Synthesis and Structure of Helical Supramolecular Arrays

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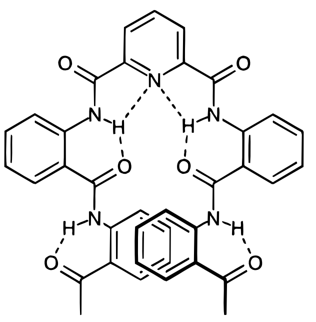
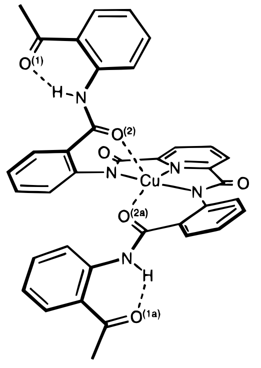
The design and synthesis of molecules that can organize into specific supramolecular assemblies in the solid state is an area of considerable interest,[1] since incorporation of well-ordered structural components into a crystal lattice may lead to new materials with desirable chemical and physical properties. However, it is still difficult to reliably predict crystal structures because individual molecules within a lattice may adopt several different, nearly degenerate, conformations depending on the specific conditions under which the crystals are grown. To develop species whose assembly is more controlled and predictable, we are investigating the formation of supramolecular assemblies with low molecular weight monometallic helical complexes.[2] We are particularly interested in using the intrinsic chirality of helical complexes to form chiral solid state supramolecular assemblies.[3,4] In this communication we report a rare example of spontaneous resolution of metallohelical complexes within individual single crystals.[5] This resolution is driven by multiple edge-to-face intermolecular aromatic interactions to form chiral supramolecular arrays.

We have reported that metal complexes of the multidentate ligand 2,6-bis[[2-[(2-acetylphenyl)carbamoyl]phenyl]carbamoyl]pyridine (H_2**1**)[6] are helical and therefore serve as appropriate starting materials.[2] The structure of the five-coordinate Cu**1** complex shows that coordination to the Cu(II) center is provided by three nitrogen donors from the pyridyl−diamidate chelate and two inner amide oxygens [O(2), O(2a)] of the appended aryl groups. The Cu−O_{amide} interactions are significant in determining the helical morphology; the unsymmetrical helix in Cu**1** results from different Cu−O_{amide} bond distances [Cu−O(2a), 1.931(4) Å; Cu−O(2), 2.315(4) Å]. Cu**1**, which crystallizes in the centrosymmetric space group $P\bar{1}$, exists as a racemic mixture of right- and left-handed helices in the solid state, as do all metallohelices of $\mathbf{1}^{2-}$ studied previously.[2,7]



H_2**1**



Cu**1**

These studies on Cu**1** suggested that modifications in helicity can occur by breaking either one or both of the structurally important Cu−O_{amide} bonds. Since these bonds are relatively weak, the O_{amide} donors should be readily substituted by more basic exogenous ligands. Substitution can indeed happen when Cu**1** is treated with pyridine ligands. Dissolving Cu**1** in neat pyridine changes the spectroscopic properties of the complex, indicating that the coordination environment about the Cu(II) center has been altered.[8a] These spectroscopic changes include (1) a red shift of the dd band in the electronic absorption spectrum from 624 nm for Cu**1** in CH_2Cl_2 to 598 when measured in pyridine and (2) shifts in the EPR parameters $g_{\perp}$ (2.00 to 2.06) and $A_{\|}$ (180 to 200 G). Similar spectroscopic changes are observed when Cu**1** is dissolved in 3,5-lutidine.[8b]

An X-ray diffraction study on Cu**1**(py) confirms that binding of a single pyridine to copper causes a significant structural rearrangement.[9,10a] The molecular structure of Cu**1**(py) is presented in Figure 1. The copper in Cu**1**(py) is bound by a pseudo square planar arrangement of nitrogen atoms provided by the pyridyl−diamidate chelate and the exogenous pyridine. Nitrogen atom N(4) of the exogenous pyridine is positioned *trans* to the pyridyl nitrogen N(3) of $\mathbf{1}^{2-}$, with the Cu−N(4) distance of 1.988(10) Å being slightly longer than the Cu−N(3) bond length [1.914(9) Å]. The Cu**1**(py) complex has exact C_2 symmetry where the axis bisects the two pyridine rings, coinciding with atoms N(3), Cu, and N(4). The two O_{amide} donors that were coordinated originally to the copper in Cu**1** [O(2) and O(2a)] are rotated away from the copper in Cu**1**(py)

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(8) (a) Cu**1**(py). Anal. Calcd (found) for $C_{42}H_{32}CuN_6O_6$: C, 64.65 (64.77); H, 4.14 (4.09); N, 10.77 (10.84). IR (KBr): ν_{CO} 1673, 1643, 1625, 1614, 1605 cm^{-1}. λ_{max} (ϵ_M) 334 (17 100), 598 (304) nm. EPR (pyridine): $g_{\|}$, 2.19 ($A_{\|}$, 198 G), $g_{\perp}$, 2.06. (b) Cu**1**(lut). Anal. Calcd (found) for $C_{44}H_{36}CuN_6O_6$: C, 65.37 (65.30); H, 4.50 (4.55); N, 10.39 (10.36). IR (KBr): ν_{CO} 1672, 1647, 1633, 1620, 1605 cm^{-1}. λ_{max} (ϵ_M) 336 (20 300), 605 (264) nm. EPR (3,5-lutidine): $g_{\|}$, 2.19 ($A_{\|}$, 190 G), $g_{\perp}$, 2.06.

(9) General crystallographic information: The refined unit cell parameters, photographic data, and systematic absences in the diffraction data sets for Cu**1**(py) and Cu**1**(lut) are uniquely consistent with a pair of enantiomeric tetragonal space groups. The space groups for Cu**1**(py) and Cu**1**(lut), initially assigned as $P4_12_12$ and $P4_32_12$, were confirmed by refinement of the η-parameter to 0.96(8) and 1.0(1), respectively. The structures were solved by directed methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Both structures lie on 2-fold axes. Non-carbon, non-hydrogen atoms were refined with anisotropic displacement coefficients. Carbon atoms were refined isotropically. Hydrogen atoms were treated as idealized contributions. Phenyl rings were refined as rigid bodies in Cu**1**(lut).

(10) (a) Diamond-shaped crystals of Cu**1**(py) were obtained by diffusing ether into a pyridine solution of Cu**1**: $P4_12_12$, $a = 10.598(2)$ Å and $c = 32.504(7)$ Å; $V = 3651(2)$ Å^3, $Z = 4$, 1089 unique data ($F_o \geq 4\sigma F_o$), R (R_w) = 0.0424 (0.0451), GOF = 1.0. (b) Diamond-shaped crystals of Cu**1**(lut) were obtained by diffusing ether into a 3,5-lutidine solution of Cu**1**: $P4_32_12$, $a = 10.990(3)$ Å and $c = 32.649(8)$ Å; $V = 3943(1)$ Å^3, $Z = 4$, 1228 unique data ($F_o \geq 4\sigma F_o$), R (R_w) = 0.0519 (0.0579), GOF = 1.1.

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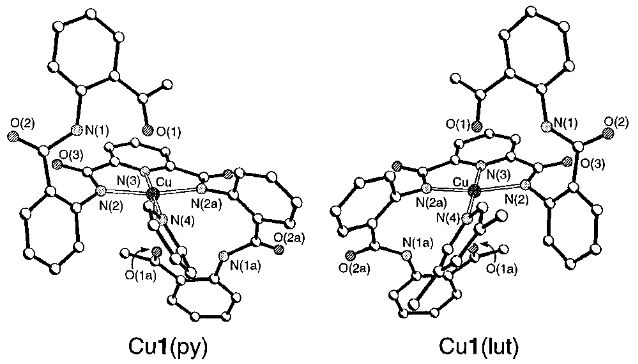

Figure 1. ORTEP diagrams of Cu**1**(py) (left) and Cu**1**(lut) (right). Hydrogens are removed for clarity. Selected distances (Å) and angles (deg) for Cu**1**(py) [Cu**1**(lut)]: Cu−N(2), 2.012(6) [1.998(7)]; Cu−N(3), 1.914(9) [1.921(10)]; Cu−N(4), 1.988(10) [1.948(9)]; Cu−O(1), 2.618(9) [2.712(10)]; N(2)−Cu−N(3), 80.1(2) [80.6(2)]; N(2)−Cu−N(4), 99.9(2) [99.4(2)]; N(3)−Cu−N(4), 180.0(1) [180.0(1)]; N(2)−Cu−N(2a) 160.2(4) [161.2(4)].

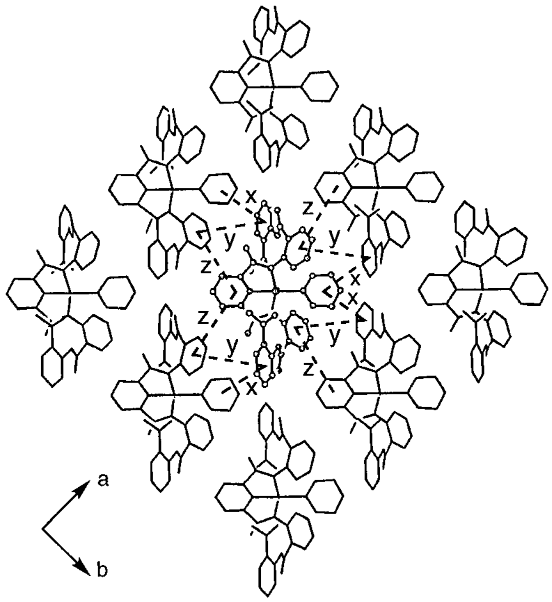

Figure 2. A portion of the crystal lattice for Cu**1**(py) (view of *a,b* plane). Selected intermolecular aromatic centroid−centroid distances (Å) [and corresponding interplane angles (deg)]: *x*, 4.98 [64.5]; *y*, 5.10 [70.7]; *z*, 5.86 [62.7].

and no longer interact with the metal ion [Cu−O(2) distance is 5.89 Å]. A chiral cleft about the exogenous pyridine is formed by the appended groups in $\mathbf{1}^{2-}$. The inner aryl moieties of the appended groups are intramolecularly π-stacked with the bound pyridine at $\text{centroid}_{\text{aryl}}-\text{centroid}_{\text{py}}$ distances of 4.37 Å, and all three rings are canted in the same direction relative to the planar pyridyl−diamidate chelate (average angle between ring planes and the chelate is −57°). The outer aryl rings of the appendages are positioned above and below the equatorial coordination plane with the acetophenone oxygens O(1) and O(1a) located 2.618(9) Å from the copper(II) center.

The most unusual feature of the crystal structure of Cu**1**(py) is that all the complexes within the lattice have the same helical chirality. Since $H_2\mathbf{1}$ is achiral in solution,[2,11] the observed helicity in Cu**1**(py) must result from spontaneous resolution as individual crystals form. Crystallization from solution should produce enantiomeric crystals in equal numbers. A crystal of the other handedness has been characterized for Cu**1**(lut); this crystal belongs to the tetragonal space group $P4_32_12$,[10b] the enantiomorph of the $P4_12_12$ space group found for Cu**1**(py). The crystal lattices of the two structures are almost identical with only slight deviations (<8%) observed in their unit cell parameters. Moreover, the obtained molecular structure of Cu**1**(lut) is similar to that described above for Cu**1**(py), the major difference being the opposite helicity (Figure 1).[12]

The similar lattice architecture shared by Cu**1**(py) and Cu**1**(lut) provides insights into the observed chiral resolution. The lattices contain ordered arrays of metallohelices in the *a,b* plane. Each metallohelix is positioned at the center of a hexagon composed of six surrounding metallohelices; between neighboring helices there are 12 edge-to-face aromatic interactions.[13] Three of these interactions are unique by symmetry, which for Cu**1**(py) are at aryl ring centroid−centroid distances of 4.98, 5.10, and 5.86 Å with corresponding interplane angles of 64.5°, 70.7°, and 62.7° (Figure 2).[14] The clustering of edge-on interactions within an array undoubtedly contributes to the stabilization of this supramolecular assembly of metallohelices.[15−17] This type of stabilization necessitates the nearly perfect alignment of helices within an array which is only possible if individual metallohelices are of the same helicity. Thus the assembly of the arrays during crystallization appears to be enantioselective for one helicity.[18]

These results demonstrate how weak intra- and intermolecular interactions can be used to assemble metal-based chiral supramolecular species. The design of Cu**1**(py) and Cu**1**(lut) allows for modifications either at the exogenous ligand site or at the appended groups of $H_2\mathbf{1}$, granting convenient synthetic access to a variety of other helical complexes. We are investigating currently how these modifications affect the assembly of supramolecular species.

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Supporting Information Available: Packing diagram for Cu**1**(lut) (Figure S1) and structure determination summaries and tables of X-ray structural data for Cu**1**(py) and Cu**1**(lut) (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(11) In solution, $H_2\mathbf{1}$ is a mixture of right- and left-handed helices which are in rapid exchange at room temperature.

(12) Physical separation of the enantiomeric crystals and further characterization of their solid state properties are under investigation.

(13) For Cu**1**(lut), two unique edge-on interactions are observed at centroid−centroid distances of 5.39 and 6.30 Å. Four weak methyl−aryl interactions between the methyl groups of the coordinated lutidine and the aromatic rings of neighboring helices are also observed at distances of 4.07 Å.

(14) Additional lattice structural parameters for Cu**1**(py): (a) Each metallohelix has two additional edge-to-face interactions with helices in adjacent arrays; centroid−centroid distances are 5.74 and 6.35 Å. (b) Two Cu−Cu distances of 14.988(3) and 10.598(2) Å are observed between neighboring metallohelices within an array.

(15) Edge-on interactions are weakly electrostatic and depend on the orientation of the two aryl rings. Theoretical investigations suggest that attractive edge-on interactions similar to those observed in Cu**1**(py) and Cu**1**(lut) can contribute between 0.5 and 2 kcal/mol (per interaction) to the stabilization of a structural motif.[16]

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(18) The structural properties observed for Cu**1**(py) and Cu**1**(lut) appear to be present only in the crystalline state. Preliminary electronic absorbance and circular dichroism results suggest that the complexes racemize upon redissolution at room temperature.