Synthesis, Structure, and Preliminary Magnetic Studies of a Cluster Polymer with a Hexacopper(II) Barrel Portion

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The synthesis and characterization of a new cluster polymer with a sodium centered hexacopper(II) barrel portion, *catena*-$[Na\subset Cu_2\{Cu(hpro)_2\}_4(ClO_4)_4](ClO_4)\cdot 4H_2O$ (hpro = 4-hydroxy-L-prolinato) are described. The central sodium ion in the barrel portion is surrounded by eight carboxylate oxygen atoms from hpro ligands, which link the central metal to the copper atoms of four $[Cu(hpro)_2]$ units. These units are in turn connected to two further apical Cu^{II} centers. The central alkali ion is therefore octahedrally surrounded by six copper atoms. The hydroxyl oxygen atoms of two hpro groups are coordinated to the axial copper atoms of two neighboring barrel portions, so that a chain complex forms. Magnetic studies indicate weak ferromagnetic coupling between copper(II) ions within the complex leading to a high spin multiplicity in the ground state.

Heteronuclear and/or polynuclear complexes are interesting materials due to their structures and properties: especially electrochemical and magnetic properties. A number of groups have been investigating the magnetic interaction between metal ions in heterometallic complexes.[1] Our group has attempted to link mononuclear and/or small polynuclear compounds into larger units. By such a strategy, some interesting systems have been prepared such as two centered icosahedral twelve-coordinate lanthanide (Sm or Eu) clusters formed by six bis(L-prolinato)nickel(II) ($[Ni(pro)_2]$) complex-ligands.[2] According to cyclic voltammetry, the nickel atoms in the cluster interact with one another. Other remarkable Ni polynuclear compounds have been reported recently in the literature, such as a Ni_{12} and a Ni_{24} wheel.[3] The Ni_{12} complex showed ferromagnetic exchange between the metal centers, resulting in an $S = 12$ spin ground state, whereas the Ni_{24} wheel exhibited weak antiferromagnetic exchange.

In this work, the preparation of a new cluster polymer with a centered sodium ion hexacopper(II) barrel portion, *catena*-$[Na\subset Cu_2\{Cu(hpro)_2\}_4(ClO_4)_4](ClO_4)\cdot 4H_2O$[4] (hpro = 4-hydroxy-L-prolinato) is presented, along with the preliminary magnetic properties.

Catena-$[Na\subset Cu_2\{Cu(hpro)_2\}_4(ClO_4)_4](ClO_4)\cdot 4H_2O$ (**1**) was prepared as follows. Sodium perchlorate, copper perchlorate, and $[Cu(hpro)_2]$ were dissolved in methanol in a molar ratio of 1:2:4, respectively. Blue parallelepiped crystals were obtained from the reaction mixture by keeping it in a desiccator containing ether for a few days at room temperature.

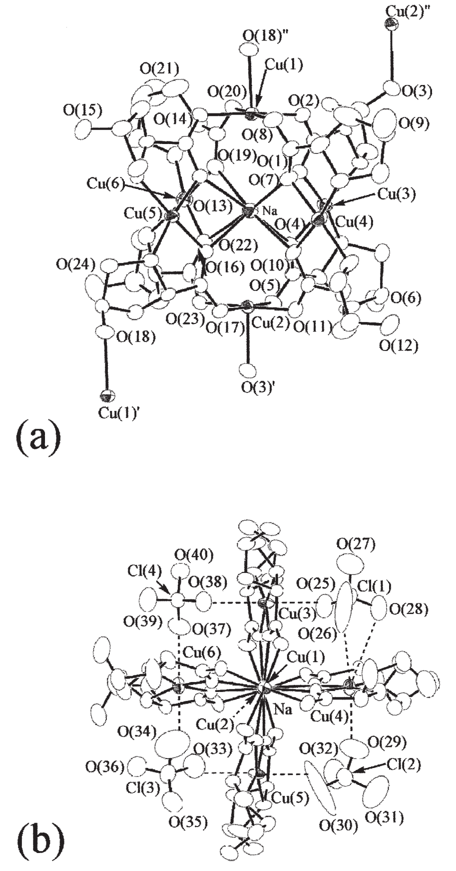

Figure 1. ORTEP representation at 30% probability level of $[Na\subset Cu_2\{Cu(hpro)_2\}_4(ClO_4)_4](ClO_4)\cdot 4H_2O$ (**1**): (a) Barrel structure, (b) Projection of the barrel along the direction piercing through Cu(1) and Cu(2). Selected bond distances (Å): Averaged; Cu_{eq}–O = 1.933, Cu_{eq}–$O_{perchlor.}$ = 2.68 or 3.55, Cu_{eq}–N = 2.006, Cu(1or2)–O = 1.951, Na–O = 2.564, Cu–O_{OH} = 2.312, Cu(1)$\cdots Cu_{eq}$ = 4.991, Cu(2)$\cdots Cu_{eq}$ = 5.001, Cu(3)$\cdots$Cu(4) = 4.953(2), Cu(3)$\cdots$Cu(6) = 5.023(2), Cu(3or4)$\cdots$Cu(5or6) = 7.129, Cu(1)$\cdots$Cu(2) = 6.998(2).

Figure 1 shows the structure of the repeating unit of **1**. In the barrel portion, $[Na\subset Cu_2\{Cu(hpro)_2\}_4]^{5+}$, Na^+ is trapped in the center. The central metal ion is surrounded by eight carboxylate oxygen atoms which link it to the copper atoms of four $[Cu(hpro)_2]$ units. These four units provide in turn the square planar environment of two further axial Cu^{II} centers *via* the other carboxylate oxygen atoms from hpro. The six Cu^{II} centers of this repeating cluster form an octahedron with idealized D_{4h} symmetry, the sodium ion being therefore approximately octahedrally surrounded by copper. Two hydroxyl groups of hpro are coordinated to the (axial) Cu(1) and Cu(2) centers of two neighboring barrel units, respectively, thereby completing their square pyramidal coordination geometry and providing the link for a chain of clusters as shown in Figure 2. Four of five perchlorate ions lie between the propellers formed by the four $[Cu(hpro)_2]$ units as shown in Figure 1(b). Two oxygen atoms from three of these perchlorate ions are weakly coordinated to the Cu center of the $[Cu(hpro)_2]$ units, occupying the axial positions of their tetragonally elongated octahedral environment. The fourth ClO_4^- ion, however, binds to one Cu through two of its oxygen atoms, and to another with one O-donor. The barrel portion, $[Na{\subset}Cu_2\{Cu(hpro)_2\}_4(ClO_4)_4]^+$ (F.W. = 1843.05), is stable and is retained in solution: in FAB mass spectroscopy, a peak corresponding to the portion (m/z = 1843) could be observed.[5] The residual ClO_4^- is on a general position between the chains. Several water molecules have been found crystallographically between the polymer and have extremely large thermal parameters. The compound can be partially dehydrated *in vacuo*.[6] Complex **1** constitutes a new example of the rare family of cluster polymers known to date.[7]

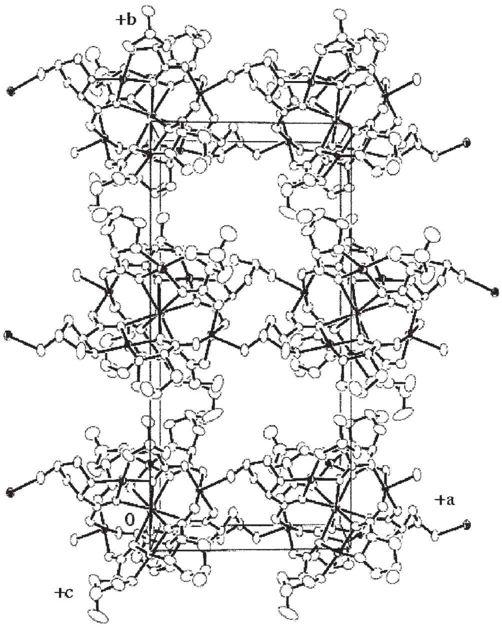

Figure 2. Crystal packing of *catena*-$[Na{\subset}Cu_2\{Cu(hpro)_2\}_4(ClO_4)_4]$-$(ClO_4){\cdot}4H_2O$ (1). Water molecules and ClO_4^- on a general position between the chains are omitted as well as hydrogen atoms.

Variable temperature bulk magnetization data were collected from a polycrystalline sample of **1**. A plot of χ_mT vs T (χ_m = magnetic susceptibility) is presented in Figure 3. At room temperature, the value of χ_mT is 2.66 cm^3 K mol^{-1}, which is slightly higher than the predicted value for six non-interacting $S = 1/2$ centers with $g = 2.1$ (2.48 cm^3 K mol^{-1}).[8] This value remains approximately constant down to *ca.* 50 K, where it starts to increase rapidly to reach 5.05 cm^3 K mol^{-1} at 1.8 K. This is consistent with the presence of weak ferromagnetic super-exchange between Cu ions within the clusters of the chain. The experimental data were fit to a Van Vleck equation[10] obtained by using a model where only a weak interaction (J) between the axial Cu^{II} ions and the equatorial Cu^{II} ions was considered. This assumption allowed us to resolve the Heisenberg Spin-Hamiltonian ($H = -2J(S_1 + S_2)(S_3 + S_4 + S_5 + S_6)$, numbering scheme as in Figure 1) for the isolated repeating unit of **1** by using the Kambe vector coupling method.[10] The best fit of the data (Figure 3, solid line), gave $J = 0.74$ cm^{-1}, and $g = 2.17$, indicating an $S = 3$ spin ground state. A detailed investigation of the magnetic properties of this system, which will include the use of EPR spectroscopy at various frequencies is under way.

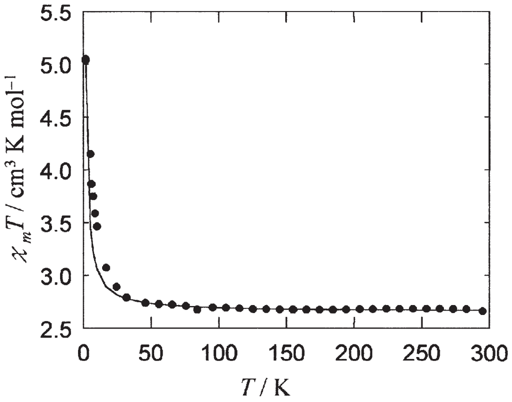

Figure 3. χ_mT vs T curve for *catena*-$[Na{\subset}Cu_2\{Cu(hpro)_2\}_4(ClO_4)_4]$-$(ClO_4){\cdot}4H_2O$ (**1**). The solid line is a theoretical fit to the experimental data (see text for details).

References and Notes

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4 Crystal and analytical data for *Catena*-$\{[Na{\subset}Cu_2\{Cu(hpro)_2\}_4(ClO_4)_5]{\cdot}4H_2O\}$, $Cu_6Cl_5NaO_{48}N_8C_{40}H_{72}$; F.W. = 2014.56; Monoclinic, $P2_1$ (#4), $Z = 2$, a = 11.746(2) Å, b = 24.872(4) Å, c = 13.064(2) Å, $\beta = 96.58(1)°$, V = 3791.5(9) Å^3, D_{calcd} = 1.764 g cm^{-3}, μ(Mo Kα) = 19.41 cm^{-1}, Final R = 0.060 (R_w = 0.082) for 7045 observed reflections ($I > 3\sigma(I)$). Measurements for diffraction data were carried out on a Rigaku AFC7R diffractometer. The structures were solved by a heavy atom method and refined by a full-matrix least-square treatment.

5 Mass spectrum of **1** was measured by means of a JEOL SX-102A mass spectrometer with FAB method using *m*-nitrobenzyl alcohol as a matrix.

6 The elemental analysis of **1** dried *in vacuo* was measured. Found: C, 24.64; H, 3.81; N, 5.34%. Calcd for $\{[Na{\subset}Cu_2\{Cu(hpro)_2\}_4(ClO_4)_5]{\cdot}2H_2O$: C, 24.28; H, 3.46; N, 5.66%.

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8 Possible reasons for this discrepancy could be; (i) the fact that g is slightly higher than 2.1 (see fit parameters), (ii) a small inaccuracy in correcting the diamagnetic contribution to the susceptibility, or (iii) the experimental error in calculating the molecular mass from elemental analysis.

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