

Formation of Chiral Solids via a Molecular Building Block Approach

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The application of principals of molecular recognition to the design of organic and inorganic solids is leading to remarkable progress in the preparation of porous and chiral materials. A new area of supramolecular complexes is metallamacrocycles, large molecules that are sewn together using metal linkages. Metallacrowns are a member of this class of inorganic complexes. In this article we develop a strategy for the preparation of solids that are chiral using metallacrowns as the centerpiece. First, we introduce the available structure types for these molecules and then proceed to describe some of the physical properties associated with this unique molecular assembly. We demonstrate that chirality can be incorporated simply and inexpensively into these molecules and then we show how the metallacrowns can be used as building blocks to make layered solids with chiral channels. Finally, we assess more general strategies that could be used to engineer truly porous and chiral materials with high metal densities. © 2000 Academic Press

INTRODUCTION

The controllable preparation of porous, metal organic solids using a small molecule building block approach is a desirable objective for modern synthetic inorganic chemists. The interest in these materials stems from applications of the solids ranging from sensors to catalysts, either through framework recognition or through incorporation of reactive guests. Examples now exist of three dimensional porous lattices that can withstand desolvation/guest removal (1). These solids are constructed from simple precursors in high yields. Concurrently, a supramolecular modular synthon approach to forming metal organic solids has been undertaken by many groups (2). As a result, chiral, acentric networks have been prepared recently (3). The preparation of noncentrosymmetric solids is desirable since nonlinear optical and ferro- and piezoelectric effects are technologically important (4). Furthermore, such lattices could provide selectivity in separation science, for example in resolution of diastereomeric pharmaceuticals. Unfortunately, it is generally difficult to incorporate chirality into an

extended solid. In some cases, stereogenic centers are incorporated either in a random manner or form racemic networks (5). Alternatively, chiral solids may resolve into two crystal habits that must be manually separated in order to realize the desired chiral material (6). Thus, the search for new chiral synthons that can be weaved into 2D or 3D frameworks to generate controllably and predictively well defined chiral solids is an important objective of solid state chemistry. In this article, we will present strategies that exploit the chemistry of metallacrowns to prepare sought-after chiral, porous materials.

WHAT ARE METALLACROWNS?

Over the past decade, inorganic chemists have applied the strategies developed since the 1960s by organic chemists to realize new molecular architectures that directly incorporate metals into a macrocyclic framework. An excellent example of this approach is the development of metallacrowns, metallamacrocycles that topologically resemble crown ethers (7). As shown in Fig. 1, both crowns and metallacrowns form macrocycles that allow oxygen atoms to sequester a metal into a preformed cavity. The metallacrown replaces the ethylene units with a nitrogen atom and a metal ion (in either the +2, the +3, or the +5 oxidation levels). Despite the clear differences in bond lengths between M–N (2.0 Å) and M–O (1.9 Å) liganding versus C–C (1.5 Å) and C–O (1.4 Å) bonds, the cavity radii of metallacrowns are nearly identical to those of crown ethers. Thus, metallacrowns are capable of the same size selectivity for central metal encapsulation as their organic precursors (8). In addition, the metallacrowns are better ligands for highly charged, hard cations than simple crown ethers because the ring oxygen atoms are bound to nitrogen and a metal rather than to carbon. This leaves residual charge on the oxygen that allows metallacrowns to bind transition ions (Mn(II), Mn(III), Fe(II), Fe(III), Cu(II), Ni(II), Y(III)), lanthanides (La(III), Nd(III), Eu(III), Gd(III), Dy(III), Ho(III), Tb(III)), and actinides (U(VI)), as well as alkali and alkaline earth cations (Li(I), Na(I), K(I), Mg(II), Ca(II), and Sr(II)). Differential anion binding has also been demonstrated by

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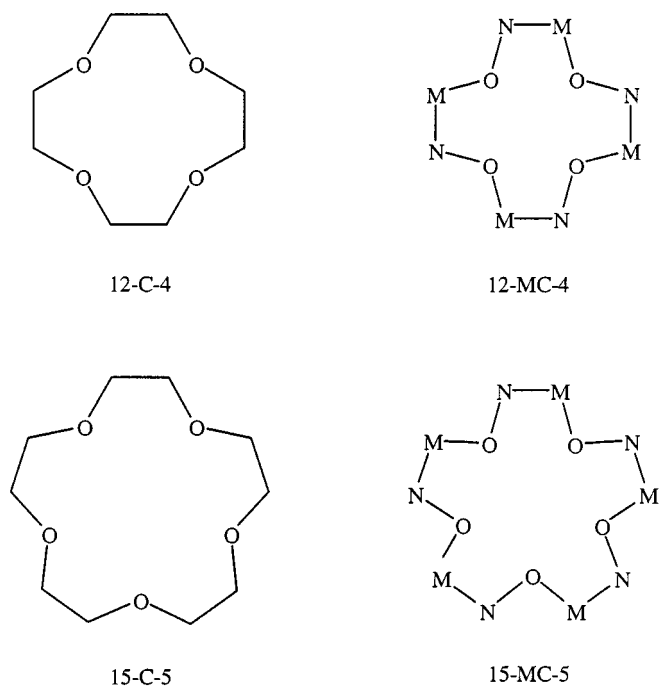


FIG. 1. The analogy between crown ethers and metallacrowns.

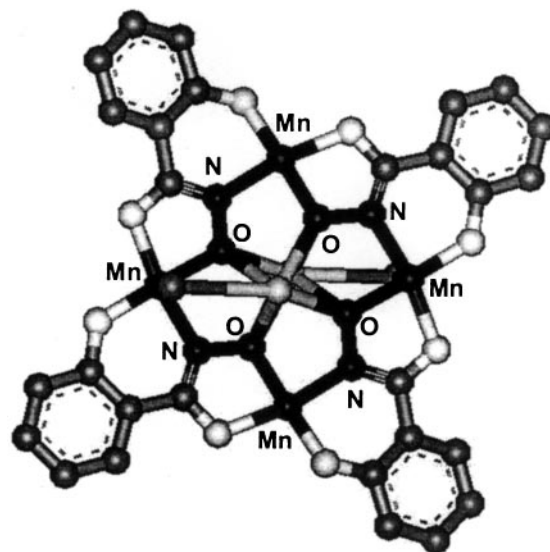


FIG. 2. Ball and stick diagrams of $(\text{NaBr})_2[12\text{-MC}_{\text{Mn(III)N}(\text{shi})-4}]$.

metallacrowns. Halides, pseudohalides (e.g., NCS^-), nitrate, carboxylates, sulfates, and even perchlorate can bind to metallacrowns. Often, the anion forms a bridge between the encapsulated metal and a ring metal, a recognition mode that would be unavailable for a simple metal-crown ether complex. Thus, metallacrowns can mimic the features of established molecular recognition agents and, in the case of anions, generate a new approach to anion-selective molecules (9).

Polynuclear metal complexes solely containing bridging hydroxylamine are unstable; therefore, metallacrowns are prepared using organic ligands usually possessing hydroxamate or oxime functionalities (although other ligand possibilities such as amidoximes have been reported). The reaction of MnBr_2 , NaBr , Na trifluoroacetate (NaTFA), and salicylhydroxamic acid (H_3shi) in DMF yields the 12-MC-4 complex in Fig. 2 (8). A weak base such as NaTFA accepts the three protons released from H_3shi as it binds to two Mn(III) ions. The recovered $(\text{NaBr})_2[12\text{-MC}_{\text{Mn(III)N}(\text{shi})-4}]$ is obtained in a one-step synthesis in 80% yield as a crystalline complex. The 12-membered macrocyclic ring is generated by linking four salicylhydroximate ligands with Mn(III) giving a Mn(III)-N-O repeat around the cycle. The two Na(I) ions are bound above and below the metallacrown plane to the four oximate oxygen atoms of the macrocyclic ring. Bromide ions bridge the Na(I) and the Mn(III) on top and bottom. The metallacrown is charge neutral because each Mn(III) compensates the negative charge of a salicylhydroximate trianion. Isostructural metallacrowns

which replace the 2 NaBr have been isolated as Li^+ , LiCl_2^- , 2 NaCl , 2 KCl , 2 KBr , 2 K(NCS) , 2 Na(NCS) , Mg(II)(acetate)_2 , Mn(II)(acetate)_2 , and Pb(II)(acetate)_2 complexes. The 12-MC-4 structures have also been prepared with Fe(III) , Cu(II) , Ni(II) , and Ga(III) as the ring metal and it is likely that other di- and trivalent metals can be substituted at this position. Many ligand types, as shown in Fig. 3, will support the 12-MC-4 structure type. The unifying feature of all these ligands is that they contain fused 5- and 6-membered chelate rings. If the metallacrown templating ligand has fused 5-membered rings, one accesses the planar 15-MC-5 structure

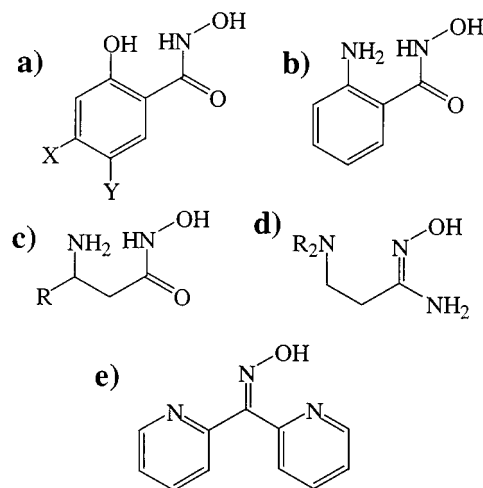


FIG. 3. Examples of 12-metallacrown-4 inducing ligands. (a) Salicylhydroxamic acids $\{X = Y = \text{H}, \text{H}_3\text{shi}\}$; (b) anthranilhydroxamic acid $\{\text{H}_2\text{anha}\}$; (c) β -aminohydroxamic acids $\{R = \text{phenyl}, \beta\text{-pheHA}\}$; (d) β -aminoamidoximes $\{R = \text{ethyl}, \beta\text{-(Et}_2\text{N)-amidox}\}$; (e) 2,2'-dipyridyl-ketonoxime $\{\text{Hpk}\}$.

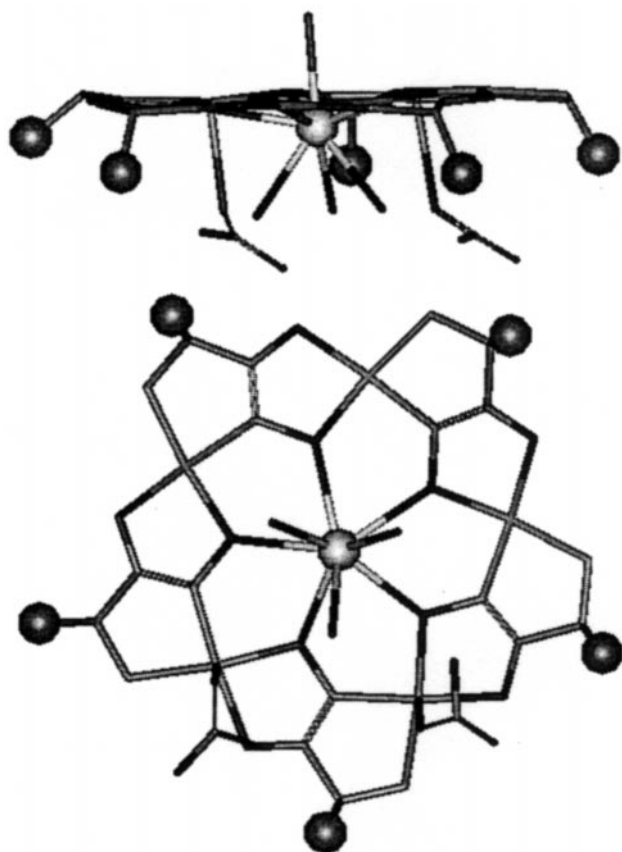


FIG. 4. Stick diagram of $\text{Nd(III)(NO}_3\text{)}[\text{15-MC}_{\text{Cu(II)N(t-alaha)-5}]^{2+}$ (top) View perpendicular to the face of the metallacrown with Nd (light sphere) emphasized. (bottom) Side view showing orientation of all peripheral methyl groups (gray spheres) on the same face.

type shown in Fig. 4 (10). The pentagonal oxygen orientation is suitable for chelating higher coordination number cations. As a consequence, Ca(II), Sr(II), and Y(III), nearly all trivalent lanthanides, and uranyl (UO_2^{2+}) ion can be accommodated by this metallamacrocycle. These examples illustrate that the size and metal composition of the isolated metallacrown is intimately dependent on the choice of organic ligand.

Metallacrowns can form chiral complexes either through the organic ligand structure or by the rotational sense of the metals in the system. Because of the cyclic $[\text{M-N-O}]_n$ orientation, clockwise (C) or anticlockwise (A) rotational isomers are possible if one differentiates one face of the metallacrown from the other. This can be realized by cation or anion binding, dimerization, or ligand functionality. The corollary of this is also true. That is, because of this rotational sense, a resolved chiral ligand must always be inserted in the same orientation generating a face differentiate metallacrown. This concept is illustrated in Fig. 4 for the 15-MC-5 structure types that are composed of α -amino hydroxamic acids. In this case, each of the methyl groups of L-alanine

hydroximate are oriented onto one face. Thus, one can prepare an amphiphilic metallacrown containing five resolved chiral centers in a one-step, bench-top synthesis that provides gram quantities of material. This approach can be extended to the 12-MC-4 structures by employing β -amino hydroxamic acids (11). In this case, the six-membered chelate ring provides more flexibility than is available for the α -aminohydroximates, which allows functional groups (e.g., phenyl) to radiate from the metallacrown ring away from either face. For this example, the 12-MC-4 structure type is amazingly similar in size and shape to Cu(II) tetraphenylporphyrin. Extending this analogy, 15-MC-5 complexes are related to the expanded porphyrins such as texaphyrins or sapphyrins; however, unlike these well known macrocycles, resolved chiral centers can be engineered into the structures of both 12-MC-4 and 15-MC-5 with relative ease. It should be emphasized that metallacrowns are prepared as resolved complexes and cannot racemize.

THE PROPERTIES OF METALLACROWNS

Because of their unique structure, metallacrowns may have applications as diverse as chemical sensing to catalysis. Due to the broad structural and compositional variability of metallacrowns, an exhaustive compilation of the physical properties is inappropriate for the present treatment; however, we will try to highlight a few aspects of this chemistry that are particularly interesting. The immediately obvious feature of metallacrowns is the very high metal density at the core. Molecules such as 12-MC-4 can restrict the nuclei of five metals ions to within a surface area of 20 \AA^2 while the 15-MC-5 species place six metals within 36 \AA^2 (12). Molecules of corresponding size and shape, such as porphyrins or phthalocyanines, have a much smaller core metal density. Thus, whether one is interested in sensor applications or catalysis, there are available multiple Lewis acid centers in close proximity to bind potential analytes or substrates. Another obvious consequence of the close metal proximity is magnetic exchange. For example, it is well known that coordination complexes containing Cu(II) and Gd(III) show ferromagnetic exchange interactions (13). Thus, it is not surprising that the $\text{Gd(III)}[\text{15-MC}_{\text{Cu(II)N-5}]^{3+}$ has an $S = 4$ ground state (14). Other metallacrowns containing Mn(II) and Mn(III) or Ni(II) have also exhibited ferromagnetic exchange (7, 15). We are presently evaluating whether molecules such as these that are linked through bridging anions will display ferrimagnetic behavior. As already discussed, chirality can be designed into metallacrowns. The resulting molecules display circular dichroism spectra demonstrating that the $d-d$ bands of copper are influenced by the organic stereocenters (10, 11) These metallacrowns show temperature-dependent changes in optical rotation and several are thermochromic. Clearly, the unique bond connectivities exhibited by the metallacrowns lead to numerous interesting

physical properties that can be engineered into the solid state.

In order to apply a building block approach for the synthesis of metal–organic solids, one must be sure that the proposed modular synthons retain their integrity in solution prior to forming the desired structure. Kurzak *et al.* have shown that Cu(II) will react with β -alanine hydroxamic acid to form thermodynamically stable 12-MC-4 complexes in aqueous solution (16). The metallacrown is completely formed by pH 6.0 and is stable in mildly basic aqueous solution (pH 10). While the stability constants for metallacrown formation have not been determined in nonaqueous systems, it is quite clear that these molecules are very stable in solvents ranging from methanol to acetonitrile and even to hexane (when long-chain alkyls are appended to the complex). A series of isotope labeling studies have demonstrated that the metallacrowns retain their composition in organic and aqueous solvents. For example if $\text{Cu(II)[12-MC}_{\text{Cu(II)N}(\text{shi})\text{-4}]^{2-}}$ and the phenyl ring deuterated analog $\text{Cu(II)[12-MC}_{\text{Cu(II)N}(\text{d}_2\text{-shi})\text{-4}]^{2-}}$ are mixed in methanol or acetonitrile and then recovered as solids as long as 2 days later, there is no evidence for the scrambling of the deuterium label (17). Had the samples dissociated in solution and then reassembled upon precipitation one would have seen a broad mass spectral envelope representative of the statistical mixture of ligands. A statistical distribution is seen, however, if one initially synthesizes the $\text{Cu(II)[12-MC}_{\text{Cu(II)N}\text{-4}]^{2-}}$ with a mixture of H_3shi and $\text{H}_3\text{d}_2\text{-shi}$. We have also shown by the same approach, using $(\text{NaBr})_2[\text{12-MC}_{\text{Mn(III)N}(\text{shi})\text{-4}]$ and $(\text{KBr})_2[\text{12-MC}_{\text{Mn(III)N}(\text{shi})\text{-4}]$, that the metallacrowns do not fall apart upon substitution of the central alkali cation or the halide with Li(I) or Cl^- , respectively (10). Furthermore, one can remove the potassium with a crown ether and then bind Na(I) or Li(I) without decomposition of the metallacrown. One can use $^1\text{H NMR}$ to evaluate solution integrity of diamagnetic and certain paramagnetic metallacrowns. Such studies have allowed us to measure exchange rates for metallacrown ligands. In all but two or three cases, the metallacrowns do not interconvert or exchange ligands on time scales less than several days. In conclusion, with all metallacrowns so far studied under a wide variety of solvent conditions, there has been little or no evidence for complex dissociation or decomposition when dissolved. Therefore, it is reasonable to expect that the structure of the metallacrown used as a modular synthon will be retained during the assembly of the metal–organic solid.

A BUILDING BLOCK STRATEGY

Successful application of a molecular building block strategy that controllably generates ordered structures requires the development of systematic plans to connect the metallamacrocyles. One can envision four approaches that

can be used individually or in conjunction to link metallacrowns in the solid state: (a) using metals, hydrogen bonds or covalent linkages to span between functionality appended to the hydroxamate ligands; (b) using neutral or anionic ligands that can bridge from metals of one metallacrown to another; (c) using the peripheral heteroatoms that bind to the metals forming the metallacrown rings to fuse two metallacrowns with an external metal unit; or (d) making chains through direct coordination between a heteroatom of one metallacrown and a metal of another metallacrown. Examples of each of these possibilities are given in Fig. 5.

There now are many examples of joining metallacrowns in a face-to-face or zig-zag chain orientation through anionic bridges. An interesting case of a face-to-face structure is illustrated with the $\text{Cu(II)[12-MC}_{\text{Cu(II)N}(\beta\text{-alaHA})\text{-4}]^{2+}}$ reported by Kurzak *et al.* (shown as Fig. 6) which shows both metallacrown dimerization and anion bridging interactions

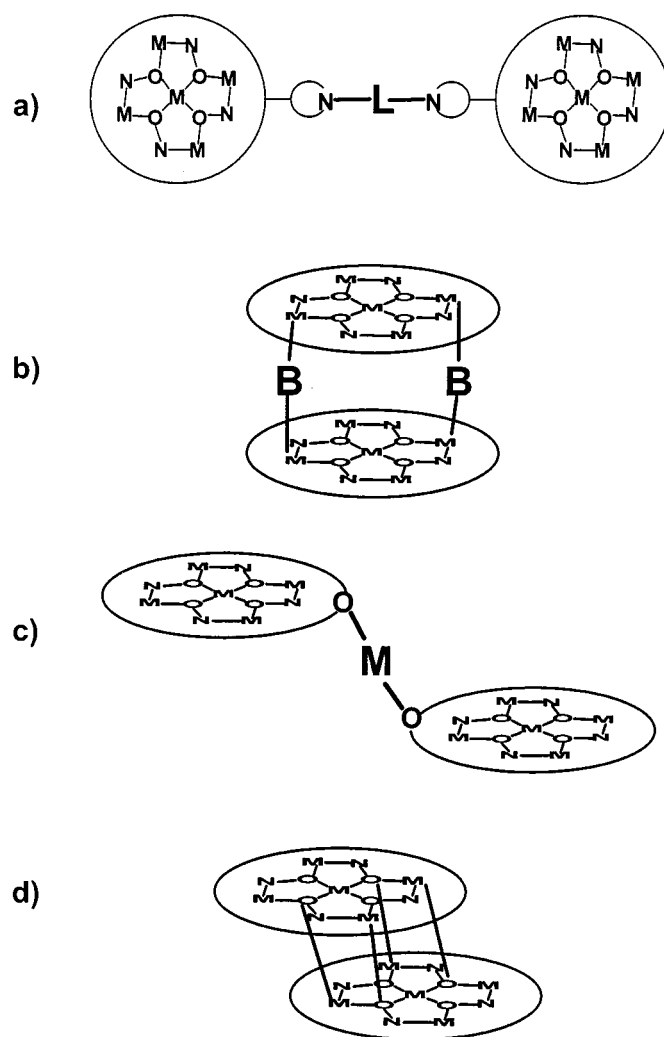


FIG. 5. Different motifs for linking metallacrowns into extended structures: (a) through the ligand periphery; (b) through bridging anions; (c) through bridging metals; (d) through direct facial interactions.

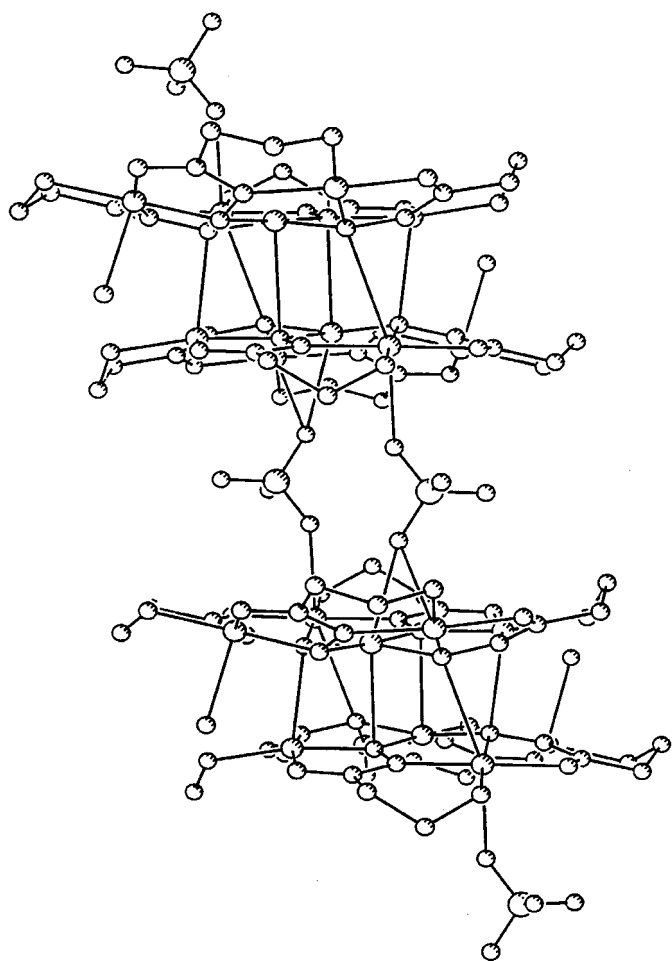


FIG. 6. A portion of the chain structure found in $\text{Cu(II)(ClO}_4\text{)}_2[12\text{-MC}_{\text{Cu(II)N}(\beta\text{-alaHA)-4}]$. In this view, two metallacrowns that have dimerized in a face-to-face orientation are linked by perchlorate anions.

(16). The metallacrowns are fused through six Cu–O bonds across the two faces to form a dimer with a face–face separation of 2.7 Å. This metallacrown dimer is then linked in a face-to-face orientation through perchlorate bridges to form an extended columnar network with the metallacrown ring planes separated by 7.2 Å through the perchlorate bridges. If a shorter plane-to-plane distance is desired, single atom bridges such as chlorides can be utilized. In a $\text{Cu(II)Cl}_2[12\text{-MC-4}]$ linked system, one should be able to obtain metallacrown ring separations as small as 5 Å. Longer separations should be realized through rigid anions such as terephthalates or even flexible linkers such as adipate. We have shown that dicarboxylate ligands can induce the formation of helices of metallacrowns using chiral $\text{Ln(III)[15-MC}_{\text{Cu(II)N}(\text{S-pheHA)-5}]^{3+}}$. An example of such an extended structure is given as Fig. 7. In this case, the hydrophilic faces of two adjacent metallacrowns are linked by the dicarboxylate ligand. Weak Van der Waal forces hold the hydrophobic faces of the structure in place, leading to

a helical column with alternating metallacrown separations of 9.4 Å (across the hydrophilic faces) and 12.0 Å (across the hydrophobic faces). Attempts to simultaneously bridge both hydrophilic and hydrophobic faces are in progress.

Assembling metallacrowns into networks through side chain functional groups has not yet been reported; however, many reasonable strategies to accomplish this goal are available. Elaboration of β -alanine to yield β -phenylalanine has two important consequences. First, as described above, β -phenylalanine has a chiral center whereas β -alanine is achiral. Second, this functionalization suggests alternative linkages between metallacrowns. For example, the preparation of β -(4-pyridyl)alanine would result in a metallacrown with a nitrogen moiety that could bind metals such as Ag(I) or Pt(II). Figure 8 shows a model of the two-dimensional network that would result from using a four-coordinate, square planar metal ion as a linking unit. Alternatively, cyano or carboxylato functionality may be introduced with β -(4-cyanophenyl)alanine or β -(4-carboxyphenyl)alanine in order to vary the metal selectivity of the ligand binding moieties. We have shown that β -(4-methoxyphenyl)alanine and β -(4-cyanophenyl)alanine will form metallacrowns with Cu(II), thus, reagents to test this strategy are now in hand.

Unlike conventional macrocycles that orient metal binding moieties solely toward a specified cavity, metallacrowns also contain heteroatoms that can be functionalized on the molecular periphery. In the case of $\text{Cu(II)[12-MC}_{\text{Cu(II)N}(\text{S-}\beta\text{-pheHA)-4}]^{2+}}$, both the carbonyl oxygen atom and the amine nitrogen atom of the β -phenylalanine are available for further elaboration either by binding metals or through covalent bond formation. Alkylation or condensation at the amine position can lead directly to 2D networks that may be linked in a third dimension by bridging anions. The isolation of $[12\text{-MC}_{\text{Cu(II)N}(\beta\text{-(Et}_2\text{N)-amidox)-4}]$ (17) demonstrates that substitution on an amine nitrogen does not disrupt metallacrown assembly. In theory, the desired solid either could be prepared by first isolating the metallacrown followed by a step coupling each metallamacrocycle or in a one-step synthesis that templated the structure together at the initial stages of synthesis. An alternative approach is to exploit the metal binding capacity of the carbonyl oxygen atoms. Bidentate complexation of metal counterions can be achieved with metallacrowns prepared from ligands such as H_3shi . For example, Na(15-C-5)^+ units can bind to the metallacrown through the hydroximate carbonyl and the phenolate oxygen atoms (8). In this case, the peripheral cations are arranged in *cis* positions and the metallacrown ring becomes domed, a conformation that is seen for many metallaporphyrins. The metallacrown dimer of $\text{Cu(II)[12-MC}_{\text{Cu(II)N}(\text{S-}\beta\text{-pheHA)-4}]^{2+}}$ provides an example of monodentate peripheral ligation of a metal ion (11). The two metallacrowns are fused into dimers through Cu–O contacts between metallacrowns across the faces of the macrocycles similar to that shown in Fig. 6 for the β -alaninehydroximate

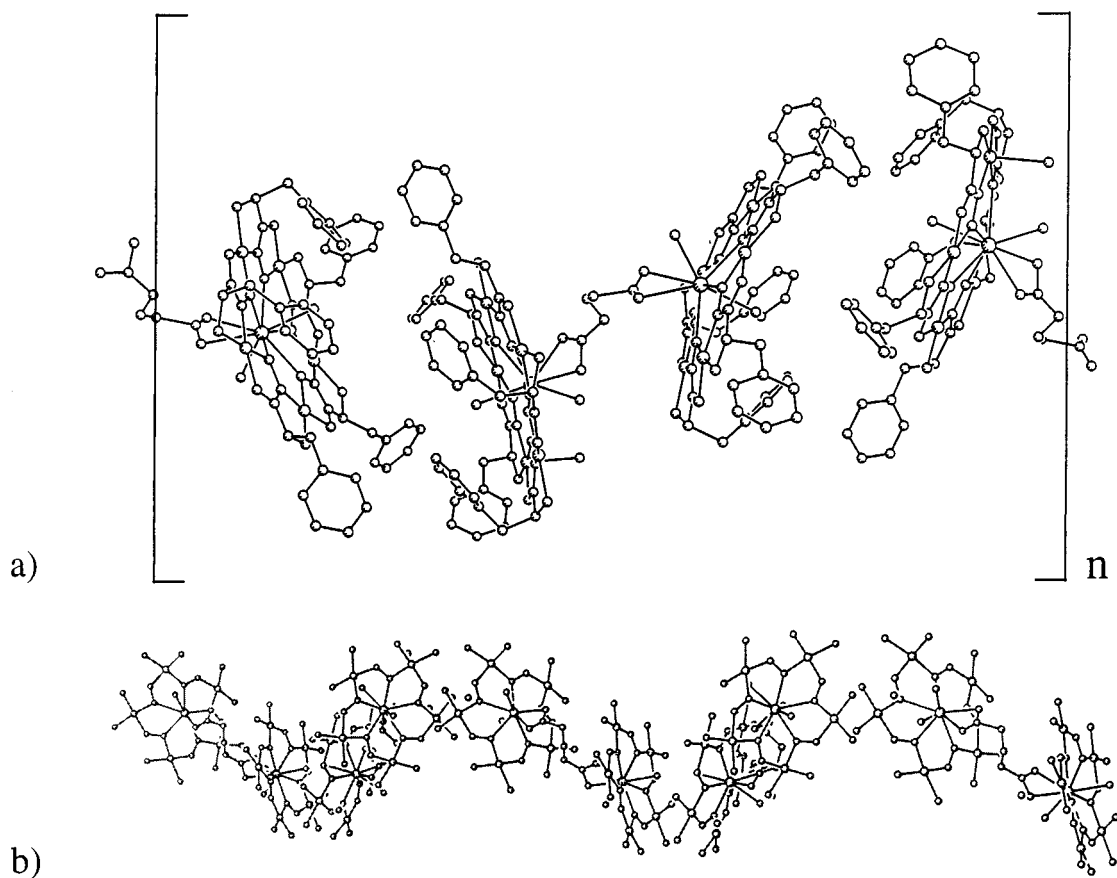


FIG. 7. PLUTO diagrams of $\text{Ln(III)[15-MC}_{\text{Cu(II)N(S-pheHA)-5}}]^{3+}$ (a) Dimers of metallacrowns linked across the hydrophilic faces by glutarate, with the hydrophobic faces interacting via Van der Waal forces. (b) A helical column of the metallacrowns viewed perpendicular to the helix axis. For clarity, only the heteroatoms of metallacrowns and dicarboxylates are shown.

case. A copper atom is appended to the carbonyl oxygen of one of the metallacrowns and stabilized through acetate bridges to a ring Cu(II) atom. In this example, the component stoichiometry is two metallacrowns and one peripheral $\text{Cu}(\text{acetate})_2$ unit coordinated to one metallacrown by a β -phenylalaninehydroximate carbonyl oxygen and a bridging acetate (charge is balanced by a bound chloride and an additional acetate in the lattice). We discuss below how a slight modification of this stoichiometry, with the same basic atom connectivity, results in the formation of extended solids.

SUCSESSES AND TARGETS

We have described above strategies that allow one to link metallacrowns. In the following discussion, we will present both an actual success story that leads to formation of extended solids and present predicted structures that are reasonable future targets for synthetic chemists.

In a paper submitted to *Inorganic Chemistry*, we have shown how chiral 2D solids may be isolated by simulta-

neously linking $\text{Cu(II)[12-MC}_{\text{Cu(II)N(R-}\beta\text{-pheHA)-4}}]^{2+}$ moieties in a face-to-face orientation with anions and in a side-to-side orientation with paddlewheel copper benzoate dimers (19). The solid forms in a noncentrosymmetric space group ($P1$) as is required by the chiral hydroximate ligands. The metallacrowns are linked in one dimension by a nitrate anion which bridges between ring copper atoms with a separation of 7.27 Å. Bridging in the second dimension is accomplished with $\text{Cu}_2(\text{benzoate})_4$ in a manner analogous to the peripheral ligation of monomeric $\text{Cu}(\text{acetate})_2$ described above. The metallacrown separation through the copper dimer bridge is 7.13 Å, with symmetrical $\text{Cu}_{\text{dimer}}-\text{O}_{\text{carbonyl}}$ distances (2.24 Å). The Cu-Cu distance between atoms of the paddlewheel dimer is 2.65 Å which is essentially the same as other molecules of this class that have axial substituents (20). The two chain directors (face-to-face and edge-to-edge) are oriented at 98.2°. As is typical for most 12-MC-4 structures, the $\text{Cu}_{\text{ring}}-\text{Cu}_{\text{ring}}$ distance is 4.72 Å and the $\text{Cu}_{\text{ring}}-\text{Cu}_{\text{central}}$ is 3.35 Å. The plane of $\text{Cu(II)[12-MC}_{\text{Cu(II)N(R-}\beta\text{-pheHA)-4}}]^{2+}$ and paddlewheel copper benzoate dimers is illustrated as Fig. 9. The subjacent layer of metal-

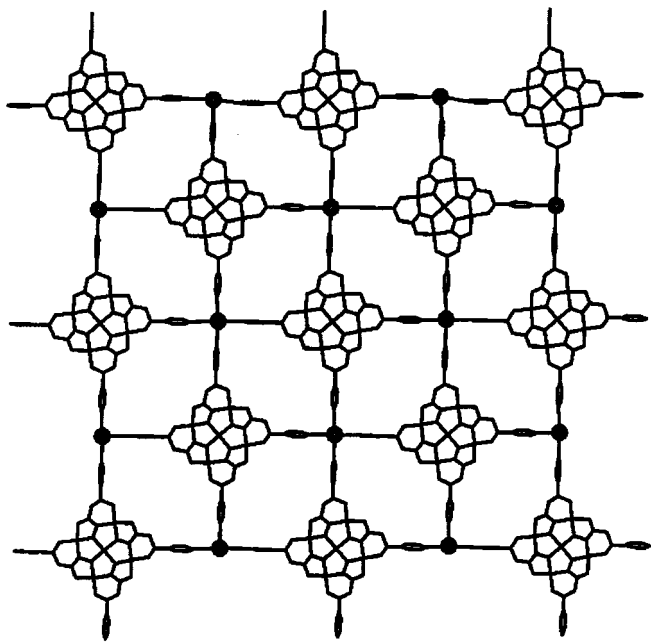


FIG. 8. Model of a metallacrown network formed via peripheral coordination of square planar four-coordinate metals. This model was made by using a crystallographically determined single metallacrown $\{\text{Cu}(\text{OAc})[12\text{-MC}_{\text{Cu}(\text{II})\text{N}(\text{S-}\beta\text{-pheHA})\text{-4}]^+\}$ and assuming reasonable Pt-N distances for the ligand with a (4-pyridyl) group in place of the phenyl group of β -phenylalaninehydroximate. The Pt-Pt distance across the rectangular "pores" is approximately 18 Å.

lacrown/copper benzoates is 16.32 Å ($\text{Cu}_{\text{central}}\text{-Cu}_{\text{central}}$) below the one that is shown. If the solid is rotated by 90°, one can observe pores (approximately 8 Å in diameter) with the

phenyl groups of the β -phenylalanine aligned along the channel. The pores are filled primarily with water and methanol; however, benzoate also serves as a guest. Each benzoate forms two strong hydrogen bonds with one metallacrown. The first hydrogen bond is between the carboxylate oxygen and a nitrogen of a coordinated amine of the β -phenylalanine, the other occurs between the same carboxylate oxygen and a water bound to a ring Cu(II). In addition to other hydrogen bonds to the entrapped water, the conformation is stabilized via van der Waal contacts between the phenyl rings of the framework and the benzoate phenyl group. The channels with all solvent guests removed is shown in the stereodiagram of Fig. 10. This view shows that the phenyl group from the chiral carbon participates directly in the formation of the channels, thus putting the site of chirality very near the surface of the channels. This simple example emphasizes the multicomponent nature of recognition available to metallacrown frameworks.

One of the beauties of this solid is the bulk incorporation of chirality into the network. Often, materials that contain stereocenters are not chiral in bulk because both hands can be found in the same lattice. Alternatively, truly chiral crystals can be obtained; however, since both enantiomorphs can be formed, there are an equal number of crystals of both handednesses, resulting in a bulk material that, unless physically separated, is also achiral. Because metallacrowns can be made chiral, incorporation of this chirality into the framework becomes trivial. In addition to the layered structure discussed in the preceding paragraph, we have also prepared seven other examples of 12-MC-4 chain compounds that crystallize in noncentrosymmetric

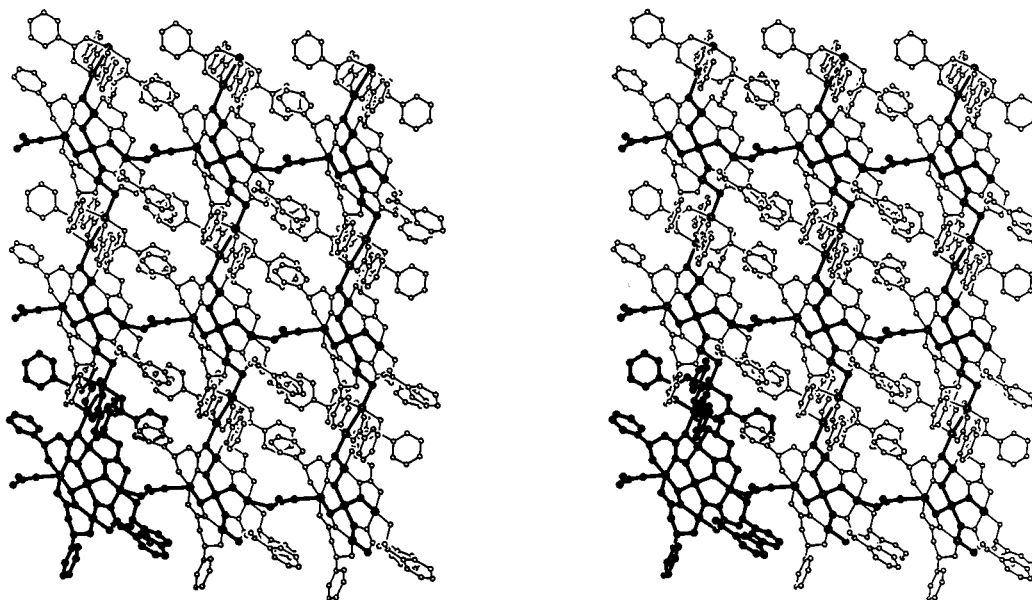


FIG. 9. Stereodiagram of the two-dimensional solid formed by $\{\text{Cu}(\text{II})(\text{NO}_3)[12\text{-MC}_{\text{Cu}(\text{II})\text{N}(\text{R-}\beta\text{-pheHA})\text{-4}]\} \{\text{Cu}_2(\text{benzoate})_4\}$. One crystallographically unique subunit (lower left) and the two-dimensional network connections are shown in bold. Solvent molecules have been removed for clarity.

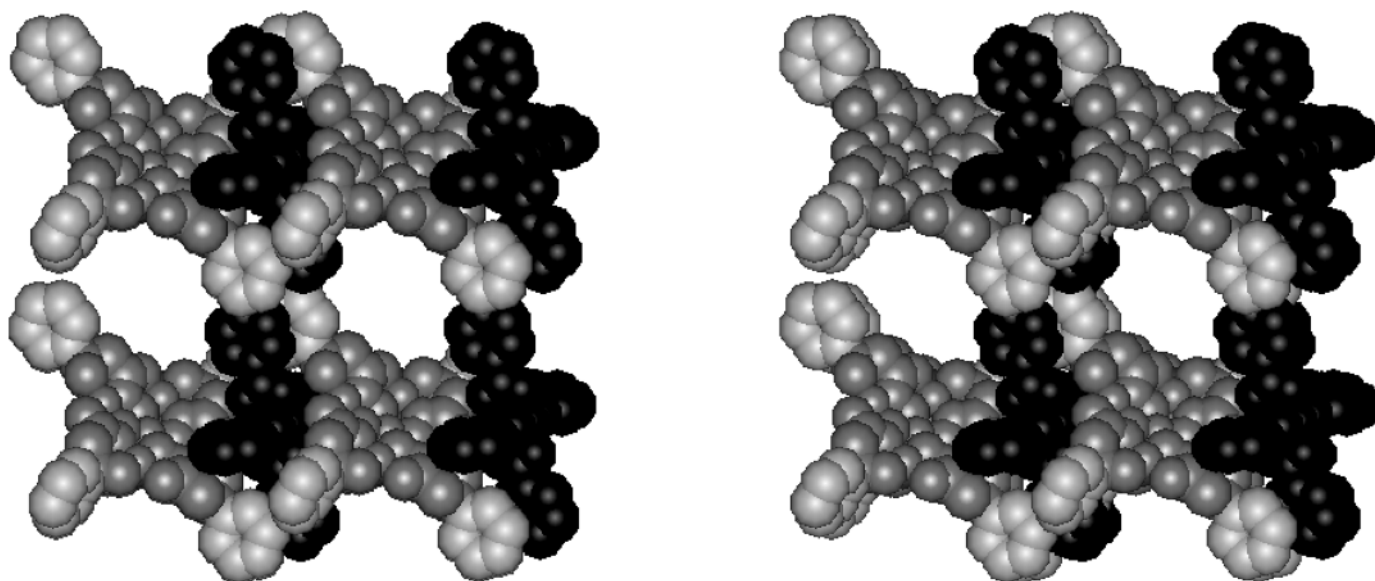


FIG. 10. Stereoview of channels in $\{\text{Cu(II)(NO}_3\text{)}[12\text{-MC}_{\text{Cu(II)N(R-}\beta\text{-pheHa)-4}}]\}\{\text{Cu}_2(\text{benzoate})_4\}$. The atoms are presented as CPK spheres. The $\{\text{Cu}_2(\text{benzoate})_4\}$ units are shown in black and the phenyl groups of the $\beta\text{-pheHa}$ ligand are in light gray. The solvents and benzoate guests in the channels have been removed for clarity.

space groups. This demonstrates the generality of this approach for the preparation of noncentrosymmetric solids.

We have also begun examining extended structures that can be obtained with chiral 15-MC-5 complexes. We have already presented one example of a chiral, helical chain in Fig. 7. If the metallacrown ligand is changed from phenylalanine to tyrosine, a second example of a chiral, helical chain is realized. In this case, the $\{\text{Gd(III)(NO}_3\text{)Cl}[15\text{-MC}_{\text{Cu(II)N(l-tyrHA)-5}]^{2+}\}_2$ is held together across the hydrophobic face by nitrate anions which bridge between coppers of the adjacent metallacrowns and by a direct coordination of a phenol from one of the metallacrown ligands to a copper atom on the other metallacrown (21). Each dimeric metallacrown then forms a columnar structure through chloride bridges on the hydrophilic face. Strong hydrogen bonds from the pendent phenols to metallacrown ligands link the structures into a three-dimensional network. The solid does not exhibit channels because the metallacrowns are tethered very tightly together by the hydrogen bonding network. This example illustrates a potential drawback of the design in these systems; however, with judicious choice of functional groups, it is likely that porous materials can be achieved even with this system.

An example of hydrogen bonding interactions being useful linkages can be seen in the solid state structure of $\text{Nd(III)(NO}_3\text{)}[15\text{-MC}_{\text{Cu(II)N(l-alaHA)-5}]^{2+}$ which is shown in Fig. 11 (10). There are two chains of metallacrowns that are formed by intermolecular bonds between the copper atom of one metallacrown and the carbonyl oxygen of the adjacent metallacrown. Each metallacrown has two of these weak bonds (at the Cu1 and Cu3 positions, dark spheres in

Fig. 11) linking it to two other metallacrowns to form an alternating chain. There are two such metallacrown chains oriented at right angles to each other which are then linked into a three-dimensional structure by a network of hydrogen bonds. One particularly strong hydrogen bonding interaction (shown as light CPK spheres for hydrogen bonded atoms) is between the coordinated water on the captured neodymium and a carbonyl oxygen of the metallacrown. The hydrogen bonds link in two dimensions the two metallacrown chains. The observer clearly sees the two sets of metallacrown chains by following the dark CPK spheres that represent the copper atoms. Perhaps most important, one can see 6-Å channels that permeate the structure along this dimension.

The ways of linking metallacrowns into two- and three-dimensional systems would seem limited only by the ingenuity of the investigator. If the linking metal species in compounds such as those represented in Fig. 5 are expanded to include tetrahedral or even octahedral coordination, the resulting three-dimensional network would contain substantial pores. One also notes that the networks in Fig. 8 rely on the assumption that all of the metallacrowns will be coplanar. Any rotation about the linking two- or four-coordinate metal centers would also give rise to three-dimensional networks. Other solids are inspired by porphyrin type networks. The large size and planarity of both macrocycles suggest that topological structures available to porphyrin might also be obtained with metallacrowns. Thus, one sees planar networks that might generate extremely large pores by linking the metallacrowns through pendent functional groups. Because the pores that would be

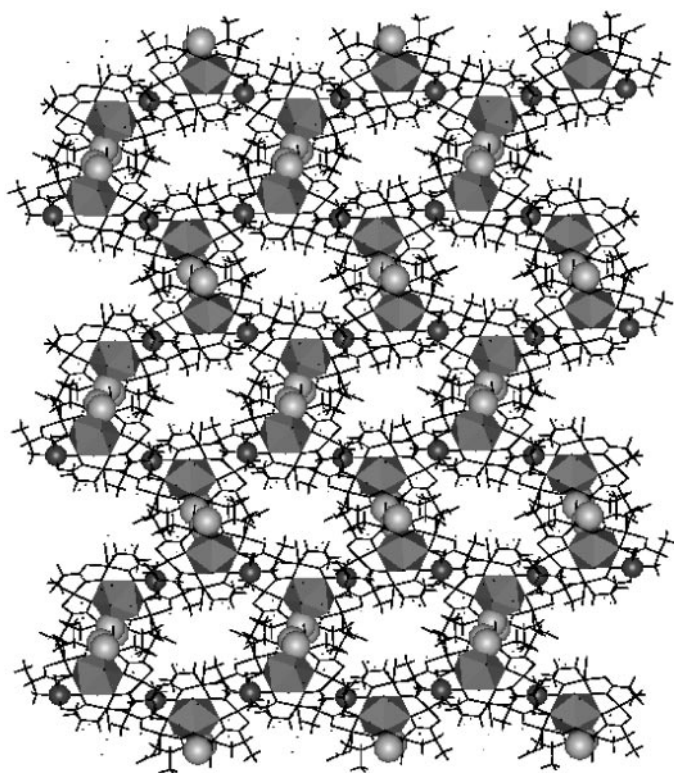


FIG. 11. Stick diagram of $\text{Nd(III)(NO}_3\text{)}_2[\text{15-MC}_{\text{Cu(II)N(l-alaHA)-5}]^{2+}$ showing channels that are formed in the solid. Dark spheres represent copper atoms that are bound to an oxygen atom on the adjacent metallacrown. This leads to a zig-zag chain of metallacrowns. The light spheres illustrate important hydrogen bonds that tie the structure into three dimensions. The polyhedra are the Nd(III) ions.

generated are so large, one might see interpenetration; however, even if this occurs, reasonably large channels should still result. Thus, it is our belief that metallacrowns provide a rational approach to making some of the next examples of chiral solids.

CONCLUSIONS

There clearly are now many reasonable approaches for designing porous solids and chiral materials. The strategy of using metallacrowns as building blocks towards such new solids represents an innovative way of incorporating chirality and interesting physical properties simultaneously. Only recently have we attempted to prepare solids incorporating chiral metallacrowns and in this short period we have seen that solids, in noncentrosymmetric space groups, can easily be obtained. These materials often have channels and always have high metal densities that present sites for small molecule recognition. We are now exploring additional features of the molecules such as ferromagnetism, thermochromicity, and optical activity. Thus, we believe that more extensive studies using this synthetic approach should lead to a new class of designed organic/inorganic solids of some potential utility.

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- Metallacrowns are named in a manner similar to the system used for organic crown ethers. The general form is $\text{M}'(A)[X-\text{MC}_{\text{M(ox)H(lig)}}-Y]$ where M' is the central metal, A is any bound counterion, X is the size of the macrocycle, Y is the number of donors, M(ox) is the ring metal and its oxidation state, H is the ring heteroatom (usually nitrogen), and (lig) is an abbreviation of the ligand used. By this method, a metallacrown composed of 5 copper(II) and 4 *S*- β -phenylalaninehydroxamic acid ligands with sulfate counterion bound would be named $\text{Cu(II)(SO}_4\text{)}_4[\text{12-MC}_{\text{Cu(II)N(S-}\beta\text{-pheHA)-4}]$
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