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Self-Assembly of a Noncovalently Bonded Dicopper(II) Complex in the Solid State and in Solution

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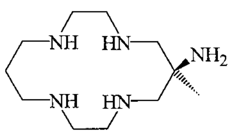
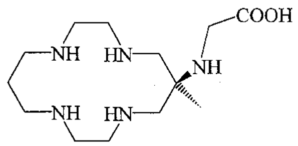
The benefits of noncovalent synthesis in the assembly of ordered supramolecular structures have been illustrated in several review articles.[1] Noncovalent synthesis typically involves hydrogen bonding, aromatic $\pi-\pi$ stacking, and weak coordinative forces, which share the common features of being short-range and reversible. It is apparent that a traditional, linear covalent synthetic approach is unfeasible if a highly ordered, extended array is sought. However, self-assembly through noncovalent forces may be directed by structural information encoded into the donor and acceptor groups. The reversibility of these interactions allows structural errors to be corrected during the assembly process.

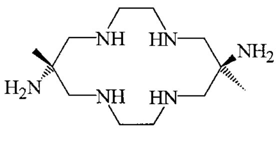
Despite the intense interest in the area of self-assembly[2] and molecular recognition, examples of noncovalently bonded assemblies, particularly those containing transition metal ions, which maintain their structure in the solid state and in solution, are still uncommon. On one hand, solid state packing forces such as H-bonding and ion dipole attraction that may hold a particular array together in a crystalline lattice are often overridden by solvation, and dissociation is the result upon dissolution. On the other hand, weakly associated solution aggregates identified by spectroscopic measurements are often difficult to crystallize, or simply precipitate in a different, but less soluble form. We now report the copper(II) complex of a pendent arm macrocyclic ligand L^2 that can be directed to self-assemble into a noncovalently bonded dimer. Furthermore, we demonstrate that this dimer persists both in the solid state and in aqueous solution, in contrast to its N-based isomer, which exists solely as a monomer.



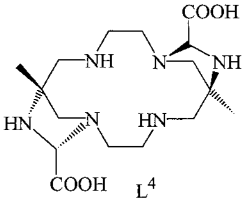
L^1



L^2



L^3



L^4

Previously, we showed[3] that reaction of the diamino-substituted analogue L^3 with glyoxylic acid gives the tricyclic bis-imidazolidine L^4 via internal nucleophilic attack on the imine intermediate by an adjacent secondary amine. To minimize formation of imidazolidine-containing byproducts, a reductive alkylation synthesis was developed[4] using water as the solvent and NaBH$_3$CN as the reductant. This hinders formation of the 5-membered aminal rings, because of solvation and protonation of the secondary amines in the macrocyclic ring, and NaBH$_3$CN is a selective reducing agent for iminium ions (over aldehydes) above pH 4.5.

The macrocyclic ligand L^2 was prepared by a reductive alkylation reaction of the parent[5] pentaamine L^1 with glyoxylic acid and NaBH$_3$CN in water. Purification was achieved by complexation of the reaction mixture with Cu(NO$_3$)$_2$•3H$_2$O and cation exchange chromatography (Sephadex C-25, 0.2 M NaClO$_4$, pH 8). After three minor bands eluted, the two isomeric Cu^{II} complexes of L^2 separated as the only bands of significance from the column. Both bands were crystallized from concentrated, aqueous NaClO$_4$ solutions acidified to pH 4.5 with HClO$_4$. The NMR spectra of the metal free ligands from each complex (obtained by precipitation of Cu^{II} with Na$_2$S) were identical.[6]

The more slowly moving major band gave deep rose colored crystals, and the X-ray crystal structure[7] (solved with SHELXS-86[8] and refined with SHELXL-97[9]) identified this to be the mononuclear complex β-[CuL^2](ClO$_4$)$_2$•3H$_2$O, a view of which is shown in Figure 1. The pendent glycine moiety is present as a zwitterion and is found in an equatorial disposition with respect to the six-membered chelate ring to which it is attached. This type of configurational isomer has been defined as β elsewhere.[10] The carboxylate group is oriented away from the metal and approximately parallel with the macrocyclic plane. Intermolecular H-bonding interactions involving the water molecules, carboxylate group, and perchlorate anions are present, but no significant cation−cation interactions are found. The equatorial Cu−N (2.010(4)−2.026(5) Å) and axial Cu−O (2.507(5) and 2.660(5) Å) bond lengths are typical of tetraazamacrocyclic copper(II) complexes with tetragonally elongated six-coordinate coordination geometries.

The X-ray crystal structure[11] of the purple isomeric complex {α-[CuL^2]$_2$}(ClO$_4$)$_4$•H$_2$O revealed a remarkable dimeric structure

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[6] L^2: ^{1}H NMR (D$_2$O) δ 1.15 (3H, s), 1.67 (2H, mult), 2.42−2.75 (16H, mult), 3.69 (2H, s); ^{13}C NMR δ 20.96 (CH$_3$), 27.21 (CH$_2$*C*H$_2$CH$_2$), 44.78, 45.51, 46.30, 46.90 (all NH*C*H$_2$), 54.67 (*C*(CH$_3$)(NH)), 54.68 (NH*C*H$_2$-CO$_2$H), 179.37 (*C*O$_2$H).

[7] Crystal data: β-[CuL^2](ClO$_4$)$_2$•3H$_2$O, C$_{13}$H$_{35}$Cl$_2$CuN$_5$O$_{13}$, $M = 603.90$, monoclinic, $P2_1/c$ (No. 14), $a = 8.023(9)$ Å, $b = 34.81(1)$ Å, $c = 9.38(1)$ Å, $\beta = 112.76(5)°$, $V = 2416(4)$ Å^3, $Z = 4$, final R1 = 0.0815, wR2 = 0.2373 for 3690 observed reflections [$|F_o| > 2\sigma|F_o|$, $2\theta < 50°$]. Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation and employing the $\omega-2\theta$ scan method. The structures were solved by Patterson methods and refined by full-matrix least squares on F^2. All non-H atoms were refined with anisotropic thermal parameters, whereas H atoms were constrained at estimated positions. Water H atoms were located from difference maps and then constrained to these positions in subsequent cycles of refinement.

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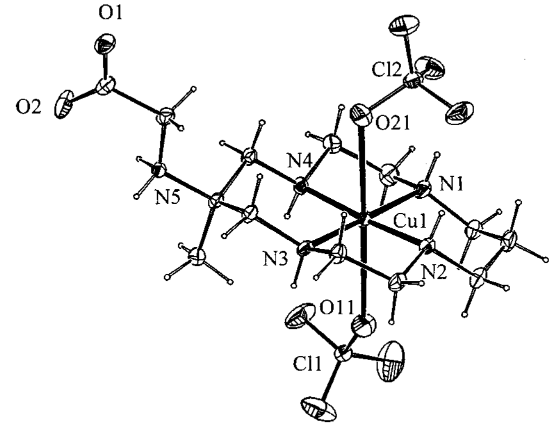

Figure 1. View of the β-[CuL^2](ClO$_4$)$_2$ complex (30% ellipsoids shown).

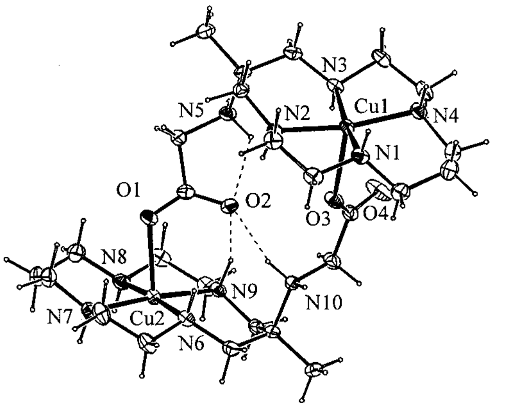

Figure 2. View of the {α-[CuL^2]$_2$}$^{4+}$ dimer (30% ellipsoids shown).

with the two crystallographically unique mononuclear units held together by both H bonds and weak axial coordinate bonds (Figure 2). Again, the pendent groups are in their zwitterionic form, but here each carboxylate group is oriented perpendicular to the macrocyclic plane. This favors an antiparallel intermolecular coordination of each carboxylate in the axial site of the adjacent Cu^{II} center. The geometries of each Cu center are effectively square pyramidal, with all equatorial Cu−N bonds in the expected range (2.006(2)−2.039(2) Å) while the axially bound carboxylates are less strongly bound (Cu1−O3 2.205(2) and Cu2−O1 2.284(2) Å). The internuclear Cu1−Cu2 separation is 7.623(1) Å. There are a number of hydrogen-bonded contacts in the crystal structure, which assist in the formation of the dimeric structure. The carboxylate oxygen O2 plays a pivotal role, forming three close contacts with adjacent amino H atoms: N5−H5B···O2 2.00 Å (N5···O2 2.562(3)), N9−H9···O2 1.88 Å (N9···O2 2.737(3)), and N10−H10C···O2 2.26 Å (N10···O2 3.027(3)).

The 77 K EPR spectrum of {α-[CuL^2]$_2$}(ClO$_4$)$_4$ (Figure 3a) measured as a 10^{-3} M H$_2$O:DMF (2:1) glass is typical of a dinuclear Cu^{II} complex, where dipole−dipole coupling between the two metal centers results in a spectrum quite different from spectra of mononuclear analogues. This spectrum was simulated (Figure 3b) using the program DISSIM,[12] which gave an internuclear distance (r) and relative orientation of the two metal ions (ξ, η, τ) identical to those obtained from the X-ray crystal structure (7.62 Å). This is remarkable since the structural integrity of the dimer is maintained in a dilute, highly polar solution, which might be expected to result in dissociation of a dimer primarily held together by H bonds and weak coordinative interactions. Moreover, there should be considerable electrostatic repulsion between the two cationic monomeric units which is evidently overcome by noncovalent forces. The integrity of the dinuclear complex under these conditions was quite unexpected. By contrast, the frozen solution EPR spectrum of β-[CuL^2](ClO$_4$)$_2$ (Figure 3c) under the same conditions is typical of a tetragonally elongated mononuclear Cu^{II} tetraamine. The spectrum simulated with EPR50F[13] is also shown in Figure 3d. In this case, disposition of the pendent glycine group is inappropriate for dimerization, so we have stereochemical control of self-assembly based upon the N-based isomeric form of the monomeric unit. In passing, we note that, over time (weeks), the monomeric β-[CuL^2](ClO$_4$)$_2$ complex isomerizes in solution to form the dimer {α-[CuL^2]$_2$}(ClO$_4$)$_4$. This suggests that the dinuclear complex is more stable, or at least that the monomeric α-isomer is the more stable, which self-assembles to give {α-[CuL^2]$_2$}(ClO$_4$)$_4$.

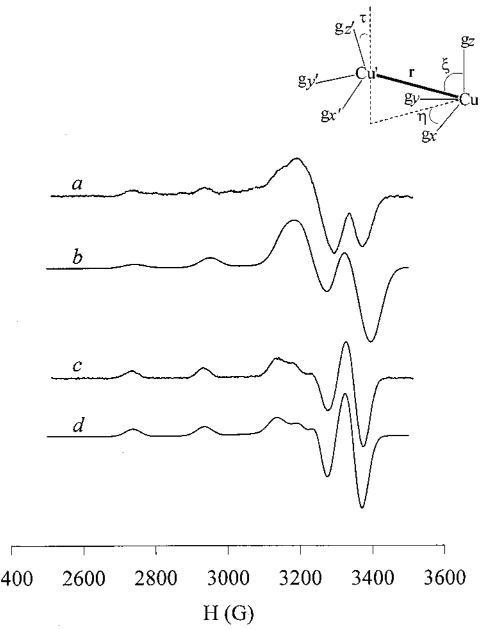

Figure 3. EPR spectra of {α-[CuL^2]$_2$}(ClO$_4$)$_4$ [(a) experimental spectrum and (b) simulated spectrum (parameters $g_\| = 2.18$ ($A_\| = 206$ G), $g_\perp = 2.06$ ($A_\perp = 16$ G), $r_{\mathrm{Cu-Cu}} = 7.62$ Å, $\xi = 45°$, $\eta = 30°$, $\tau = 18°$)] and β-[CuL^2](ClO$_4$)$_2$ [(c) experimental spectrum and (d) simulated spectrum (parameters $g_\| = 2.18$ ($A_\| = 196$ G), $g_\perp = 2.04$ ($A_\perp = 24$ G))]. Experimental conditions: $\nu = 9.299$ GHz, 10^{-3} M complex in 2:1 H$_2$O:DMF, 77 K).

The reductive alkylation reaction employed here is very versatile and offers a new route toward C-substituted cyclam ligands. The general nature of this reaction is a very useful feature, and we are currently investigating other applications of this chemistry for the further elaboration of pendent arm macrocyclic ligands and their complexes.

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Supporting Information Available: Tables of crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Crystal data: α-[CuL^2]$_2$(ClO$_4$)$_4$·H$_2$O, C$_{26}$H$_{60}$Cl$_4$Cu$_2$N$_{10}$O$_{21}$, $M = 1117.72$, triclinic, $P\bar{1}$, $a = 9.3205(9)$ Å, $b = 14.447(2)$ Å, $c = 17.185(2)$ Å, $\alpha = 78.301(9)°$, $\beta = 74.512(8)°$, $\gamma = 88.837(9)°$, $V = 2182.3(4)$ Å^3, $Z = 2$, final R1 = 0.0336, wR2 = 0.0927 for 6510 observed reflections [$|F_o| > 2\sigma|F_o|$, $2\theta < 50°$].

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