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The development of chiral metallacrowns into anion recognition agents and porous materials

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Contents

Abstract

Chiral metallacrowns can be prepared by the reaction of resolved amino hydroxamic acids with divalent metal ions. The 15-metallacrown-5 structure is achieved by the reaction of α-amino hydroxamic acids (e.g. L-alanine hydroxamic acid, L-phenylalanine hydroxamic acid and L-tyrosine hydroxamic acid) with Cu(II) and a Ln(III) ion. If a resolved ligand is used, the structure obtained contains all sidechain functional groups on the same face of the metallamacrocycle. The metallacrowns made with L-phenylalanine hydroxamic acid and L-tyrosine hydroxamic acid dimerize in the solid state, forming cavities that selectively recognize anions. If one uses resolved β-aminohydroxamic acids (which have fused 5 and 6 membered chelate rings), chiral 12-MC-4 complexes can be realized. The resultant structure with β-phenylalanine hydroxamic acid and Cu(II) is remarkably similar in size and shape to

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Cu(II) tetraphenylporphyrin. These chiral units can be linked via Cu(II) paddle wheel dimers and nitrate to form microporous layered solids. Because the of the modular synthesis strategy, grams of solid with defined chiral centers can be prepared in excellent yield.

Keywords: Chiral metallacrowns; Anion recognition agents; Porous materials

1. Introduction

Metallacrowns are among the first of a new class of molecule known as metallamacrocycles. Metallamacrocycles form cyclic structures as a consequence of key metal–heteroatom bonds that enforce a molecular architecture that can be related to previously realized organic compounds. Included in this molecular class are molecular squares [1–5] and metallacalixarenes [6,7] that resemble cyclophanes and calixarenes, respectively. Prior to the description of molecular squares and metallacalixarenes was the discovery of metallacrowns [8–10], molecules that are conceptually related to crown ethers as is illustrated in Fig. 1.

The metallacrown analogy states that macrocyclic structures containing metal ions should be obtainable by conceptually replacing the carbon atoms of a parent crown ether by a metal and a heteroatom, such as nitrogen, bound in the metal's first coordination sphere. Examining Fig. 1, the 12-MC-4 structure resembles that of 12-C-4 in that both molecules consist of 12 membered macrocycles that offer four oxygen atoms as donors to an ion that can be bound into the central cavity. Remarkably, comparison of the X-ray structures for both molecule types demonstrates that crowns and metallacrowns have similar cavity sizes despite the differences in bond lengths between C–C and C–O bonds and those of typical first row transition element M–O or M–N bonds. The difference in bond lengths is mitigated by the difference in bond angles that are typically around 109° for sp^3 carbon but

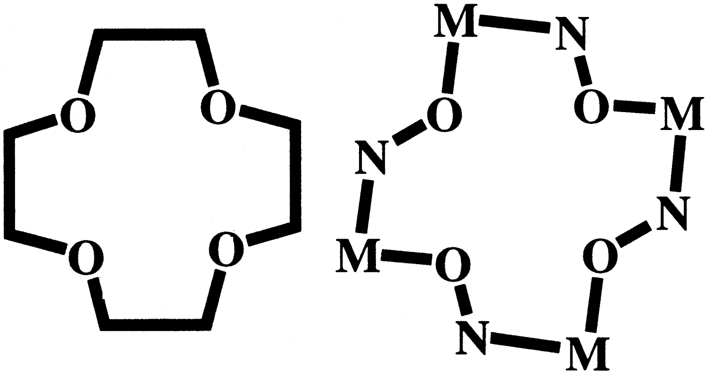
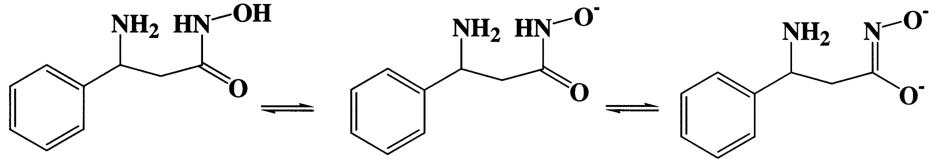


Fig. 1. Macrocyclic backbones of the organic crown ether 12-Crown-4 and the inorganic analog, 12-metallacrown-4.

only 90° for octahedral or square planar transition metal ions. Thus, crowns and metallacrowns are very suitable molecules for the complexation of ions into the central cavity. However, the metallacrowns have a much higher affinity for encapsulation of di- and trivalent ions because the oxime oxygen atoms of metallacrowns are better donors to moderate valent ions than are the neutral ether oxygen found in crowns. Recognition of the metallacrown analogy has now led to numerous examples of metallamacrocyclic structures ranging from 18-MC-6 to metallacryptates [11–18].

Another significant difference between crowns and metallacrowns is that simple structures with bridging hydroxylamine, as depicted in Fig. 1, are predicted to be very unstable, especially to hydrolysis and redox reactions. In order to make metallacrowns more robust, one must utilize functionalized hydroxylamines. Typically, we use hydroxamic acids; however, oximes, hydrazines and other functional groups have been shown to form metallacrowns. One type of metallacrown inducing ligand, β-phenylalanine hydroxamic acid (H_2β-pheHA), is shown in Fig. 2. The top row illustrates the multiple protonation states available for this ligand. It is the fully deprotonated form of the ligand that assembles into metallacrowns. The bottom row illustrates the ways that a transition ion can bind to either the 6-membered imino-amine chelate ring, the 5-membered hydroximate chelate ring or simultaneously binding to both sites as a binucleating ligand. It is this latter coordination mode that leads to metallacrowns. We can think of a 12-MC-4 as having four metals in corners of a square that are bridged by the four bifunctional hydroximate ligands. One sees the basic *–(M–N–O)–(M–N–O)–* connectivity pattern for the metallacrown in this structure. While a 12-MC-4 molecule contains four such metal-ligand units, 9-MC-3 and 15-MC-5 structures contain 3 and 5 M-L units, respectively. Molecules with one 5- and one 6-membered chelate ring orient the ring metals at approximately right angles. Thus, a ligand such as β-phenylala-

A. Protonation States



B. Metal Binding Modes

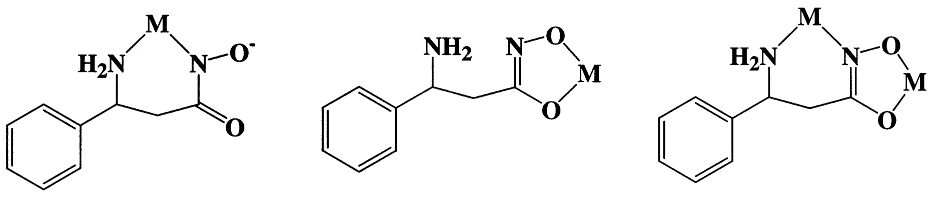


Fig. 2. Protonation states and metal binding motifs of β-phenylalaninehydroxamic acid.

nine hydroxamic acid generates with Cu(II) a flat 12-MC-4 metallamacrocycle that is formally neutral. The final charge of the structure will depend on the metal captured in the core and the anions that can bind to either the ring or core metal. While selective cation binding has received considerable attention for many years, the field of selective anion binding and recognition has not been explored as extensively [19–22] and offers some interesting opportunities in metallacrown research.

An example of the 12-MC-4 formed by β-phenylalanine hydroxamic acid and Cu(II) is shown in Fig. 3 [23]. Because metallacrowns are complex, we have adapted a nomenclature to describe simply the relevant features of the molecules. The chemical formula for **1**, neglecting bound solvents, is $Cu(II)_5(\beta\text{-pheHA})_4SO_4$. The abbreviation we use for this and all other metallacrown structures is given as $M'A[RS\text{-}MC_{M(ox)N(ligand)}\text{–}NO]$ where, within the brackets, RS is the total size of the macrocyclic ring, NO gives the total number of donor O atoms, MC designates that these are metallacrowns with a subscript that specifies the type and oxidation state of the ring metal {M(ox)}, the second bridging heteroatom (N), and the ligand that supports the metallacrown (ligand). The M′ and A outside of the brackets designate the captured metal and coordinated anions, respectively. In this example, **1** is given as $Cu(II)SO_4[12\text{-}MC_{Cu(II)N(S\text{-}\beta\text{-pheHA})}\text{-}4]$.

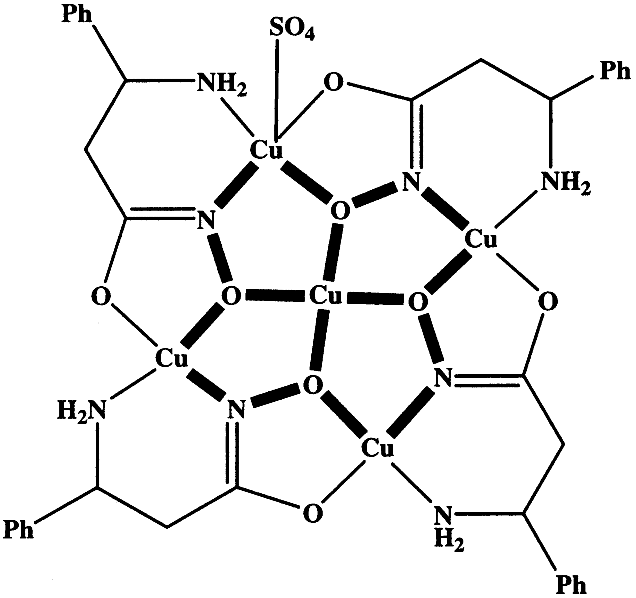


Fig. 3. Stick diagram of $Cu^{II}(SO_4)[12\text{-}MC_{Cu(II)N(\beta\text{-pheHA})}\text{-}4]$

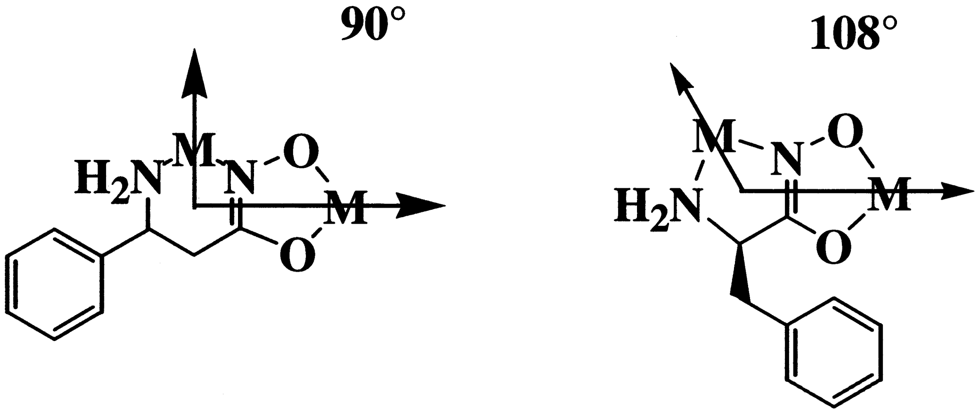


Fig. 4. Comparison of the binding geometries between the fused 6-membered/5-membered chelate rings of β-phenylalaninehydroximate and the fused 5-membered/5-membered chelate rings of α-phenylalanine-hydroximate.

2. Anion binding to chiral 15-metallacrown-5

Whereas, 12-MC-4 structures are prepared with ligands that have combined 5- and 6-membered chelate rings, planar 15-MC-5 structures can be achieved using hydroximate ligands containing two 5-membered chelate rings. This concept is illustrated in Fig. 4 in the comparison between β-phenylalanine hydroxamic and α-phenylalaninehydroximate (pheHA^2). By bisecting the chelate rings of β-pheHA^2 we see that the two metals are at ca. 90° as described above. In contrast, bisecting the pheHA^2 chelate rings illustrates that the metals form a more obtuse angle (ca. 108°). The wider angle requires that a planar metallacrown expands to a 15 membered ring. Thus, as one sees with **2**, Nd(III)[15-MC$_{Cu(II)N(alaHA)}$-5]$^{3+}$, shown in Fig. 5, a beautiful metallamacrocycle that complexes neodymium(III) can be obtained [24].

Early metallacrowns were prepared using achiral ligands such as salicylhydroxamic acid (H_3shi) and 2-picolinehydroxamic acid (H_2picHA) [8–10,25–28]. While these molecules did not contain organic ligands having chiral centers, the resultant metallacrowns could still be considered to have orientational isomers since the connectivity around the ring was directional (i.e. always $M \rightarrow N \rightarrow O \rightarrow M$). Thus, clockwise or anti-clockwise isomers were possible. The ability to incorporate chirality into the ligands ensures that the obtained metallacrown must have this rotational isomerism since the two faces of the metallacrown must be different. This concept is illustrated in Fig. 6. A consequence of this orientational symmetry is that by synthesizing a metallacrown with resolved α-aminohydroxamic acid, one should be able to obtain amphiphilic (face differentiated) metallacrowns. This is because each R group of the amino acid is required to extend from the macrocycle in the same direction. Examination of the side view of 2 in Fig. 5 emphasizes this point as each methyl group from the alaHA ligands is positioned towards the same face of

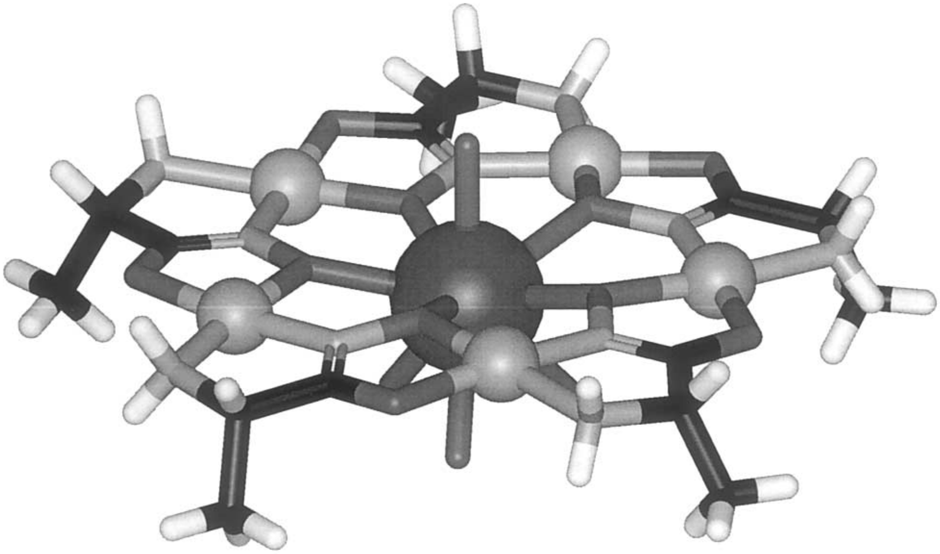


Fig. 5. Diagram of the planar $(\mathrm{Nd}[15\text{-}\mathrm{MC}_{\mathrm{Cu(II)N(alaHA)}}\text{-}5])^{3+}$ synthesized with an α-aminohydroxamic acid ligand.

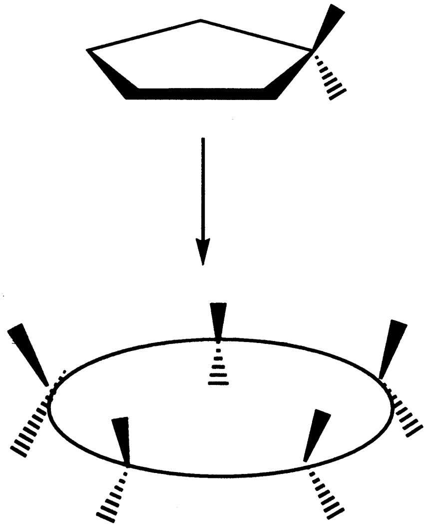


Fig. 6. Illustration of the facial differentiation which occurs when resolved α-aminohydroxamic acid ligands are used in 15-MC-5 syntheses.

the metallacrown. This suggests that a judicious choice of R group could lead to the formation of chiral cavities on one face of the metallacrown.

2.1. Differential binding of chloride and nitrate to $\{Gd(III)[15\text{-}MC_{Cu(II)N(tyrHA)}\text{-}5]\}_2^{6+}$

Facial differentiation in the 15-metallacrown-5 framework is realized upon the reaction of 5 equivalents of Cu(II) chloride, 5 equivalents of tyrosine hydroxamic acid (H_2tyrHA), 1 equivalent of Gd(III) chloride and 15 equivalents of pyridine in aqueous solution [29]. In ca. 85% yield, one may obtain the chloride salt of **3**·2Cl, $\{Gd(III)Cl[15\text{-}MC_{Cu(II)N(tyrHA)}\text{-}5]\}_2^{4+}$, which is illustrated in Fig. 7(A). This molecule is a dimer of metallacrowns. The two macrocycles are held together by weak intermolecular phenol oxygen to ring Cu(II) bonds that form across the hydrophobic faces of the two metallacrowns. The result is a cylindrical cavity with an 8.5 Å axis and an approximate radius of 6 Å. When corrected for the van der Waal radii of the metallacrown atoms, this suggests a cavity volume of over 700 $Å^3$. Each dimer represented by **3** is linked to another dimer through chloride bridges between the hydrophobic faces of the metallacrowns. If the same synthesis is carried out with nitrate salts rather than chloride salts, a closely related structure **3**·$2NO_3$, $\{Gd(III)NO_3[15\text{-}MC_{Cu(II)N(tyrHA)}\text{-}5]\}_2^{4+}$, shown in Fig. 7(B) is obtained. The essence of the metallacrown dimer is the same; however, there are important differences with respect to the anion binding. The two coordinated nitrates in **3**·$2NO_3$ perfectly fit into the cavity of the metallacrown. The two nitrate ions bridge copper atoms on either metallacrown across the hydrophobic faces without disturbing the bridging tyrosine interactions. Thus, the two metallacrowns are held in a perfect orientation to sequester nitrate. It should be recognized that the presence of competing anions such as chloride or acetate does not block the complexation of the nitrate into this cavity. As shown in Fig. 7(C) by **3**·2Cl·$2NO_3$, nitrate and chloride anions coexist on the metallacrown with little structural impact to each other or the bridging tyrosines. This simple example demonstrates how metallacrowns can be expanded into true supramolecular structures. While providing an excellent fit for nitrate, it is unlikely that larger, more complex molecules will easily fit within **3**. Therefore, we have been exploring ways to expand the chiral cavities of metallacrowns.

2.2. Differential binding of nitrate to $\{Gd(III)[15\text{-}MC_{Cu(II)N(pheHA)}\text{-}5]\}_2^{6+}$

A larger but less rigid metallacrown cavity can be achieved by using H_2pheHA. Because phenylalanine lacks the *p*-hydroxy substitution of tyrosine, the appended R groups can not serve as bridges between the metallacrowns. None-the-less, hydrophobic cavities can be obtained as illustrated in Fig. 8 with **4**·$2NO_3$, of $\{Gd(NO_3)[15\text{-}MC_{Cu(II)N(L\text{-}pheHA)}\text{-}5]\}_2^{4+}$ [30]. Compound **4** is similar to **3** in that the amino acid R groups extend toward the same side of the metallacrown generating hydrophilic and hydrophobic faces; however, the orientation of phenyl/hydroxyphenyl groups is distinctly different. In **3**, two of the ten phenol groups tuck into the hydrophobic cavity to act as bridging ligands between metallacrowns while the

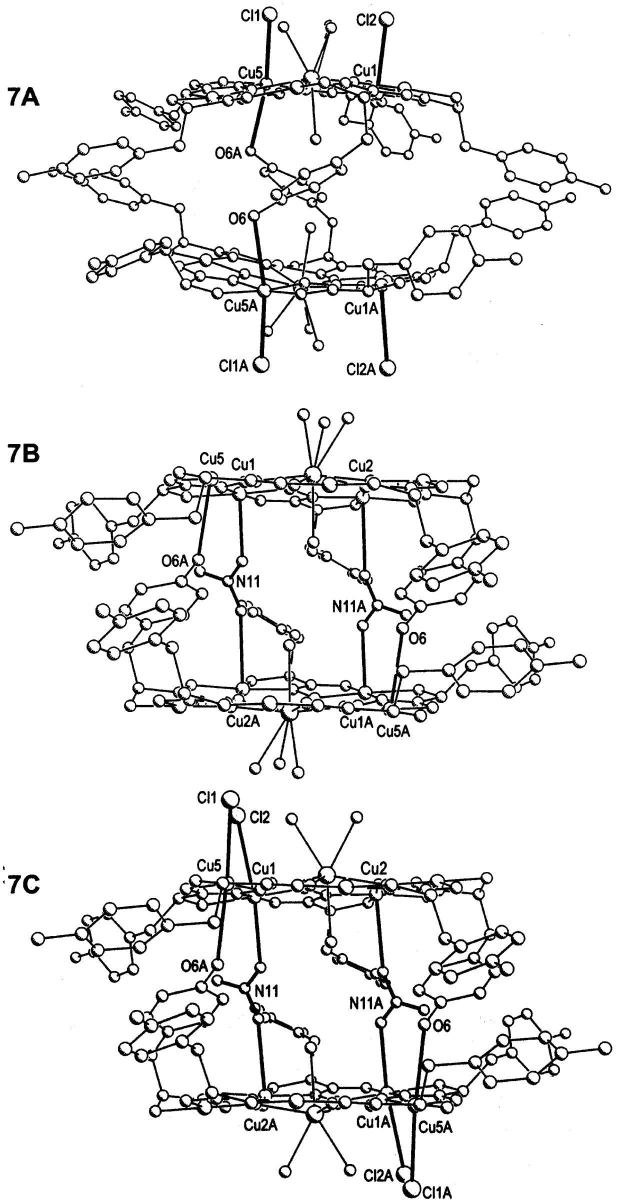


Fig. 7. Differential anion binding to $(\mathrm{Gd}[15\text{-}\mathrm{MC}_{\mathrm{Cu(II)N(tyrHA)}}\text{-}5])^{3+}$: (A) Chloride binding to the external ('hydrophilic') face of the metallacrown dimer in the absence of nitrate; (B) Nitrate binding to the internal ('hydrophobic') face of the metallacrown dimer in the absence of chloride; (C) Simultaneous, differential binding in the presence of both anions.

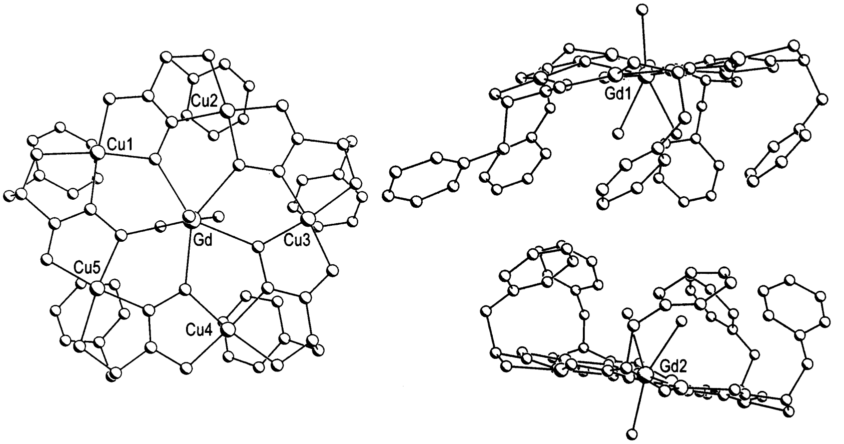


Fig. 8. Dimer formed by hydrophobic interaction between face-differentiated 15-MC-5s composed of copper(II), gadolinium(III) and α-phenylalaninehydroximate with nitrate bound in the hydrophobic cavity.

remaining eight phenols are solvent exposed forming hydrogen bonds to water through the aromatic hydroxyl group. In contrast, **4** has all ten phenyl group excluded from water. The result is that **4** has a larger cavity since the phenyl groups push the two metallacrowns apart (the cylindrical axis is ca. 11.5 Å). Furthermore, the interior of the cavity beomes much more hydrophobic. Once again, nitrate ions are captured in the cavity; however, the coordination mode is again very different than in **3**. Because the metallacrowns are no longer close enough for the anion to span the distance between the two hydrophobic faces, the nitrate group instead binds to the encapsulated gadolinium(III). Thus, we see that vastly different coordination motifs for nitrate can be obtained by simply varying the composition of the cavity.

Because **4** has a much larger cavity than **3**, we have been exploring the relative affinities of different anions for the hydrophobic interior versus the hydrophilic exterior faces of **4**. While these studies are still in progress, it appears that aliphatic carboxylates tend to bind primarily to the exterior, hydrophilic face, while carboxylates that contain unsaturation or aromatic rings bind to both the interior and exterior faces of the metallacrown. Since these metallacrowns will bind anions as large as terepthalate or pimelate, we believe that **4** represents a fertile system to begin exploring selective binding of chiral molecules such as amino acids. It should be noted that both **3** and **4** can be prepared in very high yield from commercially resolved starting materials. This is an advantage that is not shared by many other large, chiral molecules that possess preorganized cavities.

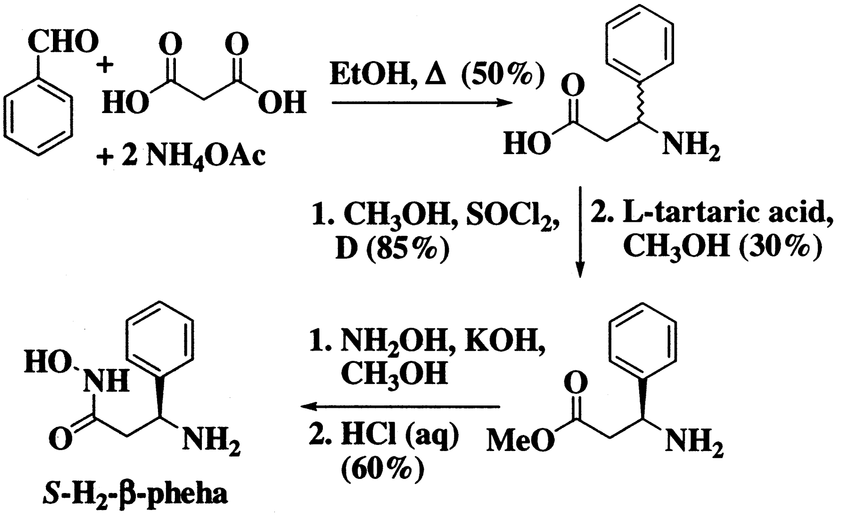


Fig. 9. Synthesis and resolution of β-phenylalaninehydroxamic acid.

3. Generation of extended structures with chiral 12-metallacrown-4

Chiral 12-MC-4 macrocycles can also be prepared using a strategy that employs aminohydroxamic acids. However, to prepare the 12-MC-4 structure type, one must use ligands that have 5- and 6-membered chelate rings. This means that the conventional α-amino acids will not be useful as precursors to the 12-MC-4 complexes. None-the-less, one can expend the synthetic investment to obtain resolved β-amino hydroxamic acids that can lead to the desired metallacrowns. Two synthetic strategies to obtain such ligands are given in Figs. 9 and 10. The first approach allows for the isolation of large quantities of resolved β-phenylalaninehydroxamic acids but suffers from a lack of functional group generality [31,32]. The second strategy allows reliable access to a broad range of α-substituted and α,β-disubstituted β-aminohydroxamic acids; however, the multistep sequence proceeding through the chiral pyrimidinone is more challenging and time consuming [33].

The reaction of Cu(II) sulfate with β-phenylalanine hydroxamic acid gives in good yield the 12-MC-4 structure **1** that was presented in Fig. 3. The obvious consequence of shifting from an α- to a β-aminohydroxamic acid is that one shifts from the 15-MC-5 structure type to that of the 12-MC-4. However, there is an equally important but more subtle change in structure that one observes by changing the chelate ring size. Whereas the aromatic side chains are oriented downward in 15-MC-5, the corresponding 12-MC-4 exhibits a radial distribution of phenyl groups. The different orientation is a direct consequence of the increased flexibility of the 6-membered chelate rings in the β-aminohydroxamic acids. The imino-amine chelate ring may adopt either of two conformations that will allow the sterically demanding phenyl group to be placed in a pseudoequatorial position. This

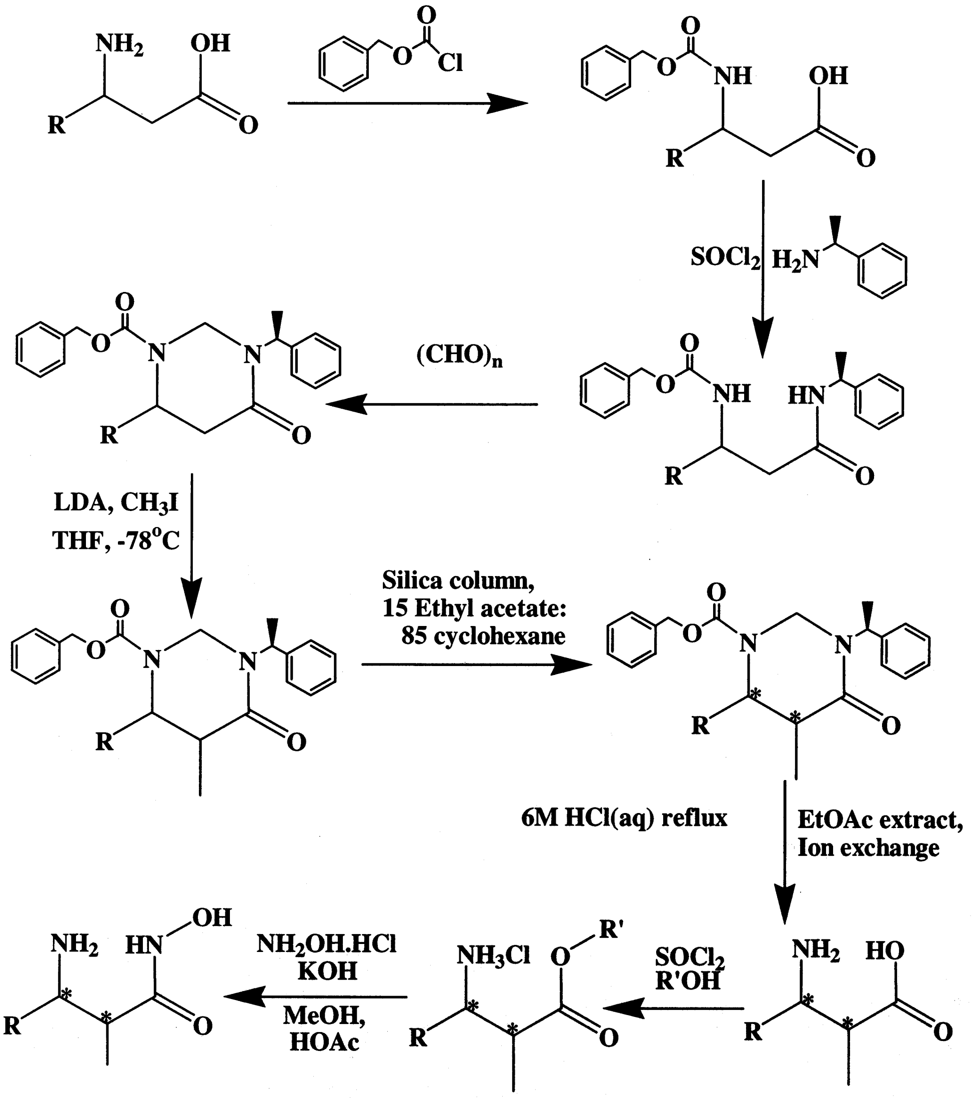


Fig. 10. Synthesis and resolution of α-substituted β-aminohydroxamic acids.

allows the phenyl group to point almost directly perpendicular to the metallacrown face. The analogous 5-membered chelate ring for the α-aminohydroxamic acids does not have this conformational freedom; therefore, the phenyl groups are forced to one face of the metallacrown.

The resultant structure for **1** is reminiscient of another common macrocyclic class, metalloporphyrins. While the electronic structure of metallacrowns and porphyrins are markedly different, the size and shape of the two molecules are quite similar. Thus, one might envision substitution of chiral metallacrowns into applications where porphyrinic molecules have already been investigated. These applications would include generating thin films of metallacrowns, preparing chiral liquid crystals and building micro- or mesoporous solids through extended networks [34]. It is the latter of these possibilities that we will discuss next.

3.1. Assembly of 12-metallacrown-4 units via facial interactions and anion bridging

In order to generate interesting solids through a modular strategy, one must be able to control the assembly of the components. In our case, this means that we must be able to controllably link metallacrowns in one, two and three dimensions. The simplest way to link metallacrowns is across the faces. This can be achieved either by direct dimerization of two metallacrowns using the oxime oxygens of one metallacrown to bind in axial positions to the metals of a second metallacrown (Fig. 11) or by using anions to bridge two metallacrowns as shown in Fig. 12. The fused metallacrown structure **5**, Cu(II)[12-$MC_{Cu(II)N(\beta\text{-alaHA})}$-4]$^{2+}$, shown in Fig. 11 has been observed for Cu(II) metallacrowns [16]. The multiple linkages between metallacrowns leads to a relatively stable dimer; however, this structure type has the disadvantage of leading to strong antiferromagnetic spin exchange and, ultimately, diamagnetic metallacrown dimers. Because we would like to exploit the paramagnetism of metallacrowns, a more convenient strategy is to assemble columns by anions that are not efficient at magnetic exchange coupling. This allows us to assemble a group of paramagnetic molecules in close proximity with weak through-bond couplings. Such an assembled system may be useful for generating soft magnetic materials.

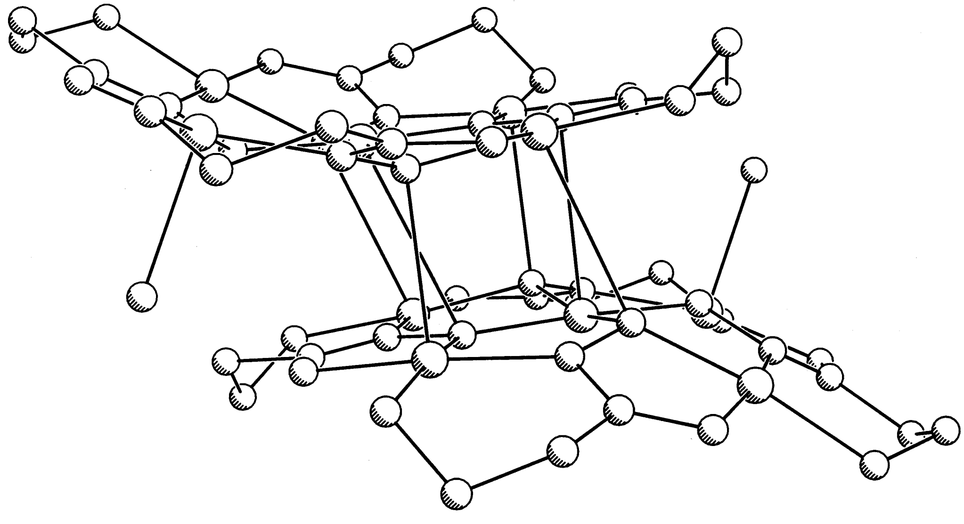


Fig. 11. Dimerization of (Cu^{II}[12-$MC_{Cu(II)N(\beta\text{-alaHA})}$-4])$^{2+}$ via axial interactions between copper and neighboring metallacrown heteroatoms.

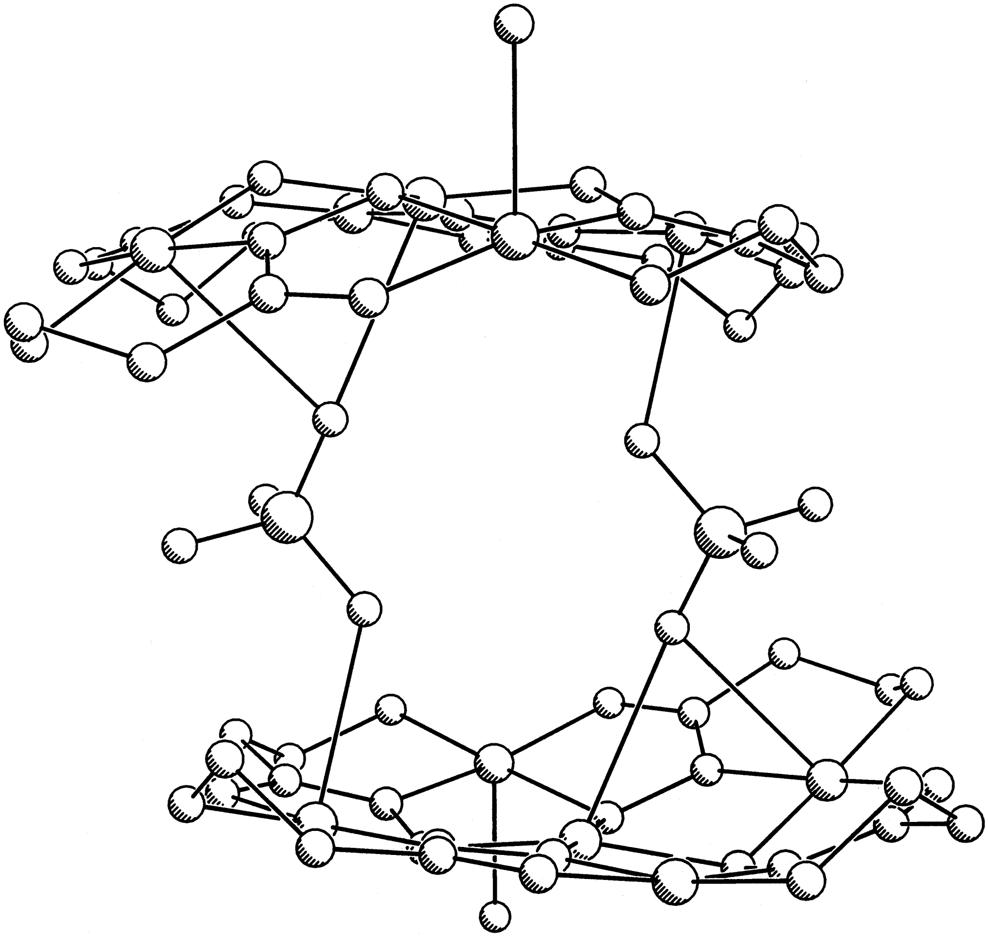


Fig. 12. Perchlorate anions bridging $(\mathrm{Cu^{II}}[12\text{-}\mathrm{MC_{Cu(II)N(\beta\text{-}alaHA)}}\text{-}4])^{2+}$.

In general, anion bridges represent a versatile method for strongly linking metallacrowns without fostering strong through-bond magnetic exchange interactions between the metallamacrocycles. The **5**·$2ClO_4$, shown in Fig. 12, using perchlorate as a bridge between metallacrowns was reported in the early 1990s [16]. Similar bridging motifs have now been described with other anions such as acetate, nitrate and sulfate. The common structural motif is that columnar structures can be generated in this way. By using anions of different charge, we can control whether we prepare neutral or ionic columns. An example of the nearly hexagonal packing of metallacrown columns is given in Fig. 13. We are exploring methods to increase the steric bulk of the appended side chains in order to convert such column solids into chiral liquid crystalline arrays. Once again, analogy for such transformations have been described in the porphyrin literature.

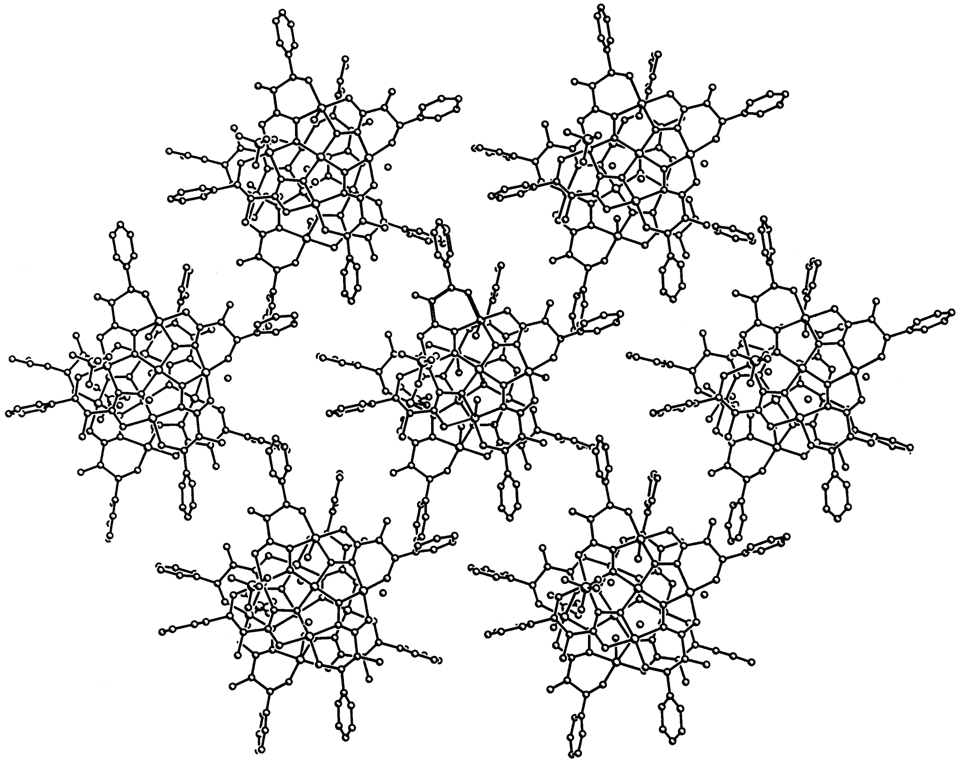


Fig. 13. Approximate hexagonal packing of 12-MC-4 columns.

3.2. Assembly of 12-metallacrown-4 units via peripheral functionalization and metal coordination

Anion bridges across the face of metallacrowns provide a mechanism for generating one dimensional solids; however, in many cases we are interested in two or three dimensional connectivities. To achieve this goal we must be able to couple metallacrowns at ca. 90° angles to the molecular four fold axis. One method would be to functionalize the phenyl groups (e.g. making this a pyridyl moiety) and then linking the metallacrowns with an appropriate metal ion. Possible structure types are shown in Fig. 14. Metals such as Ag(I) that prefer linear coordination would allow the metallacrown to achieve a more open framework (Fig. 14(a)) whereas metals that prefer square planar coordination (e.g. Cu(II), Pd(II) or Pt(II)) might provide the more compact structure shown as in Fig. 14b. These networks are again directly related to well known solids that have been reported for porphyrin mesoporous systems [34].

An alternative strategy for linking metallacrowns perpendicular to the four fold molecular axis is to build connections from the peripheral heteroatoms that bind to the ring metals. Two examples of metal binding to oxygens are shown in Fig. 15.

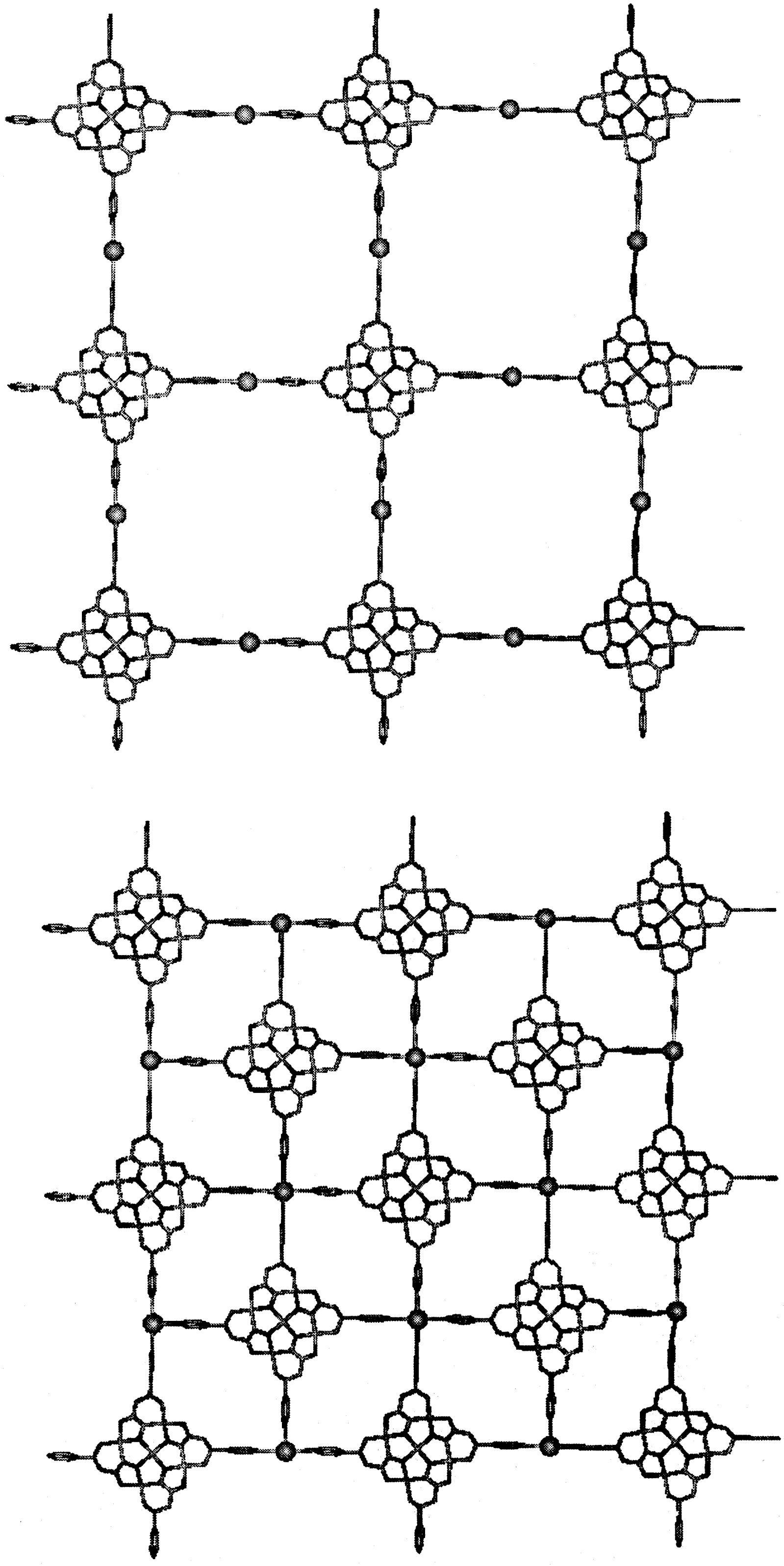


Fig. 14. Possible 2-dimensional networks consisting of pyridine-substituted 12-MC-4s linked by 2-coordinate (linear) or 4-coordinate (square planar) metals.

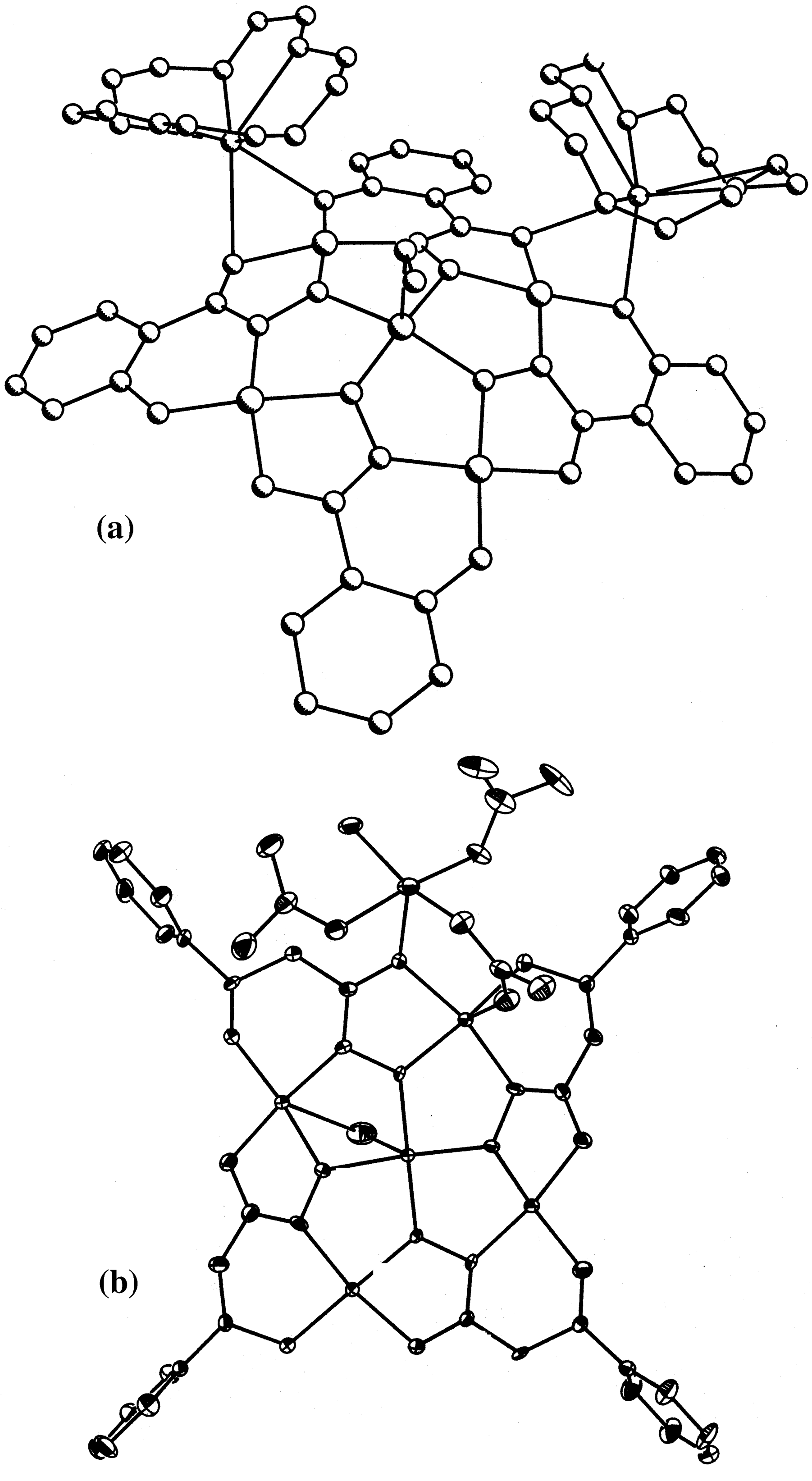


Fig. 15. Coordination of metal ions to the metallacrown periphery. Na(15-C-5) appended to $(\mathrm{Cu^{II}}[12\text{-}\mathrm{MC_{Cu(II)N(shi)}}\text{-}4])^{2-}$ (a) and $\mathrm{Cu^{II}(OAc)_2}$ appended to $(\mathrm{Cu^{II}(OAc)}[12\text{-}\mathrm{MC_{Cu(II)N(S\text{-}\beta\text{-}pheHA)}}\text{-}4])(\mathrm{Cl})$ (b).

The first example uses the achiral ligand salicylhydroxamic acid, H_3shi. The basic 12-MC-4 structure of **6**·Na(15-C-5), Cu(II)[12-$MC_{Cu(II)N(shi)}$-4]$^{2-}$, is identical to what has been previously commented upon; however, since the shi^{3-} ligand is a trianion, the metallacrown forms a dianion when Cu(II) is bound in the core, not a cation as was observed for **1**. As shown in Fig. 15(a), the extra negative charge allows a sodium counter cation that is bound to 15-C-5 to coordinate to the phenolate and carbonyl oxygen atoms of the shi^{3-} [35]. This suggested that metal ions might be directly appended from the metallacrown itself. One might reason that a phenolate oxygen atom would be a better donor to a second metal than a neutral amine nitrogen atom. Thus, by switching from H_3shi to H_2β-pheHA one should be able to switch from bidentate complexation of a peripheral cation to a monodentate coordination mode. This expectation is realized by the example shown in Fig. 15(b). Compound **7**, Cu(II)$(OAc)_2${Cu(II)(OAc)(CL)[12-$MC_{Cu(II)N(S\text{-}\beta\text{-}pheHA)}$-4]}, contains the familiar **1** as the basic metallacrown; however, appended to the carbonyl oxygen atom of one site is an additional Cu(II) ion [23]. The metal is stabilized by acetate anions that bridge from the peripheral Cu(II) to the ring metal. Both **6** and **7** illustrate that peripheral modification of a metallacrown onto atoms that stabilize the ring metal coordination does not appear to significantly destabilize the metallamacrocycle. Thus, in principle, peripheral metal binding represents an alternative strategy to generate extended solids; however, to be viable one must be able to link two metallacrowns in this manner.

While we have not yet observed the bridging of two metallacrowns with a single metal atom across carbonyl oxygen atoms, chains of metallacrowns can be isolated by using dinuclear units. Complex **8**, shown in Fig. 16, is an example of a one dimensional chain that forms between Cu(II)[12-$MC_{Cu(II)N(S\text{-}\beta\text{-}pheHA)}$-4] and $Cu(II)_2(Benzoate)_4$, a member of the well known class of 'paddlewheel' dimers [36]. Each copper of the paddlewheel dimer binds, in an axial position, to a carbonyl oxygen atom of a metallacrown (Cu–O: 2.24 Å). This leads to a series of undulating chains progressing through the solid. Each chain is separated by ca. 7.5 Å. As we will discuss in more detail below, the large number of phenyl groups in this structure leads to an interesting layering in the solid.

Armed with the recognition that metallacrowns can be linked from face to face by anions and side to side by paddlewheel dimers, one can now suggest a modular strategy for the preparation of two dimensional, chiral solids. By including nitrate in the synthesis of **8**, one can prepare compound **9** which is illustrated in Fig. 17(A). A stoichiometrically identical repeat unit $[(12\text{-MC-}4)(\text{paddlewheel})]_n$ is observed; however, the nitrate anions now serve as a guest in the lattice forming a bridge between two metallacrowns of adjacent chains [36]. While the chains move slightly closer together (7.3 Å), the essential features of **8** are retained. Thus, one can use a small anion to stitch together the solid to make a chiral layered compound. 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. The side-to-side metallacrown separation is 7.13 Å, with symmetrical Cu_{dimer}–O distances (2.24 Å). The two chain directors (face-to-face and edge-to-edge) are oriented at 98.2°. A CPK model of this 2-dimensional material shows that the plane

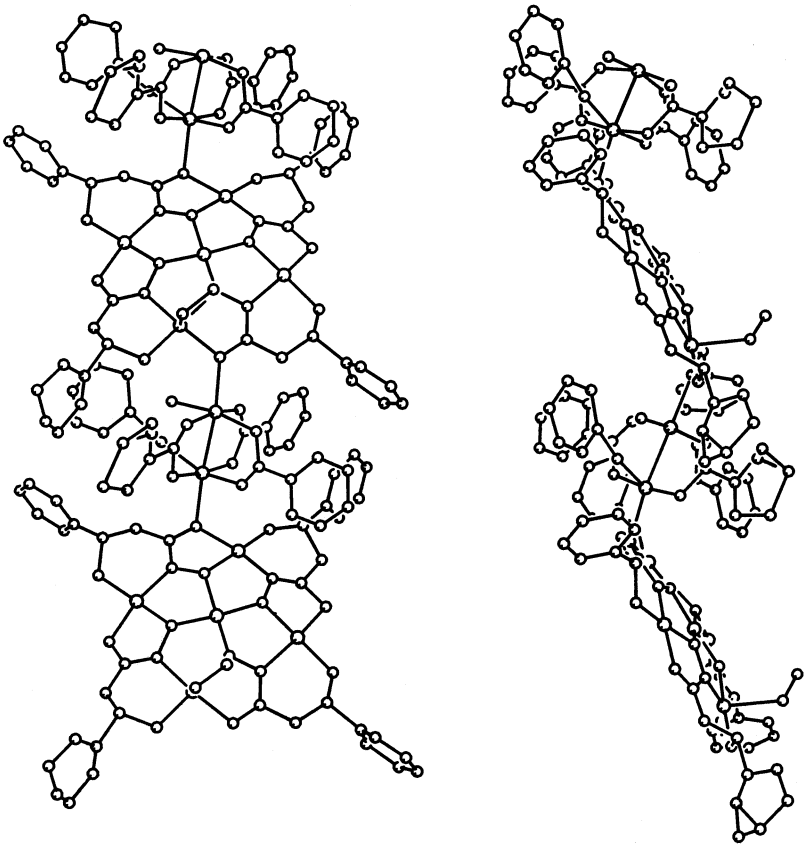


Fig. 16. Chains formed by bridging copper benzoate interactions in {Cu_2(benzoate)$_4$}:{Cu[12-$MC_{Cu(II)N(\beta\text{-pheHA})}$-4]}.

formed by the 12-MC-4, paddlewheel dimer and nitrate is very well packed (Fig. 17(B)). The subjacent layer of metallacrown/copper benzoates is 16.32 Å ($Cu_{central}$–$Cu_{central}$) below the one that is shown.

As shown in Fig. 18, a rotation of 90° reveals microporous channels that permeate the structure. The channels are slightly elliptical with dimensions 8 × 9 Å. The top and bottom of the channels are hydrophobic being lined by the phenyl groups of the benzoates and the β-pheHA of the metallacrown. The latter is a chiral molecule, so the channels have a handedness. We have collected X-ray data on both R and S isomers of Cu(II)(NO_3)[12-$MC_{Cu(II)N(\beta\text{-pheHA})}$-4] and we observe that channels which are mirror images are formed. The sides of the channels expose one face of the metallacrowns from the layer. Thus, the chiral pores in this solid have a region of hydrophobicity at top and bottom and a region of hydrophilicity/Lewis Acidity along the sides.

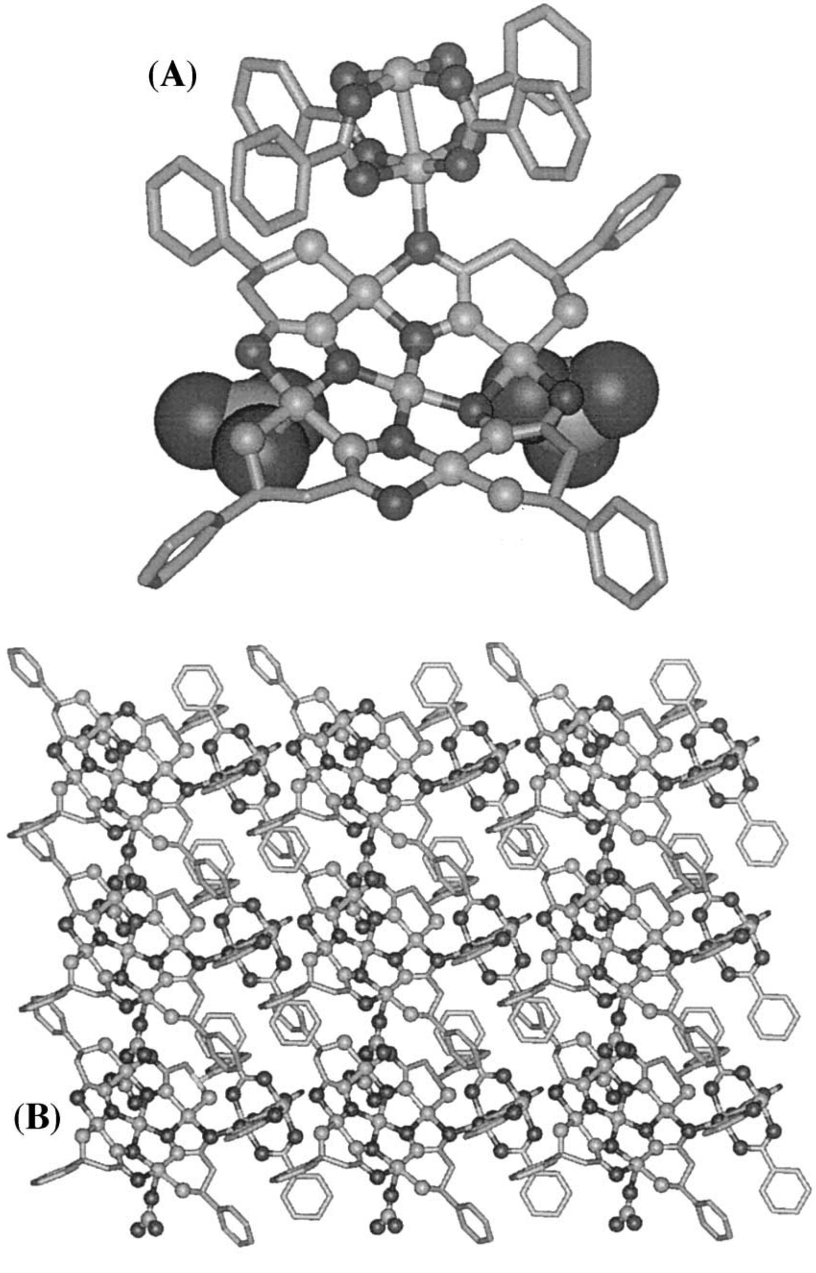


Fig. 17. (A) Unique monomeric unit of the 2-dimensional network solid {Cu_2(benzoate)$_4$}: {$Cu(NO_3)_2$[12-$MC_{Cu(II)N(\beta\text{-pheHA})}$-4]}. All heteroatoms and metals are shown as balls, with the nitrates as CPK spheres; (B) Sheet formed by bridging nitrate and copper benzoate dimer interactions.

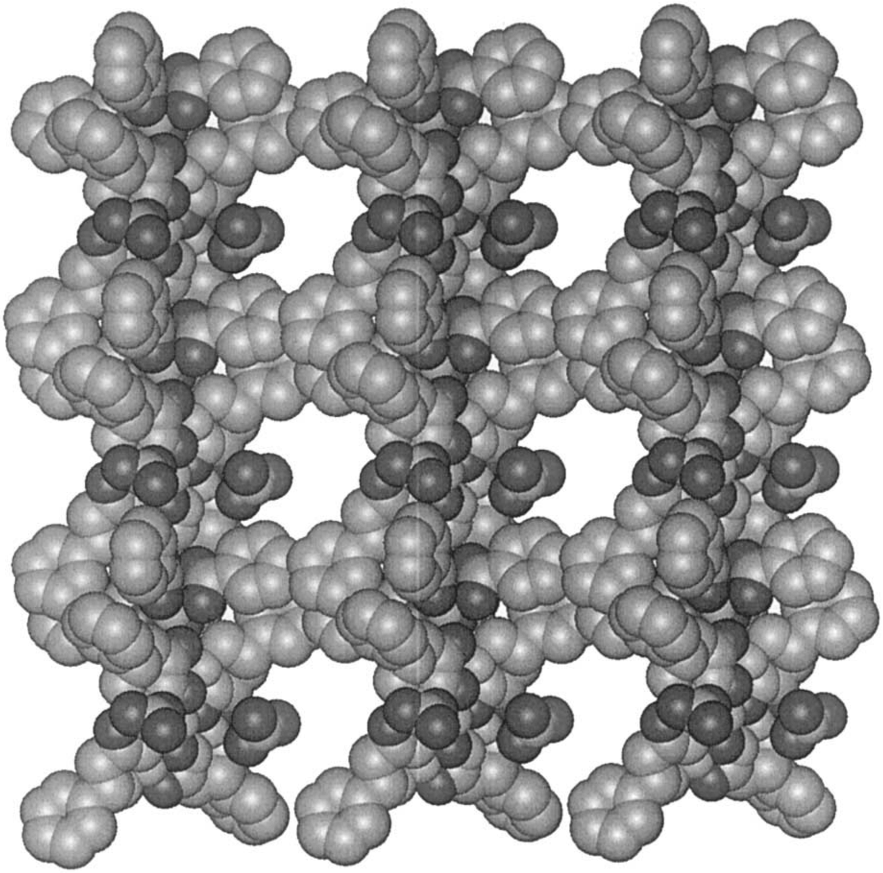


Fig. 18. Packing of $\{Cu_2(benzoate)_4\}$:$\{Cu(NO_3)_2[12\text{-}MC_{Cu(II)N(\beta\text{-}pheHA)}\text{-}4]\}$ network layers as viewed edge-on showing the channels which run through the solid.

As shown in Fig. 19, the channels are filled by solvents (methanol and water) and a benzoic acid guest molecule. In addition, a second nitrate ion is bound to the channel exposed face of the metallacrown. The included benzoic acid illustrates the major recognition elements possessed by the structure. The carboxylic acid residue forms a strong hydrogen bond to the amine nitrogen atom of the metallacrown. A second hydrogen bond is formed between the carboxylic acid and a water that is coordinated to a ring copper atom. Finally, a third longer interaction between the carboxylic oxygen and the cavity bound nitrate is observed. These three H-bond/electrostatic interactions lock the benzoic acid into the structure. At the other end of the benzoic acid molecule, the phenyl group is buried in the top of the channel and surrounded by five phenyl groups from the metallacrown and the copper benzoate dimer. The phenyl proton of the benzoic acid points directly toward the center of a metallacrown phenyl group forming a strong quadrupolar interaction. A second metallacrown-derived phenyl group points its para-proton toward the

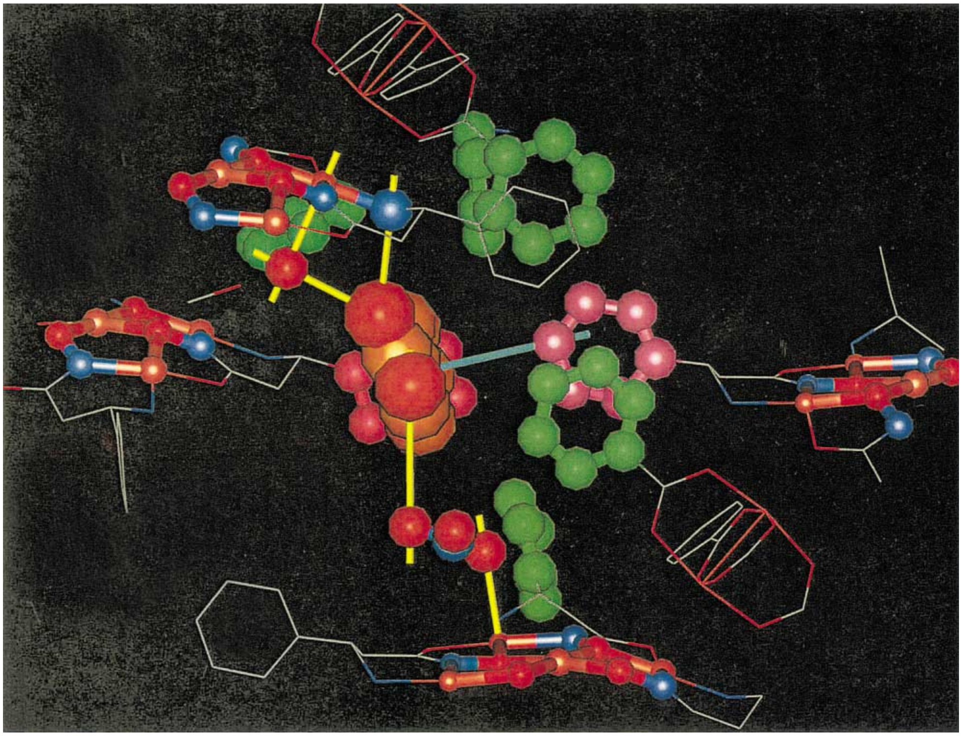


Fig. 19. Interaction of the benzoic acid (bronze/red CPK) with the channel of $\{\mathrm{Cu_2(benzoate)_4}\}:\{\mathrm{Cu(NO_3)_2}[12\text{-}\mathrm{MC}_{\mathrm{Cu(II)N(\beta\text{-}pheHA)}}\text{-}4]\}$. Yellow lines indicate important hydrogen bonding interactions and the blue line represents an orthogonal phenyl interaction between the benzoic acid guest and a ligand phenyl group. The phenyl group of the benzoic acid guest interacts with a second ligand phenyl group into the plane of the page.

interior of the benzoic acid phenyl group. The remaining phenyl groups of the cavity provide a barrier to solvent exposure. A rule of thumb for the recognition of chiral molecules is that one wants to design a material that will have multiple (at least three) contacts to distinguish molecular mixtures. This example illustrates that within this chiral channel multiple interactions between the host and guest can be achieved.

Because of the ease of metallacrown synthesis, the structure above suggests a general modular strategy for the production of chiral solids. One can envision mixing a chiral metallacrown (with various modifications such as metal substitution or embellishment of the ligand) with a preformed paddlewheel dimer (again a molecule that can vary ligand or metal) and a simple anion to achieve in high yields solids that are handed. Thus, one has the potential to create chiral solids via a combinatorial synthetic approach. The beauty of this strategy 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. Alterna-

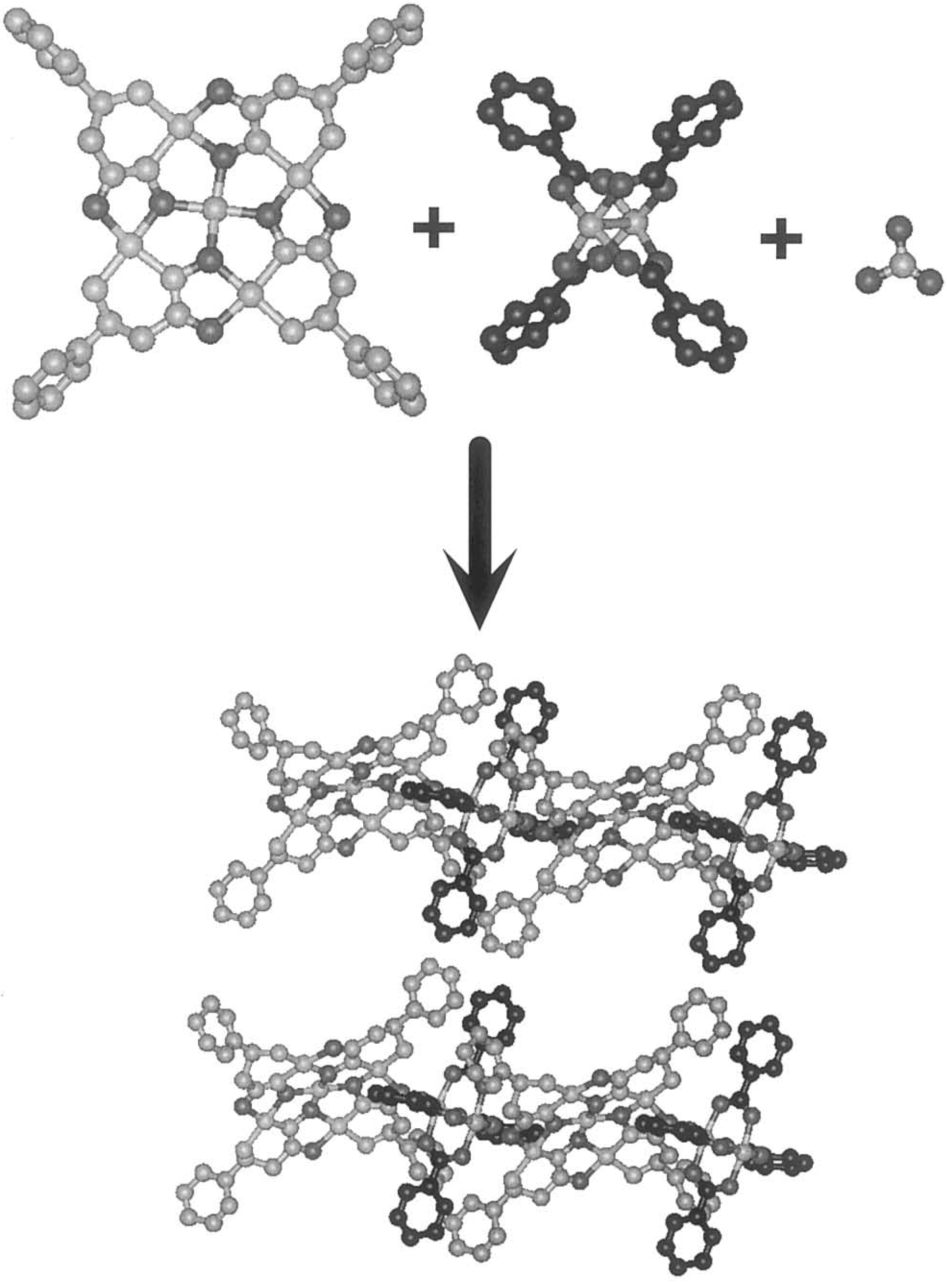


Fig. 20. Modular synthesis of $\{Cu_2(benzoate)_4\}:\{Cu(NO_3)_2[12\text{-}MC_{Cu(II)N(\beta\text{-}pheHA)}\text{-}4]\}$.

tively, truly chiral crystals can be obtained; however, since both enantiomorphs can be formed, there are an equal number of crystals of both hands resulting in a bulk material that, unless physically separated, is also achiral. Because, metallacrowns can be made chiral prior to the formation of the solid, incorporation of this chirality into the framework becomes trivial Fig. 20.

4. Conclusion

In summary, we have shown that chiral metallacrowns can easily be prepared using either α- or β-aminohydroxamic acids. While the physical properties of these molecules have not been discussed here in detail, previous reports have shown that metallacrowns can be strongly colored, highly magnetic and electroactive. The 15-MC-5 and 12-MC-4 species described herein can be used to generate amphiphilic molecules capable of binding substrates into cavities. With 15-MC-5 complexes, these are molecular species that are soluble and stable in water. The related 12-MC-4 complexes can be woven into chiral solids which also demonstrate substrate recognition. Future studies with these and other metallacrowns will explore the generality of these molecules for the application of anion recognition and chiral molecule separation.

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