Structure and Magnetic Properties of a Honeycomb-like Copper(II) Complex Containing 4-Aminopyrimidine and Methoxide Bridges

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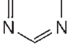
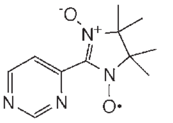
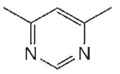
Complexation of $Cu(NO_3)_2$ with 4-aminopyrimidine (4APM) in methanol gave $[Cu(4APM)(NO_3)(OCH_3)]_n$ which crystallizes in a trigonal space group $R\bar{3}$. The three-dimensional network affords a tube-like cavity. Magnetic measurements revealed the presence of considerably large antiferromagnetic interaction due to the four-membered Cu_2O_2 structure.

Coordination compounds with three-dimensional (3D) networks and nano-sized pores attract much attention for the interest of zeolite-like functionalities.[1–3] Physical properties of porous materials can be tuned by means of supramolecular chemistry.[4,5] We have reported the host–guest chemistry of the hexanuclear complexes $[CuX_2(4PMNN)]_6$ (X = Cl, Br; see below for the molecular structure of 4PMNN) showing intermolecular ferromagnetic interactions.[6] The infinite chain $[CuBr_2(DMPM)]_n$ formed a 6_1 helix.[7] We assumed that other functional groups substituted at the 4-position of PM might play an important role in the crystal packing. We will report here another honeycomb-like complex containing a diamagnetic ligand, 4-aminopyrimidine (4APM).


PM


4PMNN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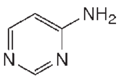
4APM

Complex $[Cu(4APM)(NO_3)(OCH_3)]$ (**1**) was very easily synthesized as follows. A methanol solution (8 mL) containing 19 mg (0.20 mmol) of 4APM and 48 mg (0.20 mmol) of copper(II) nitrate trihydrate was allowed to stand at room temperature for 3 days. Blue crystals were precipitated and separated on a filter. The yield was 14 mg (0.056 mmol; 28%). Elemental analysis indicated that 1/6 mole of methanol molecules were incorporated. Anal. Calcd. for $C_{31}H_{52}N_{24}O_{25}Cu_6[\mathbf{1}_6\cdot(CH_3OH)]$: C, 24.14; H, 3.40; N, 21.80%. Found: C, 24.16; H, 3.23; N, 21.82%.

Figure 1 shows the crystallographically independent unit together with several symmetry-related atoms in the crystal of **1**.[8] The space group was $R\bar{3}$ with $Z = 18$. The Cu1 was penta-coordinate. Two methoxide oxygens (O1 and O1*) and two pyridmidine nitrogens (N1 and $N2^{\#}$) are coordinated on a copper(II) basal plane, while a nitrate oxygen (O2) occupies an axial position.[??] The methoxide anion was introduced from the reaction solvent under the basic conditions due to the 4-aminopyrimidine base. The methoxide oxygen atom bridges Cu1 and Cu1* with the Cu1–O1 and Cu1–O1* distances of 1.917(5) and 1.969(3) Å, respectively. A four-membered ring Cu1–O1–Cu1*–O1* was formed. The Cu1–O1–Cu1* and O1–Cu1–O1* angles are 102.9(2) and 77.15(9)°, respectively.

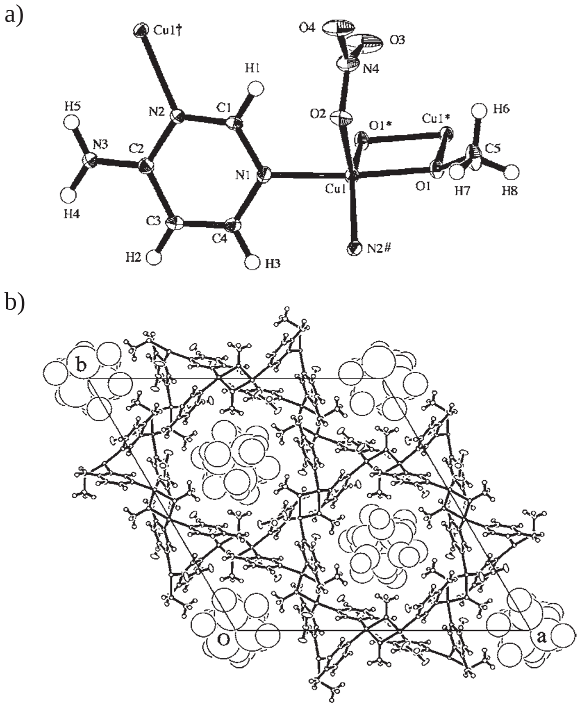

Figure 1. (a) Ortep drawing of the repeating unit in polymeric complex $[Cu(4APM)(NO_3)(OCH_3)]$ (**1**) with thermal ellipsoids at the 50% probability level. Solvent molecules were omitted for the sake of clarity. (b) Molecular arrangement in the crystal of **1** viewed along the *c* axis. Disordered solvent molecules are found in the hexagonal channel.

The amino group in 4APM was not ionized and accordingly it did not work as a ligand. Instead, some hydrogen-bonding interactions are found between the amino hydrogen and nitrate and methoxide oxygen atoms [$H5\cdots O1^{\dagger}$, 2.07; $H5\cdots O3^{\S}$, 2.24; $H4\cdots O4^{\ddagger}$, 1.96; $H4\cdots O2^{\ddagger}$, 2.53 Å], which stabilizes the macrocyclic structures.

The Cu1 ion is also coordinated with the pyrimidine nitrogen atoms (N1 and N2 with the distances of 1.973(6) and 2.088(4) Å, respectively), and the macrocyclic structures are formed; one is a 36-membered macrocyclic hexagon $[–PM–Cu–O–Cu–]_6$ and the other a 12-membered triangle $[–PM–Cu–]_3$, as shown in Figure 1b. When projected onto the *ab* plane, the figure looks like a kagomé-type lattice, but actually another bridge along the *c* axis with a 3_1 screw symmetry constructs an entirely 3D coordination network.

Magnetic susceptibilities of randomly oriented polycrystalline samples were measured on a SQUID magnetometer. Figure 2 shows the results of magnetic susceptibility measurements on the basis of the formula unit of **1**.[10] The $\chi_{mol}T$ value

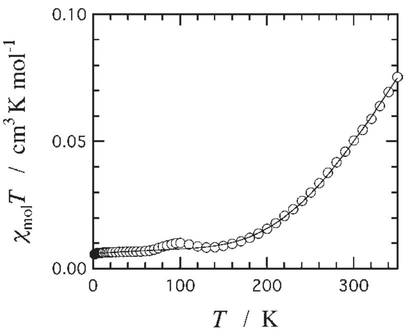

Figure 2. Temperature dependence of the product $\chi_{mol}T$ measured at 5000 Oe for $\mathbf{1}_6\cdot(CH_3OH)$. The solid line represents the theoretical fit. See the text for the equation and optimized parameters.

was much smaller than the theoretical value (typically 0.4 cm^3 K mol^{-1} per Cu^{II}) and gradually increases on heating. This behavior can be interpreted in terms of the singlet-triplet model[11] with considerably strong antiferromagnetic coupling. The bias of ca. 6×10^{-3} cm^3 K mol^{-1} is attributed to monomeric 1/2 spins. Therefore, the following equation (Eq 1) can be proposed for the analysis of the data. The first term implies the singlet–triplet model, and the second term the Curie-type impurity, where the impurity factor (p) is defined as a molar fraction of the monomeric Cu^{II} ions. The Weiss mean field parameter is introduced as θ. Assuming the g-value of 2.15 for typical Cu^{II} ions,[12] we obtained the following optimized parameters: $J/k_B = -556(1)$ K, $p = 0.0140(2)$, and $\theta = -0.16(6)$ K. The calculated curve is superposed in Figure 2.

$$\chi_{mol} = \frac{N_A g^2 \mu_B{}^2}{k_B(T-\theta)}\left[(1-p)\frac{1}{3+\exp(-2J/k_BT)} + p\frac{1}{4}\right] \quad (1)$$

The X-ray crystallographic analysis revealed that the methoxide oxygen atoms doubly bridged two copper(II) ions. The antiferromagnetic coupling is attributed to the Cu–O–Cu structure rather than the Cu–PM–Cu structure. Similar magnetic couplings in Cu–O–Cu bridges have been well investigated in connection with superexchange mechanism, and the exchange parameters (J/k_B) were reported to be −215 to −590 K.[12,13] Thus, the present value (−556 K) belongs to the largest class among the analogous structures. The Curie impurity corresponding to 1.4% of the Cu^{II} moments is attributed to the lattice defect at the dimer sites as well as isolated Cu^{II} ions in the channel as a guest.

Viewing from the distances of Cu···Cu, the magnetic coupling across the PM bridge is buried by the strong antiferromagnetic coupling across the methoxide. The PM nitrogen atoms (N1 and N2) are located at the equatorial sites of the Cu^{II} ions (Cu1 and Cu1† in Figure 1a), indicating that the PM ring may work as an antiferromagnetic coupler.[14]

As for the hexagonal cavity, the diameter defined by the opposite methyl carbon atoms is 9.4 Å. As Figure 1b shows, the solvent molecules were found as a guest in the channel, but the molecular structure of the guest could not be determined owing to severe disorder. Since the methyl groups are arranged on the inside wall of the channel, the channel is supposed to be in hydrophobic conditions. Possible host–guest chemistry is studied preliminarily.[15] The elemental analysis indicates that hexane and benzene molecules can be absorbed in **1**, and the formulas $\mathbf{1}_3\cdot(C_6H_6)$ and $\mathbf{1}_6\cdot(C_6H_{14})$ were proposed, respectively. Their magnetic data showed an increase of Curie doublet impurity compared with that of the starting material, whereas the exchange parameter (J) remained almost unchanged. This finding implies that the host structure was partially decomposed and that the Cu–O–Cu geometry stands against deformation due to guest inclusion.

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8 X-ray diffraction data of a single crystal of $\mathbf{1}_6\cdot(CH_3OH)$ were collected with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at 90 K. Selected crystallographic data: $C_6H_{12}CuN_4O_6$, trigonal, $R\bar{3}$, $a = 24.463(6)$, $c = 10.063(4)$ Å, $V = 5215(2)$ Å^3, $Z = 18$, $D_{calcd} = 1.718$ g cm^{-3}, μ(Mo Kα) $= 1.909$ mm^{-1}, $R(F)(I > 2\sigma(I)) = 0.046$, and $R_w(F^2)$(all data) $= 0.084$ for 2665 unique reflections. All the hydrogen atoms were found experimentally. Appreciable electron densities were observed in a hexagonal channel and tentatively assigned as oxygen atoms. CCDC No. 250464.

9 Symmetry operation codes. $*$) $2/3-x$, $1/3-y$, $4/3-z$. #) $2/3-y$, $1/3+x-y$, $1/3+z$. †) $1/3-x+y$, $2/3-x$, $-1/3+z$. §) $x-y$, x, $1-z$. ‡) $-1/3+y$, $1/3-x+y$, $4/3-z$.

10 A broad hump of the $\chi_{mol}T$ value between 50–100 K exhibited significant sample-dependence, probably due to absorbed oxygen.

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15 The fine polycrystalline sample of $\mathbf{1}_6\cdot(CH_3OH)$ was placed in benzene at room temperature for a week. The product was isolated on a filter and air-dried. Anal. Calcd. for $\mathbf{1}_3\cdot(C_6H_6)$: C, 30.27; H, 3.63; N, 20.17%. Found: C, 29.52; H, 3.45; N, 19.71%. After evacuation using an oil rotary pump for 1 day, the specimen was subjected again to elemental analysis. Found: C, 28.37; H, 3.20; N, 19.89%. A similar experiment in hexane showed: Anal. Calcd. for $\mathbf{1}_6\cdot(C_6H_{14})$: C, 27.09; H, 3.91; N, 21.06%. Found: C, 26.47; H, 3.98; N, 20.20%. After being pumped: Anal. Found: C, 25.78; H, 3.52; N, 20.57%.