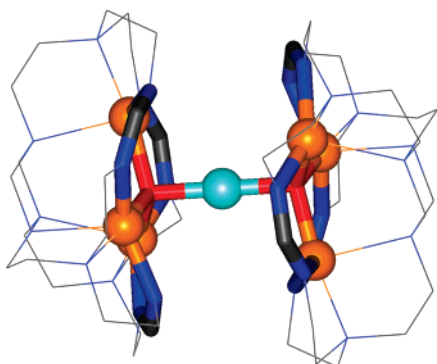


Figure 24. X-ray crystal structure of two inverse $\{(\mu_3\text{-O})[12\text{-MC}_{\text{Cu}^{\text{II}}}\text{-3}]\}^{3+}$ complexes with a bridging Cu^{I} ion. This is the same MC of Figure 23. The bridging Cu^{I} connects the MCs through the central $\mu_3\text{-O}$ atoms. Color scheme: orange sphere, Cu^{II} ; aqua sphere, Cu^{I} ; gray tube, carbon; blue tube, nitrogen; red tube, oxygen. Hydrogen atoms, ClO_4^- counteranions, and lattice solvent have been removed for clarity.²⁵³

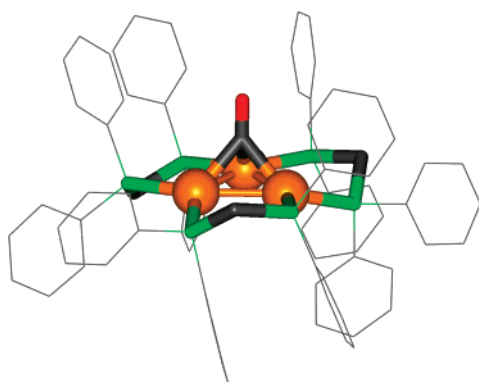


Figure 25. X-ray crystal structure of the $\{(\mu_3\text{-CO})[12\text{-MC}_{\text{Pt}}\text{-3}]\}^{2+}$ complex. Each Pt center has a $2/3+$ charge, and three Pt–Pt bonds exist in the molecule with a $\mu_3\text{-CO}$ group connecting the Pt centers. The ligand bis(diphenylphosphino)methane bridges between each Pt center. Color scheme: orange sphere, $\text{Pt}^{2/3+}$; gray tube, carbon; green tube, phosphorus; red tube, oxygen. Hydrogen atoms, PF_6^- counteranions, and lattice solvent have been removed for clarity.²⁶⁰

charges of $2/3+$ and $4/3+$ may exist. The platinum core typically binds a μ_3 -guest to the three Pt centers, although there are cases of no μ_3 -guests as noted below. Bound μ_3 -nonmetal guests include CO ^{259–263} (Figure 25), SCN^- ,²⁵⁹ sulfide,^{264,265} η_2 -acetylene^{266,267} (Figure 26), η_2 -ethyl ethynyl ether ($\eta_2\text{-HCCOCH}_2\text{CH}_3$),²⁶⁸ and hydride.^{269,270} In addition, some of the Pt_3 12-MC-3 complexes with a μ_3 -guest can bind an additional guest on the opposite face that either binds to one Pt center or bridges two Pt centers.^{261–263,269–272} In the Pt_3 12-MC-3 complexes with no μ_3 -guest, a guest will bind to one of the ring Pt centers so the MC is not completely vacant.^{273–275} Using diphosphine ligands similar to dppm, analogous Pt_3 12-MC-3 complexes have been synthesized that show binding properties similar to those of the Pt_3 dppm 12-MC-3 complexes.^{276,277} Pt_3 12-MC-3 complexes with dppm and dppm-like ligands can bind more than just μ_3 -nonmetal guests; the complexes are able to bind metal guests either by forming metal–metal bonds, by one-atom bridges between the guest metal and the ring metals, or by a combination of both methods. Groups forming metal–metal bonds with all three ring Pt centers (a μ_3 -guest) include $\text{Sn}(\text{CH}_3)_2\text{O}_2\text{PF}_2^-$,²⁷⁸ SnF_3^- ,^{278,279} $\text{AuP}(\text{CH}_3)_3^+$,²⁸⁰ $\text{Re}(\text{CO})_3^+$,^{281–284} $\text{Re}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3^-$,²⁸⁵ $\text{AuP}(\text{C}_6\text{H}_5)_3^+$,²⁸⁶ Hg ,²⁸⁷ $\text{Hg-Ru}(\eta_5\text{-C}_5\text{H}_5)(\text{CO})_2$,²⁸⁸ $\text{Ti}(\text{CH}_3\text{COCH}_2\text{COCH}_3)\text{-}$

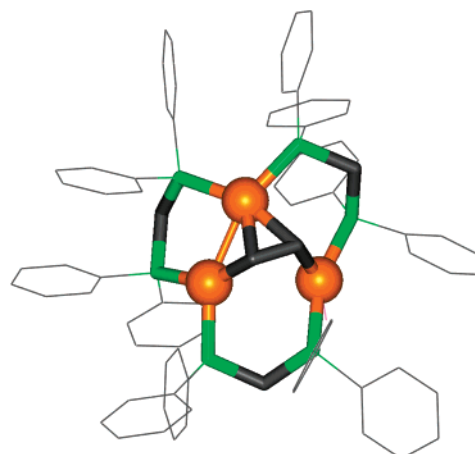


Figure 26. X-ray crystal structure of the $\{(\mu_3\text{-}\eta^2\text{-HC}\equiv\text{CH})[12\text{-MC}_{\text{Pt}}\text{-3}]\}^+$ complex. Each Pt center has a $2/3+$ charge, and one Pt–Pt bond exists in the molecule with a $\mu_3\text{-}\eta^2$ -acetylene molecule connecting the Pt centers. The ligand bis(diphenylphosphino)methane bridges between each Pt center. A chloride anion is bound to the underside of the Pt without a metal–metal bond. Color scheme: orange sphere, $\text{Pt}^{2/3+}$; gray tube, carbon; green tube, phosphorus. Hydrogen atoms and the PF_6^- counteranion have been removed for clarity.²⁶⁶

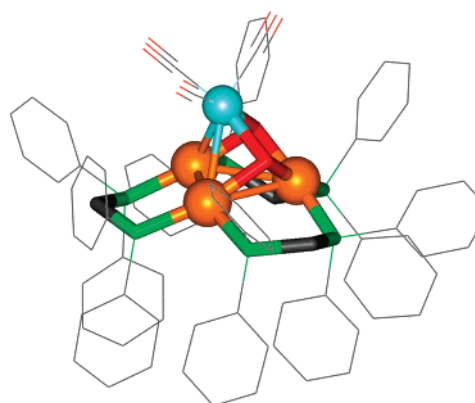


Figure 27. X-ray crystal structure of the $(\mu_3\text{-Re}(\text{CO})_3\text{O}_2)[12\text{-MC}_{\text{Pt}}\text{-3}]^+$ complex. Each Pt center has a $4/3+$ charge, and three Pt–Pt bonds exist in the molecule. The $\text{Re}(\text{CO})_3^+$ group is connected to the Pt_3 core via two Re–Pt bonds and two $\mu\text{-O}$ bridges to the third Pt center. The ligand bis(diphenylphosphino)methane bridges between each Pt center. Color scheme: orange sphere, $\text{Pt}^{4/3+}$; aqua sphere, Re^{I} ; gray tube, carbon; green tube, phosphorus; red tube, oxygen. Hydrogen atoms, PF_6^- counteranion, and lattice solvent have been removed for clarity.²⁹⁴

(OH_2) ,²⁸⁹ and $\text{Ti}(\text{CH}_3\text{COCH}_2\text{COCH}_3)(\text{O}_2\text{CCF}_3)^-$.²⁸⁹ Many of these complexes also bind a second μ_3 -guest such as a second metal group, CO, or a halide anion on the opposite face.^{278–280,284,285,287–289} In addition, $\text{Re}(\text{CO})_3^+$ groups have been attached to the Pt_3 core via three one-atom bridges between the Re and two ring Pt centers provided by two $\mu_3\text{-O}$ and one $\mu_3\text{-S}$.^{290,291} $\text{Re}(\text{CO})_3^+$ groups have also been attached to 12-MC_{Pt}-3 complexes via two or three Re–Pt bonds and two μ_3 -one atom bridges provided by $\mu_3\text{-O}$, $\mu_3\text{-S}$, or $\mu\text{-CO}$ groups (Figure 27).^{281,292–295} Furthermore, $\text{Pt}(\text{dppm})$ or $\text{Pt}\{\text{C}_6\text{H}_5\text{PCH}_2\text{P}(\text{O})\text{C}_6\text{H}_5\}$ groups have been attached to the Pt_3 core through two $\text{Pt}_{\text{central}}\text{-Pt}_{\text{ring}}$ metal bonds and two $\mu\text{-CO}$ groups that bridge the $\text{Pt}_{\text{central}}$ guest to the Pt_{ring} centers.^{296–299} The dppm and $\text{C}_6\text{H}_5\text{PCH}_2\text{P}(\text{O})\text{C}_6\text{H}_5$ ligand bound to the central Pt does not bridge to the Pt_3 12-MC-3. An $\text{Ir}(\text{dppm})$ group³⁰⁰ and an $\text{Ir}(\text{P}(\text{OC}_6\text{H}_5)_3)$ group³⁰¹ have been attached in a similar manner to a 12-MC_{Pt}-3. A Ru-

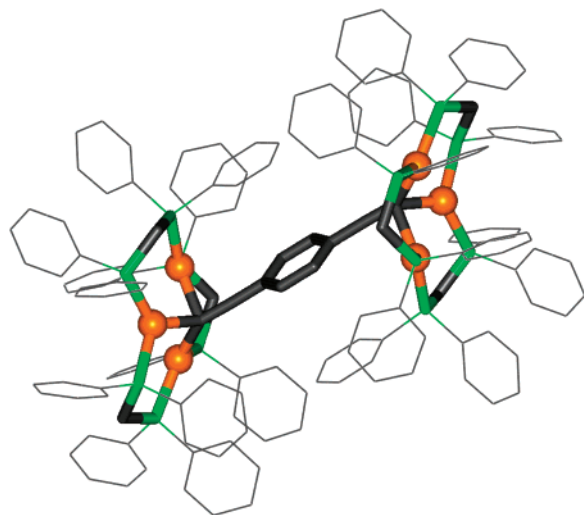


Figure 28. X-ray crystal structure of the $\{(\mu_3-\eta^1-C\equiv C_6H_4C\equiv C-p)[12-MC_{Cu^I-3}]_2\}^{4+}$ complex. The encapsulated 1,4-diethynylbenzene connects the two metallacrowns by binding to the Cu^I_3 core of each MC. The ligand bis(diphenylphosphino)methane bridges between each Cu^I center. The analogues Ag^I complex has been synthesized. Color scheme: orange sphere, Cu^I ; gray tube, carbon; green tube, phosphorus. Hydrogen atoms and BF_4^- counteranions have been removed for clarity.³¹²

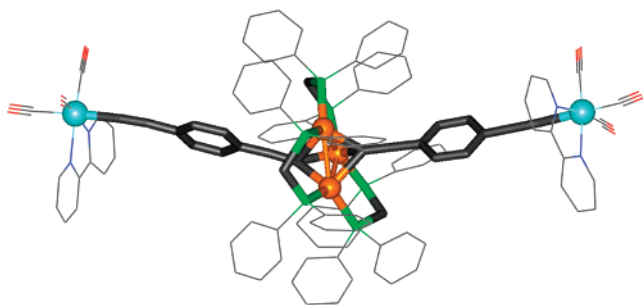


Figure 29. X-ray crystal structure of a $\{(\mu_3-\eta^1-C\equiv C_6H_4C\equiv C-p-Re(CO)_3(2,2'-dipyridyl))_2[12-MC_{Cu^I-3}]\}^+$ complex. The guests are bound on opposite faces of the Cu^I_3 core. The Cu^I-Cu^I distance is less than the sum of their van der Waals radii, suggesting metal-metal interactions. The ligand bis(diphenylphosphino)methane bridges between each Cu^I center. Color scheme: orange sphere, Cu^I ; aqua sphere, Re^I ; gray tube, carbon; green tube, phosphorus; red line, oxygen. Hydrogen atoms and PF_6^- counteranion have been removed for clarity.³¹⁴

$(CO)_2$ complex has also been bound to a $12-MC_{Pt-3}$ complex by two $Ru-Pt$ metal bonds and two $\mu-CO$ bridges.³⁰²

The chemistry of $12-MC_{Cu^I-3}$ with the ligand dppm is also quite extensive. These complexes have a $-[Cu^I-P-C-P]-$ repeat unit and readily bind one or two μ_3 -guests to the Cu^I_3 core. Nonmetal μ_3 -guests include OH ,^{303,304} η^1 -phenylacetylide ($\eta^1-C\equiv CC_6H_5$),³⁰⁵⁻³⁰⁷ chloride,³⁰⁷⁻³¹¹ η^1 -*tert*-butylacetylide ($\eta^1-C\equiv CC(CH_3)_3$),³⁰⁹ 3-methyl-8-ethylxanthine,³¹⁰ η^1 -1,4-diethynylbenzene ($\eta^1-C\equiv CC_6H_4C\equiv C-p$) [this guest connects two $12-MC_{Cu^I-3}$ complexes (Figure 28)],³¹² η^1 -*p*-tolylethynyl ($\eta^1-C\equiv CC_6H_4CH_3-4$) (this complex also contains a $\mu-\eta^1-C\equiv NC_6H_4CH_3-4$ that bridges two of the Cu^I ions),³¹³ $\eta^1-C\equiv CC_6H_4C\equiv C-p-Re(CO)_3(2,2'-dipyridyl)$ ³¹⁴ (Figure 29), bromide,^{315,316} $\eta^1-C\equiv CC_6H_4OCH_3-p$,^{317,318} $\eta^1-C\equiv CC_6H_4OCH_2CH_3-p$,³¹⁷ $\eta^1-C\equiv CC_6H_4NO_2-p$,³¹⁷ iodide,^{316,319,320} fluoride,³²¹ and nitrate.³⁰⁴ WO_4^{2-} , WS_4^{2-} , and MoS_4^{2-} anions can be bound to the $12-MC_{Cu^I-3}$ core via $Cu-O$ or $Cu-S$ bonds.^{315,322-324} Three of the O or S atoms bridge the W^{VI} or Mo^{VI} ion to each ring Cu^I ion, whereas the fourth O or S

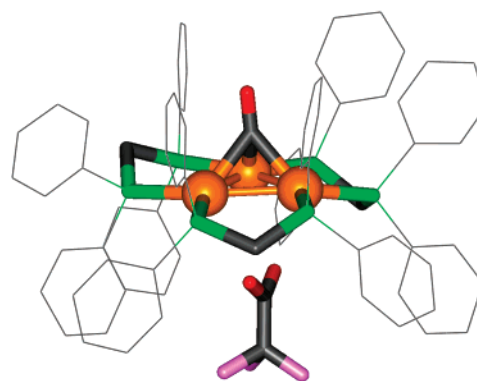


Figure 30. X-ray crystal structure of the $\{(\mu_3-CO)[12-MC_{Pd-3}]\}^{2+}$ complex. Each Pd center has a $2/3+$ charge, and three Pd-Pd bonds exist within the molecule with a μ_3-CO group connecting the Pd centers. The ligand bis(diphenylphosphino)methane bridges between each Pd center. One $CF_3CO_2^-$ anion is buried within the phenyl rings of the ligand. Color scheme: orange sphere, $Pd^{2/3+}$; gray tube, carbon; green tube, phosphorus; red tube, oxygen; magenta tube, fluorine. Hydrogen atoms, $CF_3CO_2^-$ counteranion, and lattice solvent have been removed for clarity.³²⁵

is a μ_4 -bridge between the three Cu^I ions and the encapsulated W^{VI} or Mo^{VI} ion.

The first $12-MC-3$ made with dppm consisted of a Pd_3 complex with a $-[Pd-P-C-P]-$ repeat unit with the Pd centers in a $2/3+$ oxidation state (Figure 30).³²⁵ The $12-MC_{Pd-3}$ complexes typically contain three Pd-Pd bonds, and like the Pt and Cu $12-MC-3$ structures, $12-MC_{Pd-3}$ will bind one or two μ_3 -guests such as CO ,^{263,325-330} chloride,^{326,329,331} sulfide,²⁵⁹ PF_3 ,^{331,332} dimethyl acetylenedicarboxylate ($\eta^2-CH_3O_2CC\equiv CCO_2CH_3$),³³³ iodide,^{327,332} $\eta^2-O_2CCF_3$,³²⁸ $C\equiv N-2,6-C_6H_3(CH_3)_2$,³³⁴ CH_3Cl ,³²⁹ and PF_2O_2 .³³⁰ In addition, some of the $12-MC_{Pd-3}$ complexes with one μ_3 -guest will bind an additional guest to one of the ring Pd centers such as cyanide,²⁵⁹ O_2CCF_3 ,³³³ and chloride.²⁶³

$12-MC-3$ complexes based on the dppm ligand have also been made with the metals nickel, silver, molybdenum, mercury, and ruthenium. The nickel, silver, and molybdenum $12-MC-3$ complexes also bind one or two μ_3 -guests, but they are not as common as platinum, copper, and palladium. $12-MC_{Ni-3}$ complexes have bound μ_3 -guests such as $\eta^1-C\equiv NCH_3$,³³⁵ iodide,³³⁵⁻³³⁹ $\eta^1-C\equiv CC_6H_5$,³⁴⁰ telluride,³⁴¹ CO ,³³⁷ thallium,³³⁸ $SnCl_2$,³³⁹ and $SnCl_3$.³³⁹ In addition, a $12-MC_{Ni-3}$ complex with a ligand related to dppm, bis(dimethylphosphino)methane, binds a μ_3-CO group.³⁴² $12-MC_{Ag-3}$ complexes bind μ_3 -guests such as bromide,^{343,344} chloride,^{345,346} $\eta^1-C\equiv CC_6H_5$,³⁴⁷ $\eta^1-C\equiv CC_6H_4NO_2-p$,³⁴⁸ $Fe(CO)_4$,³⁴⁹ η^1 -1,4-diethynylbenzene ($\eta^1-C\equiv CC_6H_4C\equiv C-p$) (this guest connects two $12-MC_{Ag-3}$ complexes and is isostructural to the $12-MC_{Cu^I-3}$ complex mentioned above),³¹² iodide,³²⁰ and SH .³⁵⁰ A $12-MC_{Ag-3}$ complex with a μ_3-Cl also binds a $\mu-S_2O_3$ on the opposite face.³⁴⁶ A $12-MC_{Mo-3}$ binds two μ_3-I guests within its central cavity.³⁵¹ The $12-MC_{Hg-3}$ complexes have weakly coordinated guest molecules, such as SO_4^{2-} ,³⁵² $O_3SCF_3^-$,³⁵³ SiF_6^{2-} ,³⁵⁴ PF_6^- ,³⁵⁴ and SCN^- ,³⁵⁵ within the cavity of the MC. Two $12-MC_{Ru-3}$ complexes have been synthesized with no μ_3 -guest but with the guest binding terminally to each ring Ru. In one structure each Ru is bound by two chloride anions and one bis(dimethylphosphino)methane ligand that binds bidentate to form a four-membered chelate ring³⁵⁶ (Figure 31), and in the second structure each Ru center is bound to two CO groups.^{357,358}

Several mixed-metal $12-MC-3$ complexes with the dppm ligand have been synthesized; they also bind a variety of

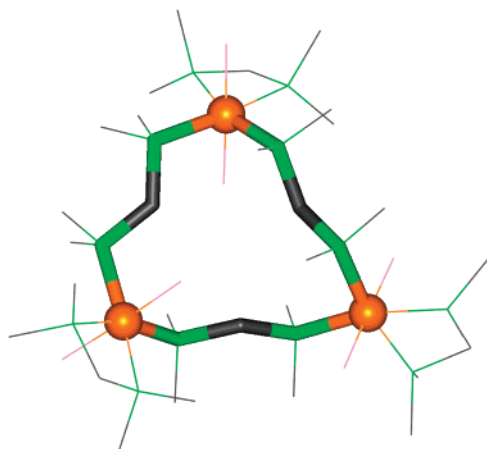


Figure 31. X-ray crystal structure of a [12-MC_{Ru^{II}-3] complex. Each Ru^{II} is surrounded by two chloride anions and one bidentate bis(dimethylphosphino)methane ligand. In addition, the dmpm ligand bridges between each Ru^{II} ion. Color scheme: orange sphere, Ru^{II}; gray tube, carbon; green tube, phosphorus; magenta line, chloride. Hydrogen atoms and lattice solvent have been removed for clarity.³⁵⁶}

guests. A 12-MC_{AuPt₂}-3 complex binds a μ_3 -sulfide.³⁵⁹ A 12-MC_{AuHg₂}-3 complex contains two CF₃SO₃⁻ anions located in cavities on opposite faces.³⁶⁰ A 12-MC_{PtIr₂}-3 complex contains in its cavity two CO groups, which bind terminally to the two Ir centers, and a μ -CO, which bridges the two Ir centers.³⁶¹ A second 12-MC_{PtIr₂}-3 complex exists with a CO arrangement similar to that of the first molecule but with an additional CO that binds terminally to the Pt center.³⁶¹ A 12-MC_{IrRu₂}-3 complex contains five CO groups and one H within the cavity.³⁶² Each Ru center is bound to two CO groups, and the Ir center is bound to a CO group and an H atom. A 12-MC_{PtCu₂}-3 binds a μ_3 - η^2 -3,4-toluenedithiolate and a μ -SH that bridges the two Cu centers.³⁶³ The isostructural 12-MC_{PtAg₂}-3 has also been synthesized.³⁶³

A number of 12-MC-3 complexes have been synthesized with P–N–P connectivity analogous to the P–C–P 12-MC-3 complexes.³⁶⁴ A trinuclear Rh^I complex made with bis(difluorophosphino)methylamine binds three μ -Cl anions in the [Rh–P–C–P]₃ ring to the three Rh^I ions.³⁶⁵ Two 12-MC_{Cu^I}-3 complexes with bis(diphenylphosphino)amine (dppa) as the bridging ligand provide a cavity to bind two guests. The central cavity is capped with either two μ_3 -Cl anions³⁶⁶ (Figure 32) or two μ_3 -SH anions.³⁶⁷ Two 12-MC_{Ni^I}-3 complexes have been synthesized that bind two μ_3 -I anions on opposite faces.³⁶⁸ A 12-MC_{Hg⁻³} complex made with dppa results in a [Hg–P–N–P]₃ macrocycle that hosts two trifluoromethanesulfonate anions within the cavity formed by the phenyl rings of the ligand.³⁶⁹ The anions are located on opposite faces of the 12-MC-3. A mixed-metal 12-MC_{CoPd₂}-3 complex with bis(diphenylphosphino)amine binds two μ_3 -CO groups on opposite faces of the macrocycle.³⁷⁰ The carbon atoms of the CO molecules are bound to the metal ions. In addition, the metals are disordered within the 12-MC-3 ring with two-thirds occupation by Pd and one-third occupation by Co. A ligand related to the dppm and dppa is (C₆H₅)₂AsCH₂As(C₆H₅)₂. This ligand is able to generate a 12-MC_{Pd}-3 complex with As–C–As bridges between the Pd^{2/3+} centers (Figure 33).³⁷¹ The 12-MC_{Pd}-3 structure contains a PF₆⁻ anion within the cavity created by the phenyl rings.

Although not as common as the above structures, 12-MC-3 metallacoronates have been synthesized with M–O–C–O

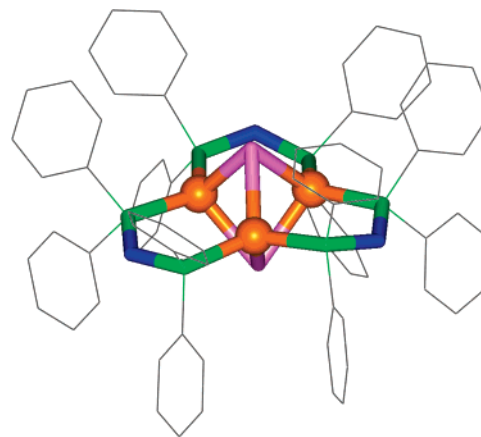


Figure 32. X-ray crystal structure of the $\{(\mu_3\text{-Cl})_2[12\text{-MC}_{\text{Cu}^{\text{I}}}\text{-3}]\}^+$ complex. The μ_3 -Cl ions bind on opposite faces of the Cu₃ core. The ligand bis(diphenylphosphino)amine bridges between each Cu^I center, and the structure is very similar to the complexes synthesized with bis(diphenylphosphino)methane. Color scheme: orange sphere, Cu^I; blue tube, nitrogen; green tube, phosphorus; magenta tube, chloride; gray line, carbon. Hydrogen atoms, Cl⁻ counteranion, and lattice solvent have been removed for clarity.³⁶⁶

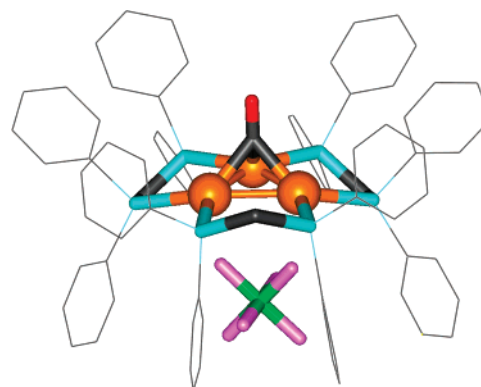


Figure 33. X-ray crystal structure of the $\{(\mu_3\text{-CO})[12\text{-MC}_{\text{Pd}}\text{-3}]\}^{2+}$ complex with bridges of As–C–As. Each Pd center has a 2/3+ charge, and three Pd–Pd bonds exist within the molecule with a μ_3 -CO group connecting the Pd centers. The ligand (C₆H₅)₂AsCAS-(C₆H₅)₂ bridges between each Pd center, and one PF₆⁻ anion is buried within the phenyl rings of the ligand. Color scheme: orange sphere: Pd^{2/3+}; gray tube, carbon; aqua tube, arsenic; red tube, oxygen; green tube, phosphorus; magenta tube, fluorine. Hydrogen atoms, a PF₆⁻ counteranion, and lattice solvent have been removed for clarity.³⁷¹

connectivity. A Fe^{II}[12-MC_{Fe^{II}}-3] metallacoronate exists in which three ring Fe^{II} ions bridged by a O–C–O moiety encapsulate a Fe^{II} central cation (Figure 34).³⁷² The three-atom repeat unit is provided by three bis(2-pyridylmethyl)glycine ligands. Three of the ring oxygen atoms bind to the central Fe^{II}. The encapsulation of the Fe^{II} is completed by three carboxylate groups from three benzoate anions that bridge each ring Fe^{II} to the central Fe^{II}. A structurally analogous compound has been made with bridging acetate anions.³⁷³ Another metallacoronate has been synthesized in which three Cu^{II} ions are connected via a O–C–O bridge from three *N*-(2-pyridylmethyl)-*S*-alanine ligands.³⁷⁴ Each 12-MC_{Cu^{II}}-3 binds one K^I within the central cavity to the ring oxygen atoms. In addition, the metallacoronates are linked together by perchlorate anions to form a one-dimensional chain. Zn^{II} ions may also construct a metallacoronate 12-MC-3 with bis(2-picolyl)glycine.³⁷⁵ The 12-MC_{Zn^{II}}-3 complex with repeat unit $-\text{[Zn}^{\text{II}}\text{-O-C-O]}-$ consists of a Zn^{II} ion in a distorted trigonal bipyramidal geometry, and the MC

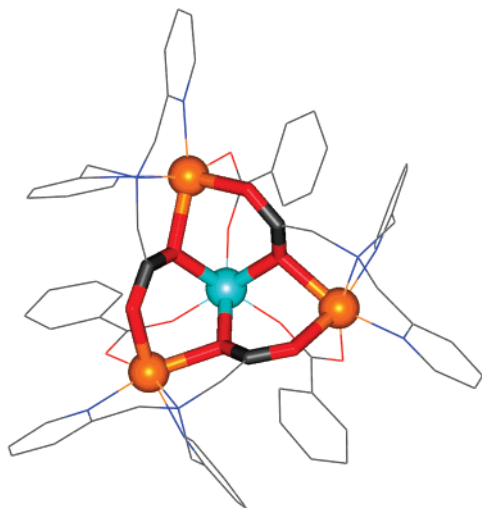


Figure 34. X-ray crystal structure of the $\{\text{Fe}^{\text{II}}[12\text{-MC}_{\text{Fe}^{\text{II}}}\text{-3}]\}^{2+}$ complex with the ligand bis(2-pyridylmethyl)glycine providing the O–C–O bridging moiety. The Fe^{II} MC ring encapsulates a Fe^{II} ion within the central cavity. Color scheme: aqua sphere, central Fe^{II} ; orange sphere, ring Fe^{II} ; red tube, oxygen; blue line, nitrogen; gray line, carbon. Hydrogen atoms and ClO_4^- counteranions have been removed for clarity.³⁷²

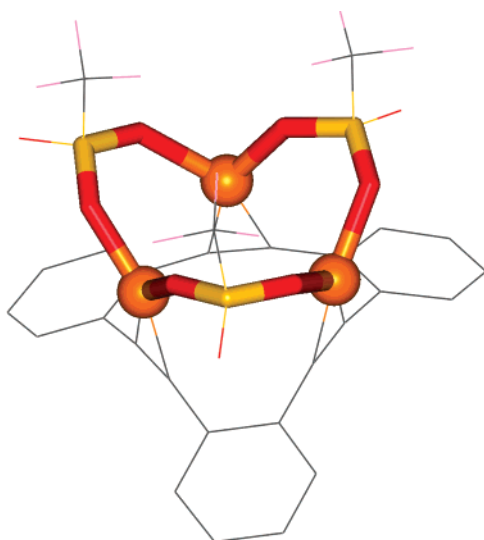


Figure 35. X-ray crystal structure of the vacant $[12\text{-MC}_{\text{Cu}^{\text{I}}}\text{-3}]$ complex. Three triflate anions (CF_3SO_3^-) provide the O–S–O bridges between the Cu^{I} ions. The bottom ring of the molecule is composed of one 1,2,5,6,9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-tri-ene ligand. Color scheme: orange sphere, Cu^{I} ; red tube, oxygen; yellow tube, sulfur; gray line, carbon; magenta line, fluorine. Hydrogen atoms have been removed for clarity.³⁷⁷

does not bind any guests within the central cavity. Along these lines a 12- $\text{MC}_{\text{V}}\text{-3}$ complex with a bridging group of O–Si–O has been synthesized. The O–Si–O bridge is provided by three di-*tert*-butylsilandiolate ligands, and the MC ring does not bind a guest within its cavity.³⁷⁶

Various 12-MC-3 complexes exist with rare three-atom bridges between the ring metals. In one structure, three Cu^{I} ions are connected by O–S–O from three triflate ligands (Figure 35).³⁷⁷ The 12-MC-3 structure is vacant. An aluminum 12-MC-3 has been synthesized with O–P–O connectivity (Figure 36).³⁷⁸ The structure consists of two 12-MC-3 rings, which bind one Na^{I} ion each with all six ring oxygen atoms. The 12-MC-3 rings then are connected by a $[\text{Na}_4\text{O}_6]^{8-}$ moiety. A final 12-MC-3 structure consists of Cu^{I} ions connected by a N–N–N bridge supplied by three

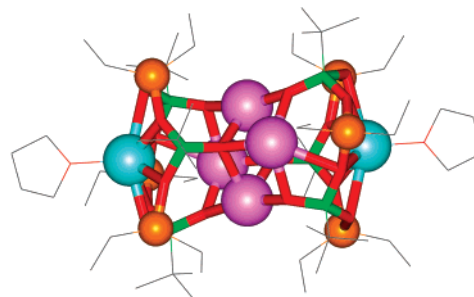


Figure 36. X-ray crystal structure of the $\text{Na}_4\text{O}_6\{\text{Na}[12\text{-MC}_{\text{Al}^{\text{III}}}\text{-3}]\}_2$ complex. The MC ring consists of a $-\text{[Al}^{\text{III}}\text{-O-P-O]}-$ repeat unit and encapsulates one Na^{I} ion within the central cavity. The two MC rings are then connected via four Na^{I} ions. Color scheme: orange sphere, Al^{III} ; aqua sphere, central Na^{I} ; magenta sphere, bridging Na^{I} ; red tube, oxygen; green tube, phosphorus; gray line, carbon. Hydrogen atoms have been removed for clarity.³⁷⁸

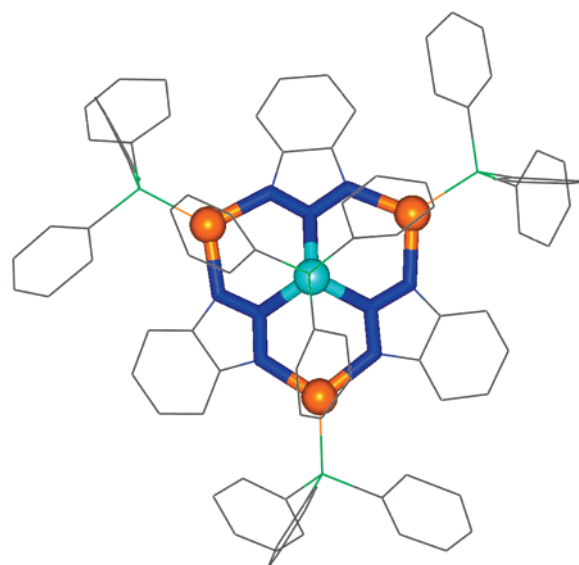


Figure 37. X-ray crystal structure of the $\{\text{Cu}^{\text{I}}[12\text{-MC}_{\text{Cu}^{\text{I}}}\text{-3}]\}^+$ complex with three benzotriazole (Hbta) ligands, which bridge the three ring Cu^{I} ions. The central Cu^{I} is bound to three N atoms from three bta ligands. The coordination sphere of each Cu^{I} is completed by a $\text{P}(\text{C}_6\text{H}_5)_3$ ligand. Color scheme: aqua sphere, central Cu^{I} ; orange sphere, ring Cu^{I} ; blue tube, nitrogen; green line, phosphorus; gray line, carbon. Hydrogen atoms, the $\text{Cu}^{\text{I}}(\text{P}(\text{C}_6\text{H}_5)_3)^+$ cation, and BF_4^- counteranions have been removed for clarity.³⁷⁹

benzotriazole ligands (Figure 37).³⁷⁹ In the central cavity, a Cu^{I} ion is bound by three nitrogen atoms from the 12-MC-3 ring and a PPh_3 group is bound axially to complete the coordination of the central Cu^{I} ion. Table 1 gathers some characteristic properties of 12-MC-3 complexes, such as metal–metal distances within the MC structure and the nature of encapsulated cationic and/or anionic guests.

2.4. 12-MC-4

The traditional 12-MC-4 complexes with M–N–O connectivity represent the first 12-MC-4 complexes to be described. The first recognized 12-MC-4 was $\text{Mn}^{\text{II}}(\text{O}_2\text{-CCH}_3)_2[12\text{-MC}_{\text{Mn}^{\text{II}}\text{N}(\text{shi})}\text{-4}]$, where shi^{3-} is salicylhydroximate (Figure 38).¹⁶⁶ When this ligand is bound as a cis isomer for a bis-bidentate chelate in a propeller configuration (either $\Lambda\Lambda\Lambda$ or $\Delta\Delta\Delta$), the 9-MC-3 structure is adopted. When the four shi^{3-} ligands are trans, the 12-MC-4 macrocycles are obtained. The structure is nearly planar with a ring connectivity of $\text{Mn}^{\text{III}}\text{-N-O}$. The planarity of the metallamac-

Table 1. Ligands and Metals Used for the Synthesis of 12-MC-3 Complexes, Their Guests (Neutral Guests Are in Bold), and M–M Distances

bridging ligand	ring-metal	cationic guest	anionic guest	av M–M distance (Å)	ref	CCDC refcode		
3-hydroxy-2-pyridone	Ru(II)			5.38	228	QOPQER		
				5.32	229	TIHJUP		
				5.46	229	TIHKOK		
				5.28	230	EFURIG		
				5.39	235	EKUTAF		
			Li	F	5.34	231	AGUHIT	
			Li	Cl	5.36	228	QOPQIV	
			Li	Cl	5.38	229	TIHKEA	
			Li	Cl	5.47	229	TIHKIE	
			Li	Cl	5.33	230	EFUROM	
			Li	HF ₂	5.37	231	AGUHUF	
			Li	BF ₄	5.41	231	AGUHAL	
			Na	Cl	5.36	228	QOPQAN	
			Na	Cl	5.34	230	EFURUS	
			Na	Br	5.38	229	TIHJOJ	
			Na	I	5.42	229	TIHKAW	
			Na	BF ₄	5.43	232	AHAKEZ	
			Na	SiF ₆	5.42	232	AHAKID	
			Rh(III)			5.34	229	TIHJID
			Li	F		5.40	231	AGUHOZ
			Li	BF ₄		5.48	231	AGUHEP
			Ir(III)			5.37	233	MODSUT
			Li	F		5.43	233	MODTAA
			Li	HF ₂		5.44	231	AGUJAN
	Li	BF ₄		5.49	233	MODTEE		
<i>N</i> -(2-hydroxy-3-pyridinyl)acetamide	Ru(II)			5.26	229	TIHJEZ		
4-piperidinomethyl-3-hydroxy-2-pyridone	Ru(II)			5.33	234	AMACEW		
5-chloro-3-hydroxy-2-pyridone	Ru(II)			5.27	236	UHUPES		
		Li	Cl	5.39	236	UHUPIW		
		Na	Cl	5.37	236	UHUPOC		
2,3-dihydroxyquinoline	Ru(II)			5.28	237	ITEBIS		
4-(morpholinomethyl)-3-oxopyridine-2(1 <i>H</i>)-one	Ru(II)			5.37	238	FAZLIC		
	Ir(III)			5.37	238	FAZMAV		
4-(4-methylpiperazinylmethyl)-3-oxopyridine-2(1 <i>H</i>)-one	Ru(II)			5.33	238	FAZLOI		
	Rh(III)			5.35	238	FAZLUO		
9-ethylhypoxanthine	Rh(III)			5.57	240	ZAPRIR		
9-methyladenine	Rh(III)			5.59	242	JUTCIK		
adenosine-5'-monophosphate	Ru(II)			5.59	246	REYXEY		
9-ethyladenine	Ru(II)			5.67	247	TIWQIZ		
	Ir(III)			5.62	248	XEDMIC		
2,6-bis[(1-methyltetrazol-5-yl)amido]pyridine	Fe(II) ₂ Ni(II)		O	3.28	251	UDAWEB		
	Fe(II) ₂ Ni(II)		O	3.29	251	UDAWIF		
1,3,5-(6,14,22-triethylene-1,3,6,9,11,14,17,19,22-nonaazacyclotetracosane)-1,3,5-triazacyclohexane	Cu(II)		O	3.11	252	SOJDUQ		
6,14,22-(1,3,5-triethylene-1,3,5-triazacyclohexane)-1,3,6,9,11,17,19,22-nonaazacyclotetracosane-1,9,17-triene	Cu(II)	Cu(I)	OH	3.26	252	SOJJOQ		
1,4,6,9,12,14,17,20,22,24,29,31-dodecaazatetracyclo(15.9.7.2 ^{9,22} .1 ^{20,24})hexatriacontane	Cu(II)		OH	3.27	254	UNAKEZ		
bis(diphenylphosphino)methane	Pt	CO	SCN	2.62	259	FAKJOQ		
		CO		2.63	260	DOSHAU		
		CO	CN	2.61	261	JURTEV		
				2.62	262	JURTEV10		
		CO	Cl	2.62	263	PUKLEM		
		CO	P(OEt)₃	2.64	271	KEHPES		
		CO	Me₂NCS₂	2.61	272	VESRUG		
		CO	Tl(H₂O)(acac)	2.64	289	XIFTIP		
		CO	Tl(F₃CCO₂)	2.64	289	XIFTOV		
			(^tBuCOCH₂COMe)					
		2 CO	PtPPh ₃	2.65	299	XISFEK		
		3 CO	IrP(OMe) ₃		300	PUFHED		
					301	PUFHED 01		
		CO(Cl)	SnF ₃	2.66	278	VAFZOR		
		S	H	2.63	264	DUVWUM		
				3.28	265	DUVWUM10		
		C₂	Cl	3.06	266	FULBIX		
		CO	EtO–C=CH	3.08	268	KIXNAG		
		P(OMe)₃	H	2.64	269	JIZBEZ		
					270	JIZBEZ10		
		2,6-xylyliso-	2,6-xylyliso-		273	JEXGAU		
		cyanido	cyanido		275	JEXGAU10		
		Me–NC	Me–NC	2.65	274	KOHXEK		

Table 1. (Continued)

bridging ligand	ring-metal	cationic guest	anionic guest	av M–M distance (Å)	ref	CCDC refcode
bis(diphenylphosphino)methane		F ₂ PO ₂ SnMe ₂		2.62	278	VAFZIL
		SnF ₃	SnF ₃	2.62	279	KISCIY
		AuPMe ₃	AuPMe ₃	2.64	280	SORHUC
		AuPPh ₃	AuPPh ₃	2.62	286	HIFFIL
		Re(CO) ₃		2.61	281	PESWIT
					283	PESWIT10
		Re(CO) ₃	2 O	3.00	281	PESWOZ
					294	PESWOZ10
		Re(CO) ₃	2 S	3.17	291	POLDAV01
					292	POLDAV
		Re(CO) ₃	I	2.60	284	ZAF CIS
		Re(CO) ₃	P(OPh)₃	2.64	285	POLMEI
					293	POLMEI10
		Re(CO) ₃	O, S	3.18	290	YIVLEW
					291	YIVLEW01
		Re(CO) ₃	O, S	3.07	291	RUNGIQ
		ReO ₃		2.60	282	YECFER
		ReO ₃		2.61	287	ZOTNEB
		ReO ₃	Hg	2.62	287	ZOTNIF
		HgOReO ₃		2.64	287	ZOTNOL
		HgRu(CO) ₂ Cp		2.65	288	HAFSEM
		Re(CO) ₂ P(OMe) ₃	2 O	3.01	295	RIJRAD
		PtPPh ₂ CH ₂ PPh ₂ O	2 CO		296	CACGES
		PtPPh ₂ CH ₂ PPh ₂ O	2 CO, H	2.65	297	FUVVUN10
					298	FUVVUN
		Ru(CO) ₂	2 CO, H	2.65	302	GUDHOC
			OH	3.19	303	CEMTUJ
			OH, NO ₃	3.18	304	DOKQID
		Cu	Ph–C ₂	3.00	305	JEBPAH
					307	JEBPAH10
			2 Ph–C ₂	2.59	306	SITNIS
					307	SITNIS10
			Ph–C ₂ , Cl	2.82	307	WARTIS
			^t Bu–C ₂ , Cl	2.82	309	WARKEF
			3-methyl-8-ethyl-xanthinato, Cl	3.22	310	YILLUA
			2 Cl	3.05	311	RIPHON
			2 Br	3.18	315	GOGKES
			2 Br	3.08	316	HOMTUY
			2 I	3.17	316	HOMVAG
			2 I	3.21	320	WOYZUF
			C ₂ –C ₆ H ₄ –C ₂	3.00	312	RUFREP
			2 Me–C ₆ H ₄ –C ₂	2.86	313	NEVWUG
			2(4,4'-bipy)Re(CO) ₃ -C ₂ –C ₆ H ₄ –C ₂	2.63	314	SACFIL
			WO ₄	3.07	323	HOSYET
			WS ₄	3.88	315	GOGJUH
			WS ₄	3.89	315	GOGKAO
			WS ₄	3.89	322	YONXUU
	MoS ₄	3.86	324	WOJBEC		
	EtO–C ₆ H ₄ –C ₂	2.60	317	GAMNEN		
	MeO–C ₆ H ₄ –C ₂					
	NO ₂ –C ₆ H ₄ –C ₂	2.67	317	GAMNIR		
	MeO–C ₆ H ₄ –C ₂					
	MeO–C ₆ H ₄ –C ₂	2.61	318	WIWZAD		
	MeO–C ₆ H ₄ –C ₂					
Pd	CO	2.60	325	CASMUE		
	CO	2.62	328	LIDLOZ		
	CO	2.59	328	LIDLUF		
	CO	2.61	330	BASFUX		
	CO	2.59	326	CUTJIK		
	CO	2.60	329	NEJFIR		
	CO	2.59	263	PUKLAI		
	CO	2.59	327	JUZRAX		
	PF₃	2.58	331	SIMBEV		
	PF₃	2.59	332	HAKTOC		
	Me ₂ -butanedioate	3.05	333	YADZOS		
	xylylisocyano	2.62	334	HEDFUR		
	S, CN	3.20	259	FAKJUW		
Ni	2 I	2.52	336	WASXAP		
			337	WASXAP10		
	2 I	2.49	336	WASWUI		

Table 1. (Continued)

bridging ligand	ring-metal	cationic guest	anionic guest	av M–M distance (Å)	ref	CCDC refcode		
bis(diphenylphosphino)methane	Ni		2 Te	2.56	337	WASWUI10		
			I	2.40	341	TEBMOC		
			CO	2.40	337	ZUCSEV		
			Me–NC	2.42	335	JEYYIV		
			TII	2.51	338	HUMXOC		
			SnCl ₂	2.50	339	XONLER		
			SnCl ₃	2.46	339	XONLAN		
			2 Ph–C ₂	2.39	340	ZESVOI		
			Ag		2 Cl	3.38	345	SAJKET
					2 Br	3.31	344	MDPAGB10
	2 I	3.24			320	WOZBAO		
	Cl, S ₂ O ₃				346	BAVVAV		
	2 Ph–C ₂	2.94			347	TEQSEN		
	4-NO ₂ –C ₆ H ₄ –C ₂	3.16			348	RUMWOL		
	(4-NO ₂ –C ₆ H ₄ –C ₂) ₂	3.01			348	RUMWUR		
	Fe(CO) ₄	2.97			349	GUCDX		
	C ₂ –C ₆ H ₄ –C ₂	3.19			350	RUFRICT		
	2 I	3.25			351	MUVFAK		
	Mo			2.78	352	VEDGUG		
				2.78	354	BILJUB		
				2.81	354	BILLAJ		
				2.75	354	BILLIR		
				2.82	354	BILLUD		
				2.78	354	BILNAL		
				2.78	354	BILPIV		
				2.82	355	WEDQUR		
				2.85	358	LAHXEX		
				2.89	358	LAHXIB		
	Hg			3.00	359	YAYWAW		
				2.77	360	YIJJAC		
				2.66	361	HICFOO		
				2.81	362	BOJWEC		
			3.36	363	ASARIV			
			3.36	363	ASASAO			
			2.98	267	VACZAA			
			2.63	276	FETPID			
			2.42	342	VESSAN			
			6.90	356	VOMSUL			
bis(diphenylphosphino)methane; 3,3-bis(diphenylphosphino)propenyl	Pt	C ₂		2.62	277	ZANJED		
				3.84	321	WEBDIQ		
bis(dimethylphosphino)methane	Pt	CO	dppm	3.86	321	WEBDOW		
				3.10	365	KASDOX10		
bis(3,5-dichlorophenylphosphino)methane	Pt	CO	6 Cl	2.99	366	JILPOJ		
			F ₃ CCO ₂	3.05	367	HACBOD		
bis(di- <i>tert</i> -butylphosphino)methane	Cu		F	2.48	368	OKELAR		
				2.46	368	OKELAV		
bis(difluorophosphino)methylamine	Rh		3 Cl	2.80	369	METQIL		
			2 Cl	2.53	370	CIGLIN		
bis(diphenylphosphino)amine	Cu		2 SH	2.60	371	ZUCZAY		
				2.58	371	ZUCZEC		
bis(diphenylphosphino)methylamine	Pd ₂ Co	2 CO	I	5.48	372	HERNOH		
				5.86	373	WEQYEW		
bis(diphenylarsino)methane	Pd	CO	3 PhCO ₂	5.25	375	YUBBAY		
			CH ₃ CO ₂	5.21	374	IKOTUX		
<i>N,N</i> -bis(2-pyridylmethyl)glycinate	Fe		O, Cl	4.92	376	WAGVOP		
				3.67	377	GEKZOL		
<i>N</i> -(2-pyridylmethyl)-L-alanine	Zn			5.80	379	SUXCIX		
^t Bu ₂ SiO ₂	V							
1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-tri- <i>yne</i>	Cu							
benzotriazole	Cu	CuPPh ₃	3 PPh ₃	5.80	379	SUXCIX		

rocycle is due to the ligand. By using fused five- and six-membered chelate rings to connect adjacent metals, the metals are placed at 90° with respect to each other. This coordination is perpetuated about the macrocycle, and the result is a nearly planar structure. The MC ring is neutral because the four shi³⁻ ligands are balanced by the four Mn^{III} ring ions. Within the central cavity a Mn^{II} ion is captured by the four ring hydroxamic oxygen atoms. The Mn^{II} is further attached to the MC ring by two acetate anions that

bridge the central Mn^{II} to two trans ring Mn^{III} ions. A Mn^{II}-[12-MC_{Mn^{III}N(shi)-4}]²⁺ complex has also been made in which two benzoate anions bridged the central Mn^{II} to two trans ring Mn^{III} ions.³⁸⁰ 12-MC_{Mn^{III}N(shi)-4} complexes can host a variety of metal ions within the central cavity including Na^I (two ions),^{381–383} Li^I (one ion) (Figure 39),³⁸² K^I (two ions),^{382,383} a Mn^{II}O₂ core,³⁸⁴ Dy^{III},³⁸⁵ and Y^{III}.³⁸⁵

12-MC-4 complexes with Cu^{II} ring metal ions have also proven to be ubiquitous. Using shi³⁻, a (TEA)₂{Cu^{II}[12-

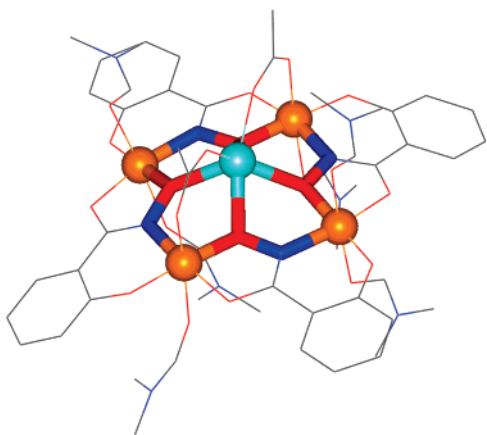


Figure 38. X-ray crystal structure of $\text{Mn}^{\text{II}}(\text{O}_2\text{CCH}_3)_2[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{Nshi})-4}] \cdot 6(\text{CH}_3)_2\text{NCHO}$. The salicylhydroximate (shi^{3-}) ligand forms fused five- and six-membered chelate rings, which place the ring metal ions at 90° with respect to each other to create a nearly planar complex. An Mn^{II} ion is captured within the central cavity and linked to the MC ring via two acetate anions. Color scheme: aqua sphere, central Mn^{II} ; orange sphere, ring Mn^{III} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.¹⁶⁶

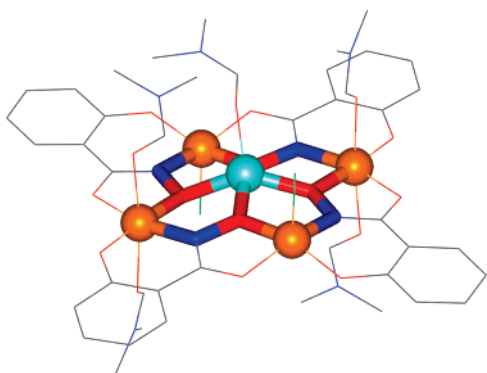


Figure 39. X-ray crystal structure of the $\text{Li}(\text{Cl})_2[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{Nshi})-4}] \cdot 5(\text{CH}_3)_2\text{NCHO}$ complex. Two chloride anions are bound to two ring Mn^{III} ions, and one Li^+ is captured within the central cavity to give the MC an overall 1^- charge, which is balanced by a Li^+ cation within the lattice. The structure has a similar topology to the $\text{Mn}^{\text{II}}(\text{O}_2\text{CCH}_3)_2[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{Nshi})-4}]$ complex. Color scheme: aqua sphere, central Li^+ ; orange sphere, ring Mn^{III} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon; green line, chloride. Hydrogen atoms, Li^+ counteraction, and lattice solvent have been removed for clarity.³⁸²

$\text{MC}_{\text{Cu}^{\text{II}}(\text{Nshi})-4}]$ complex has been synthesized (where TEA is tetraethylammonium) that has a structure very similar to that of $\text{Mn}^{\text{II}}(\text{O}_2\text{CCH}_3)_2[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{Nshi})-4}]$.³⁸⁶ Both complexes are nearly planar, but the MC ring of the $12\text{-MC}_{\text{Cu}^{\text{II}}(\text{Nshi})-4}$ has a formal charge of 4^- because each ligand is 3^- (12^- total) and there are only four ring Cu^{II} ions. A central Cu^{II} and two TEA^+ cations provide charge balance. Several other $\text{Cu}^{\text{II}}[12\text{-MC}_{\text{Cu}^{\text{II}}-4}]$ complexes with shi^{3-} type ligands have been reported.^{386–388} One complex uses the ligand 2-aminophenylhydroxamic acid (Figure 40).³⁸⁷ The ligand is very similar to H_3shi , but the hydroxyl group has been replaced by an amine group. The 2^- charge of the ligand results in a neutral MC ring, and the excess 2^+ charge is balanced by a SO_4^{2-} anion. In the solid state, the two MCs bind via two $\text{Cu}^{\text{II}}_{\text{ring}}-\text{O}_{\text{carbonyl}}$ bonds to create a “clam” structure with the MC acting as the shells of the bivalve and the $\text{Cu}^{\text{II}}_{\text{ring}}-\text{O}_{\text{carbonyl}}$ bonds as the hinge. Using β -alaninehydroxamic acid, Kurzak and co-workers synthesized a similar 12-MC-4 complex (Figure 41).³⁸⁹ The structure is very similar to the

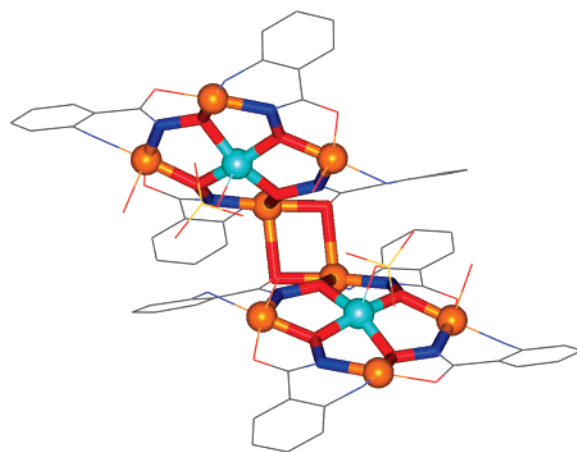


Figure 40. X-ray crystal structure of the $\{\text{Cu}^{\text{II}}\text{SO}_4[12\text{-MC}_{\text{Cu}^{\text{II}}-4}] \cdot 2\text{H}_2\text{O}\}_2 \cdot 10\text{H}_2\text{O}$ complex with the ligand 2-aminophenylhydroxamic acid. The two metallacrowns connect via $\text{Cu}^{\text{II}}_{\text{ring}}-\text{O}_{\text{carbonyl}}$ bonds to create a clam-like structure. Color scheme: aqua sphere, central Cu^{II} ; orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon; yellow line, sulfate. Hydrogen atoms and lattice solvent have been removed for clarity.³⁸⁷

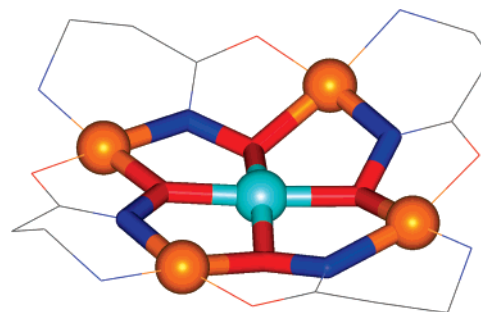
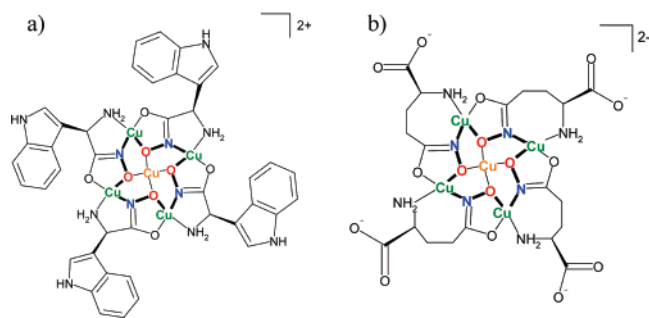


Figure 41. X-ray crystal structure of the $\text{Cu}^{\text{II}}[12\text{-MC}_{\text{Cu}^{\text{II}}-4}]^{2+}$ complex with the ligand β -alaninehydroxamic acid. Color scheme: aqua sphere, central Cu^{II} ; orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms, methyl groups of the ligand, ClO_4^- counteranions, and lattice solvent have been removed for clarity.³⁸⁹

other $\text{Cu}^{\text{II}}[12\text{-MC}_{\text{Cu}^{\text{II}}-4}]$ complexes. Like shi^{3-} , β -amino hydroxamic acids are capable of placing the ring metals at 90° with respect to each other to create a nearly planar structure. In addition, the ligands have a 2^- charge, which generates a neutral MC ring. Each ligand forms a five- and six-membered chelate ring. One Cu^{II} ion is bound by the hydroxamic nitrogen and amine nitrogen in the six-membered chelate ring, whereas the carbonyl and hydroxamic oxygens bind the second Cu^{II} in the five-membered chelate ring. Chiral $\text{Cu}^{\text{II}}[12\text{-MC}_{\text{Cu}^{\text{II}}-4}]$ may be synthesized using substituted β -amino hydroxamic acids. *S*- β -Phenylalanine has been used to create such a chiral structure.^{390,391} Similar ligands such as 3-(dimethylamino)propanamidoxime, 3-amino-3-hydroxyimino propanoic hydroxamic acid, and 3-hydroxyiminobutanoic hydroxamic acid are also capable of making $\text{Cu}^{\text{II}}[12\text{-MC}_{\text{Cu}^{\text{II}}-4}]$ by forming fused five- and six-membered chelate rings.^{392–394} $\text{Cu}^{\text{II}}[12\text{-MC}_{\text{Cu}^{\text{II}}-4}]$ structures have been proposed for pentanuclear complexes that use ligands such as α -amino hydroxamic acids^{395–400} and 2-picoline hydroxamic acid,⁴⁰⁰ which join the Cu^{II} ions via two fused five-membered chelate rings (Scheme 4). Also, *S*-glutamic- γ -hydroxamic acid⁴⁰¹ (Scheme 4) and *S*-*N*-(3-hydroxycarbonylpropionyl)-phenylalanine^{402a} have been proposed to produce a $\text{Cu}^{\text{II}}[12\text{-MC}_{\text{Cu}^{\text{II}}-4}]$ with five- and seven-membered fused chelate rings. A recent crystal structure of a $\text{Cu}^{\text{II}}[12\text{-MC}_{\text{Cu}^{\text{II}}-4}]$ with

Scheme 4. Proposed Cu^{II} [12-MC $_{\text{Cu}^{\text{II}}}$ -4] Complexes for (a) *S*-Tryptophanhydroxamic Acid with Fused Five-Membered Chelate Rings and (b) *S*-Glutamic- γ -hydroxamic Acid with Fused Five- and Seven-Membered Chelate Rings^{395,401}



γ -aminobutane-hydroxamic acid confirms the possibility of constructing 12-MC-4 structures with fused five- and seven-membered chelate rings (Figure 42).^{402b} In addition, a Cu^{II} -[12-MC $_{\text{Cu}^{\text{II}}}$ -4] with 5- and 10-membered fused chelate rings is proposed for *S*-*N*-(3-hydroxycarbonylpropionyl)proline.^{402a} These proposed structures are based on excellent potentiometric, spectrophotometric, and electrospray mass spectrometric data. Two vacant 12-MC $_{\text{Cu}^{\text{II}}}$ -4 complexes with oxime ligands, 6-amino-3-methyl-4-aza-hex-3-en-2-one and dimethylglyoxime, have been synthesized.^{403,404} The structures are not as planar as the Cu^{II} [12-MC $_{\text{Cu}^{\text{II}}}$ -4] structures but adopt a butterfly configuration. The structures contain no fused chelate rings; thus, the structure has a greater extent of flexibility. A planar, vacant 12-MC $_{\text{Cu}^{\text{II}}}$ -4 can be synthesized with the oxime ligand 1,3-dimethylvioluric acid (Figure 43).⁴⁰⁵ The ligand creates fused five- and six-membered chelate rings and provides the 12-MC $_{\text{Cu}^{\text{II}}}$ -4 with planarity.

Four structural types have been recognized for 12-MC $_{\text{Ni}^{\text{II}}}$ -4 complexes. The first type is analogous to the 12-MC $_{\text{Cu}^{\text{II}}}$ -4 complexes. (TMA) $_2\text{Ni}^{\text{II}}$ [12-MC $_{\text{Ni}^{\text{II}}\text{N}(\text{shi})}$] (TMA = tetramethylammonium) has a ring of four Ni^{II} ions with a fifth Ni^{II} ion bound in the center of the ring.⁴⁰⁶ This metallacrown has three pyridine molecules bound, two to Ni^{II} ions in the ring and the third one to the central Ni^{II} ion. The overall structure deviates from planarity in a slight bowl shape with the

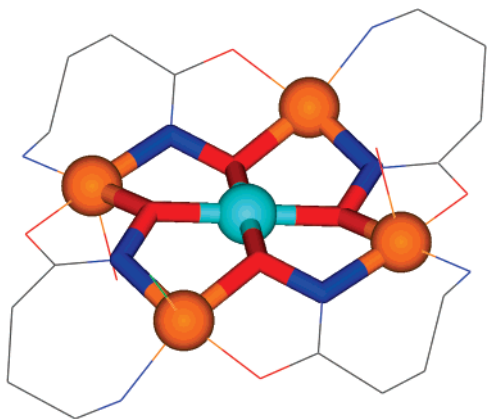


Figure 42. X-ray crystal structure of $\text{Cu}^{\text{II}}\text{Cl}_2[12\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{gabaHA})}\text{-4}]$, where gabaHA = γ -aminobutanehydroxamic acid. This is the first crystal structure using a γ -aminohydroxamic acid. Previous 12-MC-4 structures with β -aminohydroxamic acids were based upon six- and five-membered fused chelate rings. This metallacrown uses seven- and five-membered fused chelate rings to create a 12-MC-4. Color scheme: aqua sphere, central Cu^{II} ; orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon; green line, chloride. Hydrogen atoms and lattice solvent have been removed for clarity.^{402b}

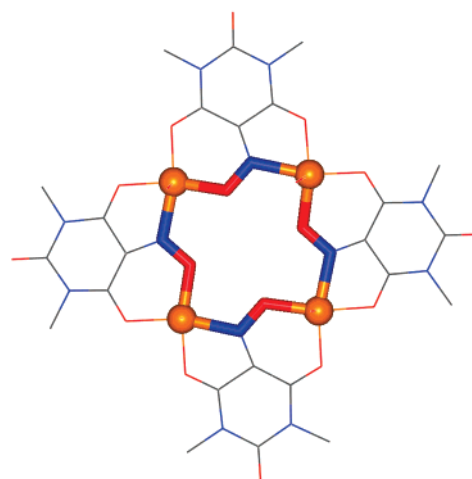


Figure 43. X-ray crystal structure of the vacant $[12\text{-MC}_{\text{Cu}^{\text{II}}}\text{-4}]^{4+}$ complex with the 1,3-dimethylvioluric acid. The fused five- and six-membered chelate rings impart planarity upon the metallacrown structure. Color scheme: orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms, ClO_4^- counteranions, and lattice solvent have been removed for clarity.⁴⁰⁵

pyridine molecules on the outside of the bowl. The central nickel ion is displaced 0.37 Å from the least-squares plane of the four metallacrown ring oxygen atoms. The cavity radius is 0.59 Å, consistent with the 0.63 Å ionic radius of five-coordinate Ni^{II} . In the similar (TMA) $_3\text{Ni}^{\text{II}}(\text{OAc})[12\text{-MC}_{\text{Ni}^{\text{II}}\text{N}(\text{nHA})}\text{-4}]$ (nHA = 3-hydroxy-2-naphthohydroxamic acid), an acetate ion bridges the central Ni^{II} ion to a ring Ni^{II} ion, making them five-coordinate. The other three Ni^{II} ions are four-coordinate in a square planar configuration. In this case, the cavity radius is smaller (0.52 Å) and the central Ni^{II} ion is displaced 0.48 Å from the least-squares planes of the four oxime oxygen atoms. The five-coordinate ring Ni^{II} ion is pulled out of the plane 0.96 Å, whereas the four-coordinate Ni^{II} ions have smaller deviations from planarity (0.11–0.35 Å). In the other three types, the complexes have a mixture of two ligands, H_3shi and di-2-pyridyl ketone oxime (Hpko). Fused five- and six-membered chelate rings can also be generated with Hpko. A $\text{Ni}^{\text{II}}[12\text{-MC}_{\text{Ni}^{\text{II}}}\text{-4}]^{2+}$ with two pko^- and two shi^{3-} ligands has been synthesized that is similar to the manganese and copper 12-MC $_{(\text{M})\text{N}(\text{shi})}\text{-4}$ complexes (Figure 44).^{407,408} Interestingly, the structure does not contain alternating five- and six-membered chelate rings about the macrocycle as in the all shi^{3-} 12-MC-4 complexes (5–6–5–6–5–6–5–6). The pko^- and shi^{3-} ligands alternate about the cyclic structure and generate a pattern of 5–5–6–6–5–5–6–6-membered chelate rings. In addition, two metallacrowns, $\text{Ni}^{\text{II}}[12\text{-MC}_{\text{Ni}^{\text{II}}\text{N}(\text{shi})_2(\text{pko})_2}\text{-4}]^{2+}$ and $\text{Ni}^{\text{II}}[12\text{-MC}_{\text{Ni}^{\text{II}}\text{N}(\text{shi})_2(\text{pko})}\text{-4}]$, can be synthesized that are fused together by eight $\text{Ni}^{\text{II}}\text{-O}$ bonds (Figure 45).^{407,409,410} One of the Ni^{II} of the neutral MC is not bound to the positive MC and vice versa. The $\text{Ni}^{\text{II}}[12\text{-MC}_{\text{Ni}^{\text{II}}\text{N}(\text{shi})_3(\text{pko})}\text{-4}]$ has a chelate ring pattern of 6–6–5–5–6–5–6–5. In addition, a vacant $[12\text{-MC}_{\text{Ni}^{\text{II}}\text{N}(\text{Hshi})_2(\text{pko})_2}\text{-4}](\text{SCN})_2$ complex may be synthesized by using two pko^- ligands and two doubly deprotonated Hshi^{2-} ligands (Figure 46).^{407,408} The structure is not planar and adopts a configuration reminiscent of a class of molecules known as molecular tweezers.^{411,412} The chelate ring pattern is 5–6–5–6–5–6–5–6.

Zinc has been used to create 12-MC-4 complexes that encapsulate both Zn^{II} ions and $\mu_3\text{-OH}$ anions. Using four pko^- ligands with Zn^{II} ions generates an inverse 12-MC-4 that binds two $\mu_3\text{-OH}$ anions (Figure 47).^{183,413,414} The *inv*MC

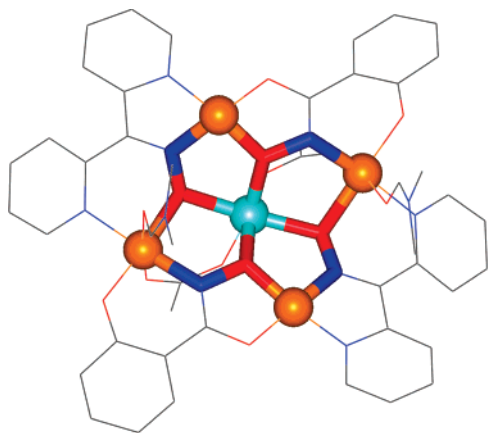


Figure 44. X-ray crystal structure of the $\text{Ni}^{\text{II}}(\text{O}_2\text{CCH}_3)_2[12\text{-MC}_{\text{Ni}^{\text{II}}\text{N}(\text{shi})_2(\text{pko})_2-4}] \cdot 2(\text{CH}_3)_2\text{NCHO}$ complex with the two shi^{3-} and two pko^- ($\text{Hpko} = \text{bis}(2\text{-pyridyl}) \text{ ketone oxime}$) ligands. The mixed ligand complex has a chelate ring pattern of 5-5-6-6-5-5-6-6. Two bridging acetate and two DMF molecules complete the coordination sphere of two ring and the central nickel ions. Color scheme: aqua sphere, central Ni^{II} ; orange sphere, ring Ni^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁴⁰⁷

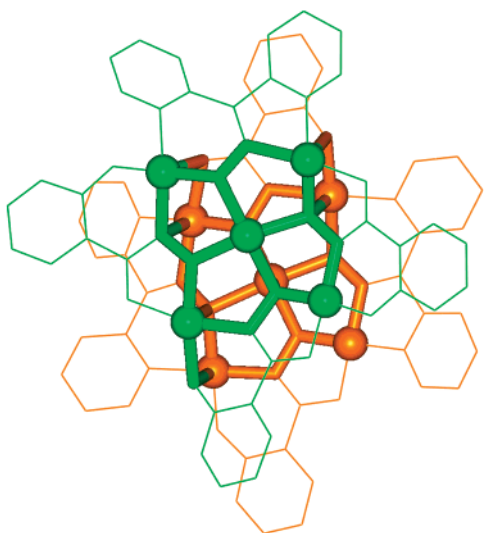


Figure 45. X-ray crystal structure of the fused metallacrowns $\text{Ni}^{\text{II}}-[12\text{-MC}_{\text{Ni}^{\text{II}}\text{N}(\text{shi})_2(\text{pko})_2-4}]^{2+}$ (orange) and $\text{Ni}^{\text{II}}[12\text{-MC}_{\text{Ni}^{\text{II}}\text{N}(\text{shi})_2(\text{pko})_2-4}]$ (green). The MCs are connected via eight $\text{Ni}^{\text{II}}\text{-O}$ bonds. One Ni^{II} of the positive MC is not bound to the neutral MC and vice versa. Hydrogen atoms, bound CH_3OH and H_2O solvent, and bound 2-methyl-4-chlorophenoxyacetate anions have been removed for clarity.⁴⁰⁹

ring connectivity, though, is different from the 12-MC-4 complexes that have a central metal ion. The ring connectivity for $\text{inv}(\mu_3\text{-O})_2[12\text{-MC}_{\text{Zn}^{\text{II}}\text{N}(\text{pko})_2-4}]$ is $[\text{N}-\text{O}-\text{M}-\text{O}-\text{N}-\text{M}]_2$ as opposed to $[\text{N}-\text{O}-\text{M}-\text{N}-\text{O}-\text{M}]_2$ for the 12-MC-4 complexes with a central metal ion. A similar $\text{inv}(\mu_3\text{-OH})_2[12\text{-MC}_{\text{Zn}^{\text{II}}\text{N}-4}]$ has been made with *syn*-2-pyridineal-doxime.⁴¹⁵ However, Zn^{II} ions may be used to synthesize 12-MC-4 complexes with typical connectivity.⁴¹⁴ An octanuclear complex centers about a $[12\text{-MC}_{\text{Zn}^{\text{II}}\text{N}(\text{pko})_2-4}]$ ring that binds two Zn^{II} ions to the hydroximate ring oxygen atoms. In addition, two of the ring Zn^{II} ions form binuclear entities with two Zn^{II} ions.

Manganese and cobalt ions have also been used to generate inverse 12-MC-4 complexes. The manganese inverse 12-MC-4 uses the ligand cyanoacetamidoximate to generate a MC ring connectivity that is similar to the inverse 12-

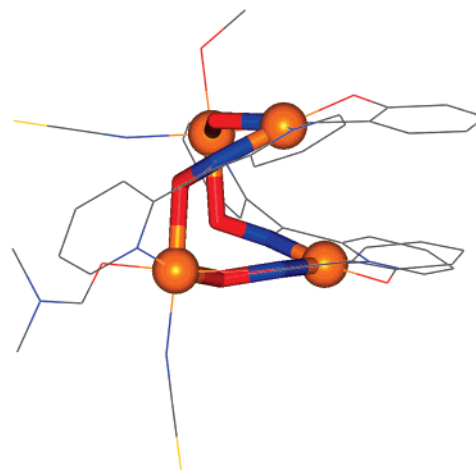


Figure 46. X-ray crystal structure of the vacant $[12\text{-MC}_{\text{Ni}^{\text{II}}\text{N}(\text{Hshi})_2(\text{pko})_2-4}](\text{SCN})_2 \cdot \text{CH}_3\text{OH} \cdot (\text{CH}_3)_2\text{NCHO}$ complex with the two Hshi^{2-} and two pko^- . The vacant MC adopts a nonplanar configuration. The chelate ring pattern is 5-6-5-6-5-6-5-6. Color scheme: orange sphere, Ni^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon; yellow line, sulfur. Hydrogen atoms have been removed for clarity.⁴⁰⁸

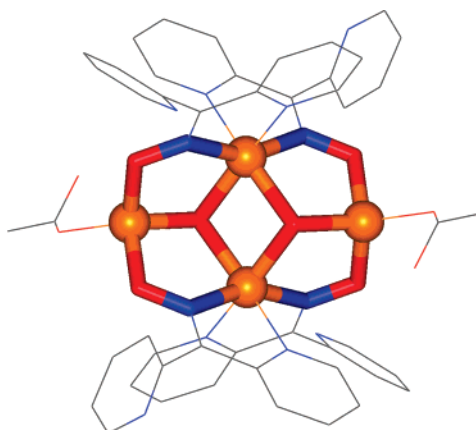


Figure 47. X-ray crystal structure of the $\text{inv}(\mu_3\text{-OH})_2(\text{O}_2\text{CCH}_3)_2[12\text{-MC}_{\text{Zn}^{\text{II}}\text{N}(\text{pko})_2-4}]$ complex. The ring connectivity follows a pattern of $-\text{[N-O-M-O-N-M]}-$ as opposed to the $-\text{[N-O-M-N-O-M]}-$ pattern in 12-MC-4 complexes with a central metal ion. Color scheme: orange sphere, Zn^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁴¹³

$\text{MC}_{\text{Zn}^{\text{II}}\text{N}(\text{pko})_2-4}$ complexes.⁴¹⁶ The *inv*MC ring consists of alternating Mn^{II} and Mn^{III} ions and binds two μ_3 -oxide oxygen atoms. The cobalt inverse 12-MC-4 has been synthesized with four pko^- ligands with *inv*MC ring connectivity similar to that of the inverse $12\text{-MC}_{\text{Zn}^{\text{II}}\text{N}(\text{pko})_2-4}$ (Figure 48).⁴¹⁷ The cobalt inverse 12-MC-4 binds two $\mu\text{-OH}$ or two $\mu\text{-OCH}_3$ anions, and the ring cobalt ions have alternating oxidation states of 2+ and 3+.

A metallacryptate-like structure can be generated from two fused $12\text{-MC}_{\text{Ga}^{\text{III}}-4}$ complexes (Figure 49).⁴¹⁸ The two $[12\text{-MC}_{\text{Ga}^{\text{III}}\text{N}(\text{shi})_2-4}]$ complexes are joined by four $\mu\text{-OH}$ anions that bridge Ga^{III} ions on opposite MCs. The MC dimer then binds three Na^{I} ions with the eight hydroximate oxygen atoms. Two of the Na^{I} ions cap the dimer on the outside faces (1.68 Å above or below the best least-squares plane of oxygens), whereas a third Na^{I} ion is bound in the cage created by the two MCs and four $\mu\text{-OH}$ anions. This central Na^{I} (1.18 Å) fits beautifully within the resultant cavity (1.07 Å) using a square prismatic orientation of the eight metallacrown ring oxygen atoms.

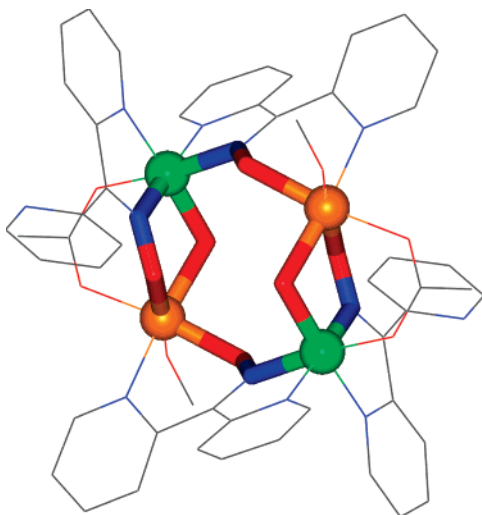


Figure 48. X-ray crystal structure of the *inv*(μ -OH) $_2$ (O $_2$ CCH $_3$) $_2$ -[12-MC $_{Co^{II}2Co^{III}2N(pkoi)-4}$] \cdot 4CH $_3$ OH \cdot 3.08H $_2$ O complex. The ring connectivity follows a pattern of $-[N-O-M-O-N-M]-$ as opposed to the $-[N-O-M-N-O-M]-$ pattern in 12-MC-4 complexes with a central metal ion. Color scheme: orange sphere, Co II ; green sphere, Co III ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁴¹⁷

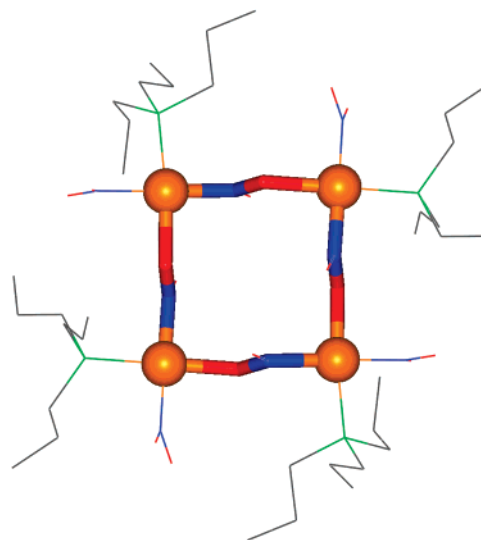


Figure 50. X-ray crystal structure of the vacant 12-MC $_{Pd^{II}-4}$ complex. Four NO $_2^-$ ligands provide N–O connectivity between the Pd II ions. The coordination about the Pd II ions is completed by four NO $_2^-$ anions and four tri-*n*-propylphosphine ligands. Color scheme: orange sphere, Pd II ; red tube, oxygen; blue tube, nitrogen; gray line, carbon; green line, phosphorus. Hydrogen atoms have been removed for clarity.⁴¹⁹

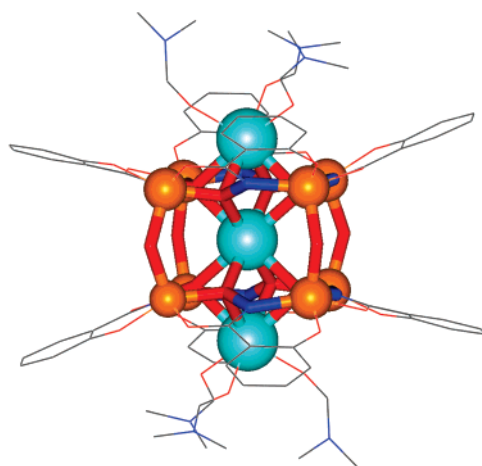


Figure 49. X-ray crystal structure of the Na $_3$ ((CH $_3$) $_2$ NCHO) $_6$ (μ -OH) $_4$ [12-MC $_{Ga^{III}2N(shi)-4}$] $_2$ complex. Two Na $^+$ ions are bound to the outside faces of the MC ring. One Na $^+$ is trapped within the cage created by the two 12-MC-4 complexes, which are joined by four μ -OH bridging between the Ga III ions. Color scheme: aqua sphere, Na $^+$; orange sphere, Ga III ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁴¹⁸

In addition, a 12-MC $_{Pd^{II}-4}$ macrocycle with N–O bridges has been generated by four NO $_2^-$ anions (Figure 50).⁴¹⁹ The [12-MC $_{Pd^{II}N(NO_2)-4}$] complex is vacant. Two terminal NO $_2^-$ anions and a tri-*n*-propylphosphine group complete the coordination environment of each Pd II ion.

Several collapsed 12-MC-4 complexes have been synthesized. Collapsed MCs contain no central guest, but instead of retaining the vacant cavity, the ring oxygens of the MC bind to ring metal ions on the opposite side of the MC ring. Thus, the vacant cavity has collapsed upon itself. Several collapsed 12-MC $_{Cu^{II}-4}$ complexes have been synthesized with oxime ligands (Figure 51).^{392,420–422} All of the complexes share the structural similarities of a nearly planar Cu $^{II}_4$ core. A $-[Cu-N-O]-$ repeat unit is observed with two nonadjacent ring oxygens binding to Cu II ions across the cavity, thus collapsing the cavity. A similar mixed-metal, mixed-

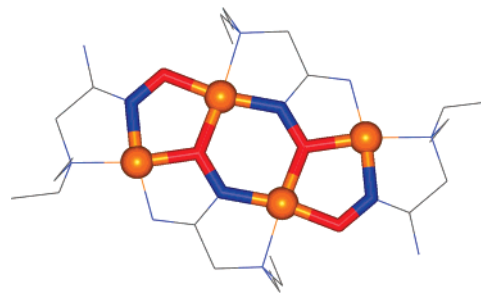


Figure 51. X-ray crystal structure of the collapsed 12-MC $_{Cu^{II}-4}$ complex with the ligand 3-(dimethylamino)propanamidoxime. Two ring oxygen atoms bind across the core to two ring Cu II ions, which causes the cavity to collapse. Color scheme: orange sphere, Cu II ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁴²²

ligand [12-MC $_{Mn^{III}2Ni^{II}2N(shi)_2(pkoi)_2-4}$] can be synthesized with alternating Mn III and Ni II ions and alternating ligands.⁴⁰⁷ The nonadjacent hydroximate oxygens bind across the cavity to the two Mn III ions. A collapsed 12-MC $_{Ni^{II}-4}$ can be made with the oxime ligand pko $^-$.⁴²³ In addition to the collapsed core, the nonadjacent Ni II ions are bridged by a pko $^-$ ligand. A different type of collapsed 12-MC-4 may be synthesized from Rh II , Zn II , and the ligand dimethyloxime.⁴²⁴ Alternating Rh II and Zn II ions with [Rh–N–O–Zn–O–N] $_2$ connectivity (just as the *inv*12-MC-4 complexes) produces a 12-MC-4. The central cavity is not collapsed by M–O bonds but by a Rh II –Rh II bond.

Aza12-MC-4 complexes are a second major group of this family of complexes, and as in the case of the aza9-MC-3 complexes, these complexes are mainly based on the pyrazole ligand and its derivatives. Aza12-MC-4 complexes with pyrazolate or its derivatives providing the bridging N–N atoms have been synthesized with Mn II ,⁴²⁵ Cu II ,^{426–432} Cu I ,^{199,201,433–435} (Figure 52), Ag I ,⁴³⁴ and Zn II .⁴²⁵ All of the complexes are very similar, with nonplanar structures that do not encapsulate a central cation. The pyrazolate anions are positioned above and below the plane created by the four ring metal ions. An interesting structure of Cu I or Ag I with

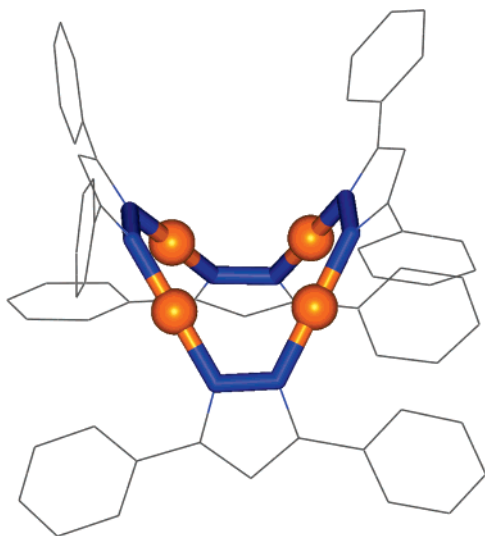


Figure 52. X-ray crystal structure of the vacant aza[12-MC_{Cu^I}-4] complex with the ligand 3,5-diphenylpyrazole. The pyrazolate ligands alternate between up and down positions about the metallamacrocycle. Color scheme: orange sphere, Cu^I; blue tube, nitrogen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁴³³

2-amino-1,2,4-thiadiazolate (atdz) consists of the four M^I ions bridged by six atdz ligands,⁴³⁴ which forms a structure that is similar in topology to paddlewheel complexes.⁴³⁶ A similar Cu^I 12-MC-4 structure has been made with pyridazine instead of atdz.⁴³⁷ In addition, 3,6-bis(2'-pyridyl)pyridazine can be used to generate Cu^I or Ni^{II} aza12-MC-4 complexes with the pyridazine moieties providing the N–N bridges.^{438,439} Hydrazone organic ligands provide a N–N bridge between metal ions because they contain diimine groups (N–N). Vacant Cu^{II},^{440–442} Ni^{II},⁴⁴³ and Li^I⁴⁴⁴ aza12-MC-4 have been generated from hydrazone ligands such as 2,6-diacetylpyridinebis(picolinoylhydrazone).⁴⁴⁰ These hydrazone-based 12-MC-4s are structurally similar to the pyrazolate 12-MC-4 complexes with the ligands positioned above and below the plane of the metal ions.

Related to the N–O and N–N MCs are three 12-MC-4 structures with M–O–P connectivity. A 12-MC_{Co^{III}Zr^{IV}}-4 complex with alternating Co^{III} and Zr^{IV} metal ions is formed from methyl phosphite or dimethyl phosphite groups.⁴⁴⁵ The MC ring connectivity is [Co^{III}–P–O–Zr^{IV}–O–P]₂, and the phosphoryl oxygen of the methyl phosphite, which is not involved in the MC ring, spans the vacant cavity to bind to the opposite Zr^{IV} ion. Platinum with *R,S*-C₆H₅P(O)CH₂CH₂P(O)C₆H₅ generates a vacant 12-MC-4 with two bridging groups between each Pt^{II} ion, O–P and P–O.⁴⁴⁶ A 12-MC_{Li₂Pt^{II}}-4 has been made with diphenylphosphine providing the P–O bridge (Figure 53).⁴⁴⁷ The 12-MC-4 binds a {Li₂-(μ-H₂O)₂}²⁺ moiety within the central cavity with the four phosphoryl oxygen atoms.

12-MC-4 complexes can be synthesized that are analogous to the 9-MC-3 complexes with a [Hg^{II}–C–C]– repeat unit from dicarbon boron cages. 12-MC_{Hg^{II}}-4 complexes, with 1,2-C₂B₁₀H₈RR' (R = H, C₆H₅, CH₂CH₃; R' = H, CH₂CH₃) cages providing the C–C bridges, bind a variety of guests to the Hg atoms within the central cavity. Encapsulated guests include chloride^{448–450} (Figure 54), bromide,^{449,451} iodide,^{449–454} *closo*-B₁₀H₁₀²⁻ cages,^{449,455} CH₃CH₂OH,⁴⁵⁰ *closo*-9-I-12-CH₂CH₃-1,2-C₂B₁₀H₁₀,⁴⁴⁹ *closo*-9,12-I-CH₂-CH₃-1,2-C₂B₁₀H₁₀,⁴⁴⁹ *closo*-9,12-CH₂CH₃-1,2-C₂B₁₀H₁₀,⁴⁴⁹

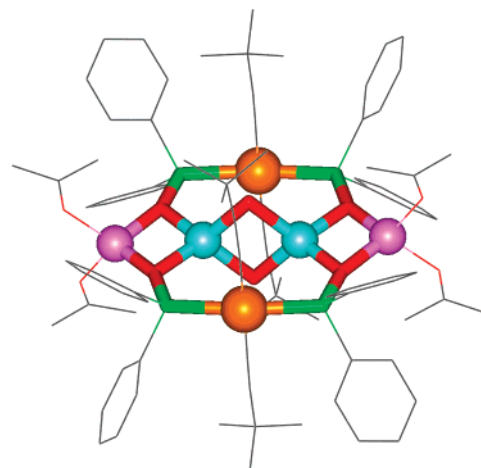


Figure 53. X-ray crystal structure of the Li₂(H₂O)₂[12-MC_{Li₂Pt^{II}}-4] complex with the ligand diphenylphosphinite providing the bridging atoms. A Li₂(H₂O)₂²⁺ core is trapped within the central cavity of the MC. The coordination of the Pt^{II} is completed by two C≡CC(CH₃)₃ ligands, and the coordination of the ring Li⁺ is completed by two (OC(CH₃)₂) groups. Color scheme: aqua sphere, central Li⁺; magenta sphere, ring Li⁺; orange sphere, Pt^{II}; blue tube, nitrogen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁴⁴⁷

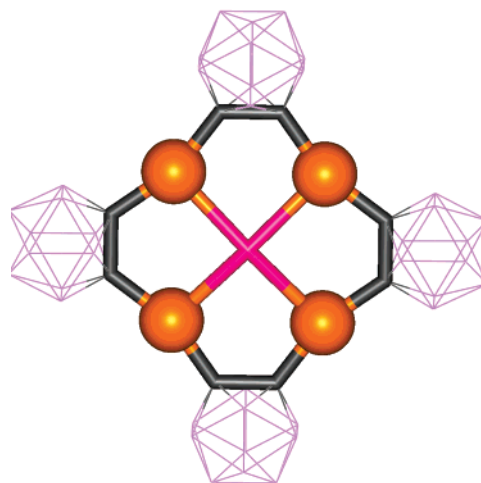


Figure 54. X-ray crystal structure of the (μ₄-Cl)[12-MC_{Hg^{II}}-4][−] complex with the carborane cages C₂B₁₀H₁₀^{2−}. A μ₄-Cl bridges the four Hg^{II} ions. Color scheme: orange sphere, Hg^{II}; magenta tube, chloride; gray tube, carbon; purple line, boron. Hydrogen atoms and the Li⁺ counteranion have been removed for clarity.⁴⁴⁸

and nitrate.⁴⁵⁶ A similar 12-MC_{Li}-4 complex has been synthesized with a [Li–B–B]– repeat unit.⁴⁵⁷ Trisho-moaromatic ligands of 1,3,5-triboracyclohexanes provide the B–B bridges, and the 12-MC-4 complex does not bind a guest within the central cavity. A similar complex can be synthesized with Ru^{II}.⁴⁵⁸ The Ru^{II} ions bridge cobalt carborane cages with a [Ru^{II}–B–B]– repeat unit to generate a 12-MC-4 complex.

2.5. 15-MC-3

A macrocyclic complex with [Re^I–O–N–N–N]₃ connectivity creates a 15-MC-3. The bridging ligand, 3-hydroxy-1,2,3-benzotriazine-4(3*H*)-one, provides a pocket in which a BF₄[−] anion is encapsulated (Figure 55).⁴⁵⁹ In addition, a [Ag(η²-C₆H₆)₃(OH₂)]⁺ cation is captured on the opposite side of the 15-MC-3, which is well shielded from the BF₄[−] anion by the metallamacrocycle. The water molecule coordinated

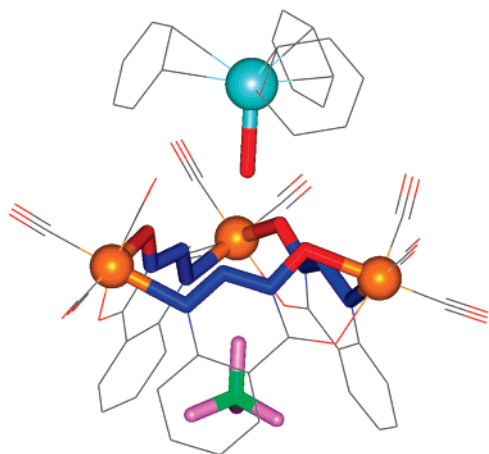


Figure 55. X-ray crystal structure of the $\text{Ag}^{\text{I}}(\eta^2\text{-benzene})_3(\text{BF}_4)^- [15\text{-MC}_{\text{Re}^{\text{I}}}\text{-3}]$ complex with the ligand 3-hydroxy-1,2,3-benzotriazine-4(3*H*)-one. The coordination sphere of Re is completed by three CO molecules. The BF_4^- anion is within the cavity created by the phenyl rings of the ligand, and it is well shielded from the Ag^{I} cation by the metallamacrocyclic. The water molecule of the Ag^{I} cation hydrogen bonds to the oxygen atoms of the MC ring. Color scheme: orange sphere, Re^{I} ; aqua sphere, Ag^{I} ; magenta tube, fluoride; green tube, boron; red tube and line, oxygen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁴⁵⁹

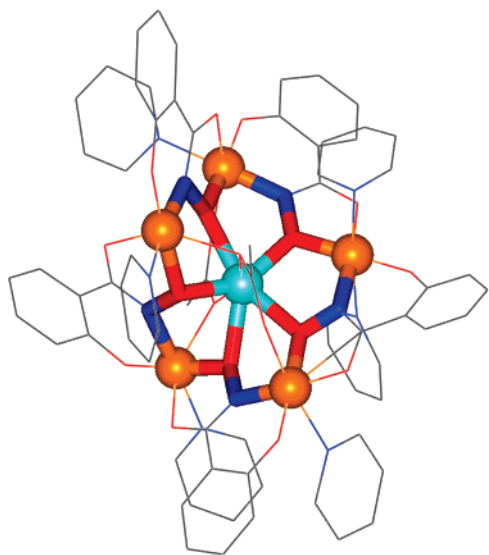


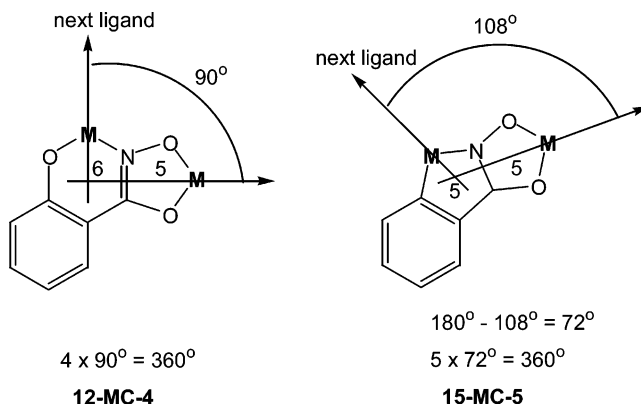
Figure 56. X-ray crystal structure of $\text{Mn}^{\text{II}}(\text{O}_2\text{CCH}_3)_2[15\text{-MC}_{\text{Mn}^{\text{III}}(\text{shi})}\text{-5}] \cdot 6\text{NC}_5\text{H}_5$. The nonplanar MC has ring Mn^{III} in three different coordination geometries with a pattern of $\Delta\Delta\Delta\text{P}_1\text{P}_1$, where P_1 is planar. A Mn^{II} ion is captured within the central cavity and linked to the MC ring via two acetate anions. Color scheme: aqua sphere, central Mn^{II} ; orange sphere, ring Mn^{III} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁴⁶⁰

to the Ag^{I} hydrogen bonds to the oxo groups of the ligand to associate the Ag^{I} cation with the 15-MC-3.

2.6. 15-MC-5

The first recognized 15-MC-5 with M–N–O connectivity was a nonplanar structure synthesized with salicylic hydroxamic acid (H_3shi) and manganese, $\text{Mn}^{\text{II}}(\text{O}_2\text{CCH}_3)_2[15\text{-MC}_{\text{Mn}^{\text{III}}(\text{shi})}\text{-5}]$ (Figure 56; Table 2).⁴⁶⁰ The neutral MC ring consists of a $-\text{[Mn}^{\text{III}}\text{-N-O]}-$ repeat unit, and the five hydroxamate oxygen atoms of the MC ring encapsulate a Mn^{II} ion within the cavity. In addition, two acetate anions

Scheme 5. Rationale for Planar 12-MC-4 and 15-MC-5 Formation



bridge the central Mn^{II} to two of the ring Mn^{III} ions. Three of the ring Mn^{III} ions have propeller configuration, whereas the other two have a planar (P_1) geometry. Similar 15-MC-5 complexes have been made with other carboxylate anions.^{380,384,461} On the basis of the relative configuration of the shi^{3-} ligands on each Mn^{III} , one observes a $\Delta\Delta\Delta\text{P}_1\text{P}_1$ pattern about the MC ring. This pattern contrasts with 9-MC-3 structures with $\Delta\Delta\Delta$ or $\Lambda\Lambda\Lambda$ configurations, which can close upon themselves to form a ring structure. By alternating the absolute stereochemistry at the metal, the two planar shi^{3-} ligands are necessary for ring closure. Although not yet realized, it is predicted that an 18-MC-6 should be accessible with shi^{3-} if the absolute stereochemistry alternates around the ring (e.g., $\Delta\Delta\Delta\Lambda\Delta\Lambda$). This precise pattern is observed for an aza-18-MC-6 described below with a different ligand. When the two shi^{3-} ligands on the same metal are oriented in a planar fashion, the metals are placed at 90° with respect to the fused six-membered and five-membered chelate rings as in the near-planar 12-MC-4 complexes (Scheme 5). UV–vis experiments demonstrate that in DMSO the $\text{Mn}^{\text{II}}(\text{O}_2\text{CH})_2[15\text{-MC}_{\text{Mn}^{\text{III}}(\text{shi})}\text{-5}]$ complex will convert over time to the related $\text{Mn}^{\text{II}}(\text{carboxylato})_2[12\text{-MC}_{\text{Mn}^{\text{III}}(\text{shi})}\text{-4}]$ complex.³⁸⁰

To achieve planarity in 15-MC-5 structures the metals must be placed at 108° with respect to each other, and this may be achieved by creating two five-membered fused chelate rings (Scheme 5). Ligands capable of this include picolinic hydroxamic acid (picHA) and α -amino hydroxamic acids (α -aminoHA). In these planar structures, the neutral ring connectivity is $[\text{Cu}^{\text{II}}\text{-N-O}]_5$ with all five of the hydroxamate oxygen atoms in the same plane. With five hydroxamate oxygen atoms in one plane, transition metal ions are not ideally suited for the central cavity due to their smaller ionic radii and preference for only four ligand atoms in the same plane. Therefore, this allows an opportunity for lanthanide and actinide ions, which, due to their larger ionic radii, can accommodate more ligand atoms in the same plane. 15-MC $_{\text{Cu}^{\text{II}}}$ -5 structures with picHA have a neutral $[\text{Cu}^{\text{II}}\text{-N-O}]_5$ MC ring that uses the five hydroxamate oxygen atoms to bind cations such as Eu^{III} (Figure 57),⁴⁶² Gd^{III} ,⁴⁶² the uranyl cation ($\text{U}^{\text{VI}}\text{O}_2^{2+}$),^{463a} Na^{I} ,^{463b} Y^{III} ,^{463b} Ag^{I} ,^{463b} Hg^{II} ,^{463b} and Pb^{II} .^{463b} Analogous 15-MC $_{\text{Ni}^{\text{II}}}$ -5 complexes have also been prepared and shown to bind Ln^{III} ions ($\text{Ln}^{\text{III}} = \text{Ce}^{\text{III}}, \text{Pr}^{\text{III}}, \text{Sm}^{\text{III}}, \text{Dy}^{\text{III}}, \text{Er}^{\text{III}}$) and Pb^{II} ions.^{463c} Moreover, by using chiral α -amino hydroxamic acids, chiral metallacrowns can be synthesized⁴⁶⁴ (achiral glycine provides achiral metallacrowns⁴⁶²). This is accomplished by each ligand placing the R group on the same face of the metallacrown, thus providing

Table 2. Ligands and Metals Used for the Synthesis of 15-MC-5 Complexes, Their Guests (Neutral Guests Are in Bold), and M–M Distances

bridging ligand	ring-metal	cationic guest	anionic (or neutral) guest	av M–M distance (Å)	ref	CCDC refcode	
salicylic hydroxamic acid	Mn(III)	Mn(II)	2 CH ₃ CO ₂	4.64	460	YOBYUJ	
			2 CH ₃ CO ₂	4.64	460	YOBZEU	
			CH ₃ CO ₂ , salicylate	4.64	460	YOBZEW	
			CH ₃ CO ₂ , 2-(2,4,5-trichlorophenoxy)acetate	4.63	461	HUHPIJ	
			2 HCO ₂	4.62	380	FILFOW	
picoline hydroxamic acid	Cu(II)	Gd(III)	2 2-(2,4-dichlorophenoxy)acetate	4.65	384	IDUYOV	
			NO ₃ , DMF	4.58	462	XEBJOD	
			2 NO ₃	4.58	462	XEBJUD	
			NO ₃ , OH	4.58	462	XEBKAQ	
			2 O	4.62	463a	REJWIM	
			Ca(II)		463a		
			Y(III)		463b		
			Na(I)		463b		
			Ag(I)		463b		
			Hg(II)	2 py	463b		
			Pb(II)	py	463b		
			Ni(II)	Pb(II)	py	463c	
					Ce(III)	463c	
					Pr(III)	463c	
					Sm(III)	463c	
Dy(III)	463c						
S-α-alanine hydroxamic acid	Cu(II)	Nd(III)	OH, 3 H₂O	4.61	464	RAPXUB	
			Eu(III)	464			
			Gd(III)	464			
R-α-alanine hydroxamic acid	Cu(II)	Nd(III)			464		
S-leucine hydroxamic acid	Cu(II)	Eu(III)			464		
			Gd(III)		464, 474		
S-tyrosine hydroxamic acid	Cu(II)	Gd(III)	4 H₂O	4.56	467	WIYLUL	
			3 H₂O	4.56	467	WIYMAS	
			3 H₂O	4.56	467	WIYMEW	
S-phenylalanine hydroxamic acid	Cu(II)	Nd(III)			464		
			Gd(III)		465a		
			Gd(III)	2 terephthalate	4.55	465a	IBODUY
			Gd(III)	isonicotinate, H₂O	470		
			La(III)	3 H₂O	4.59	465a	IBODIM
			La(III)	adipate, 2 H₂O	4.61	465a	IBODOS
			Eu(III)		464		
			Sm(III)	NO ₃ , H₂O	4.57	466	WUQZUD
			Dy(III)		465b		
			Dy(III)	isonicotinate, H₂O	470		
			Ho(III)		465b		
			Tb(III)		465c		
			Y(III)		465c		
			Y(III)	isonicotinate, H₂O	470		
			R-phenylalanine hydroxamic acid	Cu(II)	Sm(III)	NO ₃ , H₂O	4.57
S-methionine hydroxamic acid	Cu(II)	Nd(III)			464		
glycine hydroxamic acid	Cu(II)	Eu(III)			464		
			Gd(III)	NO ₃ , 2 H₂O	4.59	464, 474	YEBQIG
S- or R-mandelohydroxamic acid	Cu(II)	Nd(III)			464		
					906		

face differentiation. This R group orientation is enforced by the metallacrown repeat unit: metal–nitrogen–oxygen. If the ligand “flips” to place the R group on the opposite face, then the metallacrown connectivity is not repeated, the rotational sense is lost, and a macrocyclic complex is not synthesized. Therefore, by choosing enantiopure chiral ligands, enantiopure chiral face-differentiated metallacrowns can be synthesized. Chiral 15-MC_{Cu^{II}}-5s have been synthesized with *S*-alanine hydroxamic acid,⁴⁶⁴ *S*-phenylalanine hydroxamic acid^{465,466} (Figure 58), and *S*-tyrosine hydroxamic acid⁴⁶⁷ that host a number of Ln^{III} ions including La^{III},⁴⁶⁵ Nd^{III},⁴⁶⁴ Sm^{III},⁴⁶⁶ and Gd^{III}.^{465,467}

X-ray crystal structures have been determined for a series of {Ln^{III}(NO₃)_{3-x}[15-MC_{Cu^{II}}N(S-pheHA)-5](OH)_x}, where Ln^{III} = La^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, and Ho^{III} and *x* = 0, 1, or 1.5, allowing the effects of the lanthanide ion radius on the metallacrown structure to be determined.⁴⁶⁸ For the

lanthanide ions investigated, the ionic radius varies from 1.16 Å for La^{III} to 1.02 Å for Ho^{III} for eight-coordinate species.⁴⁶⁹ In addition, the ionic radius is highly dependent upon coordination number as the ionic radius changes from 1.10 to 1.27 Å for La^{III} as the coordination number increases from 7 to 10.⁴⁶⁹ Thus, the lanthanide radius should greatly affect the MC structure, in particular, the MC cavity radius. The MC cavity radius increases as the Ln^{III} ionic radius increases with the maximum cavity radius being 1.15 Å for La^{III} and the minimum cavity radius being 1.06 Å for Ho^{III}. In addition, the Ln^{III} ionic radius also determines the distance of the central Ln^{III} from the mean plane created by the oxygen atoms of the MC ring. The larger the Ln^{III}, the higher it resides above the mean plane of the oxygen atoms. The La^{III} ion resides 0.68 Å above the plane, whereas the smaller Ho^{III} resides only 0.19 Å above the plane. In essence, the smaller ion is better able to fit within the cavity of the MC. As the

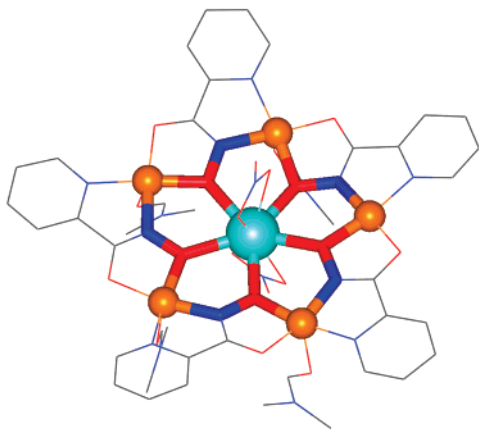


Figure 57. X-ray crystal structure of $\text{Eu}^{\text{III}}(\text{NO}_3)_2[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{picHA})}^-5]^{2+}\cdot 4(\text{CH}_3)_2\text{NCHO}$, where picHA is picolinic hydroxamic acid. The ligand forms two five-membered fused chelate rings, which place the Cu^{II} ions at 108° with respect to each other. This arrangement allows for a planar 15-MC-5 to be formed. A Eu^{III} ion is captured by the five ring oxygen atoms. Color scheme: aqua sphere, central Eu^{III} ; orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms, the NO_3^- counteranion, and lattice solvent have been removed for clarity.⁴⁶²

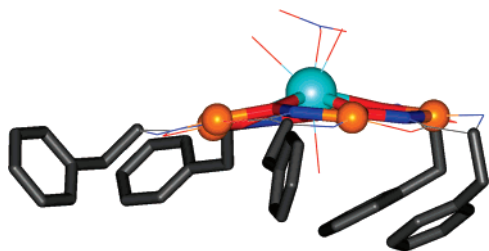


Figure 58. X-ray crystal structure of $\text{La}^{\text{III}}(\text{NO}_3)_3[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}^-5]^{2+}\cdot 4\text{H}_2\text{O}$, where pheHA is phenylalanine hydroxamic acid. The use of a chiral α -amino hydroxamic acid creates a chiral MC with one face differentiated from the other by the five phenyl rings. Color scheme: aqua sphere, central La^{III} ; orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms, the two NO_3^- counteranions, and lattice solvent have been removed for clarity.⁴⁶⁵ [This figure is modified from the supporting material of Zaleski, C. M.; Depperman, E. C.; Kampf, J. W.; Kirk, K. M.; Pecoraro, V. L. *Inorg. Chem.* **2006**, *45*, 10022.]

Ln^{III} ion increases in size, the MC attempts to increase the cavity radius to accommodate the ion. However, the MC can expand only so far; thus, the larger Ln^{III} still cannot reside close the mean plane of the oxygen atoms. As a result of this expansion, one observes that the metallacrowns adopt ruffled, planar, and bowled conformations to accommodate the central ions. Similar ring deformations have been observed with the 12-MC-4 structure types making a direct structural analogy to the chemistry of metalloporphyrins.

When crystallized from water, $\text{Ln}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}^-5]$ complexes form dimers in the solid state, where the phenyl rings of neighboring 15-MC_{Cu^{II}}-5 associate to create a hydrophobic “pocket” (Figure 59).^{465,470} In contrast, when $\text{Ln}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}^-5]$ is crystallized from a 10:1 mixture of methanol/water, helical chains of 15-MC_{Cu^{II}}-5s complexes are formed (Figures 60 and 61).⁴⁶⁶ Inside the hydrophobic pocket, a number of aliphatic and aromatic carboxylate guests can be bound, such as terephthalate or isonicotinate. Interesting to note is that whereas only one terephthalate molecule has been observed to bind inside the hydrophobic cavity of these metallacrowns, there are three guest molecules encapsulated in the case of isonicotinate. The symmetrical terephthalate guest forms bidentate carboxylate chelates to the Gd^{III}

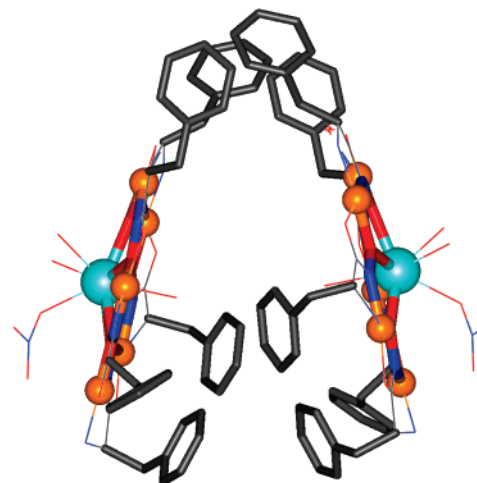


Figure 59. X-ray crystal structure of $\text{La}^{\text{III}}(\text{NO}_3)_3[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}^-5]^{2+}\cdot 4\text{H}_2\text{O}$ when crystallized from water. In the solid state the MCs associate to form dimers. A hydrophobic pocket is created by the phenyl rings of the two MCs. Color scheme: aqua sphere, central La^{III} ; orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms, the two NO_3^- counteranions, and lattice solvent have been removed for clarity.⁴⁶⁵ [This figure is modified from the supporting material of Zaleski, C. M.; Depperman, E. C.; Kampf, J. W.; Kirk, K. M.; Pecoraro, V. L. *Inorg. Chem.* **2006**, *45*, 10022.]

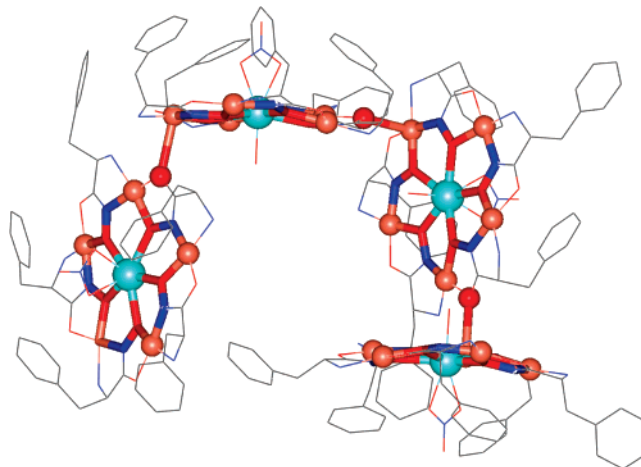


Figure 60. X-ray crystal structure of $\text{Gd}^{\text{III}}(\text{NO}_3)_3[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}^-5]^{2+}$ when crystallized from a mixture of methanol and water. The MCs bind to each other via $\text{Cu}^{\text{II}}\text{-O}_{\text{carbonyl}}$ bonds. The oxygen atoms that link the MCs together are not involved with the MC ring. The resulting helix has a positive pitch when S-pheHA is used. When R-pheHA is used to synthesize the MC, the helix has a minus pitch. Color scheme: aqua sphere, central Gd^{III} ; orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms, the NO_3^- counteranions, and lattice solvent have been removed for clarity.⁴⁶⁶ [This figure is modified from the supporting material of Zaleski, C. M.; Depperman, E. C.; Kampf, J. W.; Kirk, K. M.; Pecoraro, V. L. *Inorg. Chem.* **2006**, *45*, 10022.]

ions of each metallacrown, but the three isonicotinate molecules stretch across the two metallacrown planes within the cavity, with the pyridine nitrogen atom coordinating to the axial position of a Cu^{II} atom from one metallacrown, and the carboxylate bridging Cu^{II} and Gd^{III} ions on the other metallacrown. This different binding results in a considerably shorter Ln–Ln distance in the latter (9.7 Å) than in the former case (11.6 Å). The use of *S*-tyrosine hydroxamic acid (S-tyrHA) results in a true dimer between two 15-MC_{Cu^{II}}-5 complexes, with an even shorter Ln–Ln distance of 8.5 Å.⁴⁶⁷ One phenol group from each metallacrown binds across the

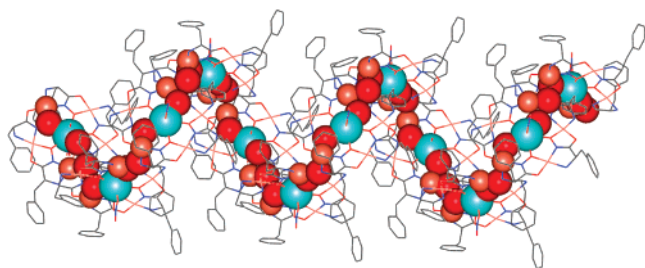


Figure 61. Another view of the X-ray crystal structure of $\text{Gd}^{\text{III}}(\text{NO}_3)[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})-5}]^{2+}$ with the helical character highlighted with spheres. The connectivity is $-\text{[Cu}^{\text{II}}\text{-O-Gd}^{\text{III}}\text{-O-Cu}^{\text{II}}\text{-O}]_n-$. Color scheme: aqua sphere, central Gd^{III} ; orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms, the NO_3^- counteranions, and lattice solvent have been removed for clarity.⁴⁶⁶ [This figure is modified from the supporting material of Zaleski, C. M.; Depperman, E. C.; Kampf, J. W.; Kirk, K. M.; Pecoraro, V. L. *Inorg. Chem.* **2006**, *45*, 10022.]

hydrophobic pocket to a ring Cu^{II} ion on the opposite MC ring. The result is a bound dimer in the solid state. Inside the cavity created by the dimer, chloride and nitrate anions may be bound. In these three examples, the smallest cavity occurs when the guest bridges Cu^{II} ions of the metallacrown (S-tyrHA); it expands with guests using both Cu^{II} and Ln^{III} as anchor points (isonicotinate), and the cavity is greatest when the guest spans both Ln^{III} ions (terephthalate).

Electrospray ionization mass spectrometry of a MeOH or H_2O solution of the isonicotinate–metallacrown complex at room temperature shows two strong peaks in the cone voltage range of 25–75 V, corresponding to a single metallacrown with one or two bound isonicotinate ligands, respectively.⁴⁷⁰ No peak attributable to a $\{\text{Gd}[\text{Cu}(\text{S-pheHA})]_5\}_2(\text{isonicotinate})_x(\text{NO}_3)_y$ species was detectable over the 0–75 V cone voltage range. Similar results were obtained with the dysprosium and yttrium analogues. Also, no peaks corresponding to pyridine adducts were detectable when a metallacrown/pyridine solution was subjected to ESI-MS under the same conditions. These experiments suggest that in solution only the carboxylate group of the guest molecule binds significantly to the metallacrown, indicating dissociation of the metallacrown compartments in solution. On the basis of the Weber and Josel definition of solid-state host–guest complexes,⁴⁷¹ the best description of the isonicotinate–metallacrown system is as a clathratocomplex because the interaction between the host and guest are retained by direct coordination bonds; however, the non-covalent association of the two metallacrowns observed in the solid state is disrupted in solution. The $[(\text{en})\text{Pt}(2\text{-hydroxypyrimidine})]_4^{4+}$ metallacrown prepared by Navarro et al. forms a similar compartmented structure, with a $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ion sandwiched between facing pairs of pinched-cone-shaped metallacrowns and held in place by multiple hydrogen bonds.⁴⁷² Likewise, the bis(double helicate) $[\text{Zn}_4\text{L}_4]$, $\text{L} = 2,2'$ -bis(1-phenyl-1*H*-tetrazol-5-yl)-1,1'-(1,3-benzenediyl)bis(ethen-1-olato), reported by Saalfrank et al. forms compartments in the solid state in which two THF molecules are entrapped.⁴⁷³ These two latter host–guest complexes also dissociate when dissolved, but in contrast to the isonicotinate–metallacrown complex, they are classified as cryptatoclathrates.

Planar $\text{Gd}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}-5}]$ complexes made with both chiral and achiral ligands have been tested for their ability to behave as MRI contrast agents.^{462,468,474} Proton relaxivity measurements indicate that the $\text{Gd}^{\text{III}}[15\text{-MC-5}]$ complexes have higher relaxivity values than $\text{Gd}^{\text{III}}\text{-DOTA}$ and $\text{Gd}^{\text{III}}\text{-DTPA}$,

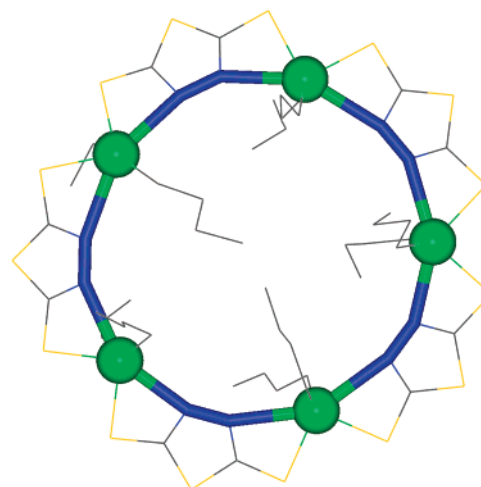


Figure 62. X-ray crystal structure of the vacant aza[15-MC $\text{Sn}^{\text{IV}}-5$] with the ligand 2,5-dimercapto-1,3,4-thiodiazole. The ligand provides a N–N bridge between the Sn^{IV} ions, and the coordination sphere about each Sn^{IV} ion is completed by two butyl groups. Color scheme: green sphere, Sn^{IV} ; blue tube, nitrogen; gray line, carbon; yellow line, sulfur. Hydrogen atoms have been removed for clarity.⁴⁷⁶

the standards upon which new MRI contrast agents are compared.⁴⁷⁵ However, many more studies are required before clinical applications can be fully assessed.

The chiral $\text{Ln}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\alpha\text{-aminoHA})-5}]$ complexes may also be generated in solution from the corresponding $\text{Cu}^{\text{II}}\text{-}[12\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\alpha\text{-aminoHA})-4}]$ (discussed earlier) complex.^{398–400} Using optical spectroscopy (UV–vis and CD), ESI-MS, and ^1H NMR several researchers have observed that $\text{Cu}^{\text{II}}[12\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\alpha\text{-aminoHA})-4}]$ complexes will convert to the corresponding $\text{Ln}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\alpha\text{-aminoHA})-5}]$ complex upon the addition of the Ln^{III} ion.^{399,400} The $\text{Cu}^{\text{II}}[12\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\alpha\text{-aminoHA})-4}]$ molecule will also convert to the $\text{UO}_2[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\alpha\text{-aminoHA})-5}]$ molecule upon addition of UO_2^{2+} .³⁹⁸ One study has observed that by adding Cu^{II} ions to the generated $\text{Ln}^{\text{III}}\text{-}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\alpha\text{-aminoHA})-5}]$ complex the original $\text{Cu}^{\text{II}}[12\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\alpha\text{-aminoHA})-4}]$ can be recovered.⁴⁰⁰ The reaction is reversible only with $\text{Ln}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\alpha\text{-aminoHA})-5}]$ complexes containing smaller Ln^{III} ions (Sm^{III} and Yb^{III}). The reaction is irreversible for $\text{Ln}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\alpha\text{-aminoHA})-5}]$ complexes with larger Ln^{III} ions (La^{III} and Nd^{III}).

One aza15-MC-5 complex has been synthesized with Sn^{IV} and 2,5-dimercapto-1,3,4-thiodiazole (bismothol-I) (Figure 62).⁴⁷⁶ Alternating units of Sn^{IV} and bismothol-I generate a metallamacrocycle with a repeat unit of $-\text{[Sn}^{\text{IV}}\text{-N-N]}-$. Each Sn^{IV} ion has a distorted octahedral geometry with two butyl and two S atoms of bismothol-I completing the coordination sphere. The $15\text{-MC}_{\text{Sn}^{\text{IV}}-5}$ complex does not encapsulate any guests within the central cavity.

2.7. 15-MC-6

Metallacoronate 15-MC-6 complexes can be synthesized with dialkyl ketipinate ligands with a $[\text{Cu}^{\text{II}}\text{-O-C-C-O}]_3$ metallamacrocycle. The MC ring is neutral because each ligand has a 2– charge. One 15-MC-6 is capable of binding one Ca^{II} cation within the central cavity.⁴⁷⁷ The Ca^{II} is bound to all six oxygen atoms of the MC ring. Similar 1:1 MC/cation complexes can be made with Na^{I} , which resides the plane of the ring oxygen atoms; however, the complexes tend to stack in the solid state to create structures similar to the fused $\text{Ni}[12\text{-MC}_{\text{Ni}^{\text{II}}-4}]$ complexes.^{53,477} The fused dimer and trimer $\text{Na}^{\text{I}}[15\text{-MC}_{\text{Cu}^{\text{II}}-3}]$ complexes have been prepared in

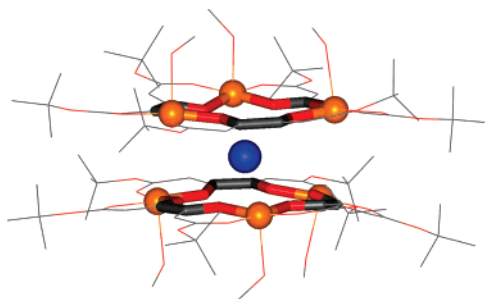


Figure 63. X-ray crystal structure of the metallacoronate [15-MC_{Cu^{II}}-3] with the ligand 1,6-di-*tert*-butoxyhexan-1,3,4,6-tetronato in which a NH₄⁺ is sandwiched between two MC complexes. The MC ring has a $-\text{[Cu}^{\text{II}}-\text{O}-\text{C}-\text{C}-\text{O}]^-$ repeat unit, and each MC is neutral. The positive charge is balanced by a hydroxide anion hydrogen bonded to a methanol molecule. Color scheme: orange sphere, Cu^{II}; blue sphere, nitrogen; gray line, carbon; red tube, oxygen. Hydrogen atoms and the ⁻OH counteranion have been removed for clarity.⁴⁷⁸

which the central Na^I of one MC binds to a ring oxygen of the opposite MC and vice versa. This coordination creates a staggered MC arrangement in both the dimer and trimer. In addition, two 15-MC-6 complexes are capable of binding one K^I or NH₄⁺ cation by forming a sandwich complex in which the cation is bound to the oxygen atoms of the MC ring (Figure 63).^{477,478}

2.8. 16-MC-4

Expanded 16-MC-4 complexes with a $[\text{M}-\text{N}-\text{C}-\text{O}]_4$ macrocycle have been synthesized with three different metals. Two 16-MC_{Pd^{II}}-4 have been synthesized from 2,3-dihydroxypyridine and 2-hydroxynicotinic acid.⁴⁷⁹ For 2,3-dihydroxypyridine, the ligand binds bidentate with two oxygen atoms to one Pd^{II} to form a five-membered chelate ring. The pyridyl nitrogen of the ligand then binds to an adjacent Pd^{II} to begin the construction of the 16-MC-4 complex with a $-\text{[Pd}^{\text{II}}-\text{N}-\text{C}-\text{O}]^-$ repeat unit. 2-Hydroxynicotinic acid uses a similar bridging mode to generate the 16-MC-4 complex except the two oxygen atoms of the ligand form a six-membered chelate ring about the Pd^{II} ion. Both 16-MC-4 complexes contain a vacant central cavity. Picoline-tetrazolamide ligands lead to 16-MC-4 complexes with either Ni^{II} or Zn^{II} (Figure 64).⁴⁸⁰ In 16-MC_{Ni^{II}}-4, the Ni^{II} ions are connected by five- and six-membered chelate rings from four ligands. Each Ni^{II} has propeller configuration with alternating Δ and Λ stereochemistry about the MC ring. The Ni^{II} ions are also connected via N-C-N bridges, so the structure could be considered an expanded aza16-MC-4 complex also. No guests are bound inside the central cavity. The Zn^{II} structure is isostructural. A sulfur derivative of a picoline-tetrazolamide ligand leads to a similar 16-MC_{Ni^{II}}-4 complex as above.⁴⁸¹ The two structures are nearly isostructural except that in the picoline-tetrazolthioamide complex the ring Ni^{II} ions are connected via N-C-S and N-C-N bridges to create the metallamacrocycle. A second 16-MC_{Ni^{II}}-4 complex with a $-\text{[Ni}^{\text{II}}-\text{N}-\text{C}-\text{O}]^-$ repeat unit can be generated via a triazine-based ligand (Figure 65).⁴⁸² Each Ni^{II} is bound to two nitrogen atoms from one ligand and two oxygen atoms of a second ligand. The octahedral geometry about each Ni^{II} is completed by two water molecules. The propeller configuration of the Ni^{II} ions alternates between Δ and Λ . The result is a nonplanar 16-membered MC ring with a vacant central cavity.

Nucleobases, nucleosides, and nucleotides are excellent ligands to construct expanded aza12-MC-3 complexes with a $-\text{[M}-\text{N}-\text{C}-\text{N}]^-$ repeat unit. By the addition of one more

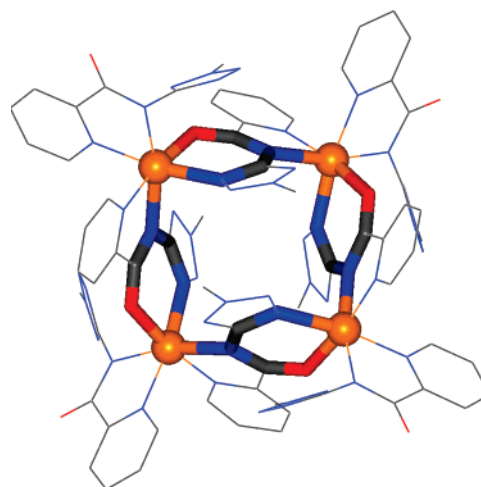


Figure 64. X-ray crystal structure of a vacant expanded 16-MC_{Ni^{II}}-4. The picoline-tetrazolamide ligand creates two bridges between the Ni^{II} ions: N-C-O and N-C-N; therefore, the metallamacrocycle could be considered either an expanded MC or an expanded azaMC. The propeller configuration of the Ni^{II} ions alternates between Δ and Λ . Color scheme: orange sphere, Ni^{II}; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁴⁸⁰

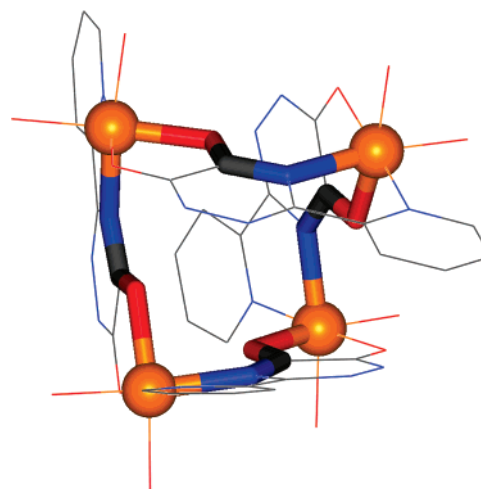


Figure 65. X-ray crystal structure of a vacant expanded 16-MC_{Ni^{II}}-4. The ligand creates one bridge between the Ni^{II} ions: N-C-O. The coordination about the Ni^{II} ions includes two O atoms from one ligand, two N atoms from a second ligand, and two water molecules. The propeller configuration of the Ni^{II} ions alternates between Δ and Λ as in the 16-MC_{Ni^{II}}-4 in Figure 64. Color scheme: orange sphere, Ni^{II}; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁴⁸²

ligand and ring metal ion, similar expanded aza16-MC-4 complexes may be generated. Moieties of Co^{III},⁴⁸³ Ru^{II} (Figure 66),^{247,484} Rh^{III},^{237,485} and Ir^{III},^{248,485} with various aromatic ligands, such as η^6 -cymene and η^5 -cyclopentadiene, alternate with ligands such as adenine to create a square aza16-MC-4 complex that does not bind a guest molecule within the central MC cavity. One key structural difference is observed between the aza12-MC-3 and aza16-MC-4 structures. In the trinuclear MCs, the N-C-N bridge is composed of the atoms in positions 1 and 6 and the N bonded to C6 of the ligand, which spans both rings of the purine-like ligand, whereas in the tetranuclear MCs, the N-C-N bridge is composed of atoms in positions 7, 8, and 9 (imidazole ring) of the ligand. This difference in binding mode leads to two different MC structures. In addition,

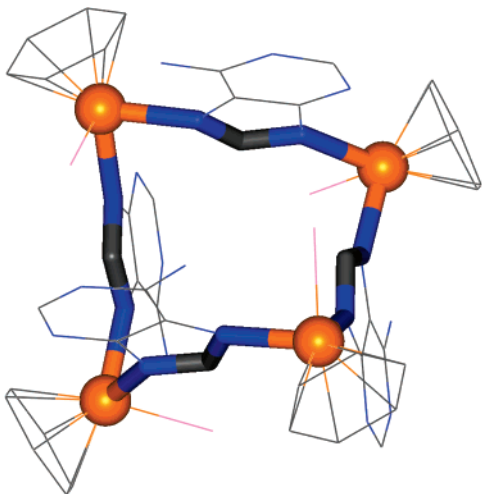


Figure 66. X-ray crystal structure of a vacant expanded aza[16-MC_{Ru^{II}}-4]. The adenine ligand provides a N–C–N bridge with the imidazole ring. Coordination about the Ru^{II} ion is completed by the η^6 -benzene and a chloride anion. Color scheme: orange sphere, Ru^{II}; blue tube, nitrogen; gray line, carbon; magenta line, chloride. Hydrogen atoms and lattice solvent have been removed for clarity.⁴⁸⁴

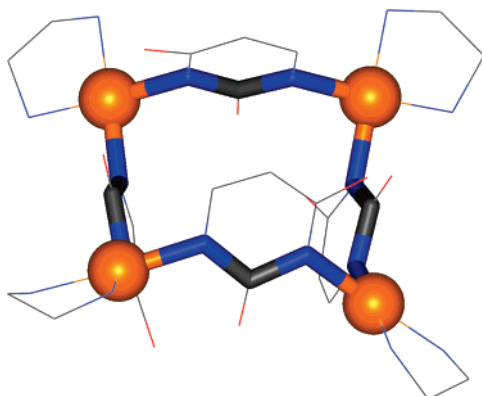


Figure 67. X-ray crystal structure of a vacant expanded aza[16-MC_{Pt^{II}}-4]⁴⁺. The monoanion of uracil provides the N–C–N bridges between the Pt^{II} ions, and coordination about the Pt^{II} ion is completed by ethylenediamine. Color scheme: orange sphere, Pt^{II}; blue tube, nitrogen; gray line, carbon. Hydrogen atoms and four NO₃[−] counteranions have been removed for clarity.⁴⁸⁶

4-imidazolecarboxylic acid can be used to generate an aza16-MC_{Rh^{III}}-4 complex that is analogous to the nucleobase examples above.²³⁷ The nucleobase uracil may also be used to generate aza16-MC-4 complexes (Figure 67).⁴⁸⁶ The monoanion of uracil can bridge four Pt^{II} ions to form a 16-MC-4 complex with a $-\text{[Pt}^{\text{II}}-\text{N}-\text{C}-\text{N}]-$ repeat unit. The coordination of the Pt^{II} ions is completed by an ethylenediamine ligand. The monoanion uracil ligands create a square MC structure with the Pt^{II} ions at the corners that do not bind a guest within the central cavity. If the dianion uracil ligand is used, a similar square aza16-MC-4 is generated but four Pt^{II}(NH₃)₂ groups bind to the MC ring at each corner.⁴⁸⁷ The Pt^{II}(NH₃)₂ groups are joined to the MC by bonding to two oxygen atoms from two dianion uracil ligands. In addition, 2-aminopyridonate can be used to construct a mixed-metal aza16-MC-4 with Pt^{II} and Pd^{II}.⁴⁸⁷ The MC complex has a $-\text{[Pt}^{\text{II}}-\text{N}-\text{C}-\text{N}-\text{Pd}^{\text{II}}-\text{N}-\text{C}-\text{N}]-$ repeat unit. Two Pd^{II}(NO₃)(H₂O) groups bind to the sides of the MC ring via bonds from two amine groups.

Ditopic ligands with central pyrimidine rings provide a N–C–N bridge, which can lead to square aza16-MC-4 complexes. The basis of the ligand is in essence two

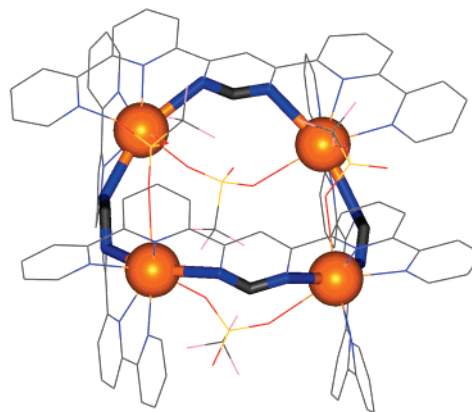


Figure 68. X-ray crystal structure of a vacant expanded aza[16-MC_{Pb^{II}}-4]⁴⁺. Four ditopic 4,6-bis(2',2'-bipyrid-6'-yl)pyrimidine ligands provide the N–C–N bridges between the Pb^{II} ions, and four triflate anions bridge between the Pb^{II} ions. Color scheme: orange sphere, Pb^{II}; blue tube, nitrogen; gray line, carbon; red line, oxygen; yellow line, sulfur. Hydrogen atoms and four CF₃SO₃[−] counteranions have been removed for clarity.⁴⁸⁹

bipyridine groups linked by a pyrimidine ring. A variety of ligand derivatives have been made with various substitutions on the bipyridine groups and the pyrimidine ring. Each ligand binds two metal ions, and the octahedral coordination sphere of the metal ion is completed by two ligands that are orthogonal to each other. The result is a $[2 \times 2]$ grid with four metal ions and four ligands, which create a $[\text{M}-\text{N}-\text{C}-\text{N}]_4$ metallamacrocycle. Guests do not bind within the central cavity. Homometallic Co^{II}⁴⁸⁸ and Pb^{II}⁴⁸⁹ (Figure 68) aza16-MC-4 complexes have been made along with heterometallic Fe^{II}₂Ru^{II}₂⁴⁹⁰ complexes. In addition, *N*-(2-methylimidazol-4-ylmethylidene)-2-aminoethylpyridine may be used to generate an aza16-MC-4 complex with a $-\text{[Cu}^{\text{II}}-\text{N}-\text{C}-\text{N}]-$ repeat unit.⁴⁹¹ The complex has a square shape similar to the aza16-MC-4 $[2 \times 2]$ grids, and like the $[2 \times 2]$ grids, guests are not bound within the central cavity.

Just as bis(diphenylphosphino)methane (dppm) can be used to construct trimeric aza12-MC-3 complexes, tetranuclear complexes can be synthesized with dppm with a similar simple metallamacrocycle of alternating metal and dppm units. 16-MC_{Pd^{II}}-4 complexes with $-\text{[Pd}^{\text{II}}-\text{P}-\text{C}-\text{P}]-$ connectivity have bound μ -chloride^{492,493} (Figure 69) and μ_4 -sulfide.^{494,495} One vacant structure has been crystallized with a possible H atom located within the central cavity.⁴⁹⁶ 16-MC_{Cu^I}-4 complexes have bound μ_4 -sulfide,^{497,498} μ_4 - η^1, η^2 -C \equiv C (acetylide),⁴⁹⁹ μ_4 -Se,⁵⁰⁰ WS₄^{2−} (Figure 70),^{315,501} WS₂^{2−},⁵⁰² MoS₄^{2−},⁵⁰¹ μ_4 -phosphinidene (PC₆H₅),⁵⁰³ μ_4 - η^2 -S₂CC(CN)P(O)(OCH₂CH₃)₂,⁵⁰⁴ and Cu^I(NS₂)₂.⁵⁰⁵ Aza16-MC_{Ag^I}-4 complexes have been synthesized that bind μ_4 -S,⁵⁰⁶ μ_4 -Se,⁵⁰⁶ μ_4 -Te (Figure 71),⁵⁰⁶ μ_4 -2,2-dicyano-1,1-ethylenedithiolate,⁵⁰⁷ μ_4 - η^2 -S₂CC(CN)P(O)(OCH₂CH₃)₂,⁵⁰⁸ μ_3 -S₂O₃,³⁴⁶ μ -S₂O₃,³⁴⁶ and μ_3 -2-mercaptopyridonate.⁵⁰⁹

Five other bridging units have been used to generate 16-MC-4 complexes. A metallacoronate with a $[\text{Cu}^{\text{II}}-\text{O}-\text{C}-\text{O}]_4$ metallamacrocycle constructs a vacant MC from a Schiff-base ligand (Figure 72).⁵¹⁰ A vacant 16-MC_{Sn^{IV}}-4 with a $-\text{[Sn}^{\text{IV}}-\text{O}-\text{P}-\text{O}]-$ repeat unit can be generated from alternating units of diphenylphosphinate and Sn(CH₃)₃⁺ (Figure 73).⁵¹¹ A $-\text{[Ga}^{\text{III}}-\text{O}-\text{Si}-\text{O}]-$ repeat unit constructs a 16-MC-4 that binds a core [Li₂O₂]^{2−} moiety within the central cavity and two [Li(THF)₂]⁺ cations to the outside of the MC ring [THF = tetrahydrofuran] (Figure 74).⁵¹² The core Li^I ions bind to the oxygen atoms of the MC ring,

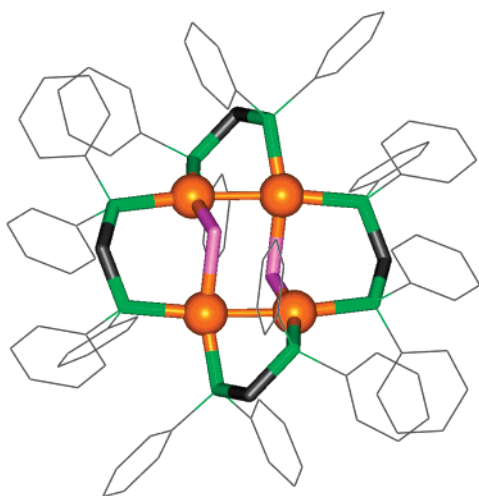


Figure 69. X-ray crystal structure of $(\mu\text{-Cl})_2[16\text{-MC}_{\text{Pd}^{\text{II}}}\text{-4}]^{2+}$ with the ligand bis(diphenylphosphino)methane, which provides a P–C–P bridge. The molecule has a rectangular shape with two short Pd–Pd bonds and two long Pd–Pd contacts. Two chloride anions provide bridges between two Pd^{II} ions. Color scheme: orange sphere, Pd^{II}; green tube, phosphorus; gray tube, carbon; magenta tube, chloride. Hydrogen atoms and two PF₆[−] counteranions have been removed for clarity.⁴⁹²

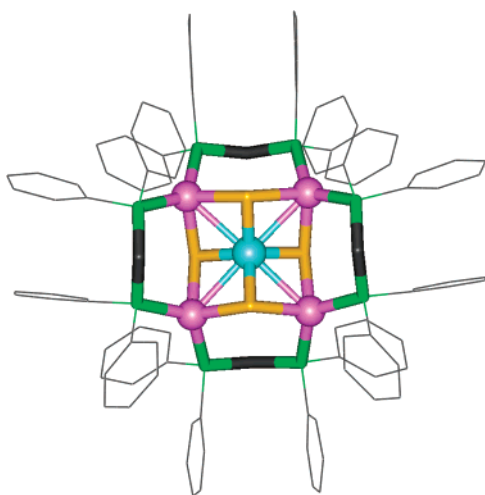


Figure 70. X-ray crystal structure of $(\mu_4\text{-WS}_4)[16\text{-MC}_{\text{Cu}^{\text{I}}}\text{-4}]^{2+}$ with the ligand bis(diphenylphosphino)methane. The WS₄^{2−} anion bridges all four Cu^I anions, and the W^{VI} bonds to all four Cu^I ions. Color scheme: magenta sphere, Cu^I; aqua sphere, W^{VI}; green tube, phosphorus; gray tube, carbon; yellow tube, sulfur. Hydrogen atoms and two PF₆[−] counteranions have been removed for clarity.³¹⁵

whereas the oxygen atoms of the core bind to the Ga^{III} ions of the MC ring. A 16-MC_{Re^V-4} complex can be synthesized from a $-\text{[Re}^{\text{V}}\text{-P-C-O]}-$ repeat unit with the ligand tris(hydroxymethyl)phosphine (Figure 75).⁵¹³ The MC ring binds four μ -oxide oxygen atoms that bridge the four Re^V ring ions. Furthermore, alternating Cr^{III} and N₂S₂ groups provide the basis for a vacant 16-MC_{Cr^{III}-4} complex with a repeat unit of $-\text{[Cr}^{\text{III}}\text{-N-S-N]}-$ (Figure 76).⁵¹⁴ This latter structure is reminiscent of the molecular square topology.

2.9. 18-MC-6

One 18-MC-6 complex has been synthesized with N–O bridges.⁵¹⁵ Using di-2-pyridyl ketone oxime (Hpko) and Cu^{II}, a complex with a [Cu^{II}–N–O]₆ metallamacrocycle can be generated that encapsulates a poorly coordinated ClO₄[−] anion (Figure 77). The molecule is shaped like a band, distinctly different from other metallacrowns constructed from pko[−].

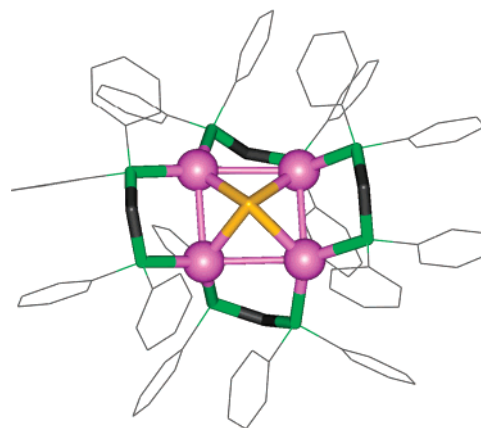


Figure 71. X-ray crystal structure of $(\mu_4\text{-Te})_2[16\text{-MC}_{\text{Ag}^{\text{I}}}\text{-4}]^{2+}$ with the ligand bis(diphenylphosphino)methane. A Te^{2−} bridges all four Ag^I ions with Ag–Ag metal bonds. Color scheme: magenta sphere, Ag^I; green tube, phosphorus; gray tube, carbon; yellow tube, Te^{2−}. Hydrogen atoms and two CF₃SO₃[−] counteranions have been removed for clarity.⁵⁰⁶

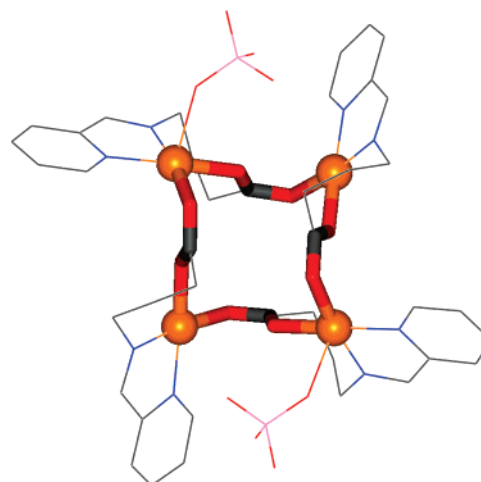


Figure 72. X-ray crystal structure of the vacant metallacoronate $[16\text{-MC}_{\text{Cu}^{\text{II}}}\text{-4}]^{2+}$ with bridges of O–C–O provided by the ligand *N*-(pyrid-2-yl)methylidene-4-aminobutanoate. Two of the Cu^{II} ions have a bound ClO₄[−] anion, whereas the other two Cu^{II} ions have only a coordination number of four. Color scheme: orange sphere, Cu^{II}; red tube, oxygen; gray tube, carbon; magenta line, chlorine. Hydrogen atoms and two ClO₄[−] counteranions have been removed for clarity.⁵¹⁰

In the 12-MC-4 and 15-MC-5 structures, the principal axis is perpendicular to the chelate rings about the metal ions, creating nearly planar complexes that encapsulate a metal ion within the central cavity. In the 18-MC_{Cu^{II}-6} complex, the principal axis is parallel to the chelate rings. This arrangement allows for a barrel-shaped molecule to be generated that captures a ClO₄[−] anion.

A series of aza18-MC-6 complexes have been made with a variety of *N*-acylsalicylhydrazide ligands. Mn^{III},^{516–522} Fe^{III},^{523,524} Co^{III},^{523,525} and Ga^{III}⁵²³ have been used as ring metal ions, and all of the structures made with different ligands and metals ions are nearly isostructural. The first *N*-acylsalicylhydrazide aza18-MC-6 was synthesized with *N*-formylsalicylhydrazidate with a $-\text{[Mn}^{\text{III}}\text{-N-N]}-$ repeat unit (Figure 78).⁵¹⁶ Each Mn^{III} is in a similar distorted octahedral coordination environment with a propeller configuration. The Mn^{III} ions have alternating Δ and Λ stereochemistry about the MC ring. The aza18-MC-6 does not bind any guests within the central cavity.

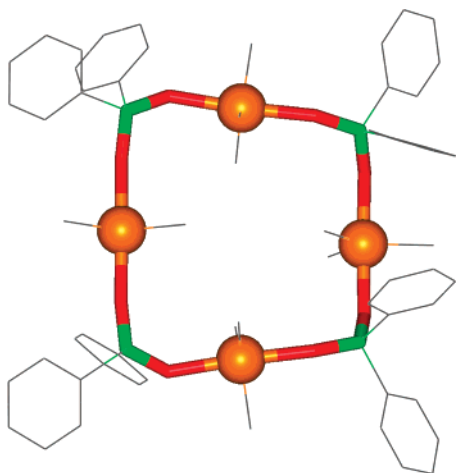


Figure 73. X-ray crystal structure of the vacant [16-MC_{Sn^{IV}-4}] complex composed of Sn(CH₃)₃⁺ groups bridged by O–P–O groups provided by the ligand diphenylphosphinate. Color scheme: orange sphere, Sn^{IV}; red tube, oxygen; green tube, phosphorus; gray line, carbon. Hydrogen atoms have been removed for clarity.⁵¹¹

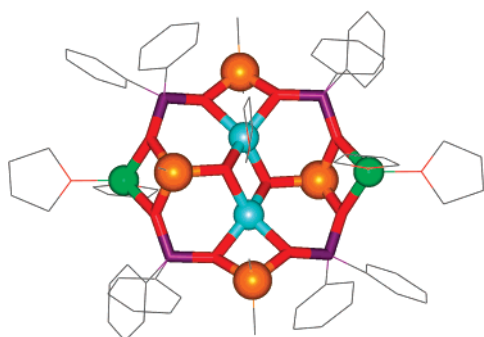


Figure 74. X-ray crystal structure of the [16-MC_{Ga^{III}-4}] complex with O–Si–O bridges provided by the ligand diphenylsilanediol. The MC ring binds a Li₂O₂²⁻ group within the core, and two Li(THF)⁺ cations (THF = tetrahydrofuran) are bound outside the MC ring. The coordination sphere around the gallium ions is completed by four methyl groups. Color scheme: orange sphere, Ga^{III}; green sphere, outer Li⁺; aqua sphere, central Li⁺; red tube, oxygen; purple tube, silicon; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁵¹²

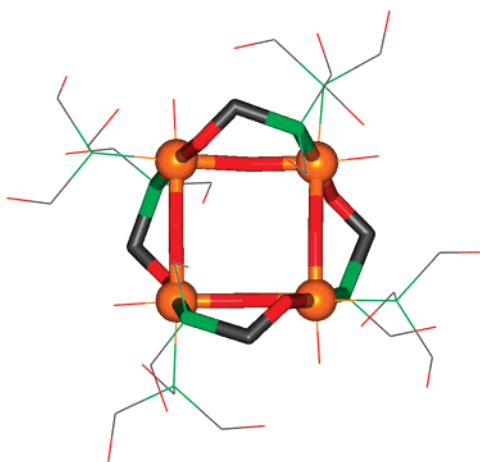


Figure 75. X-ray crystal structure of the vacant [16-MC_{Re^V-4}] complex with P–C–O bridges provided by the ligand tris(hydroxymethyl)phosphine. The four Re^V ions are also bridged by four μ -O anions. Color scheme: orange sphere, Re^V; green tube, phosphorus; red tube, oxygen; gray tube, carbon. Hydrogen atoms have been removed for clarity.⁵¹³

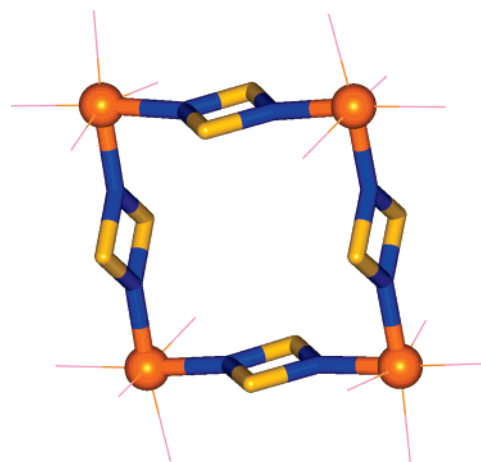


Figure 76. X-ray crystal structure of the vacant [16-MC_{Cr^{III}-4}]⁴⁻ complex with N–S–N bridges provided by N₂S₂ ligands. The coordination sphere of each Cr^{III} is completed by four Cl⁻ anions. Color scheme: orange sphere, Cr^{III}; blue tube, nitrogen; yellow tube, sulfur; magenta line, chloride. Hydrogen atoms, As(C₆H₅)₄⁺ counteranions, and lattice solvent have been removed for clarity.⁵¹⁴

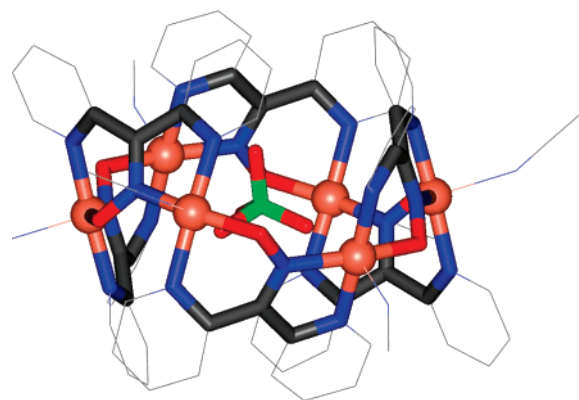


Figure 77. X-ray crystal structure of the {[ClO₄][18-MC_{Cu^{II}N(pko)-6}]}⁵⁺ complex. The ClO₄⁻ is poorly coordinated within the central cavity created by the barrel-like 18-MC-6. Each copper has a coordinated CH₃CN molecule. Color scheme: bronze sphere, Cu^{II}; blue tube, nitrogen; red tube, oxygen; gray tube, carbon; green tube, chlorine. Hydrogen atoms, ClO₄⁻ counteranions, and lattice solvent have been removed for clarity. Reprinted from ref 515, copyright 2005, with permission from Elsevier.

Two aza18-MC-6 complexes have been built from similar ligands. An aza18-MC-6 can be generated from Au^I and pyrazolate with a –[Au^I–N–N]– repeat unit (Figure 79).^{202,526} The structure consists of six Au^I ions and six pyrazolate anions. Each Au^I ion is two-coordinate with a linear geometry. An aza18-MC_{Cu^{II}}-6 can be synthesized with 4-amino-3,5-dimethyl-1,2,4-triazole (admtrz).⁵²⁷ The Cu^{II} ions are in either a distorted octahedral or a square pyramidal environment, and the admtrz ligands alternate between above or below the plane created by the six Cu^{II} ions. A solvent water molecule is contained within the central cavity.

2.10. 24-MC-6

Two 24-MC_{Cu^{II}}-6 complexes have been reported with a [Cu^{II}–N–C–O]₆ metallamacrocycle.^{528,529} The ligand 6-methyl-2-hydroxypyridine provides two N–C–O bridges between the Cu^{II} ions, which are in a distorted square-planar environment (Figure 80). One bridge has a N–C–O clockwise pattern, whereas the second bridge has an O–C–N clockwise pattern. Within the central cavity, a Na^I⁵²⁸ or Cu^{II}⁵²⁹ cation is captured by the six oxygen atoms of the MC ring. In

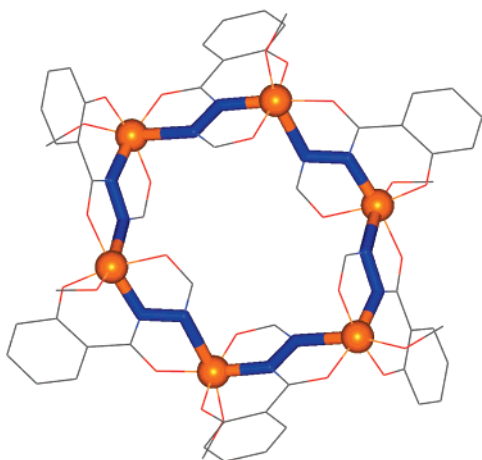


Figure 78. X-ray crystal structure of the vacant aza[18-MC_{Mn^{III}}-6] complex with the ligand *N*-formylsalicylhydrazidate. The Mn^{III} ions are connected by N–N bridges, and their coordination sphere is completed by a CH₃OH molecule. The propeller configuration about the Mn^{III} ions alternates between Δ and Λ about the ring. Color scheme: orange sphere, Mn^{III}; blue tube, nitrogen; red line, oxygen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁵¹⁶

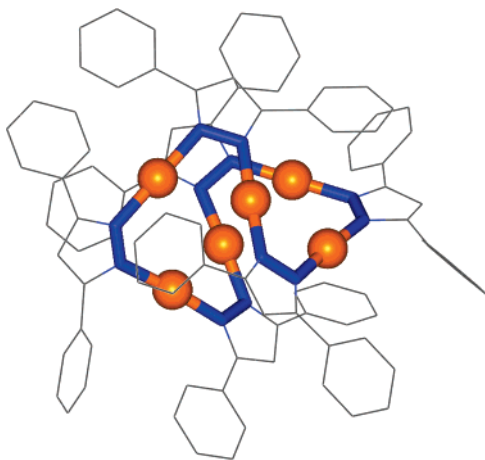


Figure 79. X-ray crystal structure of the vacant aza[18-MC_{Au^I}-6] complex with the ligand 3,5-diphenylpyrazolate. Each Au^I has a linear geometry, and the MC ring twists upon itself. Color scheme: orange sphere, Au^I; blue tube, nitrogen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁵²⁶

addition, a 24-MC_{Co^{II}}-6 complex with 6-methyl-2-hydroxypyridine captures a Na^I ion within its central cavity.⁵³⁰

Two relatively simple expanded aza24-MC-6 complexes have been synthesized with $-[M-N-C-N]-$ connectivity. An aza24-MC_{Ag^I}-6 complex can be produced with six Ag^I ions and six 2-hydroxypyrimidine (Hpymo) ligands (Figure 81).⁵³¹ Each pymo⁻ bridges between two Ag^I ions to form a MC ring that does not encapsulate any guest. The organic radical pyrimidine ligand 4-pyrimidinyl nitronyl nitroxide (4PMNN) generates an aza24-MC-6 complex with Cu^{II} ions.⁵³² As in the pymo⁻ structure, each 4PMNN bridges between the Cu^{II} ions to form a MC ring that does not bind a guest.

A more complicated expanded aza24-MC_{Cu^{II}}-6 may be produced from *N*-(2-phenylimidazol-4-ylmethylidene)-2-aminoethylpyridine.⁴⁹¹ This ligand is very similar to that used to create an expanded aza16-MC_{Cu^{II}}-4 except that a phenyl group substitutes for a methyl group at the 2-position. The use of the more sterically demanding phenyl group results in a hexameric complex instead of a tetrameric complex

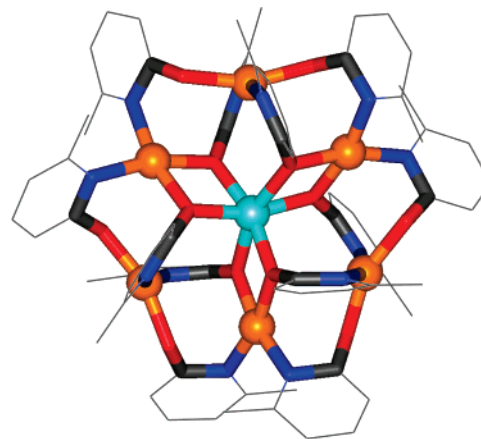


Figure 80. X-ray crystal structure of the expanded Cu^{II}[24-MC_{Cu^{II}}-6] complex with the ligand 6-methyl-2-hydroxypyridine. The Cu^{II} ions are connected by two N–C–O bridges, which proceed in opposite directions. The central Cu^{II} is bound to the oxygen atoms of the MC ring with clockwise bridges of O–C–N. Color scheme: aqua sphere, central Cu^{II}; orange sphere, ring Cu^{II}; blue tube, nitrogen; red tube, oxygen; gray line, carbon. Hydrogen atoms, [Pb^{II}(NO₃)₄]²⁻ counteranion, and lattice solvent have been removed for clarity.⁵²⁹

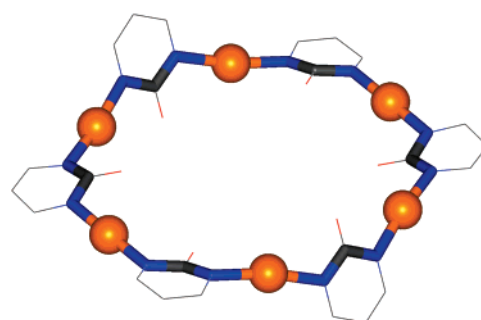


Figure 81. X-ray crystal structure of the vacant expanded [24-MC_{Ag^I}-6] complex with the ligand 2-hydroxypyrimidine. The Ag^I ions have a linear geometry, which is bridged by a N–N connectivity. Color scheme: orange sphere, Ag^I; blue tube, nitrogen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁵³¹

(methylated ligand). Also, like the aza16-MC_{Cu^{II}}-4, the aza24-MC_{Cu^{II}}-6 metallamacrocycle with a $-[Cu^{II}-N-C-N]-$ repeat unit does not bind any guests within the central cavity.

A 24-MC-6 complex with $-[Rh^{III}-S-C-N]-$ connectivity can be produced with the ligand 6-purinethione riboside (Figure 82).⁵³³ The coordination about each Rh^{III} is completed by one η^5 -cyclohexadiene, one bidentate 6-purinethione riboside to form a five-membered chelate ring with the sulfur and N(7) atoms, and the N(1) atom of an adjacent 6-purinethione riboside, which serves to bridge the Rh^{III} ions of the MC ring. The purine rings of the ligand create a cubic cavity within the center of the complex; however, the cavity hosts no central guest.

Four other unique 24-MC-6 complexes contain Cu^{II}, Pd^{II}, and Sn^{IV} ring metal ions. A cyclohexane-like complex of Cu^{II}, *N*-(2-pyridylmethyl)glycine, and *N*-(2-pyridylidene)glycine generate a 24-MC_{Cu^{II}}-6 that has a vacant central cavity.³⁷⁴ The metallacoronate 24-MC-6 consists of a $-[Cu^{II}-O-C-O]-$ repeat unit. A different 24-MC_{Cu^{II}}-6 metallacoronate may be generated with an amino-tricarboxylate ligand.⁵³⁴ The key difference is that this metallamacrocycle with a $-[Cu^{II}-O-C-O]-$ repeat unit is capable of binding a Pr^{III} ion within the central cavity using oxygen atoms not involved with the repeat unit. A 24-MC_{Pd^{II}}-6 macrocycle

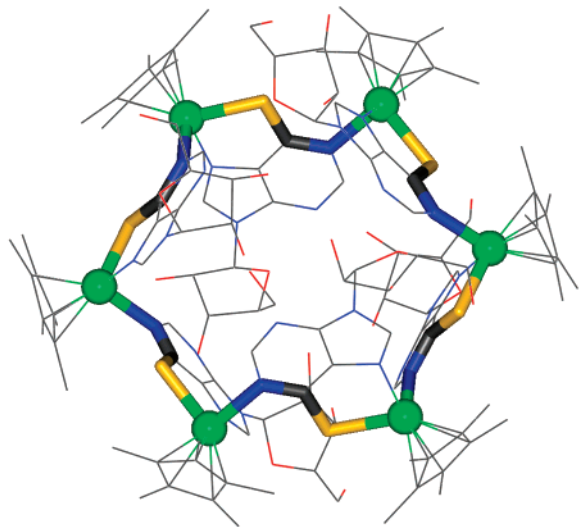


Figure 82. X-ray crystal structure of the vacant expanded $[24\text{-MC}_{\text{Rh}^{\text{III}}-6}]^{6+}$ complex with the ligand 6-purinethione riboside. The Rh^{III} ions are capped by η^2 -cyclopentadiene and connected to each other via N–C–S bridges. Color scheme: green sphere: Rh^{III} ; blue tube, nitrogen; yellow tube, sulfur; red line, oxygen; gray line, carbon. Hydrogen atoms, CF_3SO_3^- counteranions, and lattice solvent have been removed for clarity.⁵³³

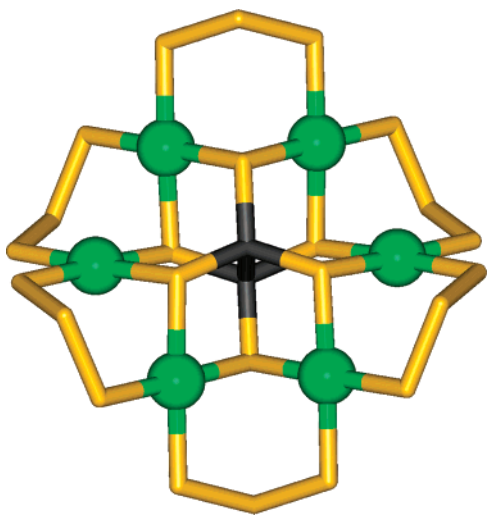


Figure 83. X-ray crystal structure of the expanded $[24\text{-MC}_{\text{Pd}^{\text{II}}-6}]^{6-}$ complex. Each Pd^{II} ion is bridging to neighboring Pd^{II} ions via a $[\text{S}-\text{S}-\text{S}]^{2-}$ bridge. The metallamacrocycle encapsulates a $(\text{C}_2\text{S}_6)^{6-}$ anion within the central cavity. Color scheme: green sphere, Pd^{II} ; yellow tube, sulfur; gray tube, carbon. The Na^+ and $\{(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}\}^+$ counteranions have been removed for clarity.⁵³⁵

consists of alternating Pd^{II} and S_3^{2-} units to construct a repeat unit of $-\text{[Pd}^{\text{II}}-\text{S}-\text{S}-\text{S}]-$ (Figure 83).⁵³⁵ The 24-MC-6 encapsulates a $\text{C}_2\text{S}_6^{6-}$ anion within the central cavity, and each sulfur atom of the $\text{C}_2\text{S}_6^{6-}$ anion bridges two of the ring Pd^{II} ions. A 24- $\text{MC}_{\text{Sn}^{\text{IV}}-6}$ is formed from six $\text{Sn}(\text{C}_6\text{H}_5)_3^+$ groups and six diphenylphosphate anions (Figure 84).⁵³⁶ The O=P–O atoms of the diphenylphosphate provide the six bridges in the MC ring. The overall metallamacrocycle has a puckered configuration with the Sn^{IV} ions in a trigonal bipyramidal geometry. The MC ring does not bind any guests within the central cavity. A similar 24- $\text{MC}_{\text{Sn}^{\text{IV}}-6}$ has been synthesized with dimethylphosphate.⁵³⁷

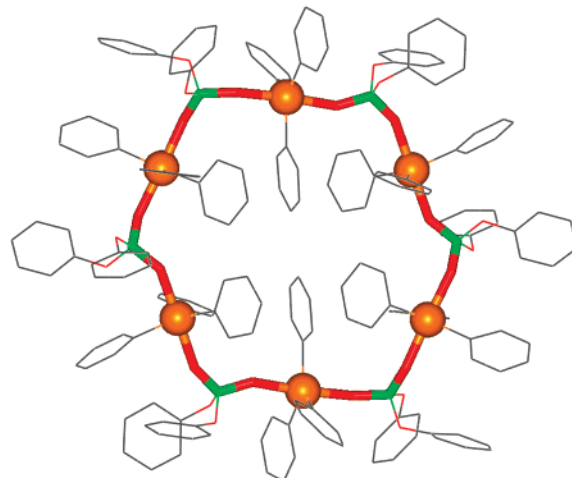


Figure 84. X-ray crystal structure of the vacant expanded $[24\text{-MC}_{\text{Sn}^{\text{IV}}-6}]$ complex with the ligand diphenylphosphate. The $\text{Sn}(\text{C}_6\text{H}_5)_3^+$ groups are connected via O–P–O bridges. Color scheme: orange sphere, Sn^{IV} ; red tube, oxygen; green tube, phosphorus; gray line, carbon. Hydrogen atoms have been removed for clarity.⁵³⁶

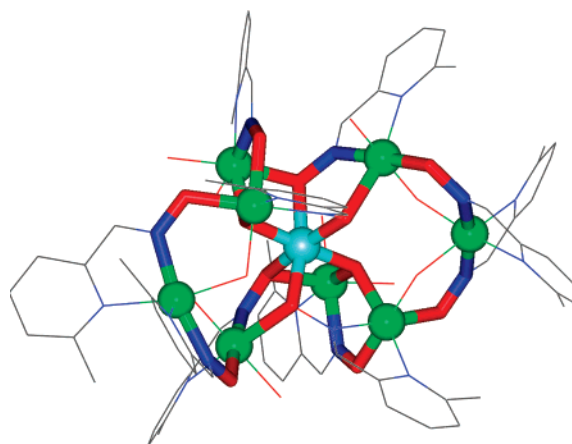


Figure 85. X-ray crystal structure of the $\text{Ni}^{\text{II}}[24\text{-MC}_{\text{Ni}^{\text{II}}-8}]^{2+}$ complex with the ligand 1-[2-(6-methylpyridyl)]ethanone oxime. The eight ring Ni^{II} ions constitute a nonplanar MC ring, which encapsulates a $\text{Ni}^{\text{II}}\text{O}_6$ core. Color scheme: aqua sphere, central Ni^{II} ; green sphere, ring Ni^{II} ; blue tube, nitrogen; red tube and line, oxygen; gray line, carbon. Hydrogen atoms, ClO_4^- counteranions, and lattice solvent have been removed for clarity.⁵³⁹

2.11. 24-MC-8

Two 24-MC-8 complexes have been synthesized with $-\text{[M}-\text{N}-\text{O}]-$ connectivity. A 24- $\text{MC}_{\text{Ni}^{\text{II}}-8}$ can be synthesized with the ligand 1-[2-(6-methylpyridyl)]ethanone oxime (Figure 85).^{538,539} The MC ring consists of connectivity $[\text{Ni}^{\text{II}}-\text{O}-\text{N}-\text{Ni}^{\text{II}}-\text{N}-\text{O}-\text{Ni}^{\text{II}}-\text{O}-\text{N}-\text{Ni}^{\text{II}}-\text{O}-\text{N}]_2$ and captures an octahedral $\text{Ni}^{\text{II}}\text{O}_6$ moiety. The second 24-MC-8 complex is made from the oxime ligand di-2-pyridyl ketone oxime (Hpko) and manganese ions.⁵⁴⁰ The manganese ions of the MC ring are in three different oxidations (2+, 3+, and 4+) with a MC connectivity of $[\text{Mn}^{\text{III}}-\text{O}-\text{N}-\text{Mn}^{\text{II}}-\text{N}-\text{O}-\text{Mn}^{\text{IV}}-\text{O}-\text{N}]_2$. In addition, the MC ring wraps around a star-shaped 16-membered ring with the connectivity of $[\text{Mn}^{\text{III}}-\text{O}-\text{Mn}^{\text{II}}-\text{O}-\text{Mn}^{\text{III}}-\text{O}-\text{Mn}^{\text{IV}}-\text{O}]_2$. Interestingly, the oxygen atoms of the MC ring and star ring originate from nonrelated ligands. The S-shaped MC ring captures a tetranuclear mixed-valent manganese core, $[\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_2(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{pko})_4]$.

An aza24- $\text{MC}_{\text{Fe}^{\text{III}}-8}$ complex can be generated from a ligand similar to that used to synthesize the *N*-acylsalicyl-

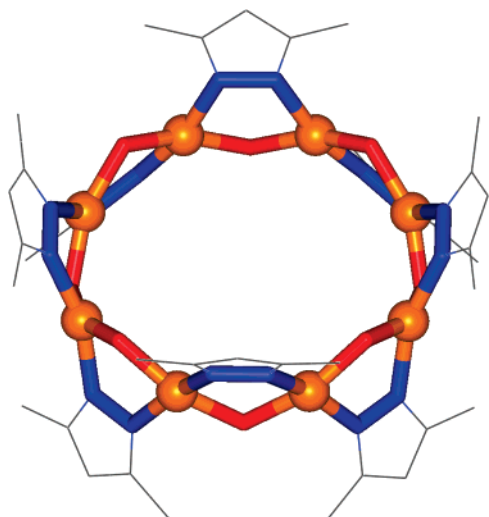


Figure 86. X-ray crystal structure of the vacant aza[24-MC_{Cu^{II}-8] complex with the ligand 3,5-dimethylpyrazole. The Cu^{II} are bridged by the pyrazolate anions and by μ -OH anions. Color scheme: orange sphere, Cu^{II}; blue tube, nitrogen; red tube, oxygen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁵⁴²}

hydrazide aza18-MC-6 complexes.⁵⁴¹ The additional steric bulk of *N*-isobutyrylsalicylhydrazidate creates the larger metallamacrocycle. Like the similar aza18-MC-6 complexes, the ring Fe^{III} ions have a propeller configuration with alternating Δ and Λ stereochemistry about the MC ring. In addition, the MC does not host any guests within the central cavity.

3,5-Dimethylpyrazole and Cu^{II} ions are also able to produce an aza24-MC-8 complex (Figure 86).^{542,543} The pyrazolate anions provide N–N bridges between the eight Cu^{II} ions, and the Cu^{II} ions are bridged by μ -OH anions. Each Cu^{II} ion has an approximately square planar geometry within the MC ring, and the pyrazolate anions alternate positions above and below the plane created by the eight Cu^{II} ions. In addition, no guest molecules could be located within the central cavity.

A decadentate diazine ligand generates an aza24-MC-8 complex with ring Ni^{II} ions.⁴⁸² Each ligand is capable of providing two N–N bridges and the coordination environment for three Ni^{II} ions; therefore, only four ligands are needed to construct the 24-membered MC ring. Each Ni^{II} ion is in a distorted octahedral environment with N₄O₂ coordination. Three water molecules are hydrogen-bonded within the central cavity. In addition, the use of the heptadentate ligand 1,5-bis(2-hydroxybenzaldehyde)thiocarbohydrazone provides an azine bridge to create an aza24-MC-8 with a $-\text{[Cu}^{\text{II}}-\text{N}-\text{N]}-$ repeat unit.⁵⁴⁴ Four of the Cu^{II} ions have a square planar geometry filled by two nitrogen atoms, one oxygen atom, and one sulfur atom. The coordination geometry of the remaining Cu^{II} ions ranges from distorted trigonal bipyramidal to trigonal bipyramidal to distorted square pyramidal to distorted octahedral. The resulting geometry depends on the location of disordered solvent molecules.

2.12. 30-MC-10

An aza30-MC-10 can be constructed with *N*-benzoylsalicylhydrazidate, which provides the N–N bridges (Figure 87).⁵⁴⁵ The complex contains a $[\text{Mn}^{\text{III}}-\text{N}-\text{N}]_{10}$ metallamacrocycle and does not encapsulate any guests within the oval-shaped cavity. The Mn^{III} ions have a propeller configuration with alternating Δ and Λ stereoconfiguration about the MC

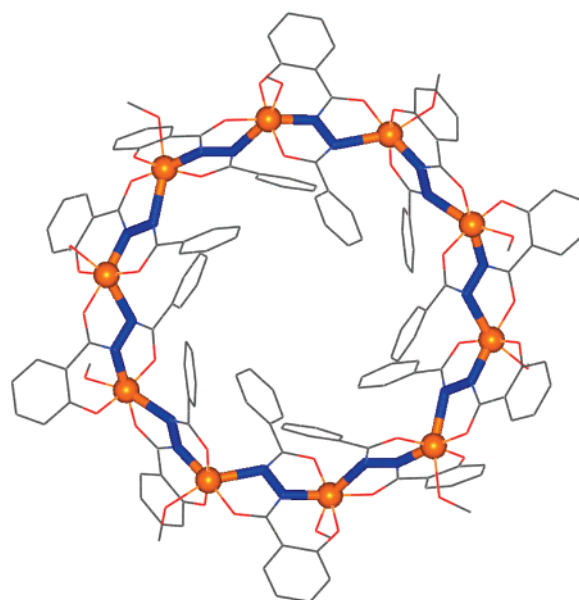


Figure 87. X-ray crystal structure of the vacant aza[30-MC_{Mn^{III}-10] complex with the ligand *N*-benzoylsalicylhydrazidate. The Mn^{III} ions have alternating propeller configurations of Δ and Λ about the MC ring. The structure has a similar connectivity with the aza-[18-MC_{Mn^{III}-6] made with *N*-formylsalicylhydrazidate (Figure 78). Color scheme: orange sphere, Mn^{III}; blue tube, nitrogen; red line, oxygen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁵⁴⁵}}

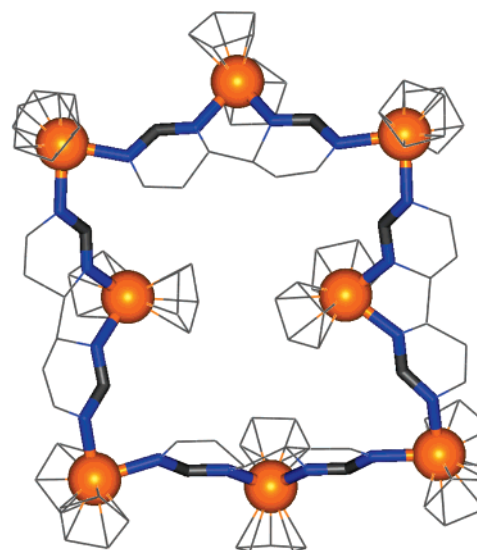


Figure 88. X-ray crystal structure of the vacant expanded aza-[32-MC_{Ti^{II}-8] complex. Two Ti^{II} coordination modes are present within the structure. “Corner” Ti^{II} ions are capped by two η^5 -cyclopentadiene ligands and bound to nitrogen atoms from two ligands. Ti^{II} ions along the sides are also capped by two η^5 -cyclopentadiene ligands, but the ions are bound by two nitrogen atoms of one ligand in a bidentate fashion. Color scheme: orange sphere, Ti^{II}; blue tube, nitrogen; gray line, carbon. Hydrogen atoms have been removed for clarity.¹²³}

ring as in the similar *N*-acylsalicylhydrazide 18-MC-6 and 24-MC-8 complexes. An isostructural Fe^{III} complex has also been synthesized.

2.13. 32-MC-8

A 32-membered ring with a $[\text{Ti}^{\text{II}}-\text{N}-\text{C}-\text{N}]_8$ metallamacrocycle with a dipyrimidine ligand forms a puckered structure with no encapsulated guest (Figure 88).¹²³ Four of the Ti^{II}

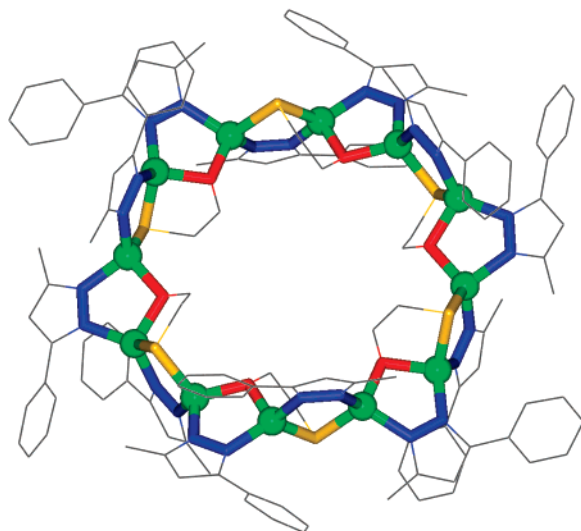


Figure 89. X-ray crystal structure of the vacant aza[36-MC_{Zn^{II}}-12] complex. The Zn^{II} ions are connected to neighboring Zn^{II} ions via N–N bridges provided by a pyrazole-based ligand and via alternating μ -O and μ -S bridges. Color scheme: green sphere, Zn^{II}; blue tube, nitrogen; red tube, oxygen; yellow tube, sulfur; gray line, carbon. Hydrogen atoms have been removed for clarity.⁵⁴⁶

are bound to two η^5 -cyclopentadiene ligands and two dipyrimidine ligands. These Ti^{II} ions alternate with a second Ti^{II} coordination mode in which the second Ti^{II} ions are bound to two η^5 -cyclopentadiene ligands and only one dipyrimidine ligand in a bidentate fashion.

2.14. 36-MC-12

Three vacant aza36-MC-12 complexes have been synthesized at the time of this review. Using 5-methyl-3-phenylpyrazole, an aza36-MC-12 with a [Zn^{II}–N–N]₁₂ metallamacrocycle can be generated (Figure 89).⁵⁴⁶ Each Zn^{II} ion is in a distorted tetrahedral coordination geometry and is also connected to neighboring Zn^{II} ions via alternating μ -S and μ -O bridges. Using a ligand that is similar to the ones used to synthesize aza18-MC-6 complexes, an aza36-MC-12 with Mn^{III} ions and *N-trans*-2-pentenoylsalicylhydrazide produce a metallamacrocycle with a –[Mn^{III}–N–N]– repeat unit (Figure 90).⁵⁴⁷ Each Mn^{III} ion has a propeller configuration with the stereochemistry having a repeat unit of [$\Lambda\Lambda\Delta\Delta$]₃ about the metallamacrocycle. This configuration is different from the similar aza18-MC-6, aza24-MC-8, and aza30-MC-10 complexes in which each Mn^{III} or Fe^{III} has alternating Λ and Δ configurations about the MC ring. The 36-MC-12 complex is vacant except for solvent molecules. Using a ligand similar to the above MC, salicylaldehyde 2-pyridinecarboxylhydrazone, an aza36-MC-12 complex can be constructed with a repeat unit of –[Ni^{II}–N–N]–. Like the Mn^{III} aza36-MC-12, the Ni^{II} ions have a propeller configuration with an absolute stereoconfiguration repeat unit of [$\Lambda\Lambda\Delta\Delta$]₃.⁵⁴⁸

2.15. 40-MC-10

A 40-membered metallamacrocycle 40-MC-10 consists of a [Pd^{II}–O–C–N]₁₀ metallamacrocycle created with the ligand 5-chloro-2,3-dihydropyridine (Figure 91).⁴⁷⁹ A similar ligand was used to construct a 16-MC-4 complex.⁴⁷⁹ The ligand binds bidentate to one Pd^{II}, forming a five-membered chelate ring, and then bridges to an adjacent Pd^{II} via the pyridyl nitrogen to generate the metallamacrocycle.

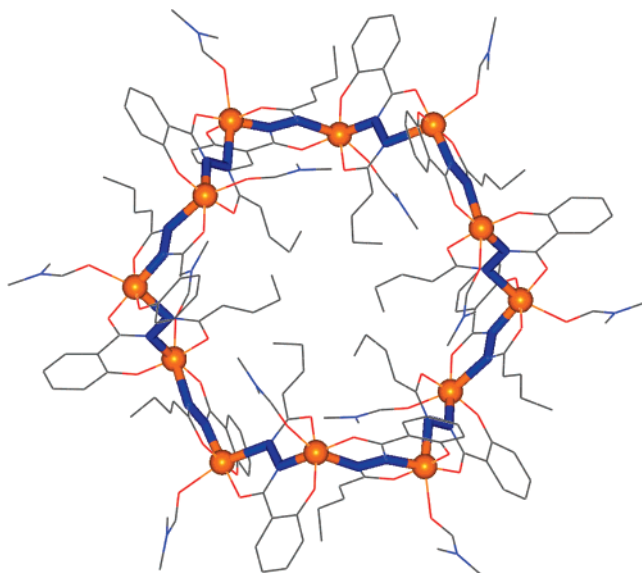


Figure 90. X-ray crystal structure of the vacant aza[36-MC_{Mn^{III}}-12] complex with the ligand *N-trans*-2-pentenoylsalicylhydrazide. The propeller configuration of the Mn^{III} ions has a repeat unit of –[$\Lambda\Lambda\Delta\Delta$]– about the MC ring. The similar aza18-MC-6, aza24-MC-8, and aza30-MC-10 complexes have alternating Δ and Λ configurations about the MC ring. Color scheme: orange sphere, Mn^{III}; blue tube, nitrogen; red line, oxygen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁵⁴⁷

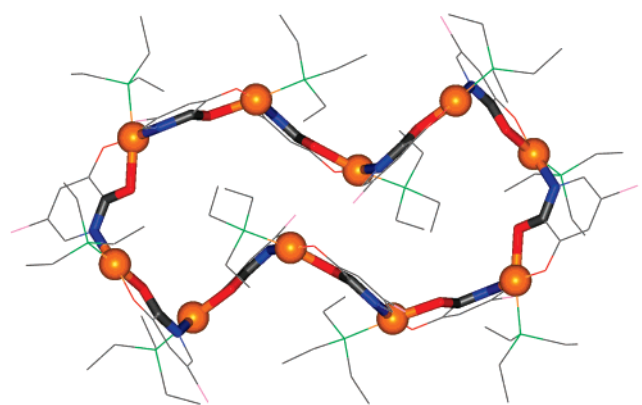


Figure 91. X-ray crystal structure of the expanded [40-MC_{Pd^{II}}-10] complex with the ligand 5-chloro-2,3-dihydropyridine. The Pd^{II} ions are connected via O–C–N bridges, and the coordination sphere of each Pd^{II} is completed by a five-membered chelate ring, a pyridyl nitrogen, and a triethylphosphine group. Color scheme: orange sphere, Pd^{II}; blue tube, nitrogen; red tube, oxygen; gray tube, carbon; green line, phosphorus; magenta line, chlorine. Hydrogen atoms and lattice solvent have been removed for clarity.⁴⁷⁹

The flexible molecule folds back upon itself to create a peanut-shaped ring, and the MC does not bind any guest within the central cavity.

2.16. 60-MC-20

The largest metallacrown structure synthesized to date is a 60-membered metalladiazamacrocycle.⁵⁴⁹ The highly puckered, *S*₄-symmetric icosanuclear manganese complex with a –(Mn^{III}–N–N)– repeat unit was synthesized using the triply deprotonated pentadentate ligand *N*-3-phenyl-*trans*-2-propenoyl-salicylhydrazide (Figure 92). All Mn^{III} ions have a distorted octahedral geometry and are in five different chemical environments. Eight of the twenty *N*-terminal 3-phenyl-*trans*-2-propenoyl groups fill in the inner cavity of the metallamacrocycle. Also, four phenoxy

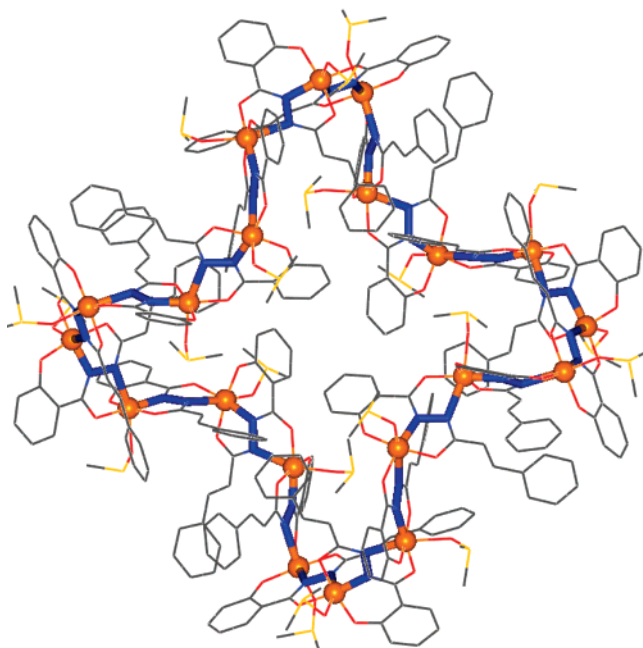


Figure 92. X-ray crystal structure of the vacant aza[60-MC_{Mn^{III}}-20] complex with the ligand *N*-3-phenyl-*trans*-2-propenoysalicylhydrazide. The propeller configuration of the Mn^{III} ions has a repeat unit of $-\text{[\Delta\Delta\Delta\Delta\Delta][\Delta\Delta\Delta\Delta\Delta]}-$ about the MC ring. The similar aza18-MC-6, aza24-MC-8, and aza30-MC-10 complexes have alternating Δ and Λ configurations about the MC ring, and the related aza[36-MC_{Mn^{III}}-12] complex has a propeller configuration repeat unit of $-\text{[\Lambda\Lambda\Delta\Delta]}-$ about the MC ring. The coordination sphere about the 20 manganese ions is completed by 18 DMSO and 2 H₂O molecules. Color scheme: orange sphere, Mn^{III}; blue tube, nitrogen; red line, oxygen; yellow line, sulfur; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁵⁴⁹

groups are directed to the inner side of the system, contrary to all previously observed metallacrowns.

2.17. Metallacrowns within Metallacrowns

Although not technically metallacrowns because each metallamacrocycle is not discrete, a series of interesting Cu^{II} metallamacrocycles have been synthesized with $-\text{[Cu}^{\text{II}}-\text{N}-\text{N]}-$ connectivity (Figure 93).⁵⁵⁰ Azametallacrowns of size 18-MC-6, 24-MC-8, 27-MC-9, 36-MC-12, and 42-MC-14 can be generated in which the Cu^{II} ions are interconnected by pyrazolate anions on the outside of the ring and by μ -OH bridges on the inside of the ring. [A Cu^{II}]₉ ring is also synthesized, but the N–N connectivity is broken by an $^-\text{O}_2\text{CCH}_3$ group; however, this ring may be considered a molecular wheel (18-MC-9) because the μ -OH bridges remain intact to give a metallamacrocycle. See below for a more extensive treatment of molecular wheels.] The MC rings are then connected to each other by the μ -OH bridges of a larger ring, which bind axially to Cu^{II} ions of a smaller ring to give the Cu^{II} ions of the smaller ring a distorted square-pyramidal geometry. The set of 36-MC-12 and 18-MC-6 azametallacrowns then dimerizes with an identical set of azaMCs to capture a Cl[−] anion between the central cavities, creating a supramolecular sandwich. Two similar supramolecular complexes have also been assembled: in one a 36-MC-12 hosts an 18-MC-6 on one face and a 27-MC-9 on the opposite face and encapsulates a CO₃^{2−} anion, whereas in the other a 42-MC-14 hosts a 24-MC-8 and a 18-MC-9 on opposite faces and encapsulates a SO₄^{2−} anion.⁵⁵⁰

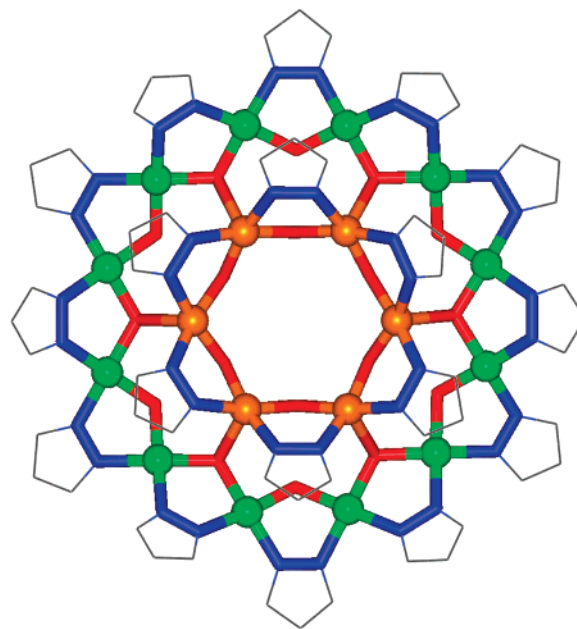


Figure 93. X-ray crystal structure of a metallacrown within a metallacrown. An aza[18-MC_{Cu^{II}}-6] is bound to an aza[36-MC_{Cu^{II}}-12] via bridging μ_3 -O atoms of the larger MC binding to Cu^{II} ions of the smaller MC. The Cu^{II} ions of each MC are connected via N–N bridges from pyrazolate anions and μ_2 -O or μ_3 -O bridges. This structure can dimerize with a second identical aza{[18-MC_{Cu^{II}}-6][36-MC_{Cu^{II}}-12]} structure to entrap a Cl[−] anion between the oxygen atoms of the smaller MCs. Color scheme: orange sphere, Cu^{II} ions of aza18-MC-6; green sphere, Cu^{II} ion of aza36-MC-12; blue tube, nitrogen; red tube, oxygen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁵⁵⁰

2.18. Molecular Wheels

2.18.1. Introduction

Molecular wheels provide unique metallamacrocycle connectivity with a one-atom bridge between metal ions; the repeat unit is $[\text{M}-\text{X}]$. The complexes typically have a circular shape; however, the shape may deviate from a perfect circle. The molecular wheels are similar to the molybdenum oxide wheel compounds pioneered by Müller.^{91,551–559} However, the molecular wheels are not nearly as large (the Müller wheels may reach sizes of 176 Mo ions⁵⁵¹), and the ring connectivity is only one-dimensional—a simple circle. The Müller wheels have a torus shape with the Mo connectivity also in a second dimension. Molecular wheels may be synthesized from *s*-, *d*-, and *f*-block metal ions, and bridging atoms include most of the *p*-block elements except the noble gases. Although not traditionally considered a metallacrown, these molecular wheels, which are typically open structures with a vacant cavity, have sometimes been referred to as MCs as some of these molecular wheels bind metals within the central cavity. When referred to as metallacrowns, these wheel complexes follow a similar naming scheme with a $2X-\text{MC}-X$ designation, where *X* is the number of bridging heteroatoms and $2X$ is the total number of atoms within the wheel. Various sized molecular wheels have been made including 8-MC-4, 10-MC-5, 12-MC-6, 14-MC-7, 16-MC-8, 18-MC-9, 20-MC-10, 22-MC-11, 24-MC-12, 28-MC-14, 32-MC-16, 36-MC-18, and 48-MC-24 (Table 3).

2.18.2. 8-MC-4

Although not wheel-shaped, 8-MC-4 complexes have the same cyclic connectivity as other molecular wheels. These

Table 3. Ligands and Metals Used for the Synthesis of Molecular Wheel Complexes, Their Cavity Radii, and Guests

bridging ligand	ring-metal	cavity radius (Å)	guest	ref	CCDC refcode
PhN(SO ₂) ₂	Mg ₆			757	LISRUA
	Al ₆			758	HUQNUC HUQPEO
bis(2-oxyethyl)(methyl)amine, oxo bis(2-oxyethyl)(2-hydroxyethyl)amine	Ti ₆	2.19		759	DAVYOO
	V ₆	1.01	Na ⁺	760, 761	CUMSEI(01)
		0.88	Mn ²⁺	762	XUTSIO
acetate, hydroxide methoxo	Cr ₆	0.68		764	AQOKAS FAGDOH
	Mn ₆	0.88	Mn ²⁺	765	PAZVER PAZVOB
2-hydroxymethylpyridine, hydroxo	Mn ₆	0.89	Mn ²⁺	766	NITBEX
		0.88	Mn ²⁺	767	IPULUA
bis(2-oxyethyl)(benzyl)amine	Mn ₆	0.92	Mn ²⁺	768	PAKPAT
bis(2-oxyethyl)(methyl)amine	Mn ₆	0.90	Mn ²⁺	768	PAKPEX
bis(2-oxyethyl)(ethyl)amine	Mn ₆	0.91	Mn ²⁺	768	PAKPIB
methoxo	Mn ₆	1.00	Na ⁺	770	NOCJEU
3-methoxy-2-salicylideneamino	Fe ₆	0.85	Fe ³⁺	771	TUSFOC
hydroxo, oxo	Fe ₆	1.34		772	WILGUT
methoxo	Fe ₆	1.05	Na ⁺	773, 774	YIYRED
					YIYRIH TUMSUP
methoxo	Fe ₆	0.90	Li ⁺	775	NECDUU
bis(2-oxyethyl)(2,5-dimethylbenzyl)amine	Fe ₆	1.01		776	ABOKUX
bis(2-oxyethyl)(ethyl)amine	Fe ₆	1.01		777	RAHBOS
bis(2-oxyethyl)[3,5-bis(4'-methoxycarbonylbenzoxy)benzyl]amine	Fe ₆	1.05		778	BEQQUK
bis(2-oxyethyl)(3,5-di- <i>tert</i> -butylbenzyl)amine	Fe ₆	1.12		778	BEQREV
	In ₆	1.23		778	BEQRAR
bis(2-oxyethyl)(3,6,9-trioxadecyl)amine	Fe ₆	1.10		779	SACZAY
bis(2-oxyethyl)(<i>n</i> -butyl)amine	Fe ₆	1.10		779	SACZEC
bis(2-oxyethyl)(ethyl)amine	Fe ₆	1.12		779	SACZIG
bis(2-oxyethyl)(3,6,9-trioxaundecyl)amine	Fe ₆	1.11		779	SACZUS
bis(2-oxyethyl)[naphth-2-yl]methylamine	Fe ₆	1.10		779	SADBEF
bis(2-oxyethyl)[naphth-1-yl]methylamine	Fe ₆	1.11		779	SADBIJ
bis(2-oxyethyl)(3-cyano-3,3-diphenylpropyl)amine	Fe ₆	1.04		779	SADBOP
bis(2-oxyethyl)(3,6-dioxaocetyl)amine	Fe ₆	1.08		779	SADBUV
bis(2-oxyethyl)(benzyl)amine	Fe ₆	1.10		779	SADCEG
bis(2-oxyethyl)(allyl)amine	Fe ₆	1.07		779	SADCIK
bis(2-oxyethyl)(hex-5-enyl)amine	Fe ₆	1.05		779	SADDAD
bis(2-oxyethyl)(<i>n</i> -hexyl)amine	Fe ₆	1.04		779	SADDEH
bis(2-oxyethyl)(<i>n</i> -octyl)amine	Fe ₆	1.03		779	SADDIL
bis(2-oxyethyl)(<i>n</i> -decyl)amine	Fe ₆	1.09		779	SADDOR
bis(2-oxyethyl)(3-oxapentyl)amine	Fe ₆	1.10		779	SADFAF
bis(2-oxyethyl)(8-phenoxy-3,6-dioxaocetyl)amine	Fe ₆	1.08		779	SADFEJ
bis(2-oxyethyl)[(5-naphth-1-yloxy)-3-oxapentyl]amine	Fe ₆	1.06		779	SADFIN
bis(2-oxyethyl)[(5-(2-(phenylethynyl)phenoxy)-3-oxapentyl]amine	Fe ₆	1.11		779	SADFOT
bis(2-oxyethyl)[3,5-bis(allyloxy)benzyl]amine	Fe ₆	1.06		779	SADFUZ
bis(2-oxyethyl)(8-phenoxy-3,6-dioxaocetyl)amine	Fe ₆	1.10		779	SACZOM
bis(2-oxyethyl)[2-(phenoxy)ethyl]amine	Fe ₆	1.11		779	SADBAB
bis(2-oxyethyl)(5-phenoxy-3-oxapentyl)amine	Fe ₆	1.01		779	SADCAC
bis(2-oxyethyl)(4- <i>tert</i> -butylbenzyl)amine	Fe ₆	1.05		779	SADCOQ
bis(2-oxyethyl)[2-(1,3-dioxan-2-yl)ethyl]amine	Fe ₆	1.06		779	SADCUW
bis(2-oxyethyl)(<i>n</i> -decyl)amine	Fe ₆	1.05		779	SADDUX
<i>n</i> -propylthioacetato	Co ₆	1.16		779	PTACCO
3-(diphenylphosphino)propionato	Co ₆	1.26		781	CAWJIT
	Ni ₆	1.25		781	CAWJEP
1,5-di- <i>p</i> -tolyl-1,4-penta-azadienido, methoxo	Co ₆	1.47		782	FIHJEL
38,41,44,47,50,53-hexamethyl-1,7,13,19,25,31-hexaazahepta-benzohexatriconta-1,3,6,9,13,15,18,21,24,27,31,33-dodecaene-4,10,16,22,28,34-hexaolato, acetato, hydroxo	Cu ₆	0.36		783	KEGRAP
bis(2-oxyethyl)(2,5-dimethylbenzyl)amine	Cu ₆	1.21	2 NaBr	785	QOZPAW
bis(2-oxyethyl)(benzyl)amine	Cu ₆	1.11	2 LiCl	785	QOZPEA
2-pyridylmethanolato	Zn ₆	0.79	Zn ²⁺	786	TUQJAJ
trifluoroacetato, ethoxo	Nb ₆	2.02		787	ERIJY
oxo, hydroxo	Sb ₆		oxalate	789	JODLET
oxo, ethoxo	Hf ₆			790	DANRUF
5,17-di- <i>tert</i> -butyl-26,28-bis(carboxymethoxy)-11,23,25,27-tetraoxocalix(4)arene	Pb ₆		6 H ₂ O	791	WOPWIH
oxo	Ni ₂ Mo ₄			793	RUNXON
2,6-bis(dimethylaminomethyl)phenylthiolato	Li ₆			794	TIBCOW
ethanethiolato	Ni ₆			795, 798	NIEMER(01, 02)

Table 3. (Continued)

bridging ligand	ring-metal	cavity radius (Å)	guest	ref	CCDC refcode
<i>N,N</i> -dimethylmercaptopropylamine	Ni ₆			797, 799	DENSEU
methanethiolato	Ni ₆			800, 802	JEZHAX
<i>n</i> -propylthiolato	Ni ₆			801	SEHXOS
					JOXMOY
					YEGSIM
1-hydroxyethane-2-thiolato	Ni ₆			804	CHESNI(01)
1,1-dicyanoethene-2-thio-2'-perthiolato	Cu ₆			671	LUDNUT
4,6-dimethylpyrimidine-2-thione	Cd ₆			805	YEDNEA
<i>n</i> -propylthiolato	Pd ₆			806	PDPRMC
2,4,6-tri-isopropylphenylthiolato	Au ₆			807, 808	SOLTES
					RUVGEU
2- <i>tert</i> -butyl-benzenethiolato	Au ₆			756	YESQIV
2,2,6,6-tetramethylpiperidide	Na ₄ Mg ₂		benzene	737	HECVEQ
			toluene	737	HECTIS
dimethylamido, fluoro	Ti ₆			809	QENVOU
2,3-dimethylbut-2-ene, chloro	Al ₆			810	SELCOB
chloro	Cu ₆		2 (1,3,5-triazine)	811	ADIHAW
bromo	Cu ₆		2 (1,1,1-tris(diphenyl-phosphino-methyl)ethane)-cyclotriphosphorus-cobalt	812	BEFD0F
diisopropyldiselenophosphato	Ag ₆			813	FIBNIN
phenylselenolato	Bi ₆		2 Br ⁻	814	LOFZIP
chloro	V ₇		2 Cl ⁻	815	GOHMIZ
(2,6-bis(benzoylamino)phenyl)phosphato	Ca ₈		<i>n</i> H ₂ O	816	EDUNOG
perfluorobenzoato, oxo	Ti ₈	2.14	toluene	817	YUZNAI
methacrylato, oxo	Ti ₈			818	SUPQOJ
acetato, ethoxo, hydroxo	V ₈	1.70		819	NAMPAS
benzoato, ethoxo, hydroxo	V ₈	1.71		820	AQUPOR
methoxo	V ₈	2.42	oxalato	821	SEJYOV
benzoato, hydroxo	Cr ₈			822	HIPGOC
acetato, hydroxo	Cr ₈			823	QEBDIK
<i>p</i> -chlorobenzoato, hydroxo	Cr ₈		<i>p</i> -chlorobenzoate, 2 H ₂ O	824	YIJTEQ
acetato, hydroxo	Cr ₈		H ₂ O	825	UCOMAA
pivalato, hydroxo	Cr ₈			826	AYUCOM
acetato, oxo	Mn ₈	1.04	Ce ⁴⁺	828	APUZOA
3,3-dimethylbutyrato, bis(2-oxyethyl)(2-hydroxyethyl)amine	Mn ₈			828	FIQSUU
tris(2-oxyethyl)amine	Fe ₈		Cs ⁺	90, 829	NEWRIQ
					OBIXOM
1,1,1-tris(oxymethyl)ethane, benzoato	Fe ₈			830	LULMIO
pivalato, phenoxo	Fe ₈		H ₂ O	831, 832	EHOQEX(01)
benzoato, phenoxo	Fe ₈		H ₂ O	831	ENEVOI
acetato, methoxo	Co ₈		NH ⁴⁺	833	PAQFAO
2-oxypropane-1,3-diyl-bis(acetylacetoniminato), hydroxo	Cu ₈			834	RUTMAU
2-oxypropane-1,3-diyl-bis(salicylalimine), hydroxo	Cu ₈			835	MUTNEU
1,3-dimethylamino-2-propanolato, isocyano, hydroxo	Cu ₈	0.65	[Cu(H ₂ O) ₂] ²⁺	619	WAHYEK
methoxo, oxo	Mo ₈			836, 838, 839, 840	DAWYAB
					PUVFAN
					WEDLAS
					WEDLIA
					ICUSII
methoxo, oxo	Mo ₈		oxalate	837	SAKPID
ethoxo, oxo	Mo ₈		oxalate	821	SEJYUB
<i>o</i> -phenylenediphosphonato	Mo ₈			841	IMAQUI
<i>p-tert</i> -butylsulfonycalix(4)arene, acetato	Gd ₈			843	BEPKEN
	Nd ₈			843	BEPKIR
	Sm ₈			843	BEPKUD
	Pr ₈			843	BEPLAK
ethoxo	Bi ₈			844	XOVPEP
oxo	W ₄ Sn ₄			846	PIYVIC
sulfido	Fe ₈			847	QADLIR
ethoxycarbonyl-methylthio	Ni ₈			848	DARGOS
2,4,6-triisopropylphenylthiolato	Cu ₈			667, 849	FIRRED
					KIDSOF
diisopropyl-dithiophosphato	Cu ₈		S ²⁻	850	ZEVFAH
bis(diphenylphosphino)methane, perfluorophenylthiolato	Pd ₈			851	LAHMUC

Table 3. (Continued)

bridging ligand	ring-metal	cavity radius (Å)	guest	ref	CCDC refcode
2-aminoethanethiolato	Co ₄ Pd ₂ Au ₂			852	LOVJOV
	Co ₄ Pd ₂ Ag ₂			852	LOVJUB
diisopropylamido	Mg ₄ Na ₄		ferrocenyl	853	ACOMEK
	Mg ₄ Na ₄		ruthenocenyl	854	BIGVET
	Mg ₄ Na ₄		osmocenyl	854	BIGVIX
1,1-bis(2-pyrrolyl)cyclohexane	Sm ₈			855	QIVGAD
pivalato, fluoro	Cr ₈	2.02		856	IFUZOY
			DMF	856	IFUZUE
			Me ₂ NC(O)Me	856	IGABAT
			Me ₂ NC(O)Me, DMF	856	IGABEX
			2 CH ₃ CN	856	IGABIB
			THF	856	IGABOH
			hexane	857	ADIZOC
		1.99	ⁿ Bu ₂ NH ₂ ⁺	859	TUSCIT
	Cr ₆ V ₂	2.01	Et ₂ NH ₂ ⁺	858	BEMCIG
	Cr ₇ Zn	1.99	Et ₂ NH ₂ ⁺	858	BEMCUS
	Cr ₇ Ni	1.99	Me ₂ NH ₂ ⁺	859	TUSBOY
		1.99	Et ₂ NH ₂ ⁺	859	TUSCAL
		1.99	ⁿ Pr ₂ NH ₂ ⁺	859	TUSCEP
		1.99	ⁿ Oct ₂ NH ₂ ⁺	859	TUSCOZ
	Cr ₇ Co	1.99	Me ₂ NH ₂ ⁺	859	TUSBUE
			Et ₂ NH ₂ ⁺	859	TUSCUF
	Cr ₇ Mn		Et ₂ NH ₂ ⁺	859	TUSDEQ
	Cr ₇ Fe		Et ₂ NH ₂ ⁺	859	TUSDIU
	Cr ₇ Cd		Et ₂ NH ₂ ⁺	859	TUSCIT
	Fe ₈	2.00	ⁿ Pr ₂ NH ₂ ⁺	861	YAPSAK
	Fe ₇ Mn		ⁿ Pr ₂ NH ₂ ⁺	861	YAPRUD
	Fe ₇ Cd		ⁿ Pr ₂ NH ₂ ⁺	861	YAPSEO
	Fe ₇ Ni		ⁿ Pr ₂ NH ₂ ⁺	861	YAPNIS
	Fe ₇ Zn		ⁿ Pr ₂ NH ₂ ⁺	861	YAPSOY
	Fe ₇ Co		ⁿ Pr ₂ NH ₂ ⁺	861	YAPSUE
	V ₇ Zn		ⁿ Pr ₂ NH ₂ ⁺	861	YAPTAL
	V ₇ Ni		ⁿ Pr ₂ NH ₂ ⁺	861	YAPTEP
2,6-bis(salicylideneaminomethyl)-4-methylphenolato	Fe ₆ Na ₃			862	MEWFOJ
pivalato, fluoro	Cr ₇ V ₂	2.41	(cyclohexyl) ₂ NH ₂ ⁺	863	FANKEL
	Cr ₈ Ni		(cyclohexyl) ₂ NH ₂ ⁺	860, 863	FANKIP
phenylthiolato	Ni ₉			864	AHAYOX(01)
chloroacetato, methoxo	Fe ₁₀			865	VIJFEZ(10)
acetato, methoxo	Fe ₁₀			866	NAHHOT
3-(4-methylbenzoyl)propionato, methoxo	Fe ₁₀			867	FAMQIT(01)
pivalato, methoxo	Fe ₁₀			831, 832	EHOQIB(01)
acetato, methoxo	Cr ₁₀			868	GUHWAH
acetato, ethoxo	Cr ₁₀			868	GUHWEL
hydroxo, sulfido	Mo ₁₀		2 Cl ⁻	870	VUZNUZ
acetato, oxo	Mo ₁₀		2 [Y(H ₂ O) ₅] ³⁺	871	CAKLIK(01)
2-methoxyethoxo	Y ₁₀			872	SEFFAK
	Dy ₁₀			873	LABDIC
acetato, methoxo	Mn ₅ Cr ₅			874	VASBEX
					VASBIB
oxo, sulfido, aqua	Mo ₁₀		2 I ⁻	876	CUCZOP
pivalato, fluoro	Cr ₈ Ni ₂	3.11	(TACN) ₂ Ni	877	FAQBOP
chloro	Cu ₁₀		CH ₃ CN	878	EFAHAU
phenylthiolato	Ni ₁₁		THF	864	AHAYAJ
					AHAYEN
borophosphato	V ₁₂	1.51	NH ₄ ⁺	879	HOTHON
		1.37	K ⁺	879	HOTHUT
bis(2-oxyethyl)(methyl)amine, acetato	Mn ₁₂			777, 880	RAHBIM(02)
					MANRID
bis(2-oxyethyl)(<i>n</i> -butyl)amine, acetato	Mn ₁₂			880	MANRAV
					MANREZ
methoxo	Fe ₁₂			881, 882	FESJAO(01)
2-hydroxo-2,2-diphenylacetato, methoxo	Fe ₁₂			883	OFUQAH
proline, methoxo	Fe ₁₂			884	ESAMOA
6-chloro-2-pyridinato, acetato	Co ₁₂			885	MUDVIQ
	Ni ₁₂			887	PONRIT(01)
biphenyl-2,2'-dicarboxylato, isonicotinato	Cd ₁₂			888	LABXAO
oxo, hydroxo	Mo ₁₂			889	RABTIT
acetato, methoxo	Mn ₆ Cr ₆			874	VASBIB
3-methylcatecholato	Sb ₆ Na ₆			890	MUBGUL
bis(2-mercatophenyl)sulfido	Fe ₁₂			891	FAFGAV
2,6-diisopropylphenylamino, ethyl	Mg ₁₂			892	ROBDUH
2-methoxyphenylimido	Sb ₁₂			893	NAFWAS

Table 3. (Continued)

bridging ligand	ring-metal	cavity radius (Å)	guest	ref	CCDC refcode
2,2,6,6-hexamethylpiperidide	Mg ₆ K ₆		6 phenyl 6 tolyl	894 894	MEHHIQ MEHHOW
pivalato, fluoro	Cr ₁₀ Cu ₂		2 Me ₂ NH ₂ ⁺	858	BEMCOM
<i>N,N,N'</i> -triisopropylguanidinato, chloro	Mg ₁₂			895	QAQSUW
tri- <i>tert</i> -butylsilylthio, chloro	Fe ₁₂			896	OHOKUR
	Co ₁₂			755	IVATEE
tri- <i>tert</i> -butyl-silylthio, bromo	Fe ₁₂			896	OHOKOL
	Ni ₁₂			755	IVATHI
<i>N</i> -(trimethylsilyl)triethylphosphanimino, chloro	Zn ₁₂			898	NEWQEL
phenylselenolato	Fe ₁₂			899	YITVUS YITWED
<i>tert</i> -butylsulfido	Ag ₁₄			900	CAYZOR(10)
1,1,1-tris(hydroxymethyl)propane, acetato, methoxo, oxo	Mn ₁₆			901	DABTOQ
bis(2-oxyethyl)(2-hydroxyethyl)amine, acetato	Mn ₁₆			828	FIQSOO
1,1,1-tris(oxyethyl)ethane, benzoato, ethoxo	Fe ₁₆			830	LULMEK
γ -cyclodextrin	Pb ₁₆		5 H ₂ O	902	POJGOK
<i>m</i> -xylylenediamine bis(Kemp's triacid imide), acetato, methoxo, hydroxo	Fe ₁₈		NO ₃ ⁻ , H ₂ O	903	NAXLAZ
3-methyl-3-pyrazolin-5-one, acetato, hydroxo	Ni ₂₄		H ₂ O	904	QEMHOF

metallamacrocycles typically have either a square or rectangular shape, although the polygon can be slightly distorted in many instances. 8-MC-4 complexes with oxygen atom connectivity have been synthesized with Li^I,⁵⁶⁰ Al^{III},^{561–563} Ti^{IV} (Figure 94),^{564–580} V^{IV},^{581,582} V^V,^{583–587} mixed-valent V^{IV}₂V^V,^{588,589} Mn^{II},⁵⁹⁰ Mn^{III},^{591,592} mixed-valent Mn^{II}Mn^{III},^{593,594} Fe^{III},^{595–601} Co^{II},⁵⁹⁰ Ni^{II},^{602,603} Cu^I,^{604–607} Cu^{II},^{590,608–619} Zn^{II},^{602,620–625} Ge^{IV},^{626,627} Nb^{IV},⁶²⁸ Nb^V,^{629–633} Mo^{IV},⁶³⁴ Mo^V,⁶³⁵ Mo^{VI},^{636,637} Ru^{II},⁶³⁸ Pd^{II},^{639,640} Cd^{II},⁶⁴¹ Ta^V,^{632,633} mixed-valent W^V₂W^{VI},⁶⁴² W^{VI},⁶⁴³ Re^V,⁵¹³ Re^{VI},⁶³² Sn^{IV},^{644–646} Sb^{III},⁶⁴⁷ Pt^{II},⁶⁴⁸ Au^{III},⁶⁴⁹ U^{IV},⁶⁵⁰ and U^{VI}.^{651,652} In addition, several mixed-metal 8-MC-4 complexes with an oxygen atom bridge have been synthesized including Li₂Al^{III},⁶⁵³ Li₂Ga^{III},⁶⁵³ Na₂Ni^{II},⁶⁵⁴ Al^{III}₂Eu^{II},⁶⁵⁵ Ti^{IV}₂Mo^{VI},⁶⁵⁶ and Re^{VI}_{1-x}Mo^{VI}_x.⁶³² 8-MC-4 complexes with sulfur atom bridges have been constructed with mixed-valent Fe^{II}₃Fe^{III},⁶⁵⁷ Co^{II},^{658,659} Ni^{II},^{657,660–663} (Figure 95), mixed-valent Ni^{II}₂-Ni^{III},⁶⁶⁴ Ni^{2.5+},⁶⁶⁴ Cu^I,^{665–676} Zn^{II},^{677–679} Ge^{IV},⁶⁸⁰ Pd^{II},^{681,682} Ag^I,^{683–692} Cd^{II},⁶⁹³ Sb^{III},⁶⁹⁴ Pt^{II},⁶⁹⁵ Hg^{II},⁶⁹³ Tl^{III},⁶⁹⁶ mixed-metal Co^{II}₂Au^I,⁶⁹⁷ mixed-metal Ni^{II}₂Au^I,⁶⁹⁸ and mixed-metal Cu^I₂-

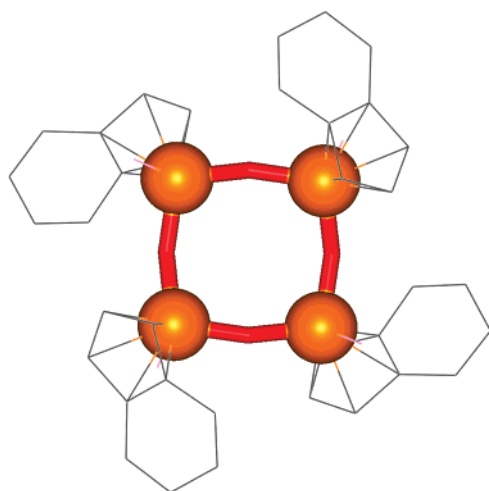


Figure 94. X-ray crystal structure of a vacant 8-MC_{Ti^{IV}}-4 complex. Ti^{IV} ions, capped by η^5 -C₉H₁₁ groups, are connected by four μ -O bridges. The coordination of each Ti^{IV} ion is completed by a Cl⁻ anion. Color scheme: orange sphere, Ti^{IV}; red tube, oxygen; gray line, carbon; magenta line, chloride. Hydrogen atoms have been removed for clarity.⁵⁶⁸

Ni⁰,⁶⁹⁹ Halide anions provide one-atom bridges for a number of 8-MC-4 complexes. Fluoride 8-MC-4s have been synthesized with Ti^{IV},^{700,701} Zr^{IV},⁷⁰² Hf^{IV},⁷⁰² mixed-valent Sn^{II}₂-Sn^{IV},⁷⁰³ mixed-valent Yb^{II}₂Yb^{III},⁷⁰⁴ Yb^{III},⁷⁰⁵ and mixed-metal Al^{III}₂Ti^{III},⁷⁰⁶ Chloride 8-MC-4 complexes include metal ions Al^{III},⁷⁰⁷ Mn^{III},^{591,592} mixed-valent Cu^I₂Cu^{II},⁷⁰⁸ Pd^{II},⁷⁰⁹ Sb^{III} (Figure 96),^{710,711} Hg^{II},⁷¹² Bi^{III},^{711,713,714} Th^{IV},⁷¹⁵ mixed-metal Li^I₂Th^{IV},⁷¹⁵ and mixed-metal Al^{III}₂Eu^{II}.⁷¹⁶ 8-MC-4 complexes with bromide include Pd^{II},⁷¹⁷ Sb^{III},⁷¹⁸ Pt^{II},⁷¹⁷ and Bi^{III},⁷¹⁹ and 8-MC-4 complexes have been synthesized with iodide bridges between Cu^I ions.⁷²⁰ 8-MC-4 complexes have been constructed with nitrogen bridging atoms with metals Li^I,^{721,722} Na^I,⁷²³ Cu^I,^{724–728} Ga^{III},^{729,730} Pd^{II},⁷³¹ Ag^I,^{727,732} Sn^{IV},⁷³³ U^{IV},⁷³⁴ mixed-metal Li^I₂Mg^{II},^{735,736} mixed-metal Na^I₂Mg^{II},^{736,737} mixed-metal K^I₂Mg^{II},⁷³⁸ and mixed-metal K^I₂Zn^{II}.⁷³⁹ The four mixed-metal alkali metal–nitrogen 8-MC-4 complexes are novel complexes that behave as inverse MCs that bind one or two oxygen atoms within the central cavity.⁷⁴⁰ 8-MC-4 complexes with phosphorus bridging atoms have been made with Al^{III},⁷⁴¹ Cu^I (Figure

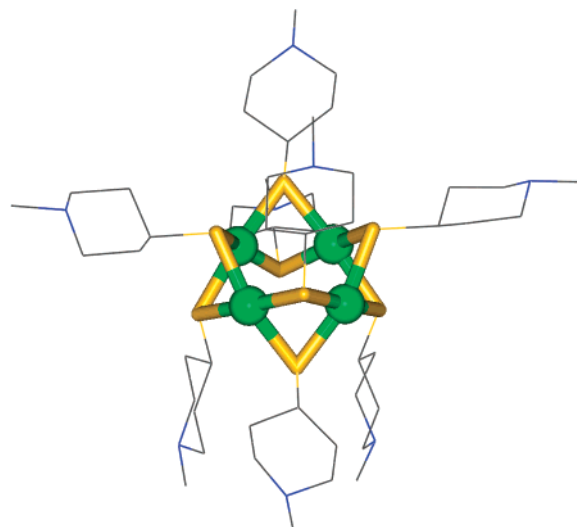


Figure 95. X-ray crystal structure of a vacant 8-MC_{Ni^{II}}-4 complex. Each Ni^{II} ion is bridged to neighboring Ni^{II} ions by two μ -*N*-methyl-4-mercaptopyperidine ligands. Color scheme: green sphere, Ni^{II}; yellow tube, sulfur; blue line, nitrogen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁶⁶⁰

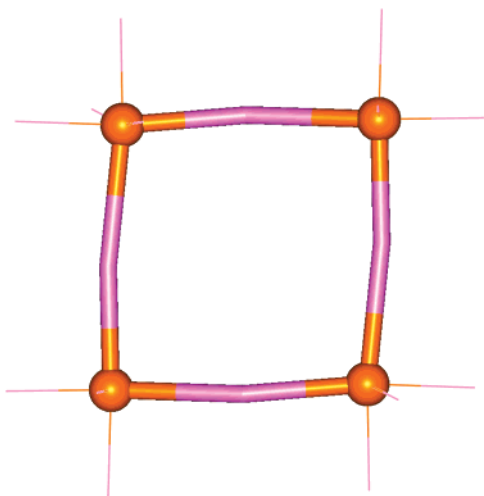


Figure 96. X-ray crystal structure of a vacant $[8\text{-MC}_{\text{Sb}^{\text{III}}}\text{-4}]^{8-}$ complex. Each Sb^{III} ion is bridged by one $\mu\text{-Cl}^-$ to neighboring Sb^{III} ions and surrounded by an additional four terminal Cl^- anions. Color scheme: orange sphere, Sb^{III} ; magenta tube, chloride. Hydrogen atoms and 2,2'-bipyridinium and 4,4'-bipyridinium counteranions have been removed for clarity.⁷¹⁰

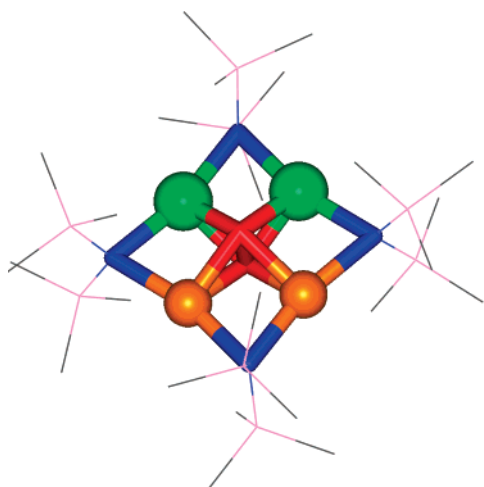


Figure 97. X-ray crystal structure of an inverse $(\mu_4\text{-O}_2)[8\text{-MC}_{\text{Li}^{\text{I}}, \text{Mg}^{\text{II}}}\text{-4}]$ complex. The s -block metals are disordered about the metallamacrocycle with 50% Li and 50% Mg occupancy at each metal site. The metal ions are connected via $\mu\text{-N}$ bridges, and the molecule encapsulates a peroxide anion within the central cavity. Color scheme: orange sphere, Li^{I} ; green sphere, Mg^{II} ; blue tube, nitrogen; magenta line, silicon; gray line, carbon. Hydrogen atoms have been removed for clarity.⁷³⁵

98),^{742,743} Ga^{III} ,⁷⁴¹ mixed-valent $\text{Au}^{\text{I}}\text{Au}^{\text{III}}$,⁷⁴⁴ Au^{I} ,⁷⁴⁵ and mixed-metal $\text{Mn}^{\text{III}}_2\text{Au}^{\text{I}}$.⁷⁴⁶ 8-MC-4 complexes have also been generated with repeat units of $-\text{[Ag}^{\text{I}}\text{-Se]}-$ ⁷⁴⁷ (Figure 99) and $-\text{[Sn}^{\text{II}}\text{-Te]}-$.⁷⁴⁸ In addition, 8-MC-4 complexes may be synthesized that contain mixed heteroatoms in the MC ring. Examples include 8-MC-4 complexes with repeat units of $-\text{[Ti}^{\text{III}}\text{-Cl-Ti}^{\text{III}}\text{-O]}-$,⁷⁴⁹ $-\text{[Fe}^{\text{II}}\text{-F-Fe}^{\text{III}}\text{-O]}-$,⁷⁵⁰ $-\text{[Mn}^{\text{II}}\text{-Cl-Mn}^{\text{II}}\text{-O]}-$,⁷⁵¹ $-\text{[Mn}^{\text{II}}\text{-N-Mn}^{\text{II}}\text{-O]}-$,⁷⁵¹ $-\text{[Cu}^{\text{I}}\text{-Br-Cu}^{\text{I}}\text{-S]}-$,⁷⁵² $-\text{[Cu}^{\text{I}}\text{-Cl-Cu}^{\text{I}}\text{-S]}-$,⁶⁶³ and $-\text{[Cu}^{\text{I}}\text{-I-Cu}^{\text{I}}\text{-S]}-$.⁷⁵³

2.18.3. 10-MC-5

Two ring-shaped 10-MC-5 complexes have been generated with a $[\text{Ni}^{\text{II}}\text{-S}]_5$ metallamacrocycle. These complexes are similar in shape and ligand type to the 8-MC-4, 12-MC-6,

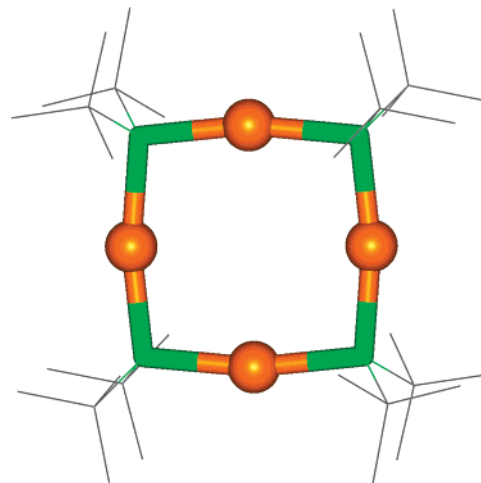


Figure 98. X-ray crystal structure of a vacant 8-MC $_{\text{Cu}^{\text{I}}}$ -4 complex. The Cu^{I} ions are bridged via a $\mu\text{-P}$ provided by four $[\text{P}(\text{CMe}_3)_2]^-$ ligands. Color scheme: orange sphere, Cu^{I} ; green tube, phosphorus; gray line, carbon. Hydrogen atoms have been removed for clarity.⁷⁴²

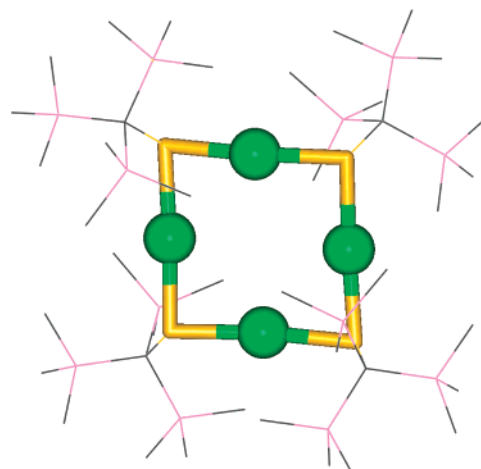


Figure 99. X-ray crystal structure of a vacant 8-MC $_{\text{Ag}^{\text{I}}}$ -4 complex. The Ag^{I} ions are bridged via a $\mu\text{-Se}$ provided by four $[\text{SeC}(\text{SiMe}_3)_3]^-$ ligands. Color scheme: green sphere, Ag^{I} ; yellow tube, selenium; magenta line, silicon; gray line, carbon. Hydrogen atoms have been removed for clarity.⁷⁴⁷

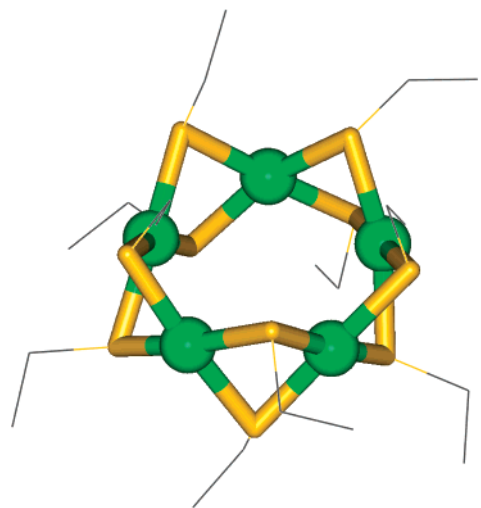


Figure 100. X-ray crystal structure of a vacant 10-MC $_{\text{Ni}^{\text{II}}}$ -5 complex. Each Ni^{II} ion is bridged to neighboring Ni^{II} ions by two $\mu\text{-ethanethiol}$ ligands. This complex is similar to the 8-MC $_{\text{Ni}^{\text{II}}}$ -4 in Figure 95. Color scheme: green sphere, Ni^{II} ; yellow tube, sulfur; gray line, carbon. Hydrogen atoms have been removed for clarity.⁶⁶¹

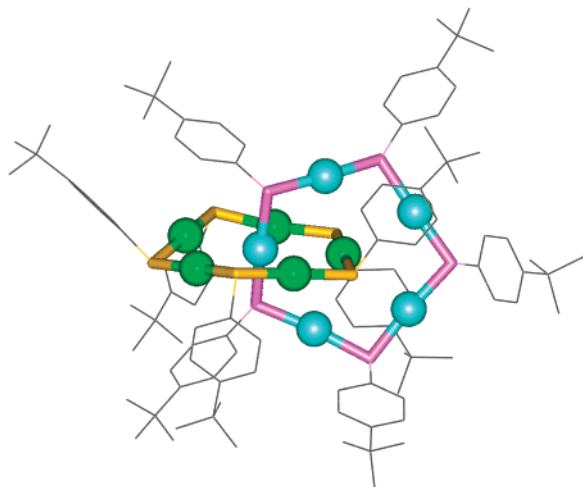


Figure 101. X-ray crystal structure of two interpenetrated 10-MCAu-5 complexes. Each Au^I ion is bridged to neighboring Au^I ions by one μ -S from *tert*-butylthiophenol. The complexes have a rare pentagon shape. Color scheme: green and aqua sphere, Au^I; yellow and magenta tube, sulfur; gray line, carbon. Hydrogen atoms have been removed for clarity.⁷⁵⁶

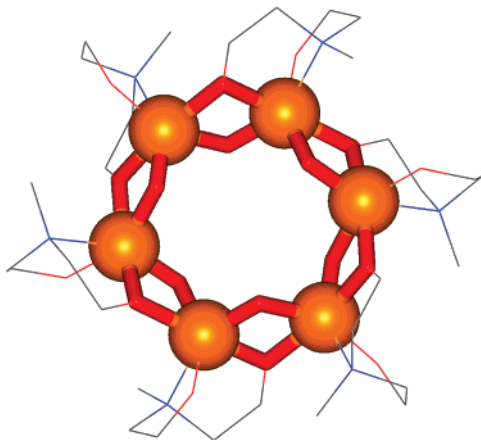


Figure 102. X-ray crystal structure of a vacant 12-MCTi^{IV}-6 complex. Each Ti^{IV} is connected to neighboring Ti^{IV} ions via one μ -O oxide and one μ -O alkoxide from the *N*-methyldiethoxamine ligand. Color scheme: orange sphere, Ti^{IV}; red tube, oxygen; blue line, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁷⁵⁹

and 16-MC-8 complexes described above and below (Figure 100).^{661,754} In addition, a $-\text{[Ni}^{\text{II}}-\text{S]}-$ repeat unit can construct a 10-MC-5 that has a pentagon shape with a Ni^{II} ion captured in the central cavity.⁷⁵⁵ Two interpenetrated 10-MC-5 complexes can be produced with a $-\text{[Au}^{\text{I}}-\text{S]}-$ repeat unit (Figure 101).⁷⁵⁶ Each Au^I has a linear geometry with *tert*-butylthiophenol providing the bridging sulfur atom. These four complexes are some of the rare examples of molecular wheel complexes that contain an odd number of ring metal ions.

2.18.4. 12-MC-6

12-MC-6 complexes with oxygen one-atom bridges can be synthesized with ring metals Mg^{II},⁷⁵⁷ Al^{III},⁷⁵⁸ Ti^{IV} (Figure 102),⁷⁵⁹ V^{IV},^{760–763} Cr^{III},⁷⁶⁴ mixed-valent Mn^{II}₂Mn^{III}₄ (disordered over all metal sites),⁷⁶⁵ mixed-valent Mn^{II}₃Mn^{III}₃,^{766–769} Mn^{III},⁷⁷⁰ Fe^{II},⁷⁷¹ Fe^{III},^{90,772–779} Co^{II},^{780–782} Ni^{II},⁷⁸¹ Cu^{II},^{783–785} Zn^{II},⁷⁸⁶ Nb^{IV},⁷⁸⁷ Mo^{VI},⁷⁸⁸ In^{III},⁷⁷⁸ Sb^V,⁷⁸⁹ Hf^{IV},⁷⁹⁰ Pb^{II},⁷⁹¹ mixed-metal Ni^{II}₂Cr^{VI}₄,⁷⁹² and mixed-metal Ni^{II}₂Mo^{VI}₄.⁷⁹³ Whereas some 12-MC-6 complexes do not have a guest within the

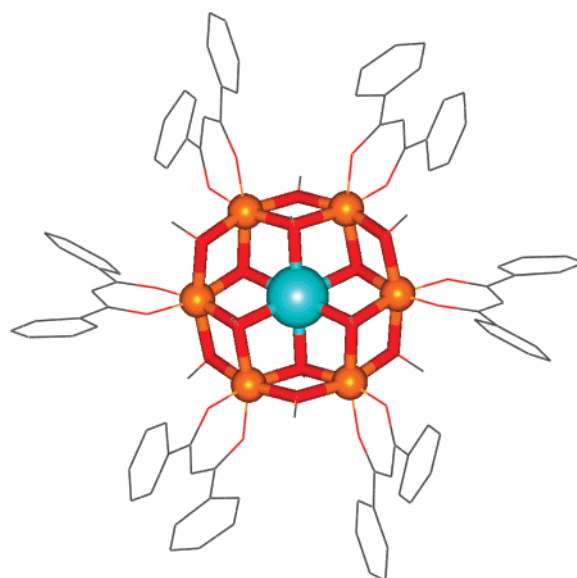


Figure 103. X-ray crystal structure of a $\{\text{Na}^{\text{I}}[\text{12-MC}_{\text{Fe}^{\text{III}}}-6]\}^+$ complex. Each Fe^{III} ion is connected to neighboring Fe^{III} ions via one μ_3 -O oxide and one μ -O methoxide. The μ_3 -O oxide bridges also bind to the encapsulated Na^I. The coordination about each Fe^{III} is completed by a bidentate dibenzoylmethane ligand. Color scheme: aqua sphere, Na^I; orange sphere, Fe^{III}; red tube, oxygen; gray line, carbon. Hydrogen atoms, Cl⁻ counteranion, and lattice solvent have been removed for clarity.⁷⁷³

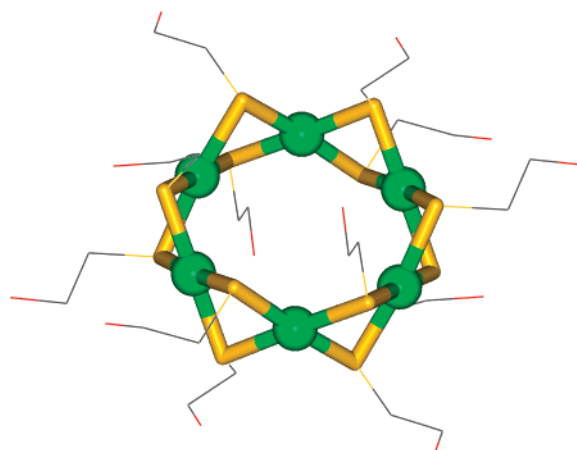


Figure 104. X-ray crystal structure of a vacant 12-MCNi^{II}-6 complex. Each Ni^{II} ion is bridged to neighboring Ni^{II} ions by two μ -1-hydroxyethane-2-thiolato ligands. This complex is similar to the 8-MCNi^{II}-4 (Figure 95) and 10-MCNi^{II}-5 (Figure 100) complexes. Color scheme: green sphere, Ni^{II}; yellow tube, sulfur; red line, oxygen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁷⁹⁶

central cavity, many 12-MC-6 complexes may trap a guest within the central cavity: 12-MCV^{IV}-6 encapsulates Na^I,^{760,761} Mn^{II},⁷⁶² and Fe^{II},⁷⁶³ 12-MCMn^{II}₂Mn^{III}₄-6 encapsulates Mn^{II},⁷⁶⁵ 12-MCMn^{II}₃Mn^{III}₃-6 encapsulates Mn^{II},^{766–769} 12-MCMn^{III}-6 encapsulates Na^I,⁷⁷⁰ 12-MCFe^{III}-6 encapsulates an Fe^{III} ion,⁷⁷¹ 12-MCFe^{III}-6 encapsulates Li^I,^{90,775} and Na^I (Figure 103),^{90,773,774} 12-MCCu^{II}-6 encapsulates two Na^I ions,⁷⁸⁵ 12-MCZn^{II}-6 encapsulates Zn^{II},⁷⁸⁶ and 12-MCMo^{VI}-6 encapsulates an Fe^{II} ion.⁷⁸⁸ Sulfur atoms may also provide one-atom bridges for 12-MC-6 complexes with metal ions Li^I,⁷⁹⁴ Ni^{II} (Figure 104),^{795–804} Cu^I,⁶⁷¹ Cd^{II},⁸⁰⁵ Pd^{II},⁸⁰⁶ and Au^I.^{756,807,808} Just as with the 10-MCAu-5 complex, an Au^I-S interpenetrated 12-MC-6 may be synthesized with interlocking

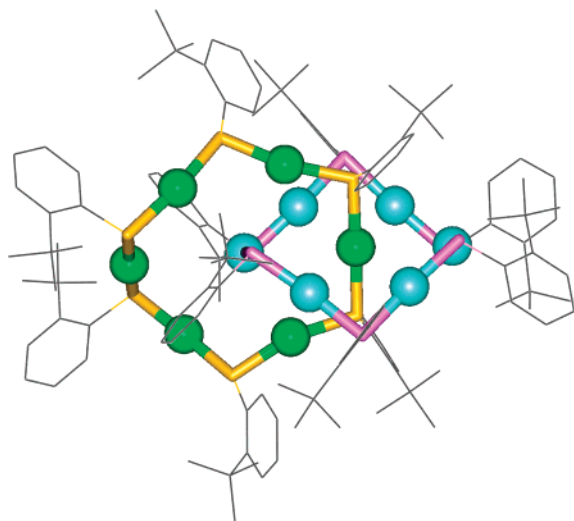


Figure 105. X-ray crystal structure of two interpenetrated 12-MC_{Au^I}-6 complexes. Each Au^I ion is bridged to neighboring Au^I ions by one μ -S atom from *tert*-butylthiophenol. The hexanuclear structure is similar to the interpenetrated 10-MC_{Au^I}-5 complexes in Figure 101. Color scheme: green and aqua sphere, Au^I; yellow and magenta tube, sulfur; gray line: carbon. Hydrogen atoms have been removed for clarity.⁷⁵⁶}}

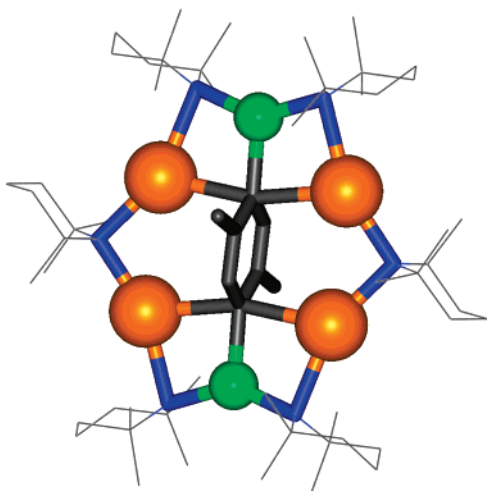


Figure 106. X-ray crystal structure of a (μ_6 -C₆H₃CH₃)[12-MC_{Na^IMg^{II}_2-6] complex. The *s*-block metals are connected via μ -N bridges from the ligand 2,2,6,6-tetramethylpiperidide. The encapsulated toluene is deprotonated at opposite ring positions with the methyl group disordered over the two sites shown. The complex is similar to the (μ_4 -O₂)[8-MC_{Li^IMg^{II}_2-4] complex in Figure 97. Color scheme: orange sphere, Na^I; green sphere, Mg^{II}; blue tube, nitrogen; gray tube, carbon. Hydrogen atoms have been removed for clarity.⁷³⁷}}

rings (Figure 105).⁷⁵⁶ 12-MC-6 complexes with other one-atom bridges include repeat units of $-\text{[Na}^{\text{I}}-\text{N}-\text{Na}^{\text{I}}-\text{N}-\text{Mg}^{\text{II}}-\text{N}]-$ (Figure 106),⁷³⁷ $-\text{[Ti}^{\text{IV}}-\text{F}]-$,⁸⁰⁹ $-\text{[Al}^{\text{III}}-\text{Cl}]-$ (Figure 107),⁸¹⁰ $-\text{[Cu}^{\text{I}}-\text{Cl}]-$,⁸¹¹ $-\text{[Cu}^{\text{I}}-\text{Br}]-$,⁸¹² $-\text{[Ag}^{\text{I}}-\text{Se}]-$,⁸¹³ and $-\text{[Bi}^{\text{III}}-\text{Se}]-$.⁸¹⁴

2.18.5. 14-MC-7

A 14-MC-7 complex has been synthesized with a metallamacrocycle of $[\text{V}^{\text{IV}}-\text{Cl}]_7$ (Figure 108).⁸¹⁵ The V^{IV} ions are connected by two μ -Cl bridges between each ion.

2.18.6. 16-MC-8

16-MC-8 complexes with oxygen atom bridges have been constructed with a variety of metal ions including Ca^{II},⁸¹⁶

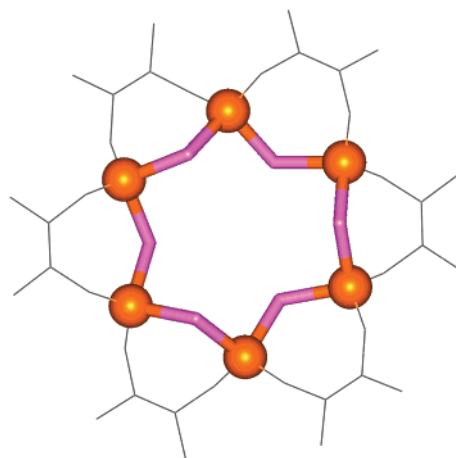


Figure 107. X-ray crystal structure of a vacant 12-MC_{Al^{III}}-6 complex. Each Al^{III} is connected by μ -Cl⁻ to neighboring Al^{III} ions. In addition, 2,3-dimethylbutene provides a bridge between each Al^{III} ion. Color scheme: orange sphere, Al^{III}; magenta tube, chloride; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁸¹⁰}

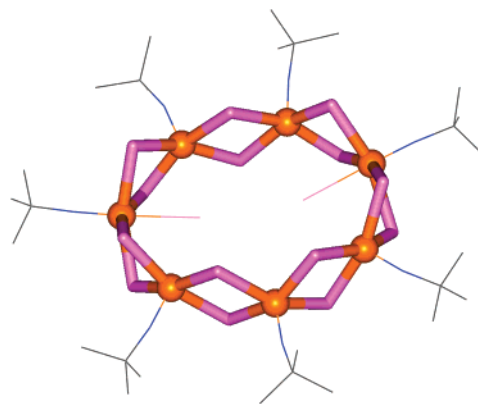


Figure 108. X-ray crystal structure of a vacant $[\text{14-MC}_{\text{V}^{\text{IV}}}-7]^{2-}$ complex. Each V^{IV} is connected to neighboring V^{IV} ions by two μ -Cl⁻ ions. Two of the ring V^{IV} ions have an additional Cl⁻ anion bound, and the coordination sphere of each V^{IV} is completed by a H₉C₄N²⁻ group. Color scheme: orange sphere, V^{IV}; magenta tube, chloride; blue line, nitrogen; gray line, carbon. Hydrogen atoms and H₉C₄NH₃⁺ counteranions have been removed for clarity.⁸¹⁵

Ti^{IV},^{817,818} V^{III},^{819,820} V^{IV},⁸²¹ Cr^{III},⁸²²⁻⁸²⁶ Mn^{III},⁸²⁷ mixed-valent Mn^{II}₄Mn^{III},⁸²⁸ Fe^{III},^{90,829-832} Co^{III},⁸³³ Cu^{II},^{619,834,835} Mo^V,⁸³⁶⁻⁸⁴⁰ mixed-valent Mo^VMo^{VI},⁸⁴¹ Cd^{II},⁸⁴² Nd^{III},⁸⁴³ Sm^{III},⁸⁴³ Gd^{III},⁸⁴³ Bi^{III},⁸⁴⁴ mixed-metal Na^ICu^{II},⁸⁴⁵ and mixed-metal W^{VI}₄Sn^{IV}.⁸⁴⁶ In addition, 16-MC_{Mn^{III}}-8 encapsulates one Ce^{IV} ion,⁸²⁷ 16-MC_{Fe^{III}}-8 may encapsulate one Cs^I ion^{90,829} (Figure 109), and 16-MC_{Cu^{II}}-8 may capture one Cu^{II} within the central cavity.⁶¹⁹ Furthermore, 16-MC_{V^{IV}}-8 encapsulates a C₂O₄²⁻ moiety (Figure 110).⁸²¹ Sulfide 16-MC-8 complexes may be constructed with Fe^{II},⁸⁴⁷ Ni^{II} (Figure 111),⁸⁴⁸ Cu^I,^{677,849,850} Pd^I,⁸⁵¹ and the mixed-metal systems [Co^{III}Pd^{II}Co^{II}Ag^I]₂⁸⁵² and [Co^{III}Pd^{II}Co^{II}Au^I]₂.⁸⁵² 16-MC-8 complexes with $-\text{[Na}^{\text{I}}-\text{N}-\text{Mg}^{\text{II}}-\text{N}]-$ repeat units encapsulate metallocenes [Fe^{II}(C₅H₃)₂]⁴⁻ (Figure 112), [Os^{II}(C₅H₃)₂]⁴⁻, and [Re^{II}(C₅H₃)₂]⁴⁻.^{853,854} A [Sm^{II}-N]₈ metallamacrocycle may also construct a 16-MC-8 complex.⁸⁵⁵ Fluoride anions can generate 16-MC-8 complexes with Cr^{III},^{856,857} mixed-metal V^{IV}₂Cr^{III}₆ (Figure 113),⁸⁵⁸ mixed-metal M^{II}Cr^{III}₇ (where M^{II} = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cd^{II}) and the metal sites are disordered over the whole ring),⁸⁵⁹ mixed-metal Ni^{II}₂Cr^{III}₆,⁸⁶⁰ and mixed-metal M^{III}M^{III}₇ systems (where M^{III} = Cr^{III} and M^{II} = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Zn^{II},}}}}

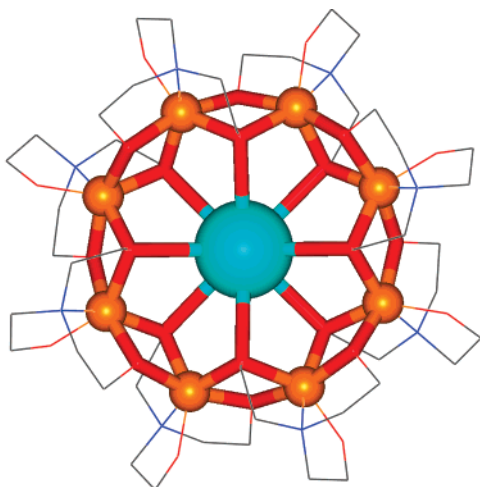


Figure 109. X-ray crystal structure of a $\{\text{Cs}^+[\text{16-MC}_{\text{Fe}^{\text{III}}}\text{-8}]\}^+$ complex. Each Fe^{III} ion is connected to neighboring Fe^{III} ions via two μ -O bridges from two different ligands of tirethanolamine. The inter-oxygen bridges also bind to the encapsulated Cs^+ ion. Color scheme: aqua sphere, Cs^+ ; orange sphere, Fe^{III} ; red tube, oxygen; blue line, nitrogen; gray line, carbon. Hydrogen atoms, Cl^- counteranion, and lattice solvent have been removed for clarity.⁸²⁹

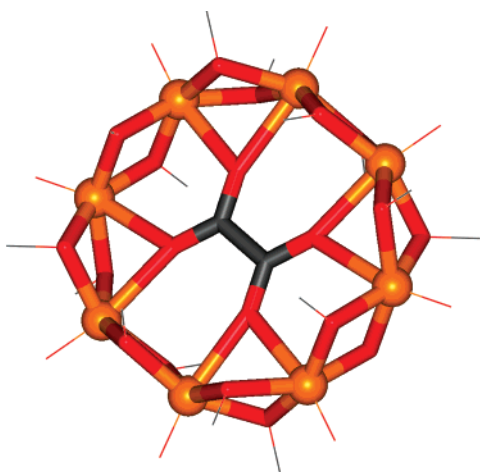


Figure 110. X-ray crystal structure of a $\{(\text{C}_2\text{O}_4)^{2-}[\text{12-MC}_{\text{V}^{\text{IV}}}\text{-6}]\}^{2-}$ complex. Each V^{IV} ion is connected to neighboring V^{IV} ions via two μ -O methoxide bridges. The four oxygen atoms of the encapsulated $[\text{C}_2\text{O}_4]^{2-}$ also bridge the V^{IV} ions. Color scheme: orange sphere, V^{IV} ; red tube, oxygen; gray tube, carbon. Hydrogen atoms, $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ counteranions, and lattice solvent have been removed for clarity.⁸²¹

Cd^{II} , Mg^{II} ; $\text{M}^{\text{III}} = \text{V}^{\text{III}}$ and $\text{M}^{\text{II}} = \text{Zn}^{\text{II}}$, Ni^{II} ; and $\text{M}^{\text{III}} = \text{Fe}^{\text{III}}$ and $\text{M}^{\text{II}} = \text{Mn}^{\text{II}}$, Fe^{II} , Co^{II} , Ni^{II} , Zn^{II} , Cd^{II} ; in all three varieties, the metal ions' positions are disordered over all metal sites).⁸⁶¹

2.18.7. 18-MC-9

A few examples exist of 18-MC-9 complexes. A 18-MC-9 complex can be generated with a $[\text{Fe-O-Fe-O-Na-O}]_3$ metallamacrocyclic,⁸⁶² whereas a connectivity of $[\text{V}^{\text{II}}\text{-F-V}^{\text{II}}\text{-F-Cr}^{\text{III}}\text{-F-Cr}^{\text{III}}\text{-F-Cr}^{\text{III}}\text{-F-Cr}^{\text{III}}\text{-F-Cr}^{\text{III}}\text{-F-Cr}^{\text{III}}\text{-F-Cr}^{\text{III}}\text{-F-Cr}^{\text{III}}\text{-F}]$ generates a different 18-MC-9 (Figure 114).⁸⁶³ A ring 18-MC-9 complex with a $-\text{[Ni}^{\text{II}}\text{-S]}-$ repeat unit has a structure similar to the ring 8-MC-4, 10MC-5, 12-MC-6, and 16-MC-8 complexes with the same repeat unit

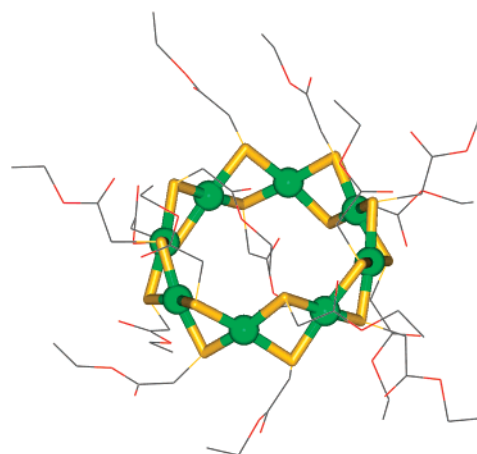


Figure 111. X-ray crystal structure of a vacant $16\text{-MC}_{\text{Ni}^{\text{II}}}\text{-8}$ complex. Each Ni^{II} ion is bridged to neighboring Ni^{II} ions by two μ -ethyl 2-mercaptoacetate ligands. This complex is similar to the $8\text{-MC}_{\text{Ni}^{\text{II}}}\text{-4}$ (Figure 95), $10\text{-MC}_{\text{Ni}^{\text{II}}}\text{-5}$ (Figure 100), and $12\text{-MC}_{\text{Ni}^{\text{II}}}\text{-6}$ (Figure 104) complexes. Color scheme: green sphere, Ni^{II} ; yellow tube, sulfur; red line, oxygen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁸⁴⁸

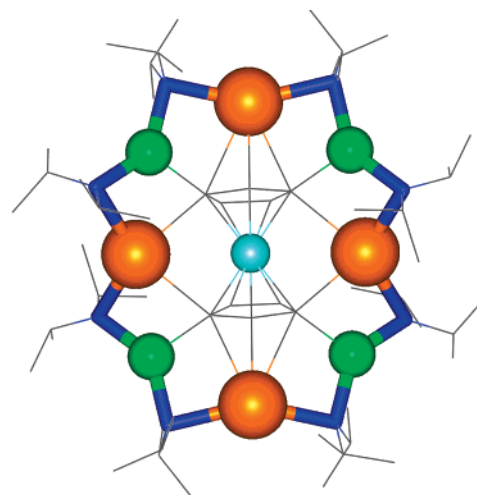


Figure 112. X-ray crystal structure of a $(\mu_8\text{-Fe}^{\text{II}}(\text{C}_5\text{H}_3)_2)[\text{16-MC}_{\text{Na}^{\text{I}}\text{Mg}^{\text{II}}}\text{-8}]$ complex. The s -block metals are connected via μ -N bridges from the ligand diisopropylamide. The encapsulated metallocene $[\text{Fe}^{\text{II}}(\text{C}_5\text{H}_3)_2]^{4+}$ is bound to all of the ring metal ions via the carbon atoms of the aromatic ring. The complex is similar to the complexes $(\mu_4\text{-O}_2)[\text{8-MC}_{\text{Li}^{\text{I}}\text{Mg}^{\text{II}}}\text{-4}]$ (Figure 97) and $(\mu_6\text{-C}_6\text{H}_3\text{CH}_3)[\text{12-MC}_{\text{Na}^{\text{I}}\text{Mg}^{\text{II}}}\text{-6}]$ (Figure 106). Color scheme: aqua sphere, Fe^{II} ; orange sphere, Na^{I} ; green sphere, Mg^{II} ; blue tube, nitrogen; gray tube, carbon. Hydrogen atoms have been removed for clarity.⁸⁵³

(Figure 115).⁸⁶⁴ Using fluoride as the bridging ligand $\text{Cd}^{\text{II}}\text{-Cr}^{\text{III}}_8$ and $\text{Ni}^{\text{II}}\text{Cr}^{\text{III}}_8$ wheels may be generated.⁸⁶⁰ In the $\text{Cd}^{\text{II}}\text{-Cr}^{\text{III}}_8$ complex, the Cd^{II} is in an ordered site as opposed to some mixed-metal wheels in which the metals are disordered over all positions.

2.18.8. 20-MC-10 and Larger Molecular Wheel Based Metallacrowns

20-MC-10 complexes with oxygen bridges can be synthesized with Fe^{III} (Figure 116),^{831,832,865-867} Cr^{III} ,^{868,869} Mo^{V} ,⁸⁷⁰ mixed-valent $\text{Mo}^{\text{V}}_4\text{Mo}^{\text{VI}}$,⁸⁷¹ Y^{III} ,⁸⁷² Dy^{III} (Figure 117),⁸⁷³ and mixed-metal $\text{Mn}^{\text{III}}_5\text{Cr}^{\text{III}}_5$ (disordered metal sites).⁸⁷⁴ A flexible, sulfur-bridged Ni^{II} wheel of formula $\text{Ni}^{\text{II}}_{10}(\mu\text{-S'Bu})_{10}(\mu\text{-SCH}_2\text{CH}_2\text{SMe})_{10}$ has been reported.⁸⁷⁵ When crystallized

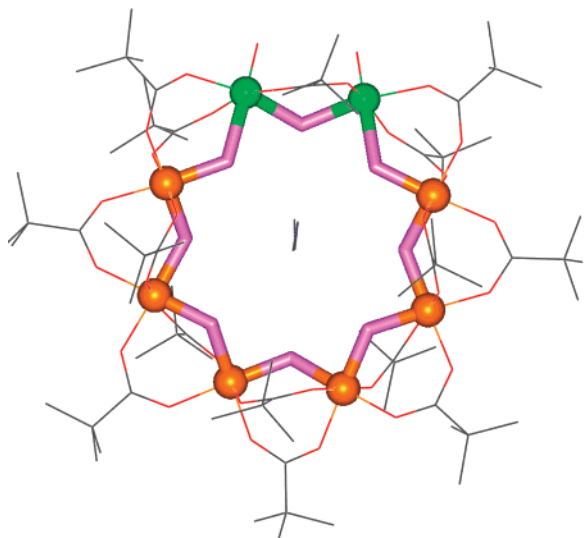


Figure 113. X-ray crystal structure of a $[16\text{-MC}_{\text{Cr}^{\text{III}},\text{V}^{\text{IV}}}\text{-8}]^{-}$ complex. The metal ions are connected to each other via bridging $\mu\text{-F}$ anions. A $(\text{CH}_3\text{CH}_2)_2\text{H}_2\text{N}^+$ cation is hydrogen-bonded within the central cavity. Pivalate anions also bridge each metal ion. Color scheme: orange sphere, Cr^{III} ; green sphere, V^{IV} ; magenta tube, fluoride; red line, oxygen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁸⁵⁸

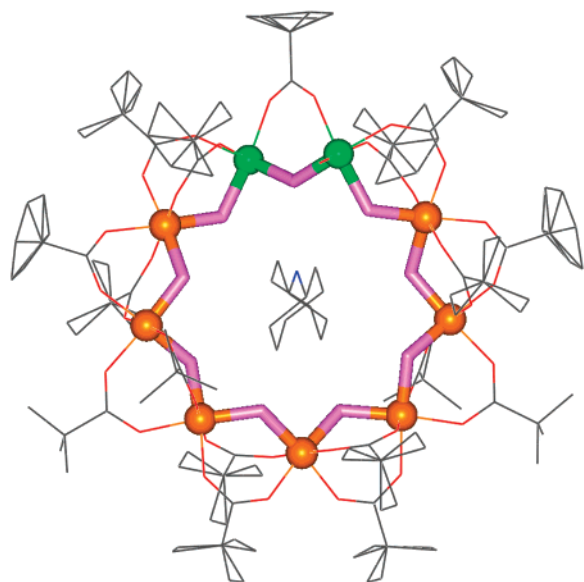


Figure 114. X-ray crystal structure of a $[18\text{-MC}_{\text{Cr}^{\text{III}},\text{V}^{\text{IV}}}\text{-9}]^{-}$ complex. The metal ions are connected to each other with bridging $\mu\text{-F}$ anions. A $(\text{C}_6\text{H}_{11})_2\text{H}_2\text{N}^+$ cation is located within the central cavity. Pivalate anions also bridge the metal ions, and the methyl groups of the pivalate anion are shown as overall disordered positions. This structure is very similar to the $[16\text{-MC}_{\text{Cr}^{\text{III}},\text{V}^{\text{IV}}}\text{-8}]^{-}$ complex in Figure 113. Color scheme: orange sphere, Cr^{III} ; green sphere, V^{IV} ; magenta tube, fluoride; red line, oxygen; blue line, nitrogen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁸⁶³

from toluene/hexamethyldisiloxane, this complex has an ellipsoidal shape (transannular $\text{Ni}^{\text{II}}\text{-Ni}^{\text{II}}$ distances = 9.50–11.11 Å), and two thioether groups of the $\text{SCH}_2\text{CH}_2\text{SMe}$ ligands penetrate into the cavity of the $\text{Ni}^{\text{II}}_{10}\text{S}_{20}$ toroid. Crystallization from benzene/hexamethyldisiloxane yields a circular form (transannular $\text{Ni}^{\text{II}}\text{-Ni}^{\text{II}}$ distances = 10.08–10.34 Å), which in contrast has a benzene molecule encapsulated in the central cavity. A mixed-bridged 20-MC-10 can be made with Mo^{V} with a repeat unit of $-\text{[Mo}^{\text{V}}\text{-}$

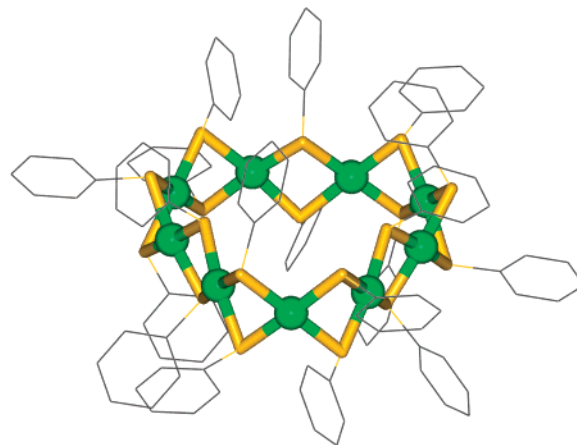


Figure 115. X-ray crystal structure of a vacant $18\text{-MC}_{\text{Ni}^{\text{II}}}\text{-9}$ complex. Each Ni^{II} ion is bridged to neighboring Ni^{II} ions by two $\mu\text{-SC}_6\text{H}_5$ ligands. This complex is similar to the $8\text{-MC}_{\text{Ni}^{\text{II}}}\text{-4}$ (Figure 95), $10\text{-MC}_{\text{Ni}^{\text{II}}}\text{-5}$ (Figure 100), $12\text{-MC}_{\text{Ni}^{\text{II}}}\text{-6}$ (Figure 104), and $16\text{-MC}_{\text{Ni}^{\text{II}}}\text{-8}$ (Figure 111) complexes. Color scheme: green sphere, Ni^{II} ; yellow tube, sulfur; gray line, carbon. Hydrogen atoms have been removed for clarity.⁸⁶⁴

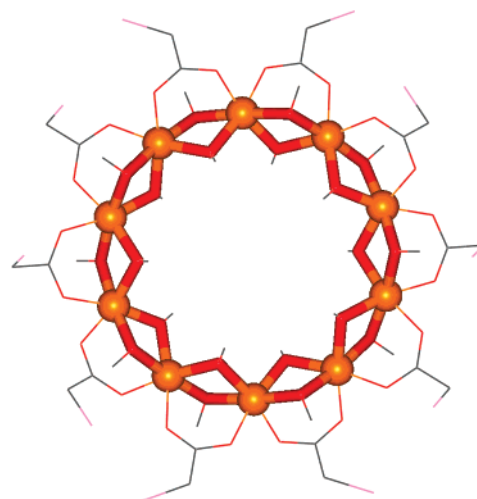


Figure 116. X-ray crystal structure of a vacant $20\text{-MC}_{\text{Fe}^{\text{III}}}\text{-10}$ complex. Each Fe^{III} ion is connected to neighboring Fe^{III} ions via two $\mu\text{-O}$ bridges from two methoxide groups. An additional chloroacetate anion bridges each Fe^{III} ion to its neighboring Fe^{III} ions. Color scheme: orange sphere, Fe^{III} ; red tube, oxygen; magenta line, chlorine; gray line, carbon. Hydrogen atoms have been removed for clarity.⁸⁶⁵

$\text{S-Mo}^{\text{V}}\text{-O}]^{-}$.⁸⁷⁶ Fluoride can be used to generate mixed-metal 20-MC-10 complexes with $\text{Ni}^{\text{II}}_2\text{Cr}^{\text{III}}_8$ ^{860,877} and $\text{Ni}^{\text{II}}\text{Cr}^{\text{III}}_9$ ⁸⁶⁰ (disordered metal sites in both complexes). A repeat unit of $-\text{[Cu}^{\text{II}}\text{-Cl}]^{-}$ constructs a 20-MC-10 complex (Figure 118).⁸⁷⁸ The analogous Br^- complex has also been synthesized.

One 22-MC-11 complex with a $-\text{[Ni}^{\text{II}}\text{-S}]^{-}$ repeat unit (Figure 119) has a ring structure similar to the other $-\text{[Ni}^{\text{II}}\text{-S}]^{-}$ molecular wheels 8-MC-4, 10-MC-5, 12-MC-6, 16-MC-8, and 18-MC-9.⁸⁶⁴

24-MC-12 complexes with oxygen bridges can be generated with ring metal ions V^{IV} (the complex encapsulates either a K^+ ion or a NH_4^+ cation),⁸⁷⁹ mixed-valent $\text{Mn}^{\text{III}}_6\text{-Mn}^{\text{II}}_6$,^{777,880} $\text{Fe}^{\text{III}}_{881-884}$ $\text{Co}^{\text{II}}_{885}$ Ni^{II} (Figure 120),^{886,887} Cd^{II} ,⁸⁸⁸ Mo^{IV} ,⁸⁸⁹ mixed-metal $\text{Mn}^{\text{III}}_6\text{Cr}^{\text{III}}_6$ (the metal ions are disordered over all the ring positions),⁸⁷⁴ and mixed-metal $\text{Na}^{\text{I}}_6\text{-Sb}^{\text{III}}_6$.⁸⁹⁰ Sulfur bridges can be used to construct a $24\text{-MC}_{\text{Fe}^{\text{II}}}\text{-12}$

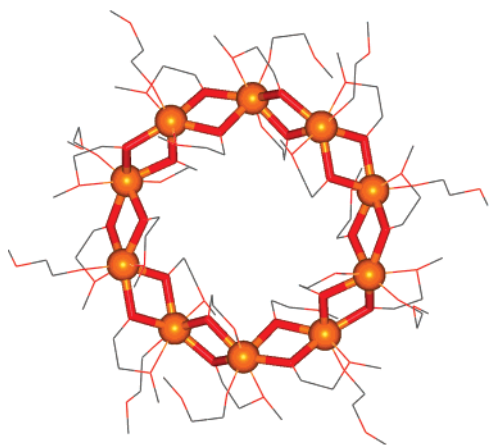


Figure 117. X-ray crystal structure of a vacant 20-MC_{Dy^{III}}-10 complex. Each Dy^{III} ion is connected to neighboring Dy^{III} ions via two μ -O bridges from two oxygen-alkoxo atoms of two methoxy-ethanol ligands. Color scheme: orange sphere, Dy^{III}; red tube, oxygen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁸⁷³

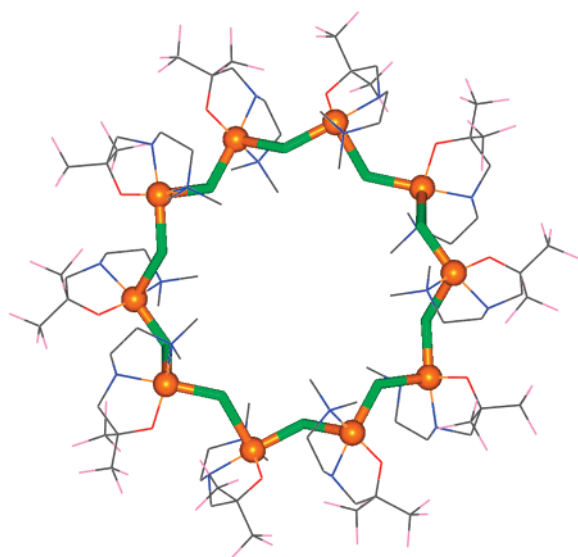


Figure 118. X-ray crystal structure of a vacant 20-MC_{Cu^{II}}-10 complex. Each Cu^{II} ion is connected to neighboring Cu^{II} ions via μ -Cl bridges. The coordination sphere of each Cu^{II} is completed by the tridentate ligand OC(CF₃)₂CH₂NHCH₂CH₂N(CH₃)₂. Color scheme: orange sphere, Cu^{II}; green tube, chloride; blue line, nitrogen; red line, oxygen; magenta line, fluorine; gray line, carbon. Hydrogen atoms have been removed for clarity.⁸⁷⁸

12 complex.⁸⁹¹ 24-MC-12 complexes with nitrogen bridges include metals Mg^{II},⁸⁹² Sb^{III},⁸⁹³ and mixed-metal K^I₆Mg^{II}₆ (Figure 121).⁸⁹⁴ Halide 24-MC-12 complexes have repeat units $-\text{[Cu}^{\text{II}}\text{-F-Cr}^{\text{III}}\text{-F-Cr}^{\text{III}}\text{-F-Cr}^{\text{III}}\text{-F-Cr}^{\text{III}}\text{-F-Cr}^{\text{III}}\text{-F}-\text{]}\text{-}$,⁸⁵⁸ $-\text{[Mg}^{\text{II}}\text{-Cl}]\text{-}$,⁸⁹⁵ $-\text{[Fe}^{\text{II}}\text{-Cl}]\text{-}$,^{896,897} $-\text{[Fe}^{\text{II}}\text{-Br}]\text{-}$,⁸⁹⁷ $-\text{[Co}^{\text{II}}\text{-Cl}]\text{-}$,^{755,897} $-\text{[Ni}^{\text{II}}\text{-Cl}]\text{-}$,⁸⁹⁷ $-\text{[Ni}^{\text{II}}\text{-Br}]\text{-}$,⁷⁵⁵ and $-\text{[Zn}^{\text{II}}\text{-Cl}]\text{-}$.⁸⁹⁸ In addition, a 24-MC-12 complex can be constructed from a $-\text{[Fe}^{\text{II}}\text{-Se}]\text{-}$ repeat unit.⁸⁹⁹

A $[\text{Ag}^{\text{I}}\text{-S}]_{14}$ metallamacrocycle constructs a 28-MC-14 complex (Figure 122).⁹⁰⁰ Each Ag^I has a linear geometry with SC(CH₃)₃ ligands providing the μ -S bridges. The MC ring consists of two twists near the ends of the molecule. One Fe^{II} 24-membered wheel exists with a halide bridge.⁸⁹⁷ The $-\text{[Fe}^{\text{II}}\text{-I}]\text{-}$ repeat unit creates a 28-MC-14.

Four 32-MC-16 structures have been synthesized with oxygen atom bridges. Metallamacrocycles of $[\text{Mn}^{\text{III}}\text{-O}]_{16}$,⁹⁰¹ $[\text{Mn}^{\text{II}}\text{-O-Mn}^{\text{III}}\text{-O}]_8$,⁸²⁸ $[\text{Fe}^{\text{III}}\text{-O}]_{16}$,⁸³⁰ and $[\text{Pb}^{\text{II}}\text{-O}]_{16}$ (Fig-

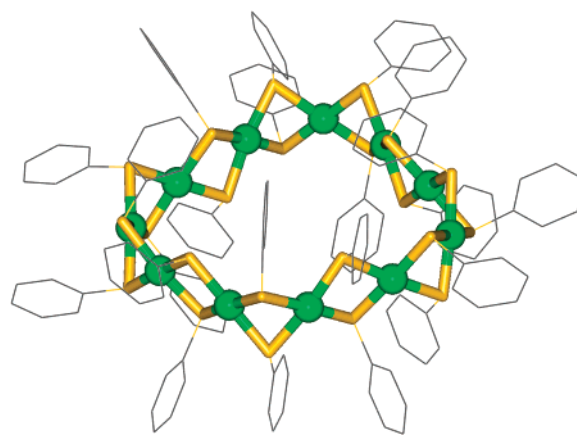


Figure 119. X-ray crystal structure of a vacant 22-MC_{Ni^{II}}-11 complex. Each Ni^{II} ion is bridged to neighboring Ni^{II} ions by two μ -SC₆H₅ ligands. This complex is similar to the 8-MC_{Ni^{II}}-4 (Figure 95), 10-MC_{Ni^{II}}-5 (Figure 100), 12-MC_{Ni^{II}}-6 (Figure 104), 16-MC_{Ni^{II}}-8 (Figure 111), and 18-MC_{Ni^{II}}-9 (Figure 115) complexes. Color scheme: green sphere, Ni^{II}; yellow tube, sulfur; gray line, carbon. Hydrogen atoms have been removed for clarity.⁸⁶⁴

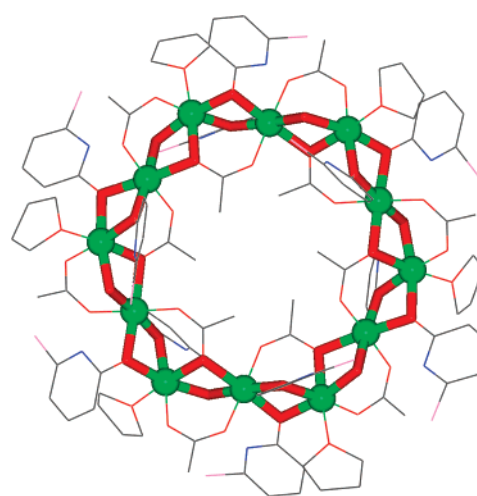


Figure 120. X-ray crystal structure of a vacant 24-MC_{Ni^{II}}-12 complex. Each Ni^{II} ion is connected to neighboring Ni^{II} ions via a μ -O of an acetate ligand and a μ -O from the 6-chloro-2-pyridonate ligand. An additional acetate anion bridges each Ni^{II} ion to its neighboring Ni^{II} ions. Color scheme: green sphere, Ni^{II}; red tube, oxygen; blue line, nitrogen; magenta line, chlorine; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁸⁸⁶

ure 123)⁹⁰² lead to molecular wheel complexes that do not bind any guests within the central cavity.

A 36-MC-18 may be generated from a $[\text{Fe}^{\text{III}}\text{-O}]_{18}$ metallamacrocycle (Figure 124).⁹⁰³ The structure is very similar to the other $-\text{[Fe}^{\text{III}}\text{-O}]\text{-}$ molecular wheels and does not bind a guest within the central cavity.

The metallamacrocycle $[\text{Ni}^{\text{II}}\text{-O}]_{24}$ constructs a 48-MC-4 molecular wheel (Figure 125).⁹⁰⁴ The structure represents to date the largest molecular wheel synthesized with 3d metal ions.

2.19. Complex Metallacrown Structures

Whereas most metallacrowns adopt relatively straightforward configurations, there are a few examples that truly contain an enormous number of atoms following a complex ring connectivity. The stereodiagram of the copper metallahelicite shown in Figure 126 contains 28 Cu^{II} ions held

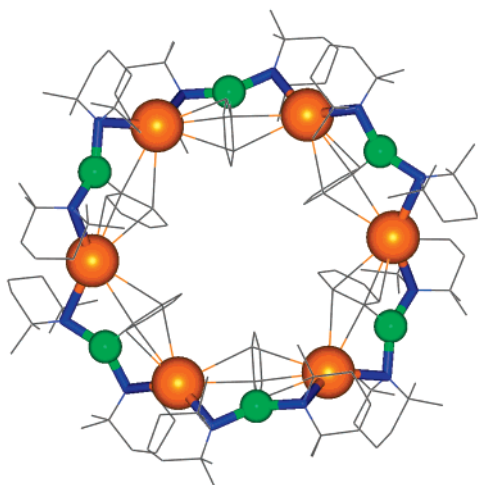


Figure 121. X-ray crystal structure of a vacant 24-MC_{K^I, Mg^{II}}⁻¹² complex. The *s*-block metal ions are connected via μ -N bridges supplied by the ligand 2,2,6,6-tetramethylpiperidide. A phenyl ring is bonded to an Mg^{II} with an *ipso* C–Mg σ bond and to two K^I through π bonds. Color scheme: green sphere, Mg^{II}; orange sphere, K^I; blue line, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁸⁹⁴

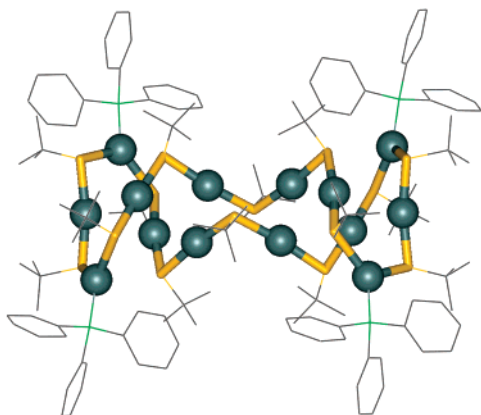


Figure 122. X-ray crystal structure of a vacant 28-MC_{Ag^I}⁻¹⁴ complex. The Ag^I ions are connected via μ -S bridges from SC-(CH₃)₃ ligands with a P(C₆H₅)₃ group completing the coordination about each Ag^I. The MC ring is twisted near the ends of the molecule. Color scheme: dark green sphere, Ag^I; yellow tube, sulfur; green line, phosphorus; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁹⁰⁰

together by 20 ligands.⁷³ This complex is prepared under conditions that are similar to those described for Ln^{III}[15-MC_{Cu^{II}N(α -aminoHA)}⁻⁵] complexes, using *S*-norvaline hydroxamic acid and Cu(OAc)₂ in the presence of NH₄Cl in methanol, but leaving Ln^{III} out of the synthetic protocol. It has been suggested, and supported with significant evidence, that the solution species under these conditions is actually a highly strained Cu^{II}[12-MC_{Cu^{II}N(α -aminoHA)}⁻⁴] structure.^{395,396,398,399,401,402} If one dissolves this metallahelicate into methanol, the observed mass spectral peaks are most consistent with the 12-MC-4 formulation, not the helicate. Nonetheless, the solid-state structure is fascinating.

The metallahelicates have been prepared with several resolved α -aminohydroxamic acids (leuHA, isoleuHA, alaHA, norvalHA). Two strands compose three structural domains. In the center of the structure is a fused core that contains eight copper ions and eight norvalHA ligands between the two strands. At either end of the helicate are two capping groups composed of two sets of wings that

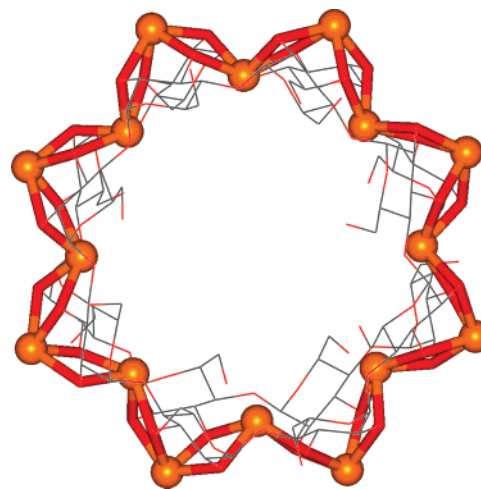


Figure 123. X-ray crystal structure of a vacant 32-MC_{Pb^{II}}⁻¹⁶ complex. The Pb^{II} ions are connected via two μ -O atoms from two γ -cyclomaltose, a cyclodextrin, ligands. Color scheme: orange sphere, Pb^{II}; red tube, oxygen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁹⁰²

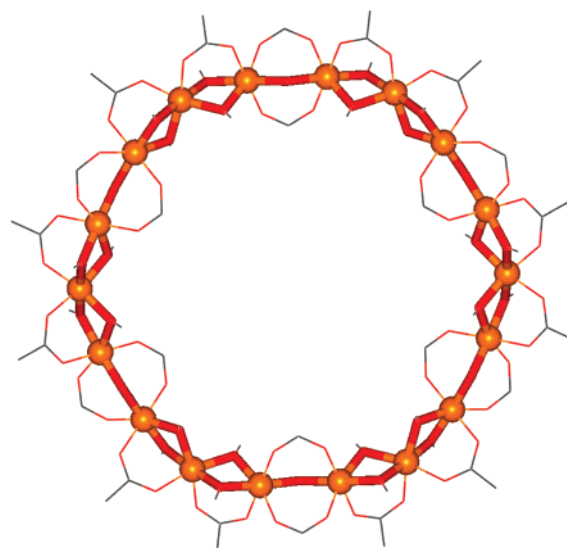


Figure 124. X-ray crystal structure of a vacant 36-MC_{Fe^{III}}⁻¹⁸ complex. The Fe^{III} ions are connected to neighboring Fe^{III} ions via two μ -O methoxide bridges or one μ -O oxide bridge. Acetate anions also bridge the neighboring Fe^{III} ions, and the ligand *m*-xylenediamine (XDK) bridges neighboring Fe^{III} ions. For the sake of clarity the XDK ligands have been reduced to only the CO₂⁻ groups. The acetate anions still have the methyl group attached to the CO₂⁻ group. Color scheme: orange sphere, Fe^{III}; red tube, oxygen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁹⁰³

demonstrate a pronounced twist. Each wing has five Cu^{II} ions and three norvalHA. One of the five Cu^{II} ions acts as a hinge between the central core and the cap. It is at this point that the copper adopts a propeller configuration that induces the structural twist of the molecule. All four copper ions of this type in the metallahelicate retain the same absolute stereochemistry (either Λ or Δ). A second copper ion of the wing forms a binuclear copper acetate capping group at the end of the molecule. Six halide ions are coordinated loosely to copper ions. Two observations point to the reproducibility of these structures. First, the metallahelicate can be prepared with a variety of α -aminohydroxamic acids. Second, the pitch of the helicate can be controlled by the choice of resolved starting hydroxamic acid. When *S*-norvalHA is used, the

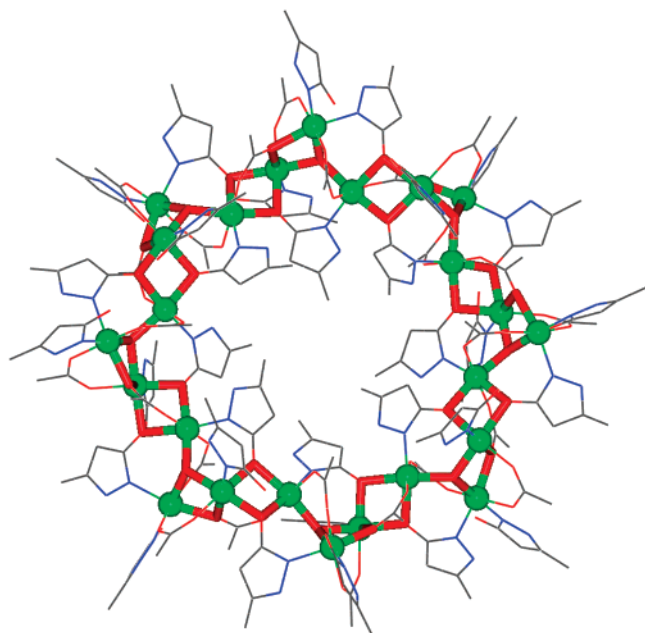


Figure 125. X-ray crystal structure of a vacant 48-MC_{Ni^{II}}-24 complex. The Ni^{II} ions are connected to neighboring Ni^{II} ions via bridging O atoms from acetate anions, hydroxide oxygen atoms, and oxygen atoms of the monodeprotonated anion of 3-methyl-3-pyrazolin-5-one. Color scheme: orange sphere: Ni^{II}; red tube, oxygen; blue line, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁹⁰⁴

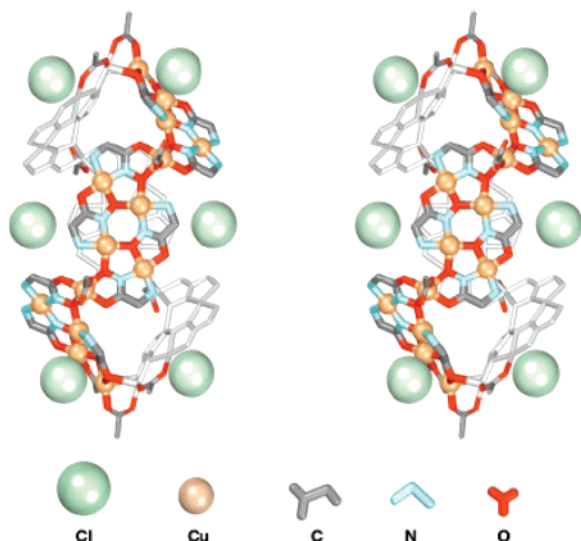


Figure 126. Stereoview of the X-ray crystal structure of metal-lahelicate [Cu₂₈(L-norvalHA)₂₀(O₂CCH₃)₁₀Cl₄(CH₃OH)₅(H₂O)₃], where L-norvalHA = L-norvalinehydroxamic acid. The traditional 15-MC-5 ligand L-norvaline (α -aminohydroxamic acid) was used to prepare a molecule that contains a collapsed 12-MC-4 core in each strand of the metal-lahelicate. Hydrogen atoms and lattice solvent have been removed for clarity. Reprinted with permission from ref 73. Copyright 2003 Wiley.

hinge atoms have the Λ absolute stereochemistry and a helicate with a positive pitch (P) is isolated. The opposite chiralities (Δ and M) are recovered from a synthesis with D-norvalHA.

A rather simple metallacryptate composed of eight Ga^{III} ions, eight shi³⁻ ligands, and three bound Na^I cations was described in section 2.4. A far more complex structure is

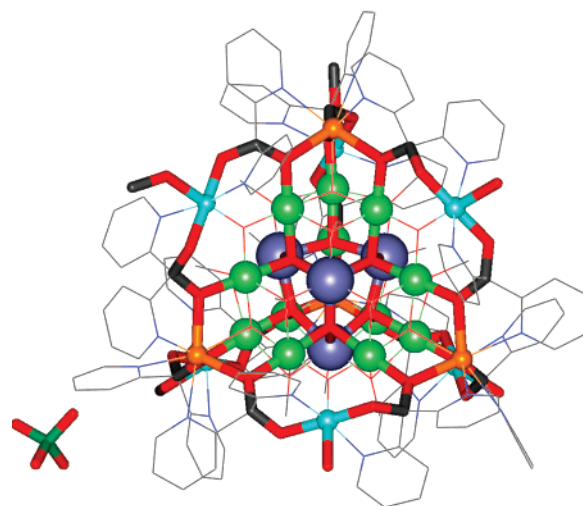


Figure 127. X-ray crystal structure of the metallacryptate [Mn^{II}₄-Mn^{III}₂₂(pdol)₁₂(μ ₃-OCH₃)₁₂(μ ₃-O)₆(μ ₄-O)₁₀(OH)₂(H₂O)(OCH₃)₃] \cdot ClO₄, where pdol²⁻ = dipyridylketonediolate ion. The core connectivity and metallacryptand strands have been highlighted. The structure contains four unique Mn ions. The core contains 16 Mn^{III} ions (purple and green), and the metallacryptand strands contain a total of 4 Mn^{II} ions (orange) and 6 Mn^{III} ions (aqua). The molecule displays slow magnetization relaxation in both the solid state and frozen solution. Color scheme: red tube, oxygen; blue tube, nitrogen; gray tube, carbon. Hydrogen atoms and lattice solvent have been removed for clarity. Reprinted with permission from ref 905. Copyright 2005 American Chemical Society.

illustrated in Figure 127.^{58,905} Unlike the previous metallahelicate, this manganese-containing metallacryptate is stable in DMF solution. In addition, it displays slow magnetic relaxation phenomena consistent with being a single-molecule magnet.

This metallacryptate contains 26 manganese ions, 22 of which are in the +3 oxidation level and 4 of which are +2 ions. Two different salts have been prepared (azide and perchlorate), and it has been shown that these have slight structural differences that lead to significant perturbations in the magnetic properties. The general structure consists of four strands having T molecular symmetry forming a metallacryptand as illustrated in the stereodiagrams of Figure 128 for the azide salt. There are four Mn^{II} ions in yellow that form the apex of tetrahedral corners. Each of these Mn^{II} ions is linked by two di-2-pyridyl methane diol ligands (pdol²⁻) and a Mn^{III} ion giving a connectivity between Mn^{II} ions that follows $-\text{[O-C-O-Mn}^{\text{III}}\text{-O-C-O]}-$. There are 4 apex positions (Mn^{II}) and 6 edges connecting these points (Mn^{III}), giving 10 manganese atoms in the metallacryptand portion of the structure. The inner core, described in Figure 127, contains an additional 16 atoms. All of these manganese ions have a +3 oxidation state. In particular, there are four Mn^{III} ions that are part of an adamantane core that are particularly important for the magnetic behavior of these molecules. The azide counterions are directly bound to the Mn^{II} ions of the cryptand portion of the structure. In contrast, the perchlorate salt has water, hydroxide, and methoxides coordinated to the Mn^{II} ions with the perchlorate in the lattice. This difference causes a breakdown of the symmetry for the perchlorate structure and leads to enhanced magnetic behavior.

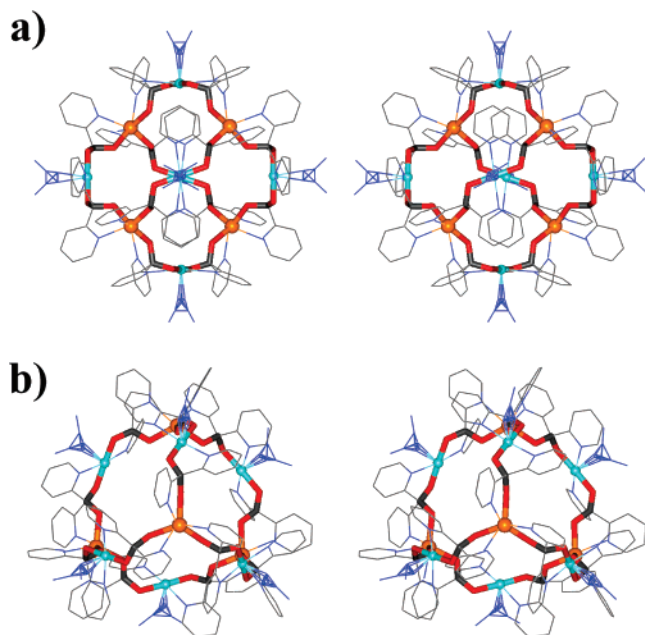


Figure 128. Stereoviews of the X-ray crystal structure of $\text{Mn}^{\text{II}}_4\text{-Mn}^{\text{III}}_{22}(\text{pdol})_{12}(\mu_3\text{-OCH}_3)_{12}(\mu_3\text{-O})_6(\mu_4\text{-O})_{10}(\text{N}_3)_6$, where pdol^{2-} = dipyridylketonediolate ion. This metallacryptate is very similar to the molecule in Figure 127. The only difference is the peripheral anions. This metallacryptate contains azide anions about the periphery, whereas the molecule in Figure 127 contains methoxide anions, hydroxide anions, and a water molecule about the periphery. Both views highlight the metallacryptand strands with the $\{\text{Mn}_{16}(\text{O}^{2-})_{12}(\text{MeO}^-)_{16}\}$ core removed. The azide analogue also possesses slow magnetization relaxation in the solid state: (a) view along the two-fold axis; (b) view along the three-fold axis. Color scheme: orange sphere, Mn^{II} ; aqua sphere, Mn^{III} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity. Reprinted with permission from ref 58. Copyright 2003 Wiley.

3. Solution Behavior of Metallacrowns

3.1. Solution Integrity Studies

As it became obvious from the previous sections, X-ray crystallography has been widely used and often is the most definitive technique for the structural characterization of metallacrowns. Nonetheless, many metallacrowns have a robust structure that is maintained in various solvents and even in the gas phase. This section is focused on metallacrown solution chemistry.

The formation of the pentanuclear $\text{Cu}(\text{II})$ -metallacrown, $[\text{Cu}_5\text{L}_4\text{H}_{-4}]^{2+}$ ($\text{HL} = \beta$ -alanine-hydroxamic acid), for which a $\text{Cu}^{\text{II}}[12\text{-MC}_{\text{Cu}^{\text{II}}-4}]$ structure had been determined by X-ray diffraction, was studied by potentiometric titration in aqueous solution.³⁸⁹ The results show that the major species in the pH range 4.5–9 is the pentanuclear species $[\text{Cu}_5\text{L}_4\text{H}_{-4}]^{2+}$, with a stability constant $\log \beta = 46.66(7)$. Below pH 4.5, the formation of a CuL^+ species is presumed, with a $\log \beta = 12.85(3)$. The stability of the pentanuclear species is also confirmed by absorption spectroscopy, which shows a d–d band at 616 nm from pH 4 to pH 9. Below pH 4 Cu^{II} is uncomplexed; the band at 616 nm is replaced by a band at 820 nm, which is characteristic for the Cu^{II} -aqua ion. At high pH values the complex decomposes due to ligand hydrolysis. The $\text{Cu}^{\text{II}}/\beta$ -alaHA system was later re-examined by another group, and similar stability constants were found by both potentiometric [$\log \beta = 47.83(5)$] and spectrophotometric

[$\log \beta = 47.42(4)$] measurements.³⁹⁶ The $[\text{Cu}_5\text{L}_4]^{2+}$ species is EPR silent at liquid nitrogen temperature or above.

Similar 12-MC-4 metallacrown structures have also been suggested to form in solution and the solid state with α -amino hydroxamic acid ligands, although no crystal structure determination has confirmed the structural identity of such species to date. Cu^{II} complexation equilibria in $\text{MeOH}/\text{H}_2\text{O}$ (9:1) solutions with *S*-phenylalanine and *S*-tryptophan hydroxamic acid ligands, along with ESI-MS studies, suggest the existence of $[\text{Cu}_5\text{L}_4]^{2+}$ species, besides other species such as $[\text{CuL}]^+$, $[\text{CuL}_2]$, and $[\text{CuL}_2]^-$.³⁹⁵ The formation constants are $\log \beta = 51.58(9)$ and $52.37(11)$, respectively. In the ESI-MS spectra, the most abundant species in both cases correspond to $[\text{Cu}_5\text{L}_4]^{2+}$. In the case of *S*- α -alanine-hydroxamic and *R*- β -aspartic hydroxamic acids, formation constants of $\log \beta = 40.16(1)$ and $\log \beta = 49.24(6)$ were found, respectively.³⁹⁶ The formation of a $[\text{Cu}_5\text{L}_4]^{2+}$ species was also suggested with *S*- γ -glutamic hydroxamic acid, $\log \beta = 39.76(7)$,⁴⁰¹ and with γ -aminobutane hydroxamic acid, $\log \beta = 36.72(6)$.^{402b} In the latter case the structure was confirmed by X-ray crystallography.^{402b}

Although single-crystal X-ray diffraction studies on metallacrowns formed with α -amino hydroxamic acids or picoline hydroxamic acid have not been able to identify 12-MC-4 structures so far, solution studies suggest the existence of such structures under certain conditions. However, the $\{\text{Cu}[\text{Cu}_4\text{L}_4]\}^{2+}$ cation cannot have a planar structure like the $\{\text{Ln}[\text{Cu}_5\text{L}_5]\}^{3+}$ cation, because the fused 5,5-membered chelate rings formed by these ligands would give rise to a strained structure. A comparative density functional theory (DFT) calculation on $\text{Cu}^{\text{II}}[12\text{-MC-4}]$ with α - and β -alanine hydroxamic acids shows that the four peripheral Cu^{II} ions in both metallacrowns form an almost planar structure.³⁹⁹ The deviation from planarity is larger in the case of the former ligand, the dihedral angles between the four Cu^{II} ions being 3.0° for the α -form and 1.4° for the β -form. Also, the central Cu^{II} ion is farther away from the quasi-plane formed by the four peripheral Cu^{II} ions in the case of the α -form (0.98 Å) than in the case of the β -form (0.50 Å). An even more pronounced difference can be seen in the coordination geometry of the Cu^{II} ions, which is nearly square-planar for the β -form but markedly distorted for the α -form. This fact is reflected in the calculated formation constants for the two metallacrowns, $\log \beta = 40$ with α -alaHA and $\log \beta = 49$ with β -alaHA.

In an attempt to crystallize such a $\{\text{Cu}[\text{Cu}_4\text{L}_4]\}^{2+}$ species ($\text{L} = \alpha$ -amino hydroxamic acid), a methanolic solution of Cu^{II} and *S*-norvaline hydroxamic acid in a 5:4 ratio in the presence of Cl^- was left to evaporate.⁷³ The crystals that grew out of this solution were characterized by X-ray crystallography as a high-nuclearity metallahelicate, with the formula $[\text{Cu}_{28}\text{L}_{20}(\text{OAc})_2\text{Cl}_4(\text{MeOH})_5(\text{H}_2\text{O})_3]$ (Fig. 126). This result suggests that the $[\text{Cu}_5\text{L}_4]^{2+}$ species observed by ESI-MS studies could also be a fragment of such a metallahelicate formed under the measurements conditions. Alternatively, the metallahelicate may convert into the proposed 12-MC-4 when dissolved. All studies agree that the ESI fragment consistent with a 12-MC-4 species can easily be converted into 15-MC-5 species upon addition of a lanthanide or uranyl ion.

Upon mixing of equimolar amounts of Cu^{II} acetate and an α -amino hydroxamic acid ligand, the initial blue color of the solution changes to dark green. The UV–vis spectrum of the final solution shows two absorption bands, one at 650–660 nm and another at 340–350 nm, whereas its ESI-

MS spectrum contains peaks that can be unambiguously assigned to $[\text{Cu}_5\text{L}_4]^{2+}$, $[\text{Cu}_5\text{L}_4(\text{H}_2\text{O})_3]\text{X}^+$, and $[\text{Cu}_5\text{L}_4(\text{LH}_2)(\text{H}_2\text{O})_2]\text{X}^+$ (where X is a monoanion).³⁹⁸ Similar results were obtained with an analogous α -hydroxy hydroxamic acid ligand, mandelohydroxamic acid, although no 12-MC-4 peaks were seen in the ESI-MS spectrum.⁹⁰⁶ Upon titration of UO_2^{2+} or a lanthanide ion into these solutions, the peaks assigned to 12-MC-4 disappear and new ones appear that can be assigned to 15-MC-5 species, $\text{GdX}[\text{Cu}_5\text{L}_5]^{2+}$ and $\text{GdX}_2[\text{Cu}_5\text{L}_5]^+$. Likewise, the absorption maximum at 650–660 nm gradually shifts to 550–560 nm with a concomitant change of the color to dark purple-blue; the observation of isosbestic points suggests the presence of only two interconverting species in the solution. The 12-MC-4 to 15-MC-5 conversion upon addition of UO_2^{2+} or a lanthanide ion was also monitored and confirmed by NMR and CD spectroscopy.

This work has recently been extended to picoline hydroxamic acid, which is also suggested to form a 12-MC-4 structure with Cu^{II} based on ESI-MS, NMR, and UV–vis spectra and elemental analysis.⁴⁰⁰ The ESI-MS spectra show peaks that can be assigned to both $[\text{Cu}_5\text{L}_4]^{2+}$ and $[\text{Cu}_5\text{L}_4]\text{X}^+$ ions. The ^1H NMR spectrum shows four lines of equal intensity that correspond to one set of pyridine-ring signals. Upon addition of a lanthanide salt, the resonances corresponding to $[\text{Cu}_5\text{L}_4]^{2+}$ disappear and four new lines corresponding to $\text{Ln}[\text{Cu}_5\text{L}_5]^{3+}$ appear. The same process was also observed by ESI-MS spectrometry. It was also shown by ESI-MS and NMR spectroscopy that addition of Ni^{II} ions to $[\text{Cu}_5\text{L}_4]^{2+}$ in DMSO solution generates a symmetrical $[\text{NiCu}_4\text{L}_4]^{2+}$ species (with the nickel ion occupying the cavity formed by the four copper ions).

The solution integrity of $[\text{12-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4}]$ and $[\text{12-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{nHA})-4}]$ metallacrowns (shi = salicylhydroxamic acid, nHA = 3-hydroxy-2-naphthohydroxamic acid) was investigated using mass spectrometry and ^1H NMR and UV–vis spectroscopy.³⁸² DMF solutions of the salt complexes $(\text{LiCl})_2[\text{12-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4}]$, $(\text{LiBr})_2[\text{12-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4}]$, and $(\text{LiTFA})[\text{12-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4}]$ (TFA = trifluoroacetate) in a 3-nitrobenzyl alcohol matrix gave strong molecular ion peaks in the FAB-MS corresponding to $\text{Li}[\text{12-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4}]$. Peaks of higher mass to charge ratio due to the binding of halide ions were also observed: $(\text{LiCl})[\text{12-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4}]$ and $(\text{LiCl}_2)[\text{12-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4}]$. In the case of $(\text{LiCl})_2[\text{12-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{nHA})-4}]$, the molecular peak corresponding to $\text{Li}[\text{12-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{nHA})-4}]$ was observed along with higher mass peaks consistent with chloride binding. In all cases, the observation of the peaks with the expected isotopic distributions at higher mass to charge ratio, consistent with anion binding, suggests that the anions remain bound to the metallacrown in solution. Similar results were obtained using ESI-MS in acetonitrile and methanol solutions. In addition, the solution integrity of $\text{Mn}(\text{OAc})_2[\text{12-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4}]$ and $\text{Mn}(\text{OAc})_2[\text{12-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{nHA})-4}]$ was confirmed by observation of molecular ions, consistent with the retention of metallacrown structure in either acetonitrile or methanol solution. Further information supporting the stability of $[\text{12-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4}]$ metallacrowns in CH_3CN , MeOH, and DMF solutions was obtained by ^1H NMR spectroscopy. The presence of only one set of signals, together with the observation that selective deuteration of the ligand in the H_5 and then in both the H_3 and H_5 positions eliminates one and then two of these resonances, demonstrates that the observed resonances are due to a single species in solution. The changes in the

chemical shifts of the proton resonances of the different salt complexes can be attributed to anions bound to the paramagnetic metal center in the case of Cl^- , Br^- , and TFA^- . Binding of anions to the Mn^{III} ions of the metallacrown ring causes a subsequent downfield shift in the H_4 resonance. These spectra further prove that the anions are bound in solution. Whereas the mass spectrometry results do not allow for conclusions about the integrity of the $(\text{NaCl})_2$, $(\text{NaBr})_2$, and $(\text{KBr})_2$ salt complexes of the metallacrown (probably due to the poor solubility and low volatility of those complexes), their ^1H NMR spectra are consistent with the retention of metallacrown structure in solution. Analogous conclusions can be drawn from the ^1H NMR data of the naphthylhydroxamic acid-based metallacrowns.

The dependence of structural integrity of the salt complexes of $[\text{12-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4}]$ on concentration was studied by UV–vis spectroscopy.³⁸² The absorbance varies linearly between 0.03 and 0.12 mM in CH_3CN , MeOH, and DMF. This adherence to Beer's law confirms that the metallacrown complexes do not dissociate at ≥ 0.04 mM concentrations.

Upon treatment of a methanolic solution of $\text{Mn}^{\text{II}}(\text{HCOO})_2 \cdot [(12\text{-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4})]$ with excess pyridine and slow evaporation, crystals of the expanded 15-MC-5, $\text{Mn}^{\text{II}}(\text{HCOO})_2 \cdot [(15\text{-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-5)(\text{py})_7)]$ were isolated.³⁸⁰ When these crystals were dissolved in DMSO, the conversion of the 15-MC-5 back to 12-MC-4 was observed, as indicated by the disappearance of the absorption band at 580 nm and appearance of a new band at 440 nm in the UV–vis spectrum. The conversion is complete in 1 h, and the final spectrum is identical to the one of an authentic $\text{Mn}^{\text{II}}(\text{HCOO})_2 \cdot [(12\text{-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4)]$ sample. The interconversion was explained by the strength of pyridine nitrogens to occupy equatorial positions of the Mn^{III} polyhedron, whereas the weak oxygen donors of DMSO prefer the Jahn–Teller axis in the distorted octahedral configuration.

The solution integrity of Cu^{II} and Ni^{II} 15-MC-5 complexes was studied by mass spectrometry and NMR, UV–vis, and circular dichroism (CD) spectroscopy.⁴⁶² Solutions of $\text{Ln}(\text{NO}_3)_3[\text{15-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{picHA})-5}]$ or $\text{Ln}(\text{NO}_3)_3[\text{15-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{glyHA})-5}]$ ($\text{Ln} = \text{La}^{\text{III}}$, Nd^{III} , Sm^{III} , Eu^{III} , Gd^{III} , Dy^{III} , Ho^{III} , Er^{III} , Yb^{III}) in H_2O , MeOH, or DMF were subjected to FAB-MS and/or ESI-MS. In each case, molecular ion peaks and intact ion peaks are observed, corresponding to mass-to-charge ratios that contain one or two nitrate ions associated with the metallacrown. Similar results were obtained for $\text{Ln}(\text{NO}_3)_3 \cdot [\text{15-MC}_{\text{Ni}^{\text{II}}\text{N}(\text{picHA})-5}]$ ($\text{Ln} = \text{Gd}^{\text{III}}$ and Nd^{III}) in DMF solutions by FAB-MS⁺. The stability of metallacrowns in DMSO and MeOH solutions was also studied by ^1H NMR of the paramagnetically shifted resonances of the ligand protons. A DMSO- d_6 solution of $\text{Ln}(\text{NO}_3)_3[\text{15-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{picHA})-5}]$ shows four distinct paramagnetically shifted resonances. Because each picoline hydroximate has four chemically distinct protons, the simplicity of the spectra—in seeing only one set of ligand resonances—can be attributed to the 5-fold pseudosymmetry of the metallacrown. Similarly, MeOH- d_4 solutions of $\text{Ln}(\text{NO}_3)_3[\text{15-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{picHA})-5}]$ or $\text{Ln}(\text{NO}_3)_3[\text{15-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{aminoHA})-5}]$ (aminoHA = glyHA, S-alaHA, S-pheHA, S-leuHA, S-tyrHA, S-valHA) showed only one set of ligand resonances immediately upon preparation and after 5 days, and no free ligand resonances were observed in the diamagnetic region. UV–vis titrations also showed that metallacrowns are intact in DMF and stable to the presence of excess lanthanide. Furthermore, the optically active metallacrowns can be conveniently studied by CD spectroscopy.

The CD spectrum of an ~ 1 mM solution of $\text{Nd}(\text{NO}_3)_3[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-alaHA})-5}]$ in either H_2O or HEPES buffer (pH 7.0) shows no evidence for decomposition for 14 days. The signal at 630 nm (the maximal negative intensity for the *S*-isomer) is lost, however, upon addition of acid (pH 2.14), D-alaha (5 equiv), or Na_2EDTA .

3.2. Selective Binding of Cations and Ion Pairs

The organometallic 12-MC-3 complexes made with a N–C–O bridge have shown alkali cation and ion-pair selectivity.²²⁷ (See Figures 16 and 17 for representative examples.) The first ionophore 12-MC-3, $[(\text{cymene})\text{Ru}^{\text{II}}(\text{hpy})_3]$ where hpy is 3-hydroxy-2-pyridone, binds Li^+ and Na^+ ; however, it does not bind K^+ .²²⁸ The complex has an affinity for LiCl twice as high as NaCl . When the aromatic group bound the metal is increased in size as in $(\text{C}_6(\text{CH}_3)_6)\text{-Ru}^{\text{II}}$, $(\text{C}_6\text{H}_3(\text{CH}_2\text{CH}_3)_3)\text{Ru}^{\text{II}}$, and $(\eta^5\text{-pentamethylcyclopentadiene})\text{Rh}^{\text{III}}$, the analogous 12-MC-3 complexes bind only Li^+ ions.²²⁹ For all metallacrowns studied, the presence of alkali metal ions can be detected electrochemically: the peak potential is shifted by >300 mV toward anionic potential upon binding. Because the metallacrowns themselves are neutral, the cations are bound as an ion-pair in the solid state, as revealed by the X-ray crystallographic results. In addition, the 12-MC-3 complexes appear to bind the alkali–halide ion pairs in solution also (CDCl_3 and CD_3OD), as evidenced by the significant downfield shift of the ^1H NMR signals of the pyridonate and the arene protons upon addition of the respective alkali–halide salt. The nature of the halide ion affects the stability constants. With the 12-MC-3 $[\text{Ru}^{\text{II}}(\text{cymene})(\text{hpy})_3]$ complex, NaCl has the highest stability constant and NaI the lowest. The 12-MC-3 $[\text{Ru}^{\text{II}}(\text{C}_6\text{H}_5\text{CO}_2\text{-CH}_2\text{CH}_3)(\text{hpy})_3]$ complex will selectively bind Li^+ in water even in the presence of large excesses of Na^+ , K^+ , Cs^+ , Mg^{II} , and Ca^{II} .²³⁰ This 12-MC-3 has a Li^+/Na^+ selectivity greater than 1000:1. When a different bridging ligand, 3-hydroxy-4-piperidino-methyl-2-(1*H*)-pyridone (hpm), is used, even greater selectivity can be achieved. 12-MC-3 metallamacrocycles with $(p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)_2)\text{Ru}^{\text{II}}$ ²³⁴ and $(\text{cymene})\text{-Ru}^{\text{II}}$ ²³⁸ can selectively bind Li^+ over Na^+ by a factor of 10000 at neutral pH.

A related iridium metallacrown, $[\text{Ir}^{\text{III}}(\eta^5\text{-pentamethylcyclopentadiene})(\text{hpy})_3]$ was developed into a fluoride-recognition agent.²³³ Whereas $(\text{LiCl})[\text{Ir}^{\text{III}}(\eta^5\text{-pentamethylcyclopentadiene})(\text{hpy})_3]$ has the same ^1H and ^7Li NMR spectrum as $(\text{LiBF}_4)[\text{Ir}^{\text{III}}(\eta^5\text{-pentamethylcyclopentadiene})(\text{hpy})_3]$ in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (2:1), indicating that the ion-separated, solvated complex is present, addition of Bu_4NF produces a distinct ^1H NMR spectrum. The selectivity was tested in the presence of a 50-fold excess of Cl^- , Br^- , I^- , and NO_3^- , and in all cases the exclusive formation of the F^- adduct was determined by ^1H and ^7Li NMR spectroscopy. These experiments show that the above-mentioned metallacrown is a high-affinity receptor for fluoride ions, comparable to cryptands.

The organometallic 12-MC-3 complexes made with a N–C–O bridge are also able to stabilize reactive molecules within the central cavity. Two 12-MC-3 complexes of $[(\text{cymene})\text{Ru}^{\text{II}}(\text{hpy})_3]$ bind a Na_2SiF_6 molecule between the two MCs (Figure 19).²³² Each central cavity uses its oxygen atoms to bind one sodium atom, and then the SiF_6^{2-} moiety connects the two Na^+ ions. This encapsulation represents one of the few examples in which Na^+ ions are coordinated to a SiF_6^{2-} anion.^{907–909} The 12-MC-3 complexes $[(\text{cymene})\text{Ru}^{\text{II}}(\text{hpy})_3]$, $[(\eta^5\text{-pentamethylcyclopentadiene})\text{Rh}^{\text{III}}(\text{hpy})_3]$, and

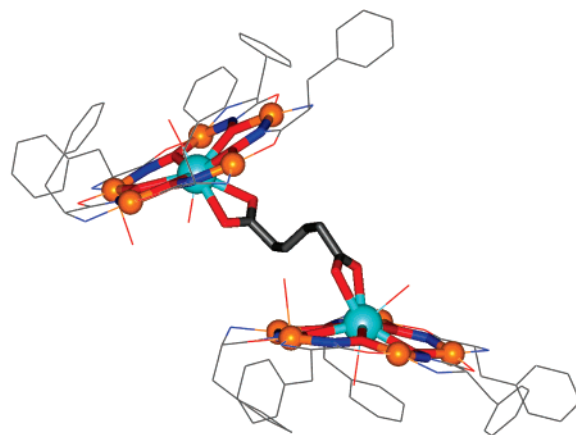


Figure 129. X-ray crystal structure of $\text{La}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})-5}]$ with the aliphatic dicarboxylate adipate anion. The adipate anion binds bidentate to each La^{III} ion but binds only on the outside faces of the MC—the adipate does not enter the hydrophobic pocket created by the phenyl rings of the *S*-phenylalanine hydroxamate ligand. Color scheme: aqua sphere, central La^{III} ; orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms, NO_3^- counteranions, and lattice solvent have been removed for clarity.^{465a}

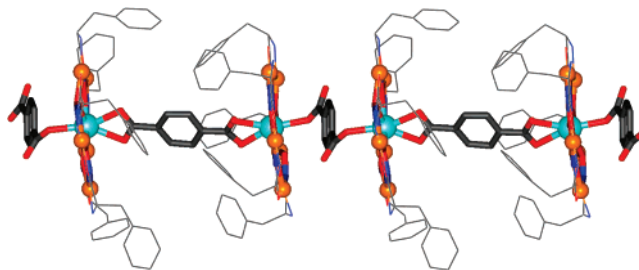


Figure 130. X-ray crystal structure of $\text{Gd}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})-5}]$ with the aromatic dicarboxylate terephthalate anion. The terephthalate anion binds monodentate to each Gd^{III} ion on the outside face of the MCs. In addition, the terephthalate enters the hydrophobic pocket created by the phenyl rings of the *S*-phenylalanine hydroxamate ligand and binds bidentate to each Gd^{III} , creating a one-dimensional chain of MCs. Color scheme: aqua sphere, central Gd^{III} ; orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms, NO_3^- counteranions, and lattice solvent have been removed for clarity.^{465a}

$[(\eta^5\text{-pentamethylcyclopentadiene})\text{Ir}^{\text{III}}(\text{hpy})_3]$ stabilize the elusive LiFHF moiety (Figure 18).²³¹ It is particularly interesting because the FHF^- anion contains a very strong hydrogen bond, and the FHF^- anion has never been captured before by a molecular host. The Li^+ binds to the ring oxygen atoms, and only one fluoride is bound to the Li^+ . The second fluoride is hydrogen-bonded to the first, and the resulting overall shape is an FHF^- anion bound in a bent fashion.

The $12\text{-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4}$ complexes also selectively bind cations and anions simultaneously.^{164,382,383} ^1H NMR and mass spectrometry indicated that the $12\text{-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4}$ complex binds Li^+ preferably over Na^+ and K^+ with K^+ ions having the lowest affinity. In addition, the $\text{M}[12\text{-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4}]^+$ ($\text{M}^+ = \text{Li}^+$, Na^+ , or K^+) has the highest affinity for Cl^- anions. Of the anions investigated the trend is $\text{Cl}^- \approx \text{SCN}^- > \text{Br}^- > \text{trifluoroacetate} > \text{F}^- \approx \text{I}^-$.

3.3. Selective Anion Binding

When synthesized from water, the $\text{Ln}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})-5}]$ complexes form a dimer in the solid state. A hydrophobic pocket forms between two MCs as a result of the interaction

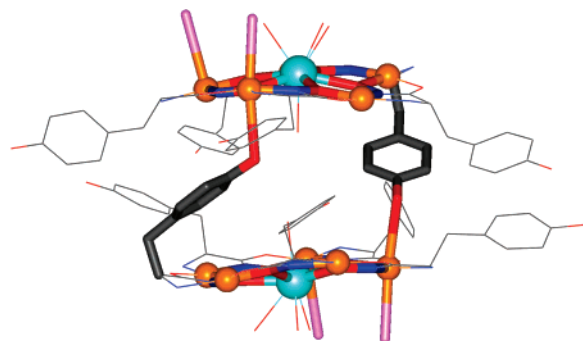


Figure 131. X-ray crystal structure of $\{Gd^{III}Cl_2[15-MC_{Cu^{II}}N(S\text{-tyrHA})\text{-}5]\}_2^{2+}$. The Cl^- anions bind only to the outside faces of the MC complexes. Two phenol oxygens bind across the hydrophobic pocket to generate a bound dimer. Color scheme: aqua sphere, central Gd^{III} ; orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; magenta tube, chloride; gray line, carbon. Hydrogen atom and lattice solvent have been removed for clarity.⁴⁶⁷

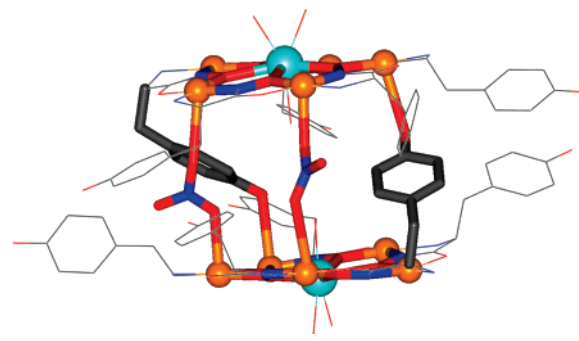


Figure 132. X-ray crystal structure of $\{Gd^{III}NO_3[15-MC_{Cu^{II}}N(S\text{-tyrHA})\text{-}5]\}_2^{4+}$. The NO_3^- anions bind only within the hydrophobic pocket of the MC complexes and bridge across the dimer to connect two ring Cu^{II} ions. Two phenol oxygens also bind across the hydrophobic pocket to generate a bound dimer. Color scheme: aqua sphere, central Gd^{III} ; orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁴⁶⁷

of the phenyl rings of opposite MC complexes. Within this hydrophobic pocket, guests may be bound. As evident from single-crystal X-ray analysis, aliphatic dicarboxylate guests bind to the outside faces of the MC dimer and aromatic dicarboxylate guests bind within the hydrophobic pocket (Figures 129 and 130).^{465,470,910,911} In $La^{III}[15-MC_{Cu^{II}}N(S\text{-pheHA})\text{-}5]$, aliphatic adipate binds bidentate to the La^{III} on the outside face of the metallacrown with one of the carboxylate groups. The second carboxylate group binds bidentate to a La^{III} ion of a second MC on the outside face. The adipate therefore joins the two dimers together to create a one-dimensional chain of “dimers of dimers”. On the other hand, aromatic terephthalate does enter the hydrophobic cavity and binds across the cavity in a bidentate fashion to the two Gd^{III} central ions of the two $Gd^{III}[15-MC_{Cu^{II}}N(S\text{-pheHA})\text{-}5]$ complexes. The terephthalate joins the two MCs together through the hydrophobic cavity. In addition, the terephthalate binds analogously to the adipate by joining the dimers through the outside faces to create a one-dimensional chain of “dimers of dimers”. Comparable aliphatic and aromatic dicarboxylate guests display a similar binding behavior.⁴⁶⁵

$Ln^{III}[15-MC_{Cu^{II}}\text{-}5]$ complexes, where $Ln^{III} = La^{III}$ and Gd^{III} , synthesized with *S*-tyrosine hydroxamic acid (*S*-tyrHA) form a true dimer because one phenol oxygen of each MC stretches across the interior cavity to bind to ring Cu^{II} ions of the opposite MC. These complexes may be made with two Cl^- anions bound to the outside faces of the MCs or two NO_3^- anions bound within the interior of the cavity (Figures 131 and 132).⁴⁶⁷ The dimer $Ln^{III}[15-MC_{Cu^{II}}N(S\text{-tyrHA})\text{-}5]$ does not have a preference for chloride anions, as when a 10:3:1 ratio of $Cl^-:NO_3^-:MC$ was crystallized, a hybrid structure that contained two Cl^- and two NO_3^- anions was recovered even though there was an excess of Cl^- anions (Figure 133). In addition, a preformed $Ln^{III}[15-MC_{Cu^{II}}N(S\text{-tyrHA})\text{-}5]$ dimer with two Cl^- anions is capable of binding an additional two NO_3^- when excess $NaNO_3$ is added to the solution of the chloride-only analogue.

The metallazaacrown complex $[(tmeda)Pd(1-MeC^--N3N4)_3\text{-}(ClO_4)_3]$ (*tmeda* = *N,N,N',N'*-tetramethylethylenediamine, 1-MeC[−] = 1-methylcytosine deprotonated at exocyclic amino group) was studied in solution by ¹H NMR for fluoride binding.²⁵⁰ Shifts of several metallazaacrown-host proton resonances were detected in the presence of fluoride ion in DMSO-*d*₆: a marked downfield shift of the N–H resonances, a moderate downfield shift of two of the four CH₃ resonances

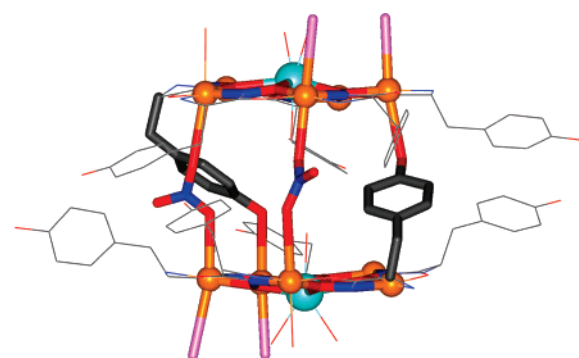


Figure 133. X-ray crystal structure of $\{Gd^{III}Cl_2(NO_3)[15-MC_{Cu^{II}}N(S\text{-tyrHA})\text{-}5]\}_2$. The structure is a hybrid of the structures with only Cl^- or NO_3^- . The NO_3^- anions still reside in the hydrophobic pocket, and the Cl^- anions still reside on the outside faces of the MCs. Color scheme: aqua sphere, central Gd^{III} ; orange sphere, ring Cu^{II} ; red tube, oxygen; blue tube, nitrogen; magenta tube, chloride; gray line, carbon. Hydrogen atoms and lattice solvent have been removed for clarity.⁴⁶⁷

of the *tmeda* ligand, and minor upfield shifts of the aromatic protons of the 1-MeC[−] ligand. Saturation was achieved after >2 equiv of F[−] was added. The downfield shift of the methyl resonances suggests either that CH^{••}F hydrogen bonding is present or that the host structure is reorganized upon fluoride binding.

3.4. Metallacrown Ligand Exchange

The solution dynamics of 9-MC-3, 12-MC-4, and 15-MC-5 in various solvents was studied by ¹H NMR spectroscopy and mass spectrometry. When 9-MC_{VO³⁺N(shi)-3 is mixed with 9-MC_{VO³⁺N(nHA)-3 in CH₃CN or with 9-MC_{VO³⁺N(4-OHshi)-3 in DMF, there is no evidence for ligand exchange after 48 h, as all of the proton peaks from the NMR spectrum of the mixture can be assigned either to one or to the other metallacrown.¹⁶⁹ These results not only indicate that the metallacrown structures are retained in the given solvents but also show that rapid dissociation equilibria that would scramble the ligands is not operative in CH₃CN or DMF solutions. However, when 9-MC_{VO³⁺N(shi)-3 is mixed with 9-MC_{VO³⁺N(nHA)-3 in MeOH, ¹H NMR shows relatively rapid exchange: after approximately 6 h, the scrambling of ligands appears to be complete and new resonances appear that are not present for the starting metallacrowns or for the ligands in protonated or deprotonated forms. The assignment of}}}}}

these resonances to mixed-ligand metallacrowns was confirmed by FAB-MS, which shows mass peaks for both starting metallacrowns and both mixed-ligand metallacrowns 9-MC_{VO³⁺N^(shi)₂(nHA)-3} and 9-MC_{VO³⁺N^(shi)(nHA)₂-3}. Kinetic studies showed that the ligand exchange is first order with an overall rate constant equal to the sum of the individual first-order rate constants from each participating species ($k = 0.31 \pm 0.02 \text{ h}^{-1}$). The kinetic lability of 9-MC_{VO³⁺N^(shi)-3} in MeOH allows it to be used as a probe of the integrity of 12-MC-4 and 15-MC-5 metallacrowns in solutions containing MeOH (vide infra).

To eliminate the thermodynamic penalties when ligand exchange reactions between metallacrowns based on different ligands are studied, thermodynamically equivalent copper 12-MC-4 complexes prepared from protio- and deuterio-salicylhydroxamic acid were used in further studies.³⁸⁶ The ESI-MS spectra of [Cu^{II}(12-MC_{Cu^{II}N^(shi)-4})] and [Cu^{II}(12-MC_{Cu^{II}N^(d₂shi)-4)] in CH₃CN were recorded separately and then in a 1:1 mixture. Both molecular ions, at m/z 919 for the former and at m/z 926 for the latter metallacrown, are observed in the initial mass spectrum. A mass spectrum of the same mixture taken 6 h later shows no observable ligand mixing between the metallacrowns, demonstrating the solution integrity of the shi³⁻-based copper metallacrown in CH₃CN.}

Further evidence demonstrating that ligand exchange does not occur with [Cu^{II}(12-MC_{Cu^{II}N^(ligand)-4})] came from ¹H NMR studies using 9-MC_{VO³⁺N^(nHA)-3}, which is known to be kinetically labile in MeOH.^{169,386} Equimolar solutions of either [Cu^{II}(12-MC_{Cu^{II}N^(shi)-4})] or [Cu^{II}(12-MC_{Cu^{II}N^(nHA)-4})] and 9-MC_{VO³⁺N^(nHA)-3} in MeOH showed no sign of ligand exchange in the ¹H NMR after 24 h. Furthermore, FAB-MS of the 1:1 solutions mentioned above showed mass peaks only for the starting metallacrowns. As a control, mixed-ligand metallacrowns were prepared directly and showed the expected mass peaks for mixed-ligand species. These results prove that the two copper 12-MC-4 complexes are kinetically inert to ligand exchange.

In the case of the manganese metallacrowns [12-MC_{Mn^{III}N^(shi)-4})] and [12-MC_{Mn^{III}N^(nHA)-4})], solution dynamics was studied by ¹H NMR spectroscopy.³⁸² A CH₃CN or DMF solution containing equimolar amounts of (NaCl)₂[12-MC_{Mn^{III}N^(d₂shi)-4})] and (NaCl)₂[12-MC_{Mn^{III}N^(shi)-4})] was monitored by ¹H NMR as a function of time. No ligand exchange was observed within 7 days. Identical results were observed for all of the other salt complexes (LiCl, LiBr, NaBr, KBr) of [12-MC_{Mn^{III}N^(shi)-4})] and [12-MC_{Mn^{III}N^(nHA)-4})] in DMF or CH₃CN. In methanol, however, a different behavior is observed: ¹H NMR of a mixture of (NaCl)₂[12-MC_{Mn^{III}N^(shi)-4})] and (NaCl)₂[12-MC_{Mn^{III}N^(nHA)-4})] shows that ligand scrambling occurs. The rate of ligand exchange was estimated by monitoring the peak area (A) for the new resonance at -5.10 ppm. Plotting $\log[(A - A_\infty)/(A - A_\infty)]$ versus time gives a line for which the slope is $2.48 \pm 0.02 \text{ h}^{-1}$, indicating that the approach to the equilibrium mixture is first-order, as in the case of 9-MC_{VO³⁺N^(shi)-3}, with an overall rate constant equal to the sum of the individual first-order rate constants from each participating species. The LiCl analogues, (LiCl)₂[12-MC_{Mn^{III}N^(shi)-4})] and (LiCl)₂[12-MC_{Mn^{III}N^(nHA)-4})], however, do not exchange ligands in methanol within 2 days as monitored by either ¹H NMR or mass spectrometry. The stability of the LiCl metallacrowns can be explained by the closeness of the lithium ion to the metallacrown core (only 0.64 Å above the best-fit plane of the four manganese ions),

which reduces the rate of ligand exchange.

In contrast to 12-MC-4 complexes, the 15-MC-5 metallacrowns appear to be more prone to ligand exchange.⁴⁶² Both NMR and ESI-MS studies show that when equimolar amounts of Nd(NO₃)₃[15-MC_{Cu^{II}N^(S-tyrHA)-5}] and Nd(NO₃)₃[15-MC_{Cu^{II}N^(S-pheHA)-5}] solutions are mixed together, ligand scrambling occurs and mixed species form—Nd(NO₃)₃[15-MC_{Cu^{II}N^(S-tyrHA)_x(S-pheHA)_y-5] with $x:y$ ratios of 5:0, 4:1, 3:2, 2:3, 1:4, and 0:5. Metal-exchange studies showed that Ca^{II} or Ln^{III} ions are replaced by the UO₂²⁺ ion in the corresponding metallacrowns with both picoline and α -amino hydroxamic acids, establishing 15-MC-5 metallacrowns as efficient uranyl-sequestering agents.^{398,463,906}}

3.5. Relaxivity Studies

The presence of tightly bound, highly paramagnetic metals in Ln^{III}[15-MC_{Cu^{II}N^(aminoHA)-5}] prompted proton relaxation enhancement studies for possible use as magnetic resonance imaging (MRI) contrast agents. The metallacrown structure has several potential advantages in this application compared to the currently used MRI contrast agents [Gd-DTPA]²⁻ and [Gd-DOTA]⁻. It has been shown that the magnetic susceptibilities of metal complexes including Cu^{II} and Gd^{III} ions can be enhanced compared to single-ion complexes. The 15-metallacrown-5 structure provides five oxygen atoms for coordination, whereas three or four other sites are possibly available for the coordination of water. Nd(NO₃)₂(OH)[15-MC_{Cu^{II}N^(S-alaHA)-5}] has four water molecules directly bound to Nd^{III}, the site that would be occupied by Gd^{III} in a MRI contrast agent. [Gd-DTPA]²⁻ and [Gd-DOTA]⁻ have only one site for the coordination of water and have relaxivities of 4.8 and 4.7 mM⁻¹ s⁻¹, respectively (at 298 K and 20 MHz),⁹¹² whereas complexes with two sites for water binding have a relaxation rate of 6.3 mM⁻¹ s⁻¹ under the same conditions.⁹¹³ Another advantage of the 15-MC-5 complexes over [Gd-DTPA]²⁻ is that they have a large planar, disk-like structure that favorably affects the reorientation rate of the molecules in solution. The reorientation rate and number of coordinating water molecules are known to have a significant effect on relaxation rate.^{912,914}

The proton relaxation rates of a series of 15-MC-5 metallacrowns, Gd(NO₃)₃[15-MC_{Cu^{II}N^(picHA)-5}], La(NO₃)₃[15-MC_{Cu^{II}N^(picHA)-5}], and Gd(NO₃)₃[15-MC_{Cu^{II}N^(S-aminoHA)-5}] (aminoHA = glyHA, S-tyrHA, S-alaHA), were measured at different concentrations in water at 20 °C and 30 MHz.⁴⁶² It was found that the larger planar structures have enhanced relaxivities, in keeping with the higher relaxivity of Gd(NO₃)₃[15-MC_{Cu^{II}N^(S-tyrHA)-5}] of 9.43 mM⁻¹ s⁻¹ compared with 4.22 mM⁻¹ s⁻¹ for the smaller, more compact Gd(NO₃)₃[15-MC_{Cu^{II}N^(S-alaHA)-5}]. In addition, the relaxivities of Gd(NO₃)₃[15-MC_{Cu^{II}N^(S-tyrHA)-5}] and Gd(NO₃)₃[15-MC_{Cu^{II}N^(picHA)-5}] (9.8 mM⁻¹ s⁻¹) are significantly higher than the relaxivity of [Gd-DTPA]²⁻ and [Gd-DOTA]⁻.

A qualitative comparison of the relaxivity of La(NO₃)₃[15-MC_{Cu^{II}N^(picHA)-5}] with the Cu^{II}-aqua ion leads to the conclusion that these metallacrowns retain their integrity in water. The relaxivity of the Cu^{II}-aqua ion is 0.81 mM⁻¹ s⁻¹.⁹¹² If the metallacrown is dissociating and binding to water, the relaxivity of La(NO₃)₃[15-MC_{Cu^{II}N^(picHA)-5}] would be equal to $5 \times 0.81 \text{ mM}^{-1} \text{ s}^{-1}$ because the concentration is per cluster and there are five copper ions per metallacrown. The relaxivity of La(NO₃)₃[15-MC_{Cu^{II}N^(picHA)-5}] ($R_1 = 0.94 \text{ mM}^{-1} \text{ s}^{-1}$) is actually closer to the relaxivity of a 5 mM solution of copper(II) ions bound in a macrocycle (CuMe₄¹⁴aneN₄, $R_1 = 0.94 \text{ mM}^{-1} \text{ s}^{-1}$), where its relaxation rate is 0.70 s⁻¹.⁴⁶²

Additional temperature- and frequency-dependent relaxivity measurements have been carried out on analogous Gd(NO₃)₃[15-MC_{Cu^{II}N(S-aminoHA)-5}] metallacrowns (aminoHA = glyHA, S-valHA, S-pheHA, S-leuHA, S-tyrHA).⁴⁷⁴ The results confirm the previous observation that the relaxivity of the gadolinium-containing 15-MC-5 complexes is approximately twice as high as the relaxivity of [Gd-DTPA]²⁻ and [Gd-DOTA]⁻ over the whole temperature and frequency range. This is in accord with the presence of two coordinated water molecules in the first coordination sphere of the metallacrown complexes, compared to one for the [Gd-DTPA]²⁻ and [Gd-DOTA]⁻ complexes. For all metallacrowns studied, the relaxivities increased by a factor of 1.65–2 as the temperature decreased from 45 to 5 °C at a magnetic field strength of 0.47 T. This indicates that the residence time of water does not limit the proton relaxivity. The relaxivities of the metallacrowns show a linear dependence on the molecular weight at magnetic field strengths of greater than 1 T. However, the relaxation profiles do not exhibit the dispersion peak at high frequency, which is characteristic for slowly rotating paramagnetic molecules.⁹¹⁵ Thus, the decrease in mobility of the metallacrowns caused by increasing their molecular weight through the attachment of larger substituents to the α-amino hydroxamic acid is insufficient to maximize the relaxation at frequencies used in clinical applications. The paramagnetic contribution of the Cu^{II} ions relative to the lanthanide ions was also investigated by measuring the relaxivity of La(NO₃)₃[15-MC_{Cu^{II}N(aminoHA)-5}] and was found to be within 2–6% depending on the magnetic field strength and ligand.

Of course, there are issues beyond simple relaxivities that are important in developing a useful MRI contrast agent. In particular, one must assess the stability of the proposed agent in the presence of biological reductants or metal-chelating agents. Using CD titrations, it has been shown that metallacrowns alone are stable in pH 7.0 solution for over two weeks with virtually no evidence of decomposition. It is also known that these molecules do not exchange hydroxamate ligands rapidly under these conditions. Transmetalation of Gd^{III} by Zn^{II} in metallacrowns was investigated by measuring proton relaxometry at 0.47 T. The results show that whereas the metallacrown complexes Gd(NO₃)₃[15-MC_{Cu^{II}N(S-aminoHA)-5}] with aminoHA = S-tyrHA, S-pheHA, or S-leuHA transmetalate more quickly than [Gd-DTPA]²⁻, the analogous metallacrowns with aminoHA = S-valHA or glyHA are characterized by transmetalation behavior intermediate between those of the open-chain [Gd-DTPA]²⁻ complex and the macrocyclic [Gd-DOTA]⁻ complex.⁴⁷⁴ Therefore, the two latter metallacrowns appear to be remarkably stable in the presence of Zn^{II} ions. However, the addition of acid (to pH 2, which might be found in the stomach) leads to immediate complex decomposition for all of the above-mentioned metallacrowns.⁴⁶² Furthermore, excess hydroxamate ligand causes decomposition of the Ln(NO₃)₃[15-MC_{Cu^{II}N(aminoHA)-5}] to Cu^{II}(hydroxamate)₂. Finally, strong chelating agents such as EDTA will quantitatively remove Cu^{II} and Ln^{III} from the metallacrown. Interestingly, the serum iron transport protein transferrin will not destroy the metallacrown. Undoubtedly this is due to slow kinetics of metal removal (the large metallacrown apparently cannot fit into the iron-binding site to initiate metal removal) because transferrin should be thermodynamically capable of removing Cu^{II} from these metallacrowns. Despite these setbacks, these metallacrowns illustrate in principle a new design strategy to both enhance

the magnetic susceptibility of a molecule and simultaneously increase the number of exchangeable Gd^{III}-bound water molecules.

4. Functional Applications of Metallacrowns

Metallacrowns have been used for a variety of functions including bioactivity, molecular recognition, catalysis of organic reactions, mimics of surface science, building blocks for one-, two-, and three-dimensional solids, liquid crystals, and single molecule magnets. This section of the review will cover this wide array of functions.

4.1. Bioactivity

12-MC_{Ni^{II}-4} complexes have shown antibacterial activity and the ability to alter the structure of pDNA. (See Figures 44–46 for representative examples.) The vacant [12-MC_{Ni^{II}N(Hshi)₂(pko)₂-4}](X)₂, where X⁻ = SCN⁻, NNN⁻, and OCN⁻, and the Ni^{II}(O₂CCH₃)₂[12-MC_{Ni^{II}N(shi)₂(pko)₂-4] complexes were tested as antibacterial agents against *Bacillus subtilis* (Gram-positive), *Bacillus cereus* (Gram-positive), *Staphylococcus aureus* (Gram-positive), *X. campestris* (Gram-negative), *Escherichia coli* (Gram-negative), and *P. mirabilis* (Gram-negative).⁴⁰⁸ All of the metallacrowns showed higher activity than simple Ni(O₂CCH₃)₂ with the vacant metallacrowns showing the highest activity. In addition, the vacant metallacrowns bound to pDNA caused concatemers to form at low concentrations of MC and precipitates to form at high concentrations of MC. The Ni^{II}(O₂CCH₃)₂[12-MC_{Ni^{II}N(shi)₂(pko)₂-4] complex did not bind to pDNA. In addition, the fused metallacrowns Ni^{II}₂X₂[12-MC_{Ni^{II}N(shi)₂(pko)₂-4][12-MC_{Ni^{II}N(shi)₃(pko)₂-4], where X⁻ = 2,4-dichlorophenoxypropionate, 2,4,5-trichlorophenoxyacetate, 2-methyl-4-chlorophenoxyacetate, 2,4-dichlorophenoxyacetate, *S*(+)-6-methoxy-α-methyl-2-naphthaleneacetate, and *S*(+)-4-isobutyl-α-methylphenylacetate (ibuprofen), were tested for antibacterial activity against *B. subtilis* (Gram-positive), *B. cereus* (Gram-positive), *S. aureus* (Gram-positive), *X. campestris* (Gram-negative), *E. coli* (Gram-negative), and *P. mirabilis* (Gram-negative).⁴¹⁰ The most active complex was the 12-MC-4 with 2,4-dichlorophenoxypropionate. The 12-MC-4 complexes with 4-dichlorophenoxypropionate, 2,4,5-trichlorophenoxyacetate, 2,4-dichlorophenoxyacetate, and *S*(+)-6-methoxy-α-methyl-2-naphthaleneacetate affect the structure of pDNA, whereas the complexes with 2-methyl-4-chlorophenoxyacetate and ibuprofen do not.}}}}

Manganese metallacrowns have also been tested for antibacterial activity. (See Figures 38 and 56 for representative examples.) MX[12-MC_{Mn^{III}N(shi)-4}], where MX = Na₂(salicylate)₂, Mn^{II}₂(O₂CH)₂, and Mn^{II}(O₂CCH₃)₂, and MX[15-MC_{Mn^{III}N(shi)-5}], where MX = Mn^{II}(2,4,5-trichlorophenoxyacetate)₂, Mn^{II}(2-methyl-4-chlorophenoxyacetate)₂, Mn^{II}(2,3-dichlorophenoxyacetate)₂, Mn^{II}(2,4-dichlorophenoxyacetate)₂, Mn^{II}(O₂CH)₂, Mn(O₂CCH₃)₂, and Mn^{II}(salicylate), were tested for antibacterial activity versus *B. subtilis* (Gram-positive), *S. aureus* (Gram-positive), *E. coli* (Gram-negative), and *P. bulgaris* (Gram-negative).⁴⁶¹ All of the metallacrowns showed more activity than simple Mn^{II}-(herbicide)₂ compounds or Mn^{II}(carboxylate)₂ salts. The complex Mn^{II}(2,4,5-trichlorophenoxyacetate)₂[15-MC_{Mn^{III}N(shi)-5}] displayed the most activity among the MCs tested. An additional study with more manganese metallacrowns, both 12-MC_{Mn^{III}N(shi)-4} and 15-MC_{Mn^{III}N(shi)-5} complexes, did

not reveal antibacterial agents superior to $\text{Mn}^{\text{II}}(2,4,5\text{-trichlorophenoxyacetate})_2[15\text{-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})\text{-5}]$.³⁸⁰

4.2. Molecular Recognition

The organometallic 12-MC-3 complexes made with a N–C–N bridge have shown molecular recognition in water at pH 7 in ^1H NMR experiments²⁴¹ (see Figure 20 for a representative complex). The 12-MC-3 complex, $[(\eta^5\text{-pentamethylcyclopentadiene})\text{Rh}^{\text{III}}(\text{L})]_3$, where L is 9-methyladenine, adenosine, 2'-deoxyadenosine, or methyl-5'-adenosine monophosphate, will accept aromatic amino acids such as *S*-phenylalanine and *S*-tryptophan only within the central cavity.²⁴⁴ *S*-Tryptophan has a higher binding constant than *S*-phenylalanine for all four 12-MC_{Rh^{III}}-3 complexes. Non-aromatic amino acids such as *S*-histidine, *S*-alanine, and *S*-proline do not interact significantly with the 12-MC_{Rh^{III}}-3 complexes. However, more hydrophobic amino acids such as *S*-isoleucine and *S*-leucine associate slightly with the 12-MC_{Rh^{III}}-3 complexes. In a more complete study, the four compounds above and $[(\eta^5\text{-pentamethylcyclopentadiene})\text{Rh}^{\text{III}}(2',3'\text{-dideoxyadenosine})]_3$ were studied with a number of guests.²⁴⁵ These additional studies reveal that all five complexes also do not bind the nonaromatic amino acids *S*-valine and *S*-glutamine. The five 12-MC_{Rh^{III}}-3 complexes do bind the aromatic carboxylic acid guests *o*-aminobenzoic acid, *m*-aminobenzoic acid, *p*-aminobenzoic acid, benzoic acid, phenylacetic acid, 4-methoxyphenylacetic acid, *o*-methoxybenzoic acid, and *o*-nitrobenzoic acid. In addition, the aliphatic carboxylic acid guest cyclohexylacetic acid and 1-adamantanecarboxylic acid do bind in the cavity just as strongly as the aromatic guests—the opposite of the aliphatic amino acids. In a competition study between phenylacetic acid and cyclohexylacetic acid with $[(\eta^5\text{-pentamethylcyclopentadiene})\text{Rh}^{\text{III}}(2'\text{-deoxyadenosine})]_3$, the host molecule did not show a preference for either guest molecule.

4.3. Catalysis

Several copper-pyrazolate-based metallacrown systems show catalytic activity. The aza12-MC_{Cu^IN(pz*)}-4, where Hpz* is 3,5-dicarbo-*sec*-butoxypyrazole, 3,5-di-*tert*-butylpyrazole, 3,5-diphenylpyrazole, catalyzes the conversion of alkenes

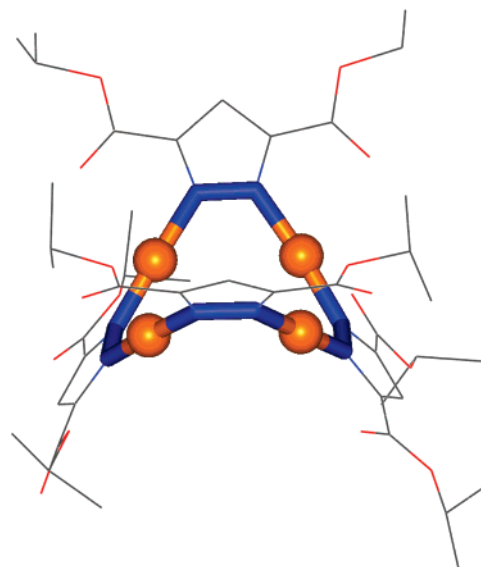
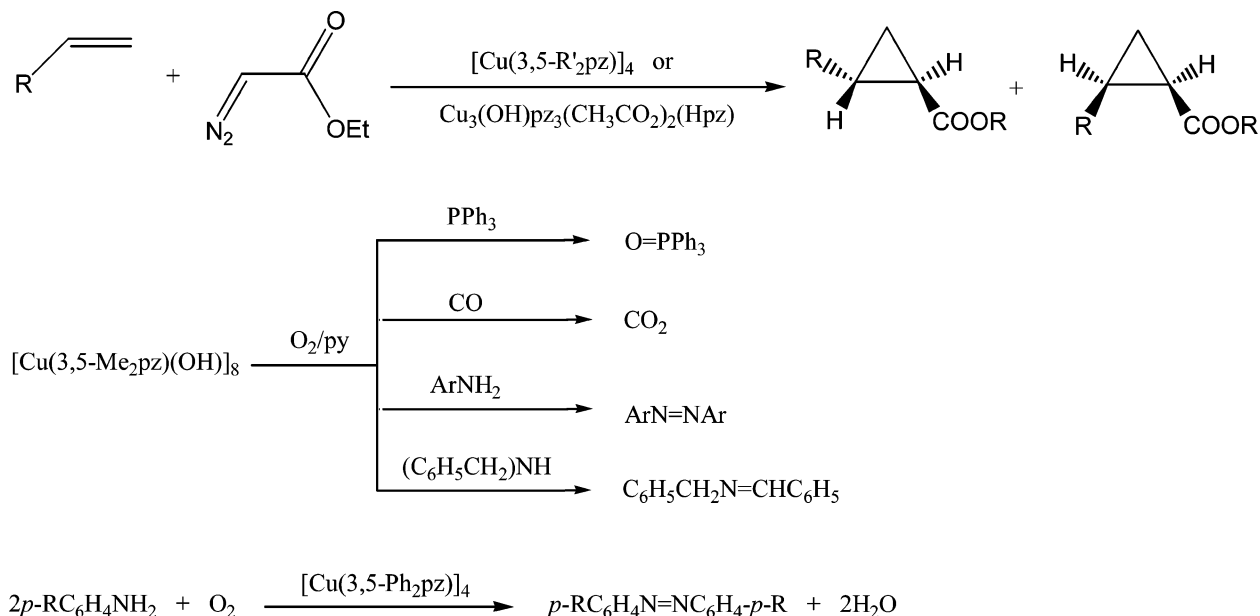


Figure 134. X-ray crystal structure of the vacant aza[12-MC_{Cu^I}-4] complex with the ligand 3,5-dicarbo-*sec*-butoxypyrazole. The MC catalyzes the conversion of alkenes into the corresponding cyclopropane derivative. Color scheme: orange sphere, Cu^I; blue tube, nitrogen; red line, oxygen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁴³⁵

into the corresponding cyclopropane derivative (Figure 134; Scheme 6).⁴³⁵ The yields are >70% and average a 3:1 diastereomeric excess (*trans*/*cis*). Three inverse aza(μ_3 -OH)-(Hpz)X[9-MC_{Cu^IN(pz)}-3] complexes, where pz is pyrazolate and X is (O₂CCH₃)₂, (O₂CCH₃)(OCH₃), or (OCH₃)₂, also catalyze the reaction of olefins with diazo compounds to form cyclopropane derivatives (Figure 135).¹⁹⁴ The yields average 73% with the X = (OCH₃)₂ 9-MC-3 performing the best with a 86% yield. These reactions proceed with a *cis*/*trans* ratio in favor of the more hindered product. The 24-MC_{Cu^{II}N(dmpz)}-8, where dmpz is dimethylpyrazolate (Figure 86), will stoichiometrically oxidize PPh₃ to O=PPh₃ at 60 °C under inert atmosphere in pyridine, toluene, or halocarbons, but at 60 °C and with a dioxygen atmosphere in pyridine, the reaction is catalytic.⁵⁴³ The 24-MC_{Cu^{II}N(dmpz)}-8 complex also catalyzes the conversion of carbon monoxide

Scheme 6. Schematic Representation of the Reactions Catalyzed by Metallacrown Complexes



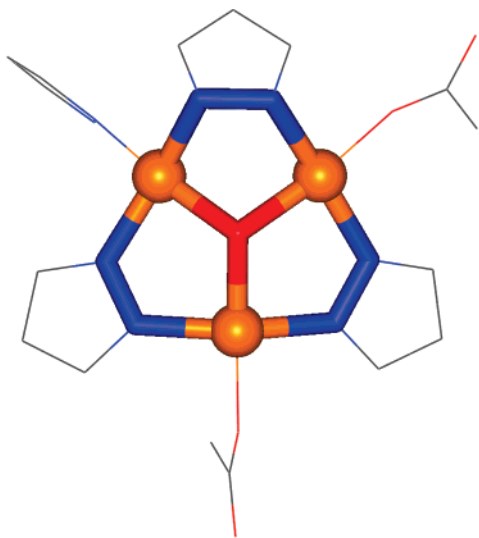


Figure 135. X-ray crystal structure of the inverse aza(μ_3 -OH)[9-MC $_{Cu^{II}}$ -3] complex with the ligand pyrazolate. One pyrazole and two $CH_3CO_2^-$ anions bind terminally to the Cu^{II} ions. The MC catalyzes the reaction of olefins with diazo compounds to form the corresponding cyclopropane derivatives. Color scheme: orange sphere, Cu^{II} ; blue tube, nitrogen; red tube, oxygen; gray line, carbon. Hydrogen atoms have been removed for clarity.¹⁹⁴

to carbon dioxide, of aromatic amines to azobenzenes, and of dibenzylamine to *N*-benzylidenebenzylamine. In addition, the aza12-MC $_{Cu^{II}}$ -4 complex with 3,5-diphenylpyrazole catalyzes the conversion of primary aromatic amines to the corresponding azobenzenes in 100% yield (Figure 52).⁴³³ In contrast to the 24-MC $_{Cu^{II}N(dmpz)}$ -8 complex, the activity of the aza12-MC $_{Cu^{II}}$ -4 complex did not decrease with time.

4.4. Mimics of Surface Science

The 12-MC-3 complexes synthesized with a $-[Pt-P-C-P]-$ or $-[Pd-P-C-P]-$ repeat unit (see Figures 25–30 for representative complexes) are excellent models for chemical reactions that may happen at metal surfaces. Extensive reviews have been written on the complete nature of these surface model systems.^{257,258} Using primarily 1H and ^{31}P NMR, activities at the Pt_3 or Pd_3 center may be followed including mimics of organic transformation chemical reactions,^{266–268,279,330} chemisorption,^{261,264,274,278,282,284,285,293} oxidation of heterometallic catalysts,^{281,290,294} and sulfidation of heterometallic catalysts.^{291,292}

4.5. Building Blocks for One-, Two-, and Three-Dimensional Solids

As noted in the section on 15-MC-5 structural types, L_n^{III} -[15-MC $_{Cu^{II}N(S-\beta\text{-pheHA})}$ -5] complexes can form one-dimensional helical chains when crystallized from a mixture of methanol and water (Figures 60 and 61).⁴⁶⁶ Within the chain a carbonyl oxygen of one metallacrown binds axially to a Cu^{II} ion of an adjacent metallacrown. The metallacrowns are placed at 90° with respect to each other, with the interior of the helix formed by the MC side without phenyl rings. Due to the pseudo-fivefold symmetry of the metallacrown, a molecular square cannot be obtained. Instead, the $O_{\text{carbonyl}}-Cu^{II}$ bond is perpetuated down a S_4 screw axis to give a helical chain. Viewed down the screw axis, the metallacrowns form the sides of a “square” with the phenyl rings directed to the outside. The solid is homochiral with the choice of ligand determining the pitch of the helix. Using the *S* enantiomer of phenylalanine hydroxamic acid results in the Plus (P) helix

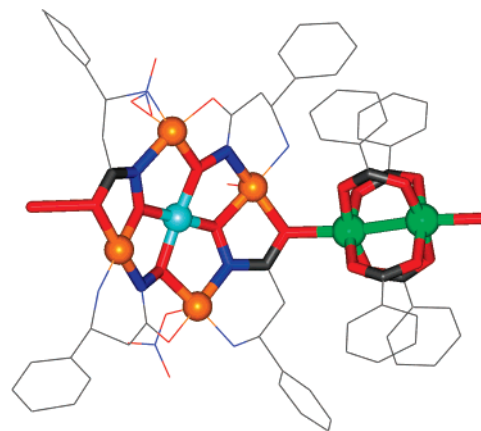


Figure 136. X-ray crystal structure of $Cu^{II}(NO_3)_2[12-MC_{Cu^{II}N(S-\beta\text{-pheHA})}-4]$, where *S*- β -pheHa is *S*- β -phenylalanine hydroxamic acid, and $Cu^{II}_2(O_2CC_6H_5)_4$, which form the monomeric unit of the two-dimensional chiral solid. A carbonyl oxygen of the MC binds to a Cu^{II} ion of the paddlewheel dimer (PD) to form a one-dimensional chain. Color scheme: aqua sphere, central MC Cu^{II} ; orange sphere, ring MC Cu^{II} ; green sphere, PD Cu^{II} ; blue tube, nitrogen; red tube, oxygen; gray tube, carbon. Hydrogen atoms, benzoic acid guest, and lattice solvent have been removed for clarity.³⁹¹

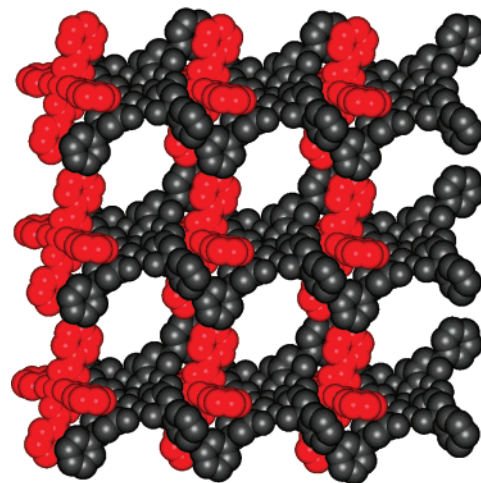


Figure 137. X-ray crystal structure of the $Cu^{II}(NO_3)_2[12-MC_{Cu^{II}N(S-\beta\text{-pheHA})}-4]-Cu^{II}_2(O_2CC_6H_5)_4$ two-dimensional chiral solid in CPK display with the view highlighting the channels created in the solid state. The nitrate anions, which form the second dimension, are perpendicular to the plane of the paper and are not visible in this view. The paddlewheel dimers are in scarlet, and the metallacrowns are in gray. Hydrogen atoms, benzoic acid guest, and lattice solvent have been removed for clarity.³⁹¹

(space group $P4_1$), whereas the use of the *R* enantiomer results in the Minus (M) helix (space group $P4_3$).

A homochiral two-dimensional network may be synthesized with $Cu^{II}(NO_3)_2[12-MC_{Cu^{II}N(S-\beta\text{-pheHA})}-4]$ and the paddlewheel dimer (PD) $Cu_2(O_2CC_6H_5)_4$ (Figures 136 and 137).^{391,910,911} An undulating one-dimensional chain is constructed of alternating units of 12-MC-4 and PD. A carbonyl oxygen of the 12-MC-4 binds axial to a Cu^{II} ion of the PD to generate a connectivity pattern of $[-O_C-Cu^{II}_{RMC}-O_H-Cu^{II}_{CMC}-O_H-Cu^{II}_{RMC}-O_C-Cu^{II}_{PD}-Cu^{II}_{PD}]_n$, where O_C is a carbonyl oxygen, O_H is a hydroxamic oxygen, Cu^{II}_{RMC} is a Cu^{II} ion of the MC ring, Cu^{II}_{CMC} is the Cu^{II} encapsulated within the central cavity of the MC, and Cu^{II}_{PD} is a Cu^{II} ion of the PD. In the second dimension, a nitrate anion binds 12-MC-4 faces to each other via a $Cu^{II}_{RMC}-O-N-O-Cu^{II}_{RMC}$ linkage. A channel of dimensions $8 \times 9 \text{ \AA}$ runs

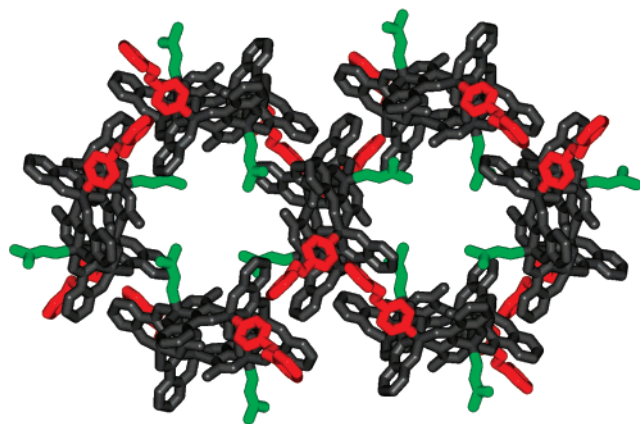


Figure 138. X-ray crystal structure of the vacant aza[18-MC_{Mn^{III}}-6] (gray) with 1,2-bis(4-pyridyl)ethane (scarlet) to create a three-dimensional solid. The view highlights the channels created along the *c*-axis in the three-dimensional framework. *N,N*-Dimethylformamide solvent (green) molecules line the inside of the channel. Hydrogen atoms and lattice solvent have been removed for clarity.⁵¹⁸

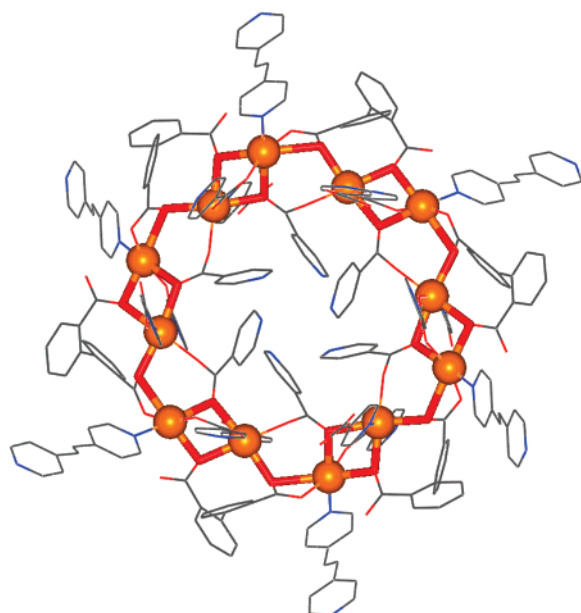


Figure 139. X-ray crystal structure of the molecular wheel 24-MC_{Cd^{II}}-12 with μ -O bridges from isonicotinate and diphenate ligands. *exo*-Tridentate isonicotinate ligands create a pillar column of molecular wheels, and then the pillars are connected via 1,2-di(4-pyridyl)ethylene ligands, which are seen on the perimeter of the above molecule, to form a three-dimensional solid. Color scheme: orange sphere, Cd^{II}; red tube, oxygen; blue line, nitrogen; gray line, carbon. Hydrogen atoms have been removed for clarity.⁸⁸⁸

perpendicular to the 12-MC-4-PD chain. The faces of the 12-MC-4 form the ceiling and floor of the channel, whereas the walls of the cavity are formed by the overlap of the phenyl rings of the MC *S*- β -pheHA ligand and the PD benzoate ligand. Inside the cavity a guest benzoic acid molecule is bound via hydrogen bonds to an amine nitrogen of the MC ring, to a water molecule, which is bound to a ring Cu^{II} ion, and to an oxygen atom of a nitrate anion, which is bound to a ring Cu^{II} ion (this nitrate is not involved in bridging the MC faces to form the second dimension). The benzoic acid guest is also involved in two quadrupolar interactions with phenyl rings of the 12-MC-4 complex. Additional solvent molecules are also located within the cavity. Furthermore, if the *R*-isomer of β -phenylalanine

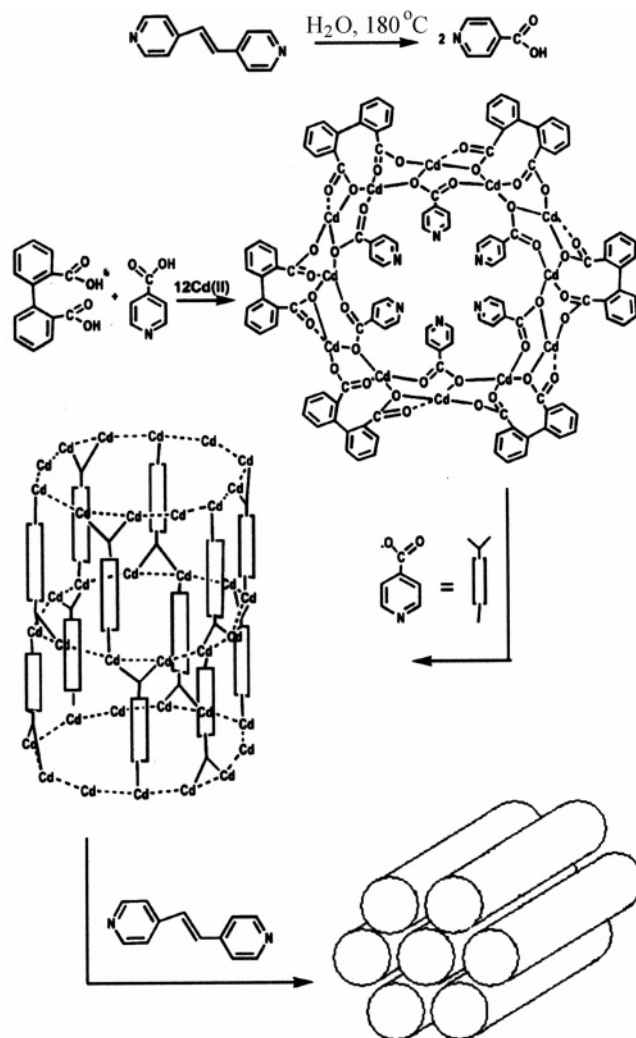


Figure 140. Schematic of how the 24-MC_{Cd^{II}}-12, *exo*-tridentate isonicotinate, and di(4-pyridyl)ethylene molecules combine to form a three-dimensional solid. Reprinted with permission from ref 88. Copyright 2003 Royal Society of Chemistry.

hydroxamic acid is used to construct the solid, the mirror image homochiral two-dimensional network is produced.

Aza18-MC-6 complexes made with *N*-acetylsalicylhydrazide ligands can be used to generate three-dimensional solids. Using *N*-acetylsalicylhydrazidate (H₃ashz) and Mn^{III}, a hexanuclear metallamacrocycle can be synthesized.⁵¹⁸ This aza18-MC-6 complex can then be connected with 1,2-bis(4-pyridyl)ethane (bpea) to form a three-dimensional network (Figure 138). The bpea binds to four of the ring Mn^{III} ions of one aza18-MC-6 and then bridges to adjacent complexes to create the three-dimensional network. The aza18-MC-6 acts as a helical tecton in which the bpea ligand bridges with 4₁/4₃ screw symmetry. The ~ 16 Å channels are filled with *N,N*-dimethylformamide (DMF) solvent molecules, and the DMF molecules may be exchanged with other organic solvents. When *N*-lauroylsalicylhydrazide is used as the ligand, a similar aza18-MC-6 is produced, but when the 18-MC-6 complex is combined with bpea, two different three-dimensional networks are obtained.⁵²⁰ One network is exactly the same as with H₃ashz—the metallamacrocycle acts as a helical tecton that is bridged by the bpea ligand with 4₁/4₃ screw symmetry. In the second network, the metallamacrocycle still acts as a helical tecton but the bpea bridges via 3₁/3₂ screw symmetry. This results in solvent-filled channels with a size of 2.0 nm. Both solids retain their crystallinity

Table 4. Transition Temperatures (°C), Enthalpies (kJ·mol⁻¹; in Parentheses), and Lattice Parameters (Å) for the Hexagonal Columnar Mesophases^a

compound	phase transition behavior	X-ray data	ref
Au ₃ [(3,5-bis(3',4'-di- <i>n</i> -decyloxyphenyl)pyrazole) ₃]	<i>K</i> 59 (112.1), Col _h 64 (2.8), <i>I</i>	32.4 (±0.2)	208
Au ₃ [(3-(3',4',5'-tri- <i>n</i> -decyloxyphenyl)-5-(3'',4''-di- <i>n</i> -decyloxyphenyl)pyrazole) ₃]	<i>K</i> 36.5, Col _h 59 (5.8), <i>I</i>	31.7 (±0.2)	208
Au ₃ [(3-(2',3',4'-tri- <i>n</i> -decyloxyphenyl)-5-(3'',4'',5''-tri- <i>n</i> -decyloxyphenyl)pyrazole) ₃]	Col _h 22 (5.9), <i>I</i>	31.1 (±0.2)	208
Au ₃ [(3,5-bis(3',4',5'-tri- <i>n</i> -decyloxyphenyl)pyrazole) ₃]	<i>K</i> 35 (6.8), Col _h 58 (4.9), <i>I</i>	30.8 (±0.2)	208
Au ₃ [(3,5-bis(methyl)-4-(<i>n</i> -heptyl)pyrazole) ₃]	heating <i>K</i> 71 (5.4), <i>K'</i> 116 (12.1), <i>I</i> cooling <i>I</i> 112 (3.4), Col _h 99 (8.9), <i>K</i>		209
Au ₃ [(3,5-bis(methyl)-4-(<i>n</i> -octyl)pyrazole) ₃]	heating <i>K</i> 56 (1.8), <i>K'</i> 112 (31.2), <i>I</i> cooling <i>I</i> 85 (3.5), Col _h 61 (26.7), <i>K</i>		209
Au ₃ [(3,5-bis(methyl)-4-(<i>n</i> -nonanyl)pyrazole) ₃]	heating <i>K</i> 82 (27.1), <i>K'</i> 90 (2.6), <i>I</i> cooling <i>I</i> 39 (22.3), <i>K</i>		209
Au ₃ [(3,5-bis(methyl)-4-(<i>n</i> -undecanyl)pyrazole) ₃]	heating <i>K</i> 87 (7.9), <i>I</i> cooling <i>I</i> 14 (23.4), <i>K</i>		209
Au ₃ [(3,5-bis(<i>n</i> -octyl)pyrazole) ₃]	heating <i>K</i> 58 (9.2), <i>K'</i> 80 (48.6), <i>I</i> cooling <i>I</i> 52 (55.4), <i>K</i>		209

^a *K*, *K'*, crystalline phase; Col_h, hexagonal columnar mesophase; *I*, isotropic phase.

upon removal of channel solvent; however, when the solvent is reintroduced, the networks do not retain their crystallinity. Additional studies of similar solids have shown that these networks are capable of binding guests with size and podality selectivity.⁵²¹

A three-dimensional solid may also be generated from a molecular wheel 24-MC_{Cd^{II}}-12 complex, [$\{Cd^{II}_2(dpa)(pya)\}_6-(pya)_6(dpe)_6$]_{*n*}, where H₂dpa is diphenic acid, Hpya is isonicotinic acid, and dpe is 1,2-di(4-pyridyl)ethylene (Figures 139 and 140).⁸⁸⁸ The 24-MC-12 has a repeat unit of $-[Cd^{II}-O]-$ with the oxygen atoms provided by the dpa and pya ligands. The metallamacrocycles are linked together in one dimension to form a pillared structure. An above MC is bound to a below MC via six *exo*-tridentate isonicotinate ligands, which bridge between two above Cd^{II} ions (the carboxylate group bridges two Cd^{II} ions of the same MC) and one below Cd^{II} (pyridyl nitrogen of the ligand coordinates). The pillars are then linked in the second and third dimensions via six dpe ligands, which bind to every other Cd^{II} ion of one MC ring.

4.6. Liquid Crystals

Liquid crystals have formed a very important technological area that affects all of us daily. The ability to control the properties of such phases is an area of constant industrial and academic research. In particular, the ability to control the addressability of such materials using polarization, photochemical, and electrochemical or magnetochemical switching is of particular interest. For this reason, the field of metallomesogens (metal-containing liquid crystals) has developed because metals offer an attractive method for altering these physical properties. Numerous metal motifs have been attached to mesogen-inducing ligands, notably metalloporphyrins, and recent studies that have developed mesogenic metallacrowns have been reported.

Aza9-MC_{Au^I}-3 structures of the formula $[Au^I(3,4,5-R_1,R_2,R_3-pz)]_3$ synthesized from 3,4,5-*R*₁,*R*₂,*R*₃-pyrazole (*R*₁, *R*₃ = methyl, *n*-octyl, 3',4'-di-*n*-decyloxyphenyl, 2',3',4'-tri-*n*-

decyloxyphenyl, 3',4',5'-tri-*n*-decyloxyphenyl; *R*₂ = H, *n*-heptyl, *n*-octyl, *n*-nonanyl, *n*-undecanyl) form hexagonal columnar mesophases at room temperature.^{208,209} Although the parent pyrazole ligands are not mesogenic, coordination to gold results in complexes with liquid crystal behavior. The nuclearity of these complexes was confirmed by molecular weight and mass spectrometry measurements, whereas the liquid crystalline behavior was studied by polarizing optical microscopy (with an attached heating-cooling stage), differential scanning calorimetry, and X-ray diffraction.

Optical microscopy under polarized light reveals that the texture of these compounds is fanlike and pseudo-focal-conic, characteristic of hexagonal columnar mesophases. On cooling, these complexes exhibit a hysteresis phenomenon, and the liquid crystal phases remain metastable for long periods at room temperature. The hexagonal columnar structures of the liquid crystalline phases are clearly demonstrated by X-ray diffraction analysis. Transition temperatures and enthalpies, as well as lattice parameters for the discotic mesogens, are presented in Table 4. These complexes stack into columns not only in the mesophase but also in the crystalline state, as confirmed by a single-crystal X-ray diffraction measurement of $[Au^I(3,5-Me_2-4-(n-octyl)-pz)]_3$. In this complex, the three Au atoms form an almost perfect equilateral triangle with Au...Au separations of 3.335(1)–3.356(1) Å, and they lie in a plane with the three pyrazolate rings. As expected, the peripheral *n*-octyl groups attached to the pyrazolate ligands are severely disordered. Interestingly, the complex forms “dimers” through intermolecular Au...Au contacts of 3.255(2) Å, which are stacked in a tilted fashion to form columns in the crystal phase. These tilted columnar stacks are converted to flat columnar stacks during the phase change. Thus, Au–Au interactions seem to play an important role in forming the hexagonal columnar structures of the mesophases.

4.7. Single-Molecule Magnets (SMMs)

The first SMM, $\text{Mn}^{\text{III}}_3\text{Mn}^{\text{IV}}_4\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4$ (Mn_{12} -acetate), was first synthesized in 1980 by Lis⁹¹⁶ and then recognized as an SMM in 1993 by Christou, Hendrickson, Gatteschi, and co-workers.^{917,918} The field of SMMs has been intensely studied ever since.^{919–923} The term “single-molecule magnet” was coined by chemists, but the phenomenon has been studied for a number of years using nanoparticles under the designation superparamagnetism. Superparamagnetism is the phenomenon in which a single magnetic domain is located within a solid. Transition metal nanoparticles such as $\text{Fe}^{\text{III}}_2\text{O}_3$ with a diameter of ≤ 60 nm contain no magnetic domain walls; thus, the nanoparticles contain only one magnetic domain and are known as superparamagnets.^{924–929} In oscillating magnetic fields, superparamagnets will display a frequency-dependent magnetic signal as the magnetization of the sample is slow to relax upon switching of the field. The slow magnetization relaxation is due to ordering of the spin within the sample. The idea of a single magnetic domain can be extended to isolated molecules. If a molecule is sufficiently isolated from its neighbors so as to have negligible intramolecular magnetic interactions and if the molecule is anisotropic with a net magnetic spin, then each individual molecule may behave as a single magnetic domain—a superparamagnet or a single-molecule magnet.

The properties of SMMs are derived from the slow relaxation of magnetization over a thermal energy barrier. The energy barrier height is determined from the spin of the molecule and the amount of molecular magnetoanisotropy, D , with the relation $E = S^2|D|$. The molecular D parameter arises from summation of the individual anisotropy of each magnetic center. High-spin molecules typically behave as SMMs; however, if the molecule is completely isotropic, that is, a spherical complex, the molecule will not behave as an SMM because the individual anisotropies of each magnetic center will negate each other. At low enough temperatures, only the ground state of the complex will be occupied and the distribution will be equal between the “up” and “down” ground spin states. In an applied field, all of the molecules will align with the field. As the field is reversed at a certain frequency, the magnetization of the molecule will begin to realign to the opposite ground state by “climbing” the thermal energy barrier. However, if the barrier is sufficiently large, then the magnetization will not be able to realign at the same frequency of the magnetic field. This can be manifested in ac magnetic susceptibility experiments by the observation of a frequency-dependent signal. As the frequency is lowered, the temperature at which the magnetization will not be able to keep in-phase with the oscillating field will also lower because at high temperatures the magnetization is realigning at a faster rate. Therefore, for Mn_{12} -acetate with an $S = 10$ ground spin state and a molecular D of 0.47 cm^{-1} , the theoretical blocking temperature (temperature at which frequency dependency is first observed) would be 47 cm^{-1} ($\sim 68 \text{ K}$).^{917,918} The theoretical blocking temperature is also known as the effective blocking temperature or the effective energy barrier to magnetization relaxation, U_{eff} . However, blocking temperatures are never observed at these theoretical values due to quantum tunneling of the magnetization. In an applied magnetic field, the energy diagram becomes shifted with the spin states aligned with the magnetic field becoming lower in energy and the states aligned against the magnetic field becoming higher in energy. If spin states in opposite wells of the spin ladder align, then the magnetization

may tunnel through the barrier instead of being thermally activated to the other side. This tunneling therefore increases the rate of magnetization relaxation and decreases the observable blocking temperature considerably. The tunneling manifests itself in magnetic hysteresis experiments, where step-like behavior is observed in the coercive sweeps. Because the tunneling causes the magnetization to drop rapidly, steps are observed in the hysteresis curves instead of smooth lines, which indicate thermal transitions. Due to the tunneling process, the highest observable blocking temperature is 7 K at 500 Hz for Mn_{12} -acetate.^{917,918}

SMMs have been made with a variety of transition metal ions including manganese,⁹²⁰ iron,^{921,922} cobalt,^{930–932} nickel,^{933–935} vanadium,⁹³⁶ and variety of heterometallic transition metals.^{937–944} However, SMMs based on Mn^{III} ions have been the most popular because Mn^{III} has four unpaired electrons per ion ($S = 2$) and large anisotropy due to its Jahn–Teller axis. The main area of research has focused upon manganese carboxylate complexes.⁹²⁰ A recent avenue into the field of SMMs has been the inclusion of lanthanide ions within complexes.^{945–952} Lanthanide ions are highly attractive because they not only potentially provide a large number of unpaired electrons but also are highly magnetoanisotropic due to spin–orbit coupling.

Metallacrown structures represent a logical extension of the previous work in the field of single-molecule magnetism. Metallacrown complexes typically have a large number of metal ions contained within a small volume; thus, the metal centers can interact to provide a large spin for the molecule. In addition, certain metallacrown frameworks have proven to be generic with the substitution of a variety of metal types into a ligand framework being feasible. Furthermore, metallacrowns are capable of containing both transition metal ions and lanthanide ions within a single complex. This area of SMM research has just begun to be explored.

Other reviews have extensively detailed the single-molecule magnet properties of molecular wheels,^{953–955} a type of metallacrown, so only a general listing will be given below. The focus of this review has been cyclic metal complexes with two atom bridges between metal centers; thus, the single-molecule magnetism portion of this review will focus on traditional metallacrowns.

Molecular wheels have greatly expanded the field of single-molecule magnetism. The structural basis is very similar in all of the complexes with one-atom bridges between metal centers, and the structures have been described above. The complexes $\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_4 \{ \text{Mn}^{\text{II}}[12\text{-MC}_{\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_3-6}] \}$,⁷⁶⁹ $\text{Mn}^{\text{III}}_8 \{ \text{Ce}^{\text{IV}}[16\text{-MC}_{\text{Mn}^{\text{III}}_8-8}] \}$,⁸²⁷ $\text{Mn}^{\text{II}}_8\text{Mn}^{\text{III}}_8 \{ 32\text{-MC}_{\text{Mn}^{\text{II}}_8\text{Mn}^{\text{III}}_8-16} \}$,⁸²⁸ $\text{Mn}^{\text{II}}_6\text{Mn}^{\text{III}}_6 \{ 24\text{-MC}_{\text{Mn}^{\text{II}}_6\text{Mn}^{\text{III}}_6-12} \}$,^{777,880,956} and $\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_{18}\text{Mn}^{\text{IV}}_2 \{ 32\text{-MC}_{\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_{18}\text{Mn}^{\text{IV}}_2-16} \}$ ⁹⁰¹ represent manganese molecular wheels that behave as SMMs. In addition, the complex $\text{Ni}_{12} \{ 24\text{-MC}_{\text{Ni}^{\text{II}}_{12}-12} \}$ represents a molecular wheel that behaves as a SMM (Figure 120).^{886,887,957} Recently, a Co^{II}_7 complex $\{ \text{Co}^{\text{II}}[12\text{-MC}_{\text{Co}^{\text{II}}_7-6}] \}$ has been identified as a single-molecule magnet.⁹⁵⁸ A very interesting fusion between molecular wheels and metallacrowns has been described by Saalfrank.^{776,959} One can see conversion of the ferric corannulene to ferric wheels. They represent an interesting path to making heteronuclear assemblies. In addition, the molecular stars have recently been shown to behave as SMMs.^{959b}

Just like the first identified SMM, many years passed between synthesis and recognition of SMM behavior for the first 12-MC-4. The $\text{Mn}^{\text{II}}(\text{O}_2\text{CCH}_3)_2[12\text{-MC}_{\text{Mn}^{\text{II}}\text{N}(\text{shi})-4}]$ complex possesses a frequency-dependent ac magnetic suscep-

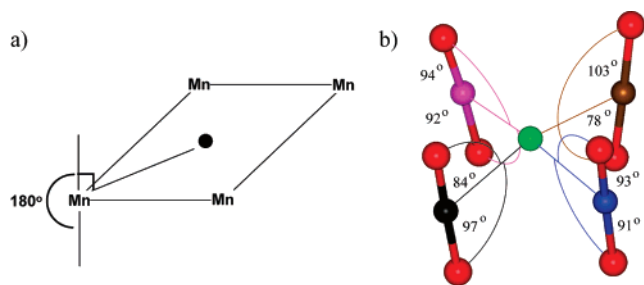


Figure 141. (a) Schematic of an ideal Mn^{III}_4 plane in $\text{Mn}^{\text{II}}[12\text{-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})}\text{-4}]$. The individual D parameters of each Mn^{III} ion are directed along the Jahn–Teller axis of the ion, which is perpendicular to the plane of the four Mn^{III} ions. The black dot in the middle of the square represents the center of the plane. (b) Measured $\text{O}_{\text{Jahn-Teller}}\text{-Mn}^{\text{III}}\text{-center}$ angles of $\text{Mn}^{\text{II}}[12\text{-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})}\text{-4}]$ in relation to the center of the plane. Color scheme: red sphere, oxygen atoms; green sphere, estimated center; black, blue, magenta, and brown spheres, ring Mn^{III} ions.

tibility signal in both the solid state and a frozen N,N -dimethylformamide solution.⁹⁶⁰ The energy barrier to magnetization relaxation (U_{eff}) is 21.1 K. Moreover, the complex displays hysteresis below 1 K with the width of the hysteresis loop increasing with increasing magnetic field sweep rates; the widening of the hysteresis loop indicates that the slow relaxation of the magnetization is due to SMM behavior and not magnetic ordering. The $\text{Mn}^{\text{II}}(\text{O}_2\text{CCH}_3)_2\text{-}[12\text{-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})}\text{-4}]$ complex is a planar square of four MC ring Mn^{III} ions with a Mn^{II} ion encapsulated within the central cavity. The complex provides an opportunity to directly control the molecular magnetoanisotropy, D , of a SMM. Most SMM complexes approach spherical symmetry; thus, the individual D components of each ion tend to cancel one another. However, in the 12-MC-4 topology, the salicylhydroxamic acid (H_2shi) ligand enforces a planar arrangement among the Mn^{III} ions of the metallacrown ring. Therefore, each individual D component of each Mn^{III} can be combined to create a large molecular D parameter (Figure 141). Examination of the exchange coupling within the complex reveals that the four ring Mn^{III} ions are antiferromagnetically coupled to each other ($J = -6.0 \text{ cm}^{-1}$) and that the Mn^{III} ions are antiferromagnetically coupled to the central Mn^{II} ($J = -4.2 \text{ cm}^{-1}$). The overall ground spin state of the molecule is only $S = 1/2$; however, the large amount of molecular magnetoanisotropy due to each Mn^{III} ion ($D = -3.0 \text{ cm}^{-1}$) allows the MC to behave as a SMM. The central Mn^{II} is of paramount importance to the SMM behavior because the $\{\text{Li}(\text{Cl})_2[12\text{-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})}\text{-4}]\}^+$ analogue does not behave as an SMM. The $\text{Mn}^{\text{II}}(\text{O}_2\text{CCH}_3)_2[12\text{-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})}\text{-4}]$ complex is a rare example of a method to directly control the molecular D parameter. Most efforts in the field of SMMs are directed toward increasing the ground spin state. The $\text{Mn}^{\text{II}}[12\text{-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})}\text{-4}]$ complex instead strives to increase deliberately the amount of molecular magnetoanisotropy by controlling the topology of the complex through alignment of single ion magnetoanisotropy.

Planar $15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}\text{-5}$ complexes are capable of binding a multitude of Ln^{III} ions within the central cavity. This capability now allows for the investigation of lanthanide-based SMMs. Although not the first SMMs to combine lanthanide ions and transition metals,⁹⁵⁰ $\text{Ln}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}\text{-5}]$ complexes create the opportunity to perturb only one variable with the structure; thus, the SMM properties can be investigated within a ligand framework. Furthermore, the $\text{Ln}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}\text{-5}]$ complex can be

crystallized in two different polymorphs: dimer units and helical chains. Thus, not only can the effect of the central Ln^{III} be investigated but also the effect of the metallacrown solid state arrangement. $\text{Ho}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}\text{-5}]$ and $\text{Dy}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}\text{-5}]$ were investigated for potential SMM behavior^{465b} because previous Ho^{III} and Dy^{III} $[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{picHA})}\text{-5}]$ complexes possessed high magnetic moments.⁴⁶² In the solid state, the Ho^{III} and Dy^{III} $[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}\text{-5}]$ complexes in either polymorph displayed a frequency-dependent ac magnetic susceptibility signal, a hallmark of SMMs. However, the solid state behavior could also be caused by magnetic ordering, glassy behavior, or a combination of both effects. In addition, the observable blocking temperatures (below 4.5 K for Dy^{III} complexes and 6 K for Ho^{III} complexes) were independent of polymorph type. This indicates that the polymorph type had no effect on the magnetic properties. To clarify the solid state observations, the complexes were dissolved in methanol. This process also eliminates the polymorph differences. Only the frozen solution of the $\text{Dy}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}\text{-5}]$ complex retained the frequency-dependent magnetic behavior. Therefore, only the $\text{Dy}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}\text{-5}]$ can be considered a SMM. In addition, because the polymorph type had little bearing on the magnetic properties, the one-dimensional helical chain of MCs can be considered a chain of SMMs. The $\text{Ln}^{\text{III}}[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}\text{-5}]$ system provides an excellent model to study central ion effects and polymorph effects on magnetic properties. Future work will likely focus on the effect of other Ln^{III} ions within the $[15\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S-pheHA})}\text{-5}]$ ligand framework.

The first metallacrown structural type with more than one atom bridges to behave as a SMM was a set of manganese metallacryptate structures: $[\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_{22}(\text{pdol})_{12}(\mu_3\text{-OCH}_3)_{12}(\mu_3\text{-O})_6(\mu_4\text{-O})_{10}(\text{N}_3)_6]$, Mn_{26}N_3 , and $[\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_{22}(\text{pdol})_{12}(\mu_3\text{-OCH}_3)_{12}(\mu_3\text{-O})_6(\mu_4\text{-O})_{10}(\text{OH})_2(\text{H}_2\text{O})(\text{OCH}_3)_3]\cdot\text{ClO}_4$, $\text{Mn}_{26}\cdot\text{ClO}_4$.^{58,905} The overall topologies of both complexes are very similar. The metallacryptand structure can be considered a three-dimensional structure consisting of six strands with repeat units of $[\text{O}-\text{C}-\text{O}-\text{Mn}^{\text{III}}-\text{O}-\text{C}-\text{O}]$, which are connected by four Mn^{II} ions. The resulting adamantoid structure creates a [4]-metallacryptand. The metallacryptand encapsulates a $\{\text{Mn}_{16}(\text{O}^{2-})_{12}(\text{MeO}^-)_{16}\}$ core. In the solid state, both structures possess a frequency-dependent ac magnetic susceptibility signal. In addition, a frozen solution of the $\text{Mn}_{26}\text{ClO}_4$ complex dissolved in dimethyl sulfoxide also possesses a frequency-dependent ac magnetic susceptibility signal; thus, the $\text{Mn}_{26}\text{ClO}_4$ complex is a SMM.⁹⁰⁵ The Mn_{26}N_3 complex is insoluble in most common solvents; thus, no frozen solution experiments could be conducted. However, due to the similarity of the two complexes, it can be safely proposed that the Mn_{26}N_3 complex is a SMM. In the solid state, the $\text{Mn}_{26}\text{ClO}_4$ complex has higher energy barrier to magnetization relaxation (U_{eff}) than the Mn_{26}N_3 complex, $U_{\text{eff}} = 36.2 \pm 2.0 \text{ K}$ for $\text{Mn}_{26}\text{ClO}_4$ and $U_{\text{eff}} = 16.5 \pm 0.7 \text{ K}$ for Mn_{26}N_3 . On the surface these values are intuitive. The Mn_{26}N_3 molecule has T symmetry due to the peripheral azide anions. In the $\text{Mn}_{26}\text{ClO}_4$ molecule, the azide anions are replaced with a mixture of hydroxide ions, a water molecule, and methoxide anions; thus, the symmetry is lower in the $\text{Mn}_{26}\text{ClO}_4$ molecule. The Mn_{26}N_3 molecule has a greater degree of symmetry, so it should have a lower amount of molecular magnetoanisotropy and a smaller U_{eff} because $U_{\text{eff}} = S^2|D|$. The $\text{Mn}_{26}\text{ClO}_4$ should have the higher U_{eff} value because the molecule is less symmetrical and possesses a

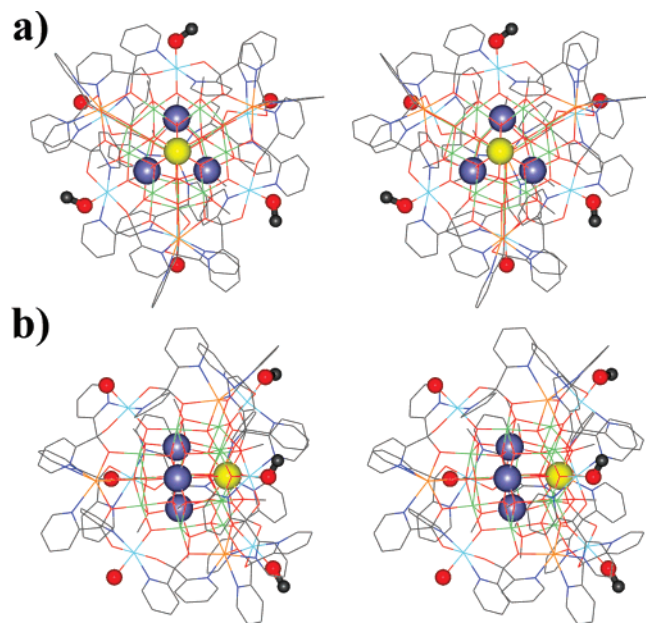


Figure 142. Stereoviews of $\text{Mn}_{26}\text{ClO}_4$ indicating how the peripheral anions affect the Mn^{III}_4 core: (a) view down the pseudo- C_3 axis; (b) side-on view. Note that one of the Mn^{III} ions is unique compared to the other three. One Mn^{III} ion (yellow) is directed toward the methoxide ligands, whereas the other three are directed toward the water/hydroxide anions. Color scheme: yellow and blue spheres, Mn^{III} ; gray spheres, carbon; red sphere, oxygen. Hydrogen atoms, perchlorate anion, and lattice solvent removed for clarity. Reprinted with permission from ref 905. Copyright 2005 American Chemical Society.

higher molecular D value. The ground spin state was presumed to be the same for both molecules since only the peripheral anions have been perturbed. Thus, the change in U_{eff} is due to only a change in symmetry. However, analysis of the in-phase ac magnetic susceptibility data reveals that $S = 4$ or 5 for Mn_{26}N_3 and $S = 7$ for $\text{Mn}_{26}\text{ClO}_4$. A closer inspection of the Mn^{III}_4 inner core of the metallacryptate reveals the discrepancy of the ground spin states. In the Mn_{26}N_3 complex, the Mn^{III}_4 core has T_d symmetry. If all of the metal centers are antiferromagnetically coupled, the ground spin state of the core is $S = 0$. In the $\text{Mn}_{26}\text{ClO}_4$ molecule, the Mn^{III}_4 core only has C_{3v} symmetry. The change in the peripheral anions causes a structural change that is perpetuated to the inner core of the molecule! One of the Mn^{III} ions of the core is unique compared to the other three Mn^{III} ions, with differing bond distances and bond angles (Figure 142). This structural perturbation of the core causes a change in the coupling strength between the Mn^{III} ions. The result is a core with an $S = 2$ or $S = 3$ ground spin state. Therefore, the change in the core magnetic coupling accounts for the discrepancy between the ground spin states of the two molecules. Consequently, the larger U_{eff} for the $\text{Mn}_{26}\text{ClO}_4$ molecule is due to not only an increase in the D parameter but also an increase in the S parameter. These two complexes illustrate an excellent example of how simple changes of the peripheral structure of a molecule can cause gross changes in the magnetic properties.

Although not traditional metallacrowns, the $\text{Ln}^{\text{III}}_6\text{Mn}^{\text{III}}_4\text{Mn}^{\text{IV}}_2(\text{H}_2\text{shi})_4(\text{Hshi})_2(\text{shi})_{10}(\text{CH}_3\text{OH})_{10}(\text{H}_2\text{O})_2$ ($\text{Ln}^{\text{III}} = \text{Tb}^{\text{III}}$, Dy^{III} , and Gd^{III}) complexes contain remnants of traditional metallacrowns. The complexes are made with the familiar metallacrown ligand salicylhydroxamic acid (H_3shi) and have a repeat unit of $[\text{Mn}^{\text{IV}}-\text{O}-\text{N}-\text{Mn}^{\text{III}}-\text{N}-\text{O}-\text{Mn}^{\text{III}}-\text{N}-\text{O}-\text{Ln}^{\text{III}}-\text{O}-\text{Ln}^{\text{III}}-\text{O}-\text{N}]_2$, a 28-MC-10 ring (Figure 143).⁹⁶¹

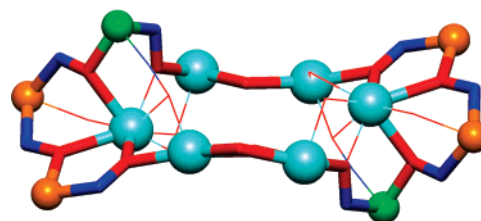


Figure 143. 28-MC-10 ring of $\text{Ln}^{\text{III}}_6\text{Mn}^{\text{III}}_4\text{Mn}^{\text{IV}}_2$. Color scheme: aqua sphere, Dy^{III} ; orange sphere, Mn^{III} ; green sphere, Mn^{IV} ; red tube, oxygen; blue tube, nitrogen.⁹⁶¹

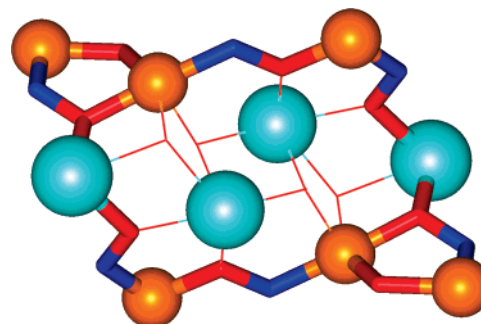


Figure 144. 22-MC-8 ring of $\text{Ln}^{\text{III}}_4\text{Mn}^{\text{III}}_6$. Color scheme: aqua sphere, Ho^{III} ; orange sphere, Mn^{III} ; red tube, oxygen; blue tube, nitrogen.⁹⁶²

The three manganese ions of the repeat unit are bound by the ligands in a fashion comparable with, but not identical to, that of $\text{Mn}^{\text{II}}(\text{O}_2\text{CCH}_3)_2[12\text{-MC}_{\text{Mn}^{\text{III}}\text{N}(\text{shi})-4}]$. Additionally, the metallacrown-type ring captures two Ln^{III} ions. The Dy^{III} analogue possesses a frequency-dependent ac magnetic susceptibility signal in the solid state below 4 K, whereas the Tb^{III} and Gd^{III} do not exhibit a frequency-dependent behavior above 1.8 K. Furthermore, the Dy^{III} analogue is highly magnetoanisotropic as evident from nesting behavior in isothermally variable-field magnetization studies. Because only one of the three molecules possesses SMM behavior, the manganese ions alone cannot be the source of the observed magnetic behavior. The interaction of the anisotropic Dy^{III} ions with the manganese ions is crucial. However, the identity of the Ln^{III} ion is vital as not any anisotropic Ln^{III} will lead to SMM behavior, i.e., Tb^{III} . The Dy^{III} analogue is the first SMM to contain both lanthanide ions and manganese ions and only the second SMM to contain transition metal ions mixed with lanthanide metal ions.⁹⁵⁰ Thus, the metallacrown analogy provided an opportunity to create large mixed d-f metal complexes that behaved as SMMs.

The related complexes, $\text{Ln}^{\text{III}}_4\text{Mn}^{\text{III}}_6(\text{H}_2\text{shi})_2(\text{shi})_6(\text{sal})_2(\text{O}_2\text{-CCH}_3)_4(\text{OH})_2(\text{CH}_3\text{OH})_8$, where H_2sal is salicylic acid, are daughter compounds of the $\text{Ln}^{\text{III}}_6\text{Mn}^{\text{III}}_4\text{Mn}^{\text{IV}}_2(\text{H}_2\text{shi})_4(\text{Hshi})_2(\text{shi})_{10}(\text{CH}_3\text{OH})_{10}(\text{H}_2\text{O})_2$ complexes.⁹⁶² Again, these metallacrown-like molecules are based on the salicylhydroxamic acid ligand (some of the H_3shi hydrolyzed to salicylate during the synthesis). The molecules do not have the traditional metallacrown repeat unit, but instead possess a repeat unit of $[\text{Mn}^{\text{III}}-\text{N}-\text{O}-\text{Ln}^{\text{III}}-\text{O}-\text{N}-\text{Mn}^{\text{III}}-\text{O}-\text{Mn}^{\text{III}}-\text{N}-\text{O}]_2$, a 22-MC-8 ring (Figure 144). In addition, the metallacrown ring encapsulates two Ln^{III} ions. For the Dy^{III} and Ho^{III} analogues, both molecules possess a frequency-dependent ac magnetic susceptibility signal in the solid state. However, when frozen N,N -dimethylformamide solutions of both complexes were investigated, only the Dy^{III} analogue retained the frequency-dependent magnetic behavior. Thus, only the

Dy^{III}₄Mn^{III}₆ analogue can be considered a SMM. Like the parent complexes, the manganese ions alone are not creating the SMM behavior; the identity of the anisotropic Ln^{III} is crucial. In addition to confirming the solid state observations, the frozen solution measurements provided insight into possible magnetic interactions in the solid state. In the Ho^{III} analogue, magnetic ordering or glassy behavior may be causing the frequency-dependent magnetic behavior. The packing of the molecules is compact within the solid state as the metal centers on neighboring molecules closely approach one another. Along the *b*-axis, a Ho^{III} ion of one molecule is only 5.52 Å from a Ho^{III} of a neighboring molecule. Along the *a*-axis, two Mn^{III} ions of different molecules are separated by 7.83 Å. In addition, a water molecule serves as a hydrogen-bond bridge between methanol molecules that are coordinated to Mn^{III} ions on separate molecules. When the Ho^{III} analogue is placed in frozen solution, these intramolecular interactions are removed; thus, the frequency-dependent magnetic behavior is not observed. For the Dy^{III} analogue in frozen solution, the frequency-dependent magnetic behavior is actually enhanced. A blocking temperature is observed and U_{eff} can be estimated as 16 K. In the solid state, the magnetic ordering and/or glassy behavior may be suppressing the SMM behavior of the Dy^{III} analogue. When placed in frozen solution, the true SMM behavior can be revealed because the mechanisms by which the magnetic ordering and glassy behavior operate have been removed.

The metallacrown family of complexes is a viable route to developing new types of SMMs. Along with molecular wheel complexes, the traditional metallacrown types possess SMM properties. The 12-MC_{Mn^{III}N^(sh)}-4 scaffold provides a rare opportunity to control the magnetoanisotropy within a molecule; the 15-MC_{Cu^{II}N^(S-pheHA)}-5 complexes provide a structural framework in which the central Ln^{III} ion can be varied and the properties of the molecule can be perturbed; the Mn₂₆ metallacryptate structures display a wonderful example of how simple changes in anions can greatly affect the ground spin state of a molecule; and the Ln^{III}₆Mn^{III}₄Mn^{IV}₂ and the Ln^{III}₄Mn^{III}₆ complexes are examples of large transition metal–lanthanide molecules behaving as SMMs.

5. Conclusion

Metallacrown chemistry has grown from the initially identified 9-MC_{V^N(sh)}-3 to include a vast array of metal-lamacrocycles. The initial 9-MC-3 was scrutinized and believed to be a chance of luck. However, the $-\text{[M-N-O]}-$ repeat unit has proven to be quite general in inorganic chemistry. Now the connectivity has grown to include a great variety of bridges including but not limited to $-\text{[N-N]}-$, $-\text{[O-P]}-$, $-\text{[N-C-O]}-$, $-\text{[N-C-N]}-$, $-\text{[O-C-O]}-$, and $-\text{[X]}-$ (where X is a nonmetal). After the initial thrust to synthesize many types of structural types, the latest chemistry has focused on using these unique molecules for some type of application ranging from MRI contrast agents, to single molecule magnets, to building blocks of one-, two-, and three-dimensional solids. Metallacrown chemistry obviously has much potential for growth, and we look forward to these new discoveries.

6. References

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