Inorg. Chem. **2006**, *45*, 505–507

Inorganic Chemistry
Communication

Unique Asymmetric (Cu^{II}_4) Double-Stranded Helicate from a Hexadentate Piperazine-Based Ligand: Ligand Conformation Isomerism upon Coordination

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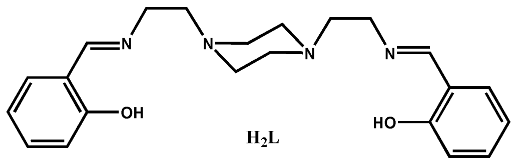
Received August 25, 2005

In methanol, the reaction of $Cu(ClO_4)_2\cdot 6H_2O$ and a sterically constrained piperazine imine phenol ligand (H_2L), in the presence of NEt_3, affords a novel tetranuclear copper(II) complex of formula $[Cu^{II}_4(\mu_3\text{-}L)_2(\mu\text{-}OH)_2(H_2O)_2](ClO_4)_2\cdot H_2O$ (**1**). The X-ray structure of this complex shows an elongated Cu_4 quasi-tetrahedron coordinated to two hexadentate *chair*-(e,a)-μ_3-piperazine bridging ligands. Variable-temperature magnetic studies show an $S_t = 0$ spin ground state resulting from antiferromagnetic interactions between Cu^{II} ions within the complex.

Tetranuclear copper(II) complexes, known for some time and studied extensively,[1] are interesting in bioinorganic modeling, multielectron transfer, catalysis, and magnetostructural research. Currently, efforts are being made to rationalize the involvement of a novel tetranuclear copper cluster in the catalytic cycle of N_2O reduction to N_2.[2] In trying to isolate and study new forms of such aggregates, we have been exploring the reactivity of the hexadentate, sterically restricted Schiff base ligand H_2L {(2-hydroxobenzylidene)-[2-(4-{2-[(2-hydroxobenzylidene)amino]ethyl}-piperazin-1-yl)ethyl]amine} towards Cu^{II}. Substituted 1,4-piperazine can assume different types of bridging conformations in both boat and chair forms, of which the latter is thermodynamically more favorable.[3] While in the boat form, it can coordinate one or bridge two metal ions to give mononuclear and cis dinuclear complexes, respectively.[4] In the chair form, the most important bridging modes are equatorial–equatorial (e–e)[5] and equatorial–axial (e–a), analogous to the syn–syn and syn–anti coordination modes of bridging acetates.[6] From the reaction of H_2L with copper(II) perchlorate hexahydrate, we succeeded in obtaining the novel tetranuclear complex $[Cu^{II}_4(L)_2(OH)_2(H_2O)_2](ClO_4)_2\cdot H_2O$ (**1**), featuring *chair*-piperazine (e–a), terminal phenolato, and hydroxo bridging. The ligand H_2L can exist in three different conformations, A–C (Figure 1),[7] and has been shown to transform from A to B during dicopper complex formation, leading to a trans-coordination mode (complex **2** in Figure 1).[5] Now for the first time the conformation C, responsible for cis coordination, has been identified in a Cu_4 complex. The ligand shows unprecedented conformational isomerization at the piperazine coordination as a result of the self-assembly process.



H_2L

Complex **1** was synthesized in ~85% yield from chloroform–methanol (1:1) under aerobic conditions at room temperature by stirring $Cu(ClO_4)_2\cdot 6H_2O$, H_2L (prepared from 2 mol of salicylaldehyde and 1 mol of 2-[4-(2-aminoethyl)-piperazin-1-yl]ethylamine[8] in methanol), and NEt_3 in a 2:1:3

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10.1021/ic051455y CCC: $33.50 © 2006 American Chemical Society
Published on Web 12/24/2005

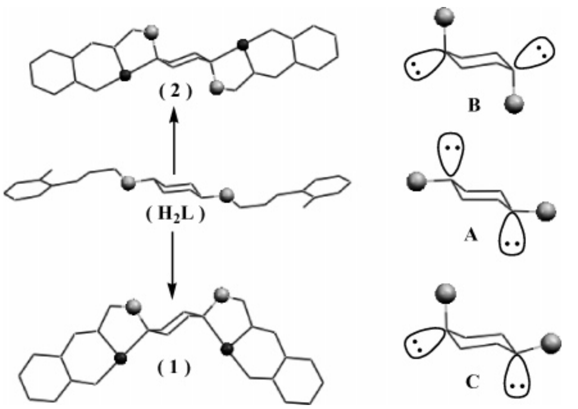

Figure 1. (Left) Molecular structure of H_2L, a portion of a reported Cu_2L complex (**2**; ref 5a) and a relevant part of complex **1**: gray ball, α-C; black ball, Cu. Structures were generated by a mercury X-ray crystallography software package (version 1.3). (Right) *chair*-Piperazine backbone of the ligand with α-C and available lone pairs in three different conformations: A (a,a), B (e,e), and C (e,a) (a, axial; e, equatorial).

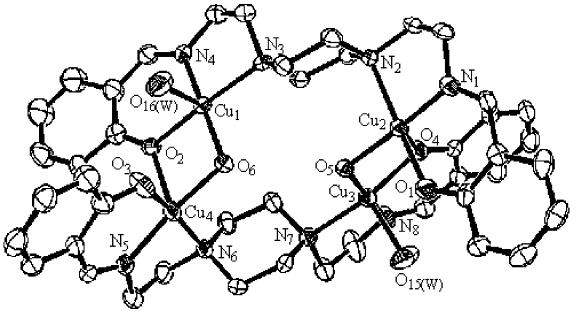

Figure 2. Labeled ORTEP view of $[Cu^{II}_4(\mu_3\text{-}L)_2(\mu\text{-}OH)_2(H_2O)_2]^{2+}$ (cation of **1**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

molar ratio for 1 h. The complex precipitates directly from the reaction mixture as a dark-green solid. Elemental analysis, solution electrical conductivity, and room-temperature magnetic susceptibility data are consistent with the formula of complex **1**. The presence of two bridging hydroxo groups is attributed to the deprotonation of adventitious water present in the solvents. The strong unsplit band $\nu(ClO_4^-)$ at around 1107 cm^{-1} is due to the ν_3 mode of perchlorate anions in T_d symmetry, thus suggesting no coordination of perchlorate ions.[9,10] Single crystals suitable for structure determination were obtained by slow evaporation of a methanol−chloroform (1:1) solution of the complex. A labeled molecular view of the complex cation of **1** is shown in Figure 2. The complex consists of a dication unit $[Cu^{II}_4(L)_2(OH)_2(H_2O)_2]^{2+}$ and two uncoordinated perchlorate anions with one water of crystallization. The core of the complex is composed of two piperazine-bridged $[Cu_2O_2]$ units (Figure S1 in the Supporting Information) wrapped around by two ligand strands in the formation of a tetranuclear double-helical structure (Figure S2 in the Supporting Information) in which the four metals constitute an elongated pseudo-tetrahedron. Each hexadentate N_4O_2 donor ligand binds three Cu centers asymmetrically. The N−Cu−N and N−Cu−O bite angles average 83.64° and 92.36°, respectively, whereas the averages of the Cu−O−Cu angles for the hydroxo and phenolato oxygen bridges are 93.45° and 106.30°, respectively. The coordination geometry about the metals is very close to square-pyramidal (τ parameter from 0.02 to 0.08). Very interestingly, the apical position of one type of Cu^{II} is occupied by H_2O and oriented perpendicular to the $[Cu_2O_2]$ unit, whereas the long axis of the other Cu^{II} is contained within the bridge and is taken by the oxygen of one bridging phenoxide. Thus, complex **1** is one of the very rare examples displaying a $[Cu_2O_2]$ moiety where, of the four bonds linking the metals, three are basal (short) and one axial (long). The longer $Cu-N_{amine}$ distances (avearge 2.126 Å) than the $Cu-N_{imine}$ distances (average 1.929 Å) are mainly due to the different states of hybridization of N. The $Cu-O_{hydroxo}$ distances, in the 1.923(5)−1.945(4)-Å range, are comparable to those reported for other μ-hydroxo-bridged tetranuclear complexes.[11] The short $Cu-O_{phenolato}$ distances are 1.921(6) and 1.951(5) Å, whereas the axial such distances are 2.251(5) and 2.333 (5) Å.[10] In its free form, the ligand H_2L is present in conformation A and undergoes conformational isomerization to C within this reaction system. Unsymmetrical e−a coordination of the *chair*-piperazine ring actually triggers unsymmetrical binding of the two tridentate halves of the ligand. Equatorial coordination is strong compared to the axial one and may be responsible for phenolate bridging, which is not observed on the axial coordination side. The X-ray structure of H_2L was also determined in order to compare the structural parameters.[12] In the present complex, the average Cu···Cu distance along the ligand backbone is 5.655 Å, which is short compared to 6.908 and 6.881 Å in reported *chair*-piperazine-bridged Cu_2 complexes having trans coordination.[5] The average intradimer hydroxo-bridged Cu···Cu distance is 3.094 Å. A double-stranded helicate is formed from the ligand twisting at the *chair*-piperazine. The C=N and C−O distances of the salicylaldimine fragments are consistent with the coordination of the deprotonated form of the salicylaldimine functionalities.[5b,13] Intramolecular hydrogen bonds were observed between the coordinated water and the terminal nonbridging phenolate oxygens at distances of 2.680(10) ($O_1\cdots O_{15}$) and 2.722(9) ($O_3\cdots O_{16}$) Å, respectively. Intermolecular anion−hydrogen bonds connect two Cu_4 units via lattice water molecules (Figure S3 in the Supporting Information). The crystal lattice contained ∼911.3-$Å^3$ (or ∼15.5%) void volume per unit cell.

Magnetic susceptibility data in the temperature range 2−300 K at 1 T were collected for a polycrystalline sample of complex **1**. The results are represented in Figure 3 as $\chi_M T$

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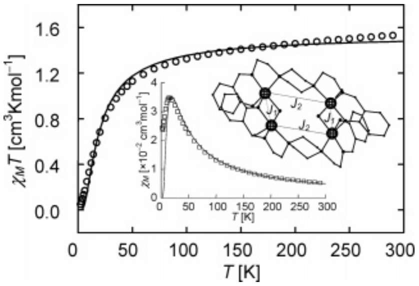

Figure 3. Plot of $\chi_M T$ vs T per molecule of **1**. The solid line is the best fit to the experimental data (see the text for details). Inset: Plot of χ_M vs T and fit. The chart shows the spin-coupling scheme used to model the magnetic behavior of the compound.

and χ_M vs T plots (χ_M is the paramagnetic susceptibility after subtraction of the diamagnetic contributions). At room temperature, $\chi_M T$ corresponds to the value for four uncoupled Cu^{II} ions with $g = 2.03$, and it slowly decreases upon cooling, down to approximately 60 K, where the drop occurs more sharply. This indicates the presence of antiferromagnetic interactions. To describe quantitatively this behavior, the spin-coupling scheme depicted in the inset of Figure 3 was considered, which leads to the following Heisenberg spin Hamiltonian for the magnetic superexchange; $H = -2J_1(S_1S_2 + S_3S_4) - 2J_2(S_1S_4 + S_2S_3)$. A fit to the experimental data (solid lines in Figure 3) was performed from the best $\chi_M = f(T)$ possible expression obtained through a numerical procedure based on the matrix diagonalization of the above Hamiltonian, using the program CLUMAG.[14] The fit on the χ_m vs T representation appears less accurate at low temperature, presumably because of the presence of a small amount of paramagnetic impurity, particularly visible in antiferromagnetic systems at low temperature, which could not be modeled with this program. The fit parameters were $J_1 = J_2 = -16.9$ cm^{-1} and $g = 2.03$. In addition, a temperature-independent paramagnetism (TIP) term was also allowed to optimize during the fit, reaching a value of TIP $= 258 \times 10^{-6}$ cm^3 mol^{-1}. The magnitude of g is slightly smaller than the one obtained from X-band solid-state EPR measurements ($g = 2.11$; Figure S4 in the Supporting Information). Both optimized coupling constants are exactly the same as the mathematical consequence of the fact that they play the exact same role in the model and that they are expected to be physically similar. Indeed, the few documented cases of a [Cu$_2$(μ-O)$_2$] bridge with the novel geometric features found in **1** (see above) display coupling constants in the range of -11 to -19 cm^{-1}, whereas the three reported cases of piperazine-bridged Cu^{II} ions show J values of -10.2, -13.9, and -14.7 cm^{-1}. The value resulting from the fit must thus be regarded as an "average" and only orientative. Both kinds of Cu···Cu links seen in this complex are very rare. The first is a substituted piperazine ring in a chair conformation, with piperazine itself having been described on very rare occasions as a means to propagate magnetic exchange interactions.[5,15] The other link is formed by two μ-O atoms: one is basal−basal (hydroxide) and the other axial−basal (phenolate). Bridged pairs of the type [Cu$_2$(μ-O)$_2$] featuring such a combination of equatorial and axial bonds also have very few precedents, and the magnetic coupling taking place within them has therefore been largely unexplored.[16,17] The geometry of Cu in **1** (square pyramidal) is very similar to that of the reported examples with the same bridge. In all cases, given the long Cu···Cu separation, the coupling needs to occur via superexchange. Given their relative orientation, the overlap between the magnetic orbitals of Cu^{II} (d$_{x^2-y^2}$) can only occur through the atomic orbitals from the O-donor bridging in the basal−basal manner (Scheme SI in the Supporting Information). The coupling through the other oxygen atom (basal−axial bridge) might not be negligible despite being axially bound because the Cu−O−Cu angle of the hydroxo bridge (93.45°) is close to that leading to accidental orthogonality in [Cu$_2$(μ-OH)$_2$] systems. As for the piperazine bridge, compound **1** is the first example of this kind where the Cu^{II} centers are not in a square-planar coordination geometry. Also, it is the first studied case where the bridge is *chair*-piperazine in the C conformation (Figure 1). In all of the previous cases, the coupling has taken place through the piperazine B conformation. It has been suggested that conformation B favors a mechanism of exchange through the σ network of the ring whereas conformation C would favor an interaction through space (direct N-to-N delocalization).[5b] The J value in **1** is slightly larger than those in all previously studied examples; thus, the reduction of the through-bond mechanism and increase of the through-space pathway is not detrimental to the intensity of the coupling.

In conclusion, we have been able to provide here a rare example of terminal phenolate and a *chair*-(e,a)-piperazine-bridged double-stranded Cu$_4$ system with an overall antiferromagnetic interaction. The deprotonated ligand L^{2-}, showing conformational isomerism for cis coordination, assembles four Cu^{II} ions in an elongated quasi-tetrahedron.

Acknowledgment. We are thankful to the Council of Scientific and Industrial Research, New Delhi, India, for financial support. G.A. acknowledges the financial support from the Spanish Government.

Supporting Information Available: Crystallographic data, tables of selected bond lengths and angles, CIF, Figures S1−S4, Schemes SI and SII, and synthesis and characterization of ligand H$_2$L and complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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