

Structural Chemistry of Pyridonate Complexes of Late 3d-Metals

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Only recently has interest in polymetallic complexes of metals in moderate oxidation states begun to rival the attention given to high-nuclearity species of metals in low or high oxidation states. Low-oxidation metal clusters containing carbonyl or chalcogenide ligands are well-known,^{1,2} and clusters containing as many as 146 metal atoms³ have been structurally characterized. Equally, high-valent species such as polyoxometalates have been studied for a number of years,⁴ producing fascinating structural chemistry, redox chemistry, and photochemistry. The highest nuclearity species structurally characterized contains 154 metal centers.⁵ In all these studies the bridging ligands are mono- or diatomic.

Moderate oxidation state coordination assemblies fall far short of this size, yet the work reported in the last decade or so provides a solid basis for future expansion, and early physical studies of such complexes are intriguing. As the metal centers are in moderate oxidation states, they may be paramagnetic, and this has led to exciting magnetic properties.^{6–13} Most molecular species with high-spin ground states belong to this class of compounds, and ground states as high as $S = 33/2$ have been reported.⁶ Perhaps the most significant results have been found for a dodecanuclear manganese compound which has an $S = 10$ ground state.¹³ The compound displays surprising magnetic relaxation effects,¹⁴ with the magnetization induced by an applied field remaining “frozen” in the preferred orientation after the field is removed. Such behavior could provide the basis for information storage at a molecular level and provides opportunities for studies of phenomena such as macroscopic quantum tunneling.

The challenge for a synthetic chemist is to provide more such compounds for study. Several groups are pursuing elegantly designed routes to such compounds. Loosely the field can be regarded as dominated by two

types of ligands. Carboxylate ligands are used because their ability as 1,3-bridging ligands is well-documented. Thus, for iron^{6–10} and manganese^{11–13} a large number of compounds have been synthesized using ligands such as benzoate. For earlier transition metals and for p-block metalloids high-nuclearity assemblies with alkoxide ligands have been made because alkoxides can bridge *via* μ_2 - or μ_3 -oxygen donors.^{15,16} Both carboxylates and alkoxides, and polyfunctional versions of these ligands, are well-behaved species, with fairly regular coordination chemistry. This allows prediction of likely products and some level of design of synthetic routes.

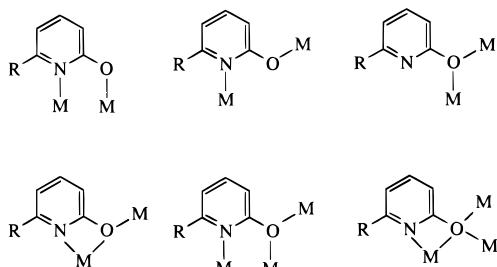
Our work has involved a much less well-behaved ligand. Derivatives of 2-pyridone (2-hydroxypyridine, Hhp) once deprotonated show at least six coordination modes as illustrated in Chart 1, and frequently several different modes within the same complex. Although many pyridonate complexes of the 4d- and 5d-metals had been reported,¹⁷ prior to our studies few reactions involving 3d-metals had been described.^{18–25} The most relevant in this context gave the cobalt complex $[\text{Co}_{12}(\text{OH})_6(\text{mhp})_{12}(\text{O}_2\text{CMe})_6]_n$,²⁵ which is the product of incomplete displacement of acetate by incoming pyridonate ligands in the reaction between fused Hmhp (MP 128 °C) and cobalt acetate.

Our strategy has therefore been to target heteroleptic carboxylate/pyridonate complexes of Co, Ni, and Cu. In many senses this is a “try and see” exercise as, *a priori*,

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Simon Parsons gained a B.Sc. degree in 1987 from the University of Durham, U.K., and a Ph.D. in 1991 from the University of New Brunswick, Canada, under the supervision of Professor J. Passmore. After postdoctoral research at the University of Oxford, U.K. (with Dr. A. J. Downs), he was appointed to a postdoctoral position in crystallography at the University of Edinburgh in 1993. In 1995 he was appointed Staff Crystallographer in the same department.

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Chart 1. Coordination Modes of Pyridonate Ligands^a

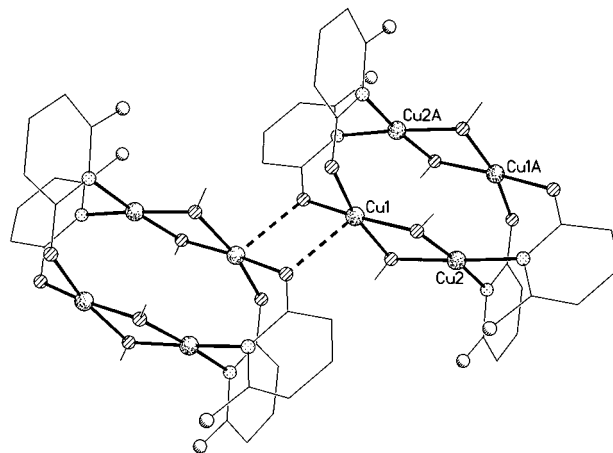
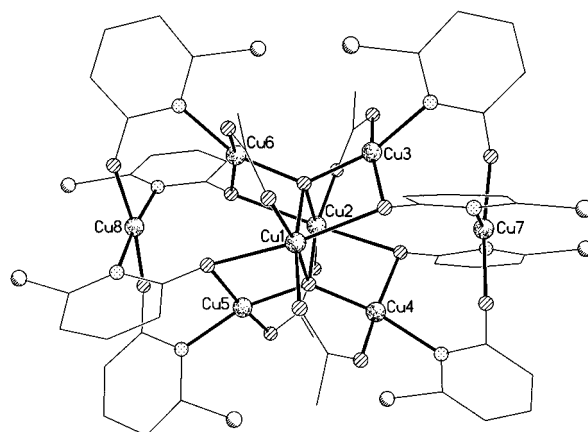
^a Abbreviations for ligands: R = Me, mhp; R = Cl, chp; R = Br, bhp; R = F, fhf; R = H, hp.

there is no means of predicting the outcome due to the flexibility of the pyridonate groups. While the only way to learn about unpredictable ligands is through trying unpredictable reactions, this may appear to be strategic weakness. The result, whatever is thought of the approach, is a range of products of unprecedented structural diversity. We hope that this illustration of what is possible through very simple coordination chemistry may provoke examination of other unpredictable ligand blends as means of stabilizing high-nuclearity coordination assemblies.

Copper Complexes of Pyridonates

The chemistry of copper with a pyridonate ligand has been more thoroughly examined than that of any 3d-metals with the possible exception of chromium. A number of dinuclear species of formula $[\text{Cu}_2(\text{xhp})_4(\text{S})_2]$ have been reported^{21,22} (xhp = hp or 3-ethyl-2-pyridonate, S = DMSO or DMF), which have "lantern" structures related to copper acetate. A tetranuclear Cu(I) complex has also been synthesized by Garner and co-workers.²³ We have extended this range of complexes to two heptametallic assemblies,^{26,27} both based on a "Star of David" of six Cu centers encapsulating a further metal, either a sodium²⁶ or a copper.²⁷ We also demonstrated that a dimeric species of formula $[\text{Cu}_2(\text{chp})_4]$ could be synthesized without axially coordinated solvent molecules,²⁸ and that the related species with 6-fluoro-2-pyridone (Hfhf) crystallizes as a tetranuclear entity formed by dimerization of two dinuclear units.²⁹ These dimers react readily with methanol to give either tetranuclear species of formula $[\text{Cu}_4(\text{OMe})_4(\text{chp})_4]$ ³⁰ or one-dimensional polymers of tetranuclear units, $[\text{Cu}_4(\text{OMe})_4(\text{fhf})_4]_n$ ²⁹ (Figure 1).

The reaction of copper carboxylates with molten pyridones leads to a series of octanuclear species (Figure 2) of general formula $[\text{Cu}_8(\text{O})_2(\text{xhp})_8(\text{O}_2\text{CR})_4]$ (where R = Me or Ph and xhp = mhp, chp, or bhp).³¹ The structure involves a hexametalllic edge-sharing bitetrahedral core of copper centers, with each tetrahedron containing a μ_4 -

FIGURE 1. $[\text{Cu}_4(\text{OMe})_4(\text{fhf})_4]_n$.FIGURE 2. $[\text{Cu}_8(\text{O})_2(\text{chp})_8(\text{O}_2\text{CMe})_4]$.

oxo group. The external edges of the bitetrahedron are bridged alternately by carboxylates functioning in a 1,3-fashion, or by μ_2 -oxygen atoms from xhp ligands. These latter groups attach the final two copper atoms to the central core.

Examination of the formation of this octanuclear species using thermogravimetric analysis³¹ strongly suggested that the reaction proceeded *via* complete displacement of carboxylate groups from the copper carboxylate complexes in a first step, giving dinuclear copper pyridonate species $[\text{Cu}_2(\text{xhp})_4]$ which on dissolution reacted with residual $[\text{Cu}_2(\text{O}_2\text{CR})_4]$ moieties to generate octanuclear species. This was confirmed by performing the reaction of copper acetate in the molten pyridonates for much longer periods, repeatedly removing carboxylates by vacuum distillation and replenishing the pyridone ligand in the reaction flask. This led to formation of $[\text{Cu}_2(\text{xhp})_4]$ complexes. We could also react $[\text{Cu}_2(\text{xhp})_4]$ directly with copper carboxylates to generate octanuclear species. Curiously we have been unable to crystallize $[\text{Cu}_2(\text{mhp})_4]$ despite good evidence for its existence; in all cases it has crystallized as a heptametallic $[\text{Cu}_6\text{Na}(\text{mhp})_{12}][\text{NO}_3]$ compound.²⁶

The bitetrahedral core is new in copper(II) chemistry, and the magnetic behavior of these complexes³¹ indicates that a complex series of exchange interactions leads to spin frustration within the central Cu_6O_2 core. The spin ground state for these species is not yet clear, and it

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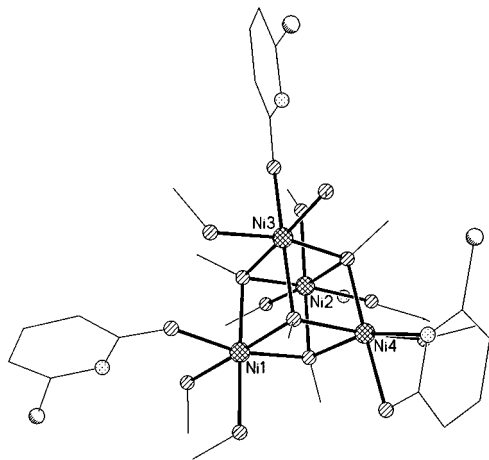


FIGURE 3. $[\text{Ni}_4(\text{OMe})_4(\eta^2\text{-chp})(\text{chp})_3(\text{MeOH})_7]$.

appears possible that the ground state differs between the complexes with differing pyridonate derivatives.

The copper chemistry therefore shows a limited range of structural types, with octanuclear assemblies resulting whenever carboxylate/pyridonate mixtures were examined. Five of these octanuclear complexes have been structurally characterized, and spectroscopic evidence is sufficient for the remaining complexes to be unambiguously identified.

Nickel Complexes of Pyridonates

Much greater structural diversity has been displayed by nickel(II) with these ligand mixtures. In addition to involvement of pyridonate and carboxylate, we have found a strong dependence on the solvent used in recrystallization, with protic solvents such as MeOH leading to smaller nuclearities than weaker bonding solvents such as THF or CH_2Cl_2 .

Linear trinuclear complexes of formula $[\text{Ni}_3(\text{xhp})_4(\text{O}_2\text{CR})_2(\text{R}'\text{OH})_6]$ ($\text{xhp} = \text{chp}$ or bhp ; $\text{R} = \text{Me}$ or Ph ; $\text{R}' = \text{Me}$ or Et) are found when the product of the reaction of nickel acetate or benzoate with Hchp or Hbhp is recrystallized from MeOH/ether,³² or by reaction of nickel acetate with Na(chp) in an alcohol. The presence of the terminal ROH groups presumably limits the nuclearity of the assembly, preventing formation of larger species. Such linear trinuclear arrays are common in nickel chemistry.

Reaction of nickel trichloroacetate with Na(chp) or Na(bhp) followed by recrystallization from MeOH/ether leads to a tetranuclear assembly containing a Ni_4O_4 cube with the general formula $[\text{Ni}_4(\text{OMe})_4(\eta^2\text{-xhp})(\text{xhp})_3(\text{MeOH})_4]$ (Figure 3)³² (where $\text{xhp} = \text{chp}$ or bhp). The presence of one chelating xhp group is intriguing and suggests that these cubanes are one of a series of four such cubanes varying from $[\text{Ni}_4(\text{OMe})_4(\eta^2\text{-xhp})_4(\text{MeOH})_4]$ to $[\text{Ni}_4(\text{OMe})_4(\text{xhp})_4(\text{MeOH})_8]$, although we have only been able to isolate the complex with one chelating pyridonate and seven terminal alcohol ligands. Cubane complexes are not uncommon in nickel chemistry, with the other vertices

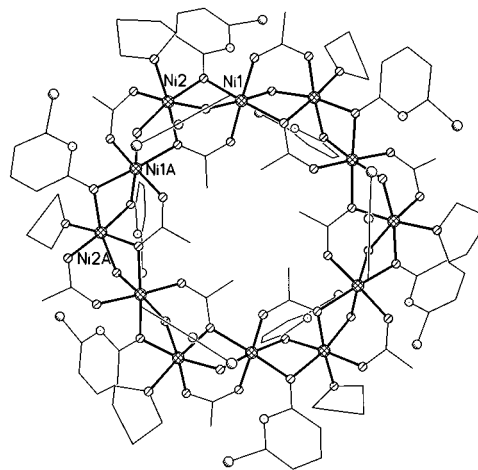


FIGURE 4. $[\text{Ni}_{12}(\text{chp})_{12}(\text{O}_2\text{CMe})_{12}(\text{H}_2\text{O})_6(\text{THF})_6]$.

of the cube occupied by hydroxide, methoxide, or azide.³³ The trinuclear and cubane complexes show expected magnetic behavior:³² antiferromagnetic exchange in the linear species and ferromagnetic exchange in the cubes which is explicable given the small Ni–O–Ni angles at the $\mu_3\text{-OMe}$ groups.³³

If we carry out the recrystallization step from a non-protic solvent, the structural chemistry becomes more unusual. Recrystallization of the reaction of nickel acetate with Hchp or Hbhp from THF leads in both cases to cyclic dodecanuclear species, $[\text{Ni}_{12}(\text{xhp})_{12}(\text{O}_2\text{CMe})_{12}(\text{H}_2\text{O})_6(\text{THF})_6]$ ($\text{xhp} = \text{chp}$ or bhp) (Figure 4).³⁴ The assembly is in some ways most closely related to the "ferric wheel" $[\text{Fe}_{10}(\text{OMe})_{20}(\text{O}_2\text{CCH}_2\text{Cl})_{10}]$ reported by Lippard and Taft,⁹ in that each metal···metal vector is bridged by one carboxylate and two μ_2 -oxygen atoms; however, in this case the oxygen atoms are derived from a number of sources. Again the pyridonate ligand binds only through the exocyclic oxygen atom, behavior which had not been observed for the deprotonated ligand with 4d- and 5d-metals despite a large number of structure determinations.¹⁷ For nickel this coordination mode is the most common.

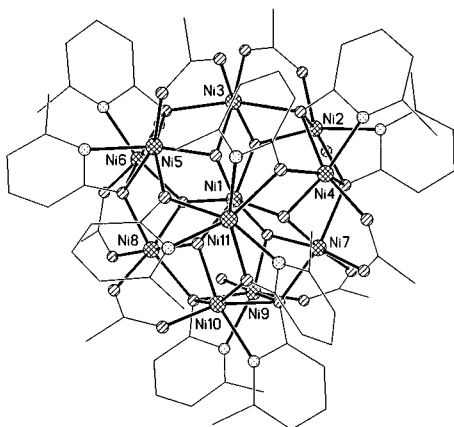
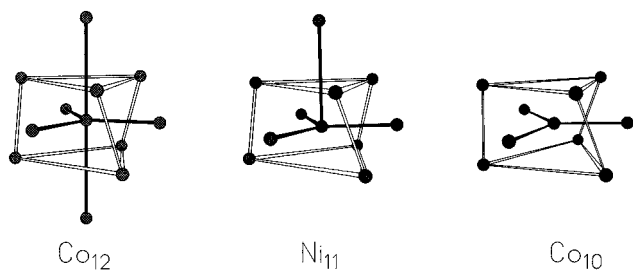
The cyclic dodecanuclear species shows ferromagnetic coupling between Ni centers, giving the assembly a spin ground state of $S = 12$.³⁴ This is among the highest known for a molecular species, only definitely exceeded by an Fe_{19} species synthesized by Powell and co-workers.⁷ It is also the highest spin state for a nickel species, and for a species where the coupling is exclusively ferromagnetic; previous molecules with very high spin states have contained either manganese or iron, and the ground state has been the result of antiferromagnetic interactions.

Nickel complexes involving the mhp ligand show a greater tendency for binding through both N and O donors when compared with the chp derivative. An example is the undecanuclear species $[\text{Ni}_{11}(\text{OH})_6(\text{mhp})_{12}(\text{O}_2\text{CMe})_3(\text{H}_2\text{O})_3]$ (Figure 5),³² made from reaction of nickel acetate with Hmhp followed by crystallization from CH_2Cl_2 /hexane or CHCl_3 /hexane. The structure is similar to $[\text{Co}_{12}(\text{OH})_6(\text{mhp})_{12}(\text{O}_2\text{CMe})_6]$,²⁴ merely lacking one of the

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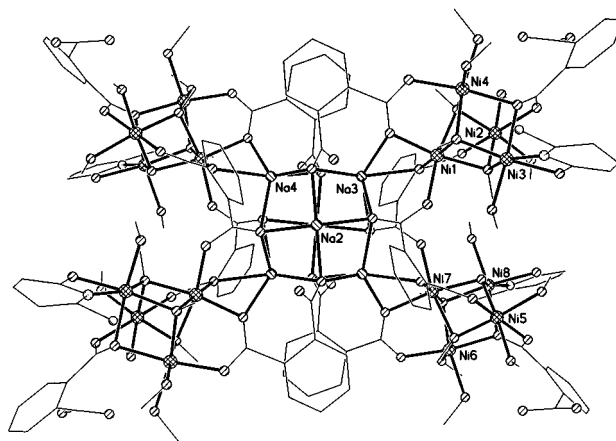
FIGURE 5. $[\text{Ni}_{11}(\text{OH})_6(\text{mhp})_{12}(\text{O}_2\text{CMe})_3(\text{H}_2\text{O})_3]$.Chart 2. Metal Polyhedra in Co_{12} , Ni_{11} , and Co_{10} Species, Illustrating the Close Relationship between These Structures

metal sites (Chart 2). The metal array is a centered tricapped trigonal prism, with Ni(1) at the center of the array, the sides of the prism comprising Ni(2), Ni(4), Ni(5), Ni(6), Ni(9), and Ni(10), and the Ni(3), Ni(7), and Ni(8) at the centers of the square faces. Ni(11) is attached through mhp units to the exterior of the polyhedron on the noncrystallographic 3-fold axis running through the metal array. Three different crystal structures have been determined which contain such a Ni_{11} assembly; in one of the three the undecanuclear units crystallize with strong H-bonding contacts between units, leading to dimers of undecanuclear species. In the second, strong H bonds attach a $\text{Ni}(\text{mhp})_3$ unit to the top of a Ni_{11} cage.

We can extend the nickel chemistry still further by reactions using a dicarboxylate ligand rather than a monocarboxylate.³⁵ Reaction of $\text{Na}(\text{chp})$ and sodium phthalate with nickel chloride in MeOH leads to a complex of formula $[\text{Ni}_{16}\text{Na}_6(\text{chp})_4(\text{phth})_{10}(\text{Hphth})_2(\text{OMe})_{10}(\text{OH})_2(\text{MeOH})_{20}]$ which is best regarded as an assembly of five cages (Figure 6), the five cages being four Ni_4 cubanes and one Na_6 octahedron. The assembly is held together by eight phthalate ligands which each bond from the central Na_6 octahedron to the peripheral Ni_4 units. The Ni_4 cubanes involve bridging methoxides at three of the vertices, with the Ni coordination spheres completed by molecules of MeOH solvate and chp ligands.

Cobalt Complexes of Pyridonates

Yet more novel structural types are exhibited by the cobalt pyridonates, and this in part is due to the coordinative flexibility of the metal. In the complexes described above nickel is always six-coordinate, and rarely deviates greatly

FIGURE 6. $[\text{Ni}_{16}\text{Na}_6(\text{chp})_4(\text{phth})_{10}(\text{Hphth})_2(\text{MeO})_{10}(\text{OH})_2(\text{MeOH})_{20}]$.

from ideal octahedral coordination, whereas we observe cobalt to be variously four-, five-, and six-coordinate. There are nevertheless several points of similarity with the nickel systems; in particular linear trinuclear and tetranuclear cobalt cubes can be made in the presence of methanol which are isostructural to the nickel species. The major difference between these cobalt and nickel species is in the metal...metal separation which is always greater for cobalt. For example, in the trinuclear species the Ni...Ni distances vary from 3.087(2) to 3.118(2) Å, while in $[\text{Co}_3(\text{chp})_4(\text{O}_2\text{CMe})_2(\text{MeOH})_6]$ the Co...Co distance is 3.164(2) Å. We have also prepared a Co_{10} complex,³⁶ $[\text{Co}_{10}(\text{OH})_6(\text{mhp})_6(\text{O}_2\text{CPh})_7\text{Cl}(\text{Hmhp})_3(\text{MeCN})]$, which completes the series of tricapped centered trigonal prisms (see Chart 2) comprises by Garner's Co_{12} complex and our own Ni_{11} complexes in lacking both caps on the pseudo-3-fold axis. The reason for this appears to be related to steric effects of the benzoate ligands which hinder access to the triangular faces of the prism.

Reactions using cobalt carboxylates as substrates have been less successful than the corresponding nickel chemistry, and the route from cobalt chloride or nitrate reacted with $\text{Na}(\text{O}_2\text{CR})$ and $\text{Na}(\text{chp})$ in MeCN has been more productive.

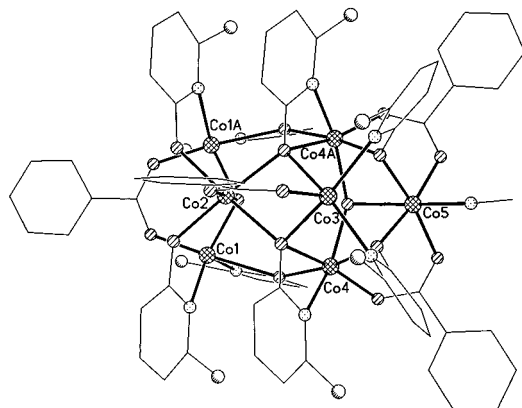
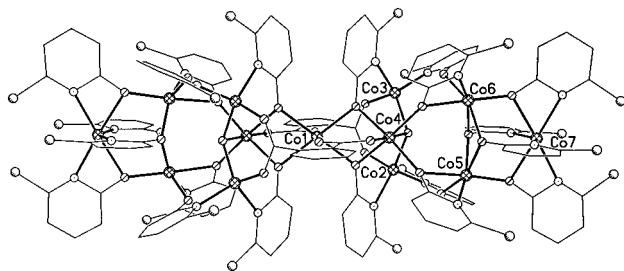
A heptanuclear species³⁷ results from the reaction of cobalt chloride with $\text{Na}(\text{O}_2\text{CPh})$ and $\text{Na}(\text{chp})$ in MeCN. The product $[\text{Co}_7(\text{OH})_2(\text{O}_2\text{CPh})_4(\text{chp})_8(\text{MeCN})]$ contains a capped distorted trigonal prism of cobalt centers (Figure 7). The cap is placed on one of the triangular faces rather than on a square face, and the structure is unrelated to other polymetallic species based on centered trigonal prisms. The structure is held together by a mixture of 1,3-bridging benzoates and chp units which chelate to one metal through both N and O donors and bridge two further metals through the exocyclic oxygen.

The analogous reaction using disodium phthalate $[\text{Na}_2(\text{phth})]$ in place of $\text{Na}(\text{O}_2\text{CPh})$ results in a tridecanuclear cobalt complex, $[\text{Co}_{13}(\text{chp})_{20}(\text{phth})_2(\text{OH})_2]$ (Figure 8) which can be regarded as two heptametallic units with Co(1) common to both. The central region of this structure, encompassing Co(2), Co(3), Co(4), their symmetry equivalents, and Co(1), is dominated by two tetra-

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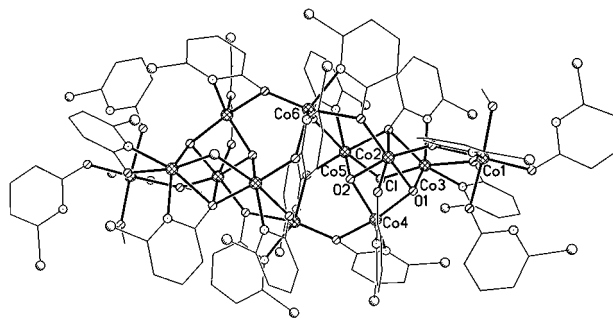
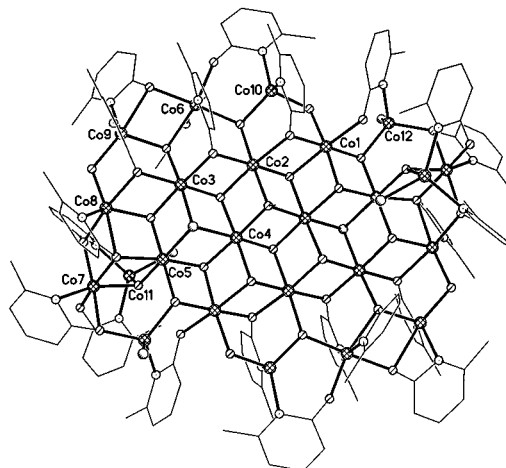
FIGURE 7. $[\text{Co}_7(\text{OH})_2(\text{O}_2\text{CPh})_4(\text{chp})_8(\text{MeCN})]$.FIGURE 8. $[\text{Co}_{13}(\text{chp})_{20}(\text{phth})_2(\text{OH})_2]$. The resemblance to $[\text{Co}_7(\text{OH})_2(\text{O}_2\text{CPh})_4(\text{chp})_8(\text{MeCN})]$ can be seen by comparing the polyhedron defined by Co(2), Co(4), Co(3), Co(6), Co(7), and Co(5) in this structure with Co(1), Co(2), Co(1a), Co(4a), Co(5), and Co(4), respectively, in the former structure (Figure 7).

nucleating phthalates, which serve to link the two Co_7 fragments. The remaining Co atoms in the molecule are bound to this region through bridging chp groups.

Within this structure the cobalt coordination is varied: Co(1), Co(4), Co(5), Co(6), and Co(7) are all six-coordinate, while Co(2) and Co(3) are four-coordinate. The chp ligands demonstrate three coordination modes: trinucleating, e.g., bound to Co(1), Co(3), and Co(4); binucleating, e.g., connecting Co(3) and Co(6); chelating and binucleating, e.g., chelating to Co(5) and additionally attached to Co(4). It is the presence of a tetranucleating dicarboxylate, as opposed to the binucleating carboxylates used in previous reactions, which leads directly to this higher nuclearity array and suggests that many further, larger complexes should be accessible using this strategy. Similar results have been reported for Mn chemistry.¹²

Reaction of CoCl_2 with 2 equiv of $\text{Na}(\text{chp})$ in methanol, followed by evaporation to dryness leads to a purple compound which we have not fully characterized, but which we believe contains cobalt cubanes plus some other cobalt species. Prolonged heating of this material, which presumably drives off methanol, followed by recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ gives $[\text{Co}_{12}(\text{chp})_{18}(\text{OH})_4(\text{Cl})_2(\text{Hchp})_2(\text{MeOH})_2]$.³⁷

This centrosymmetric dodecanuclear assembly (Figure 9) retains two $[\text{Co}_4\text{O}_3\text{Cl}]$ units. They are linked by an eight-membered ring involving four cobalt atoms and four μ_2 -oxygen atoms derived from chp ligands. Co(5) and Co(5a) are each part of a cube and of the eight-membered ring, with Co(6) and Co(6a) the other cobalt atoms within the eight-membered metalocycle. The other three cobalt atoms in the cube are Co(2), Co(3), and Co(4), and both

FIGURE 9. $[\text{Co}_{12}(\text{chp})_{18}(\text{OH})_4(\text{Cl})_2(\text{Hchp})_2(\text{MeOH})_2]$.FIGURE 10. $[\text{Co}_{24}(\mu_3\text{-OH})_{14}(\mu_2\text{-OH})_4(\mu_3\text{-OMe})_2(\mu_3\text{-Cl})_2(\text{Cl})_4(\text{mhp})_{22}]$.

Co(2) and Co(4) share μ_2 -oxygen atoms with Co(6) or its symmetry equivalent. The cube is not ideal as the chloride group only bridges Co(3) and Co(4).

The final unique cobalt site [Co(1)] is found at the periphery of the molecule, attached to the cube by two μ_2 -oxygen atoms shared with Co(2) and Co(3). This bridging is identical to that between Co(6) and the cube, and suggests that larger oligomers involving cubes bridged by further Co atoms should be possible. In the formation of this complex nearly all methanol has disappeared except for molecules attached to Co(1) and Co(1a), and the coordination chemistry is dominated by bridging and chelating chp ligands. Additionally four μ_3 -hydroxides [O(1), O(1a), O(2), O(2a)] are found as part of the two $\text{Co}_4\text{O}_3\text{Cl}$ cubes.

A still larger cobalt complex results when cobalt chloride is reacted with $\text{Na}(\text{mhp})$ in MeOH, followed by recrystallization from damp ethyl acetate.³⁸ The compound of formula $[\text{Co}_{24}(\mu_3\text{-OH})_{14}(\mu_2\text{-OH})_4(\mu_3\text{-OMe})_2(\mu_3\text{-Cl})_2(\text{Cl})_4(\text{mhp})_{22}]$ is a layer structure containing Co centers bridged by, in the main, μ_3 -hydroxides surrounded by a peripheral sheath of mhp ligands (Figure 10). These bridging groups are derived from the ethyl acetate solvent, which contains 0.1% water by weight and thus appears ideal for the slow introduction of bridging hydroxides. A similar procedure allowed synthesis of a heptadecanuclear iron-oxo array.³⁹ The cobalt centers can all be regarded as six-coordinate; however, the degree of distortion in-

(38) Brechin, E. K.; Harris, S. G.; Harrison, A.; Parsons, S.; Whittaker, A. G.; Winpenny, R. E. P. Manuscript submitted to *J. Chem. Soc., Chem. Commun.*

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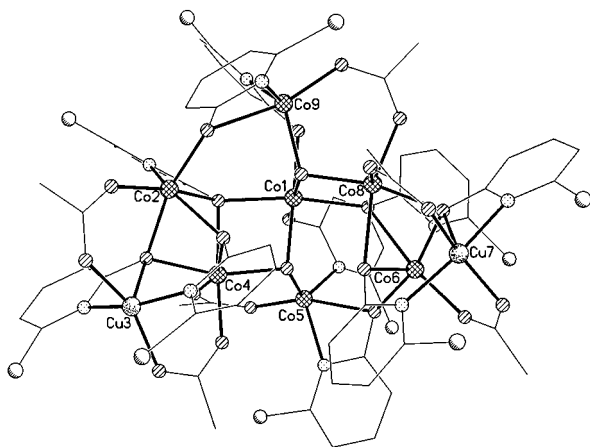


FIGURE 11. $[\text{Co}_7\text{Cu}_2(\text{OH})_2(\text{chp})_{10}(\text{O}_2\text{CMe})_6]$.

creases markedly on moving from the center of the cluster to the edge. The central metal sites are bound to exclusively monodentate ligands, and have approximately octahedral geometries. The external Co centers are bound to two chelating mhp groups and two monodentate ligands, and their geometries are best described as tetrahedral distorted by two additional long contacts. This complex is the highest nuclearity cobalt compound known, and initial identifications are that the magnetochemistry of the compound may also be novel. Studies indicate a high-spin ground state, of around $S = 9$ (the spin state is difficult to estimate given the high g values common to cobalt), and there is a divergence below 4 K between field-cooled and zero-field-cooled susceptibility. This may indicate superparamagnetic behavior, but many further studies will be necessary to fully understand this result.

Comparing the cobalt and nickel chemistry, we have uncovered two striking features. The first is the tendency of the pyridonate ligands to use both N and O donors to coordinate to cobalt, but only O donors to bind to nickel. It is possible that this apparent trend simply reflects the small number of compounds thus far prepared and crystallized. If genuine, it would be unexpected as no great difference in preference for N or O donors is expected for these two metals. Secondly, nickel is exclusively six-coordinate in all the polynuclear compounds characterized while cobalt is more flexible.

Heterometallic d-Block Complexes

A further structural twist can be achieved by mixing different metal carboxylates prior to reaction with molten pyridones. Thus far, we have fully characterized two mixed Co–Cu species from such reactions.⁴⁰

Reaction of cobalt acetate and copper acetate with Hchp in a 1:1:4 mole ratio prior to heating to 130 °C gives a paste from which crystals can be obtained using CH_2Cl_2 /ether. A nonmetallic species $[\text{Co}_7\text{Cu}_2(\text{OH})_2(\text{chp})_{10}(\text{O}_2\text{CMe})_6]$ is found (Figure 11); the metal coordination sites were assigned to the differing metals on the basis of structure refinement and elemental analysis by atomic absorption spectroscopy. The cobalt sites are a mixture of five six-coordinate sites, each with a geometry based on a distorted octahedron, and two five-coordinate sites

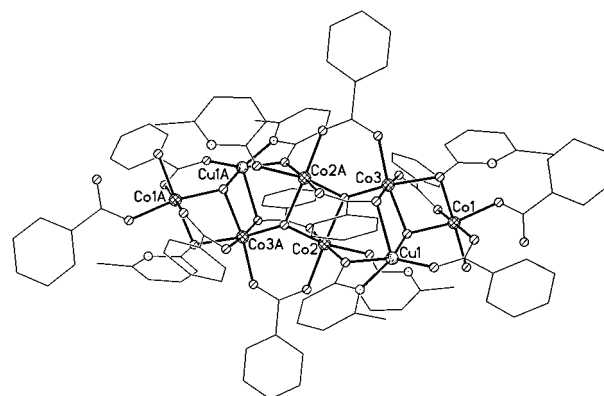


FIGURE 12. $[\text{Co}_6\text{Cu}_2(\text{OH})_4(\text{mhp})_2(\text{O}_2\text{CPh})_{10}(\text{Hmhp})_4(\text{H}_2\text{O})_2]$.

$[\text{Co}(5)$ and $\text{Co}(9)]$. The remaining two sites are also five-coordinate with extremely distorted geometries, typical of copper(II). All five coordinate sites are bound to two N and three O donors, $\text{Co}(2)$ and $\text{Co}(6)$ are bound to one N and five O atoms, and the remaining three Co sites are bound exclusively to O donors.

The polyhedron defined by the metal sites is extremely irregular (Figure 11). The Co sites belong to four oxygen-centered Co triangles, with $\text{Co}(1)$ a vertex of all four triangles. Thus, $\text{Co}(1)$, $\text{Co}(2)$, and $\text{Co}(4)$ and $\text{Co}(1)$, $\text{Co}(6)$, and $\text{Co}(8)$ form triangles about μ_3 -oxygen atoms from chp ligands. $\text{Co}(1)$, $\text{Co}(4)$, and $\text{Co}(5)$ and $\text{Co}(1)$, $\text{Co}(8)$, and $\text{Co}(9)$ describe triangles about μ_3 -hydroxides. This Co_7 array is far from planar, with $\text{Co}(2)$, $\text{Co}(4)$, $\text{Co}(6)$, and $\text{Co}(8)$ within one plane, and $\text{Co}(1)$, $\text{Co}(5)$, and $\text{Co}(9)$ considerably above this plane. The two Cu atoms are also part of O-centered triangles; $\text{Cu}(3)$, $\text{Co}(2)$, and $\text{Co}(4)$ and $\text{Cu}(7)$, $\text{Co}(6)$, and $\text{Co}(8)$ each define triangles about μ_3 -oxygens from chp units. The Cu atoms lie below the plane of $\text{Co}(2)$, $\text{Co}(4)$, $\text{Co}(6)$, and $\text{Co}(8)$.

The reaction utilizing benzoate salts reacted with Hmhp at 130 °C produces, after crystallization from dichloromethane/ether, $[\text{Co}_6\text{Cu}_2(\text{OH})_4(\text{mhp})_2(\text{O}_2\text{CPh})_{10}(\text{Hmhp})_4(\text{H}_2\text{O})_2]$ (Figure 12).⁴⁰ Again the structure is dominated by oxygen-centered metal triangles. At the midpoint of the complex is a bitriangular unit sharing an edge, with $\text{Co}(2)$ and $\text{Co}(2a)$ in the common edge and $\text{Co}(3)$ or its symmetry equivalent completing the triangles. $\text{Co}(3)$ and $\text{Co}(3a)$ are present in the other crystallographically unique triangle, made up of $\text{Co}(3)$, $\text{Co}(1)$, and $\text{Cu}(1)$. At the center of each triangle is a μ_3 -hydroxide. The three crystallographically unique Co sites are all bound to an octahedral array of O donors, while the one Cu site is bound to four O donors and one N atom. Again assignment of metal sites was made on the basis of both X-ray refinement and elemental analysis.

These preliminary results on mixed-metal systems again illustrate the extraordinary structural flexibility of mixed carboxylate/pyridonate systems. The ratio of metals in the reaction mixture does not appear to affect the reaction product. In both cases a side product of the reaction appears to be a homometallic copper pyridonate complex such as $[\text{Cu}_2(\text{chp})_4]$.

Conclusions

The bewildering assortment of polyhedral arrays described above were derived from minor variations on quite simple

(40) Brechin, E. K.; Harris, S. G.; Parsons, S.; Winpenny, R. E. P. Manuscript submitted to *J. Chem. Soc., Chem. Commun.*

synthetic themes. This very diversity means that it is difficult to draw practical conclusions about the best way to make complexes of a given nuclearity at present. This can be excused in a new field, but it is important to recognize that our current knowledge rests on structures derived from the reaction products which happened to be crystalline, while almost no mechanistic information is available. It is becoming clear, though, that whereas most homoleptic pyridonate complexes are dinuclear,¹⁷ large complexes are frequently produced with heteroleptic ligand blends which can be derived from the primary reactants (i.e., metal salts and ligands added to the reaction mixtures), from the solvent, and from water in the solvent or hydrated starting materials. It seems that this mixture of ligands plays an important role, possibly by stabilization of a framework via favorable interligand interactions (e.g., H bonding). Yields, however, tend to be in the range 10–20%, and it is frequently the case that the ratio of reactants which gives the best yield does not relate to that found in the crystalline product. Much work remains to be done to understand these reactions.

The immense structural diversity of these complexes stems from the ability of the pyridonate ligands to exhibit no less than six distinct coordination modes: terminally bound through the O-donor; 1,3-bridging through both N and O atoms; 1,1-bridging through the exocyclic oxygen alone; chelating through N and O; chelating plus 1,1-bridging through O; chelating plus 1,1,1-bridging through O. Where the N donor is not bound to a metal it is always involved in H bonding to another ligand. Neutral pyridone ligands also display terminal and bridging modes through oxygen while the N atom is protonated. Such versatility is observed neither in pyridonate complexes of the 4d- and 5d-metals, where the 1,3-bridging mode is the rule, nor among carboxylate and alkoxide ligands which have dominated previous studies of polyoxometallic complexes. The structural diversity and unpredictability

of the chemistry thus go hand in hand, and both are due to the coordinative flexibility of pyridonates.

The metallic assemblies which characterize these complexes invite comparisons with carbonyl clusters, metal chalcogenide clusters, and supramolecular compounds. The progress made in rationalizing the structures of cluster compounds stands as one of the principal achievements of inorganic chemistry. Many reflect electronic preferences of the metal, and often contain fragments of some archetypal metal or mineral. The structures of supramolecular complexes are controlled by the rigidity and geometry of the ligands. The versatility of the pyridonate ligand means that the structure of these polymetallic complexes is far less predictable. By contrast to naturally-occurring systems the metal–oxo core frequently appears quite asymmetric, and it is rare that series of metal polyhedra can be interrelated by reference to common polyhedra (although the series based on centered tri-capped trigonal prisms is an exception).

The purpose of an Account such as this is to shed light on a novel area of modern research. There is still much work to do, but it seems clear that the prospects for the synthesis of very high nuclearity complexes are very good; indeed, the Ni₁₆Na₆³⁵ and Co₂₄ complexes³⁸ were characterized during the preparation of this Account. Placing the synthesis and structures of these complexes within a coherent conceptual framework forms one ultimate aim of this research. Exploring, explaining, and exploiting the novel high-spin magnetic ground states exhibited by these molecules form another.

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