Cage-Type Hexacopper(II) Complex Formed by Chloride Template

Asako Kamiyama, Takashi Kajiwara, and Tasuku Ito*
Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578

(Received July 4, 2002; CL-020555)

A novel cage complex $[Cu_6Cl(MeO)_2(pz)_9]$ (**1**) was synthesized via a chloride ion template reaction and structurally characterized. In **1**, two trinuclear units, $\{Cu_3(MeO)(pz)_3\}^{2+}$, are linked by three pyrazolate ligands, six copper(II) ions form a trigonal prism, and a chloride ion is located at the center of the cage. **1** shows rather strong antiferromagnetic coupling between the copper(II) ions through the MeO^- and pyrazolate ligands.

Metal ion assembled compounds have interesting properties such as magnetic,[1] electrochemical,[2] and catalytic[3] functions. To assemble metal ions in a single molecule, anionic cyclic-polyamines such as pyrazolate (pz^-) are often utilized to prevent accumulation of positive charges in the resulting compound. There have been several reports concerning multicopper(II) complexes prepared with use of pyrazolate as a bridging ligand.[4] As well, monoatomic anions such as a halide ion have been used to make discrete multinuclear complexes.[5] Anion control in the self-assembly of a cage coordination complex is often refered to as anion templation. In this letter, we describe a novel hexacopper(II) complex $[Cu_6Cl(MeO)_2(pz)_9]$ (**1**) where a chloride anion is used as a template. The synthesis, structure, and magnetic behavior are reported.

Reaction of pyrazole, $Cu(ClO_4)_2\cdot 6H_2O$, and $Et_4NCl\cdot H_2O$ in methanol (3 : 2 : 3 molar ratio) followed by addition of a methanolic solution of triethylamine afforded dark green crystals of **1**. Excess chloride ion was essential in order to obtain **1** in good yield.[6]

Figure 1 shows the crystal structure of **1**.[7] The hexacopper(II) cage consists of two tricopper(II) units, $\{Cu_3(\mu_3\text{–}OMe)(pz)_3\}^{2+}$ (shown with filled bonds in Fig. 1), and three perpendicular pyrazolates (shown with open bonds, $pz_{\perp}^-$) which bridge the two tricopper(II) units. Six copper(II) ions form a trigonal prismatic array. The chloride anion is located at the center of the prism and weakly bound to the six copper(II) ions in a μ_6–mode. There are two perpendicular crystallographic mirror planes passing through Cl, which divide the trigonal prism vertically, passing through Cu1, O1, N4, and Cl, and horizontally, passing through Cl and the center of the N–N bonds of $pz_{\perp}^-$. In the tricopper(II) unit, copper(II) ions are bridged by pyrazolate ligands ($pz_{\parallel}^-$) being almost coplanar to the Cu_3 triangle, and by a μ_3–methoxy group capping from ca. 1.0 Å above the tricopper(II) plane. Each copper(II) atom is in an axially elongated square pyramidal environment with a basal N_3O donor set including two nitrogens from two $pz_{\parallel}^-$ ligands (Cu1–N1 = 1.935(5), Cu2–N2 = 1.931(5), and Cu2–N3 = 1.941(5) Å), a nitrogen from a $pz_{\perp}^-$ (Cu1–N4 = 1.992(7) and Cu2–N5 = 1.990(5) Å), and an oxygen from a μ_3-OMe^- (Cu1–O1 = 2.085(6) and Cu2–O1 = 2.083(4) Å). The apical position of the pyramid is occupied by Cl with long Cu–Cl separation (2.623(2) Å for Cu1 and 2.6032(13) Å for Cu2, respectively).

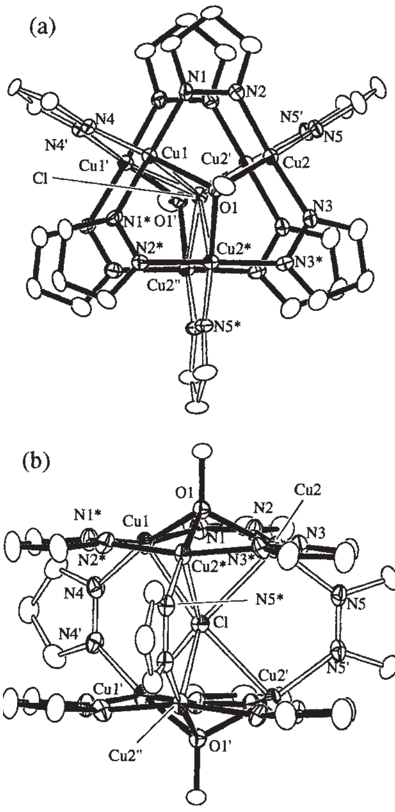

Figure 1. ORTEP drawing of **1** with thermal ellipsoids at 50% probability ((a) overview and (b) sideview). Hydrogen atoms are omitted for clarity. The moiety with solid bonds represents the tricopper(II) unit (see text). Selected atom-atom distances (Å): Cu1···Cu2, 3.2331(12); Cu2···Cu2*, 3.209(1); Cu1–N1, 1.935(5); Cu2–N2, 1.931(5); Cu2–N3, 1.941(5); Cu1–N4, 1.992(7); Cu1–O1, 2.085(6); Cu2–N5, 1.990(5); Cu2–O1, 2.083(4); Cu1–Cl1; 2.623(2); Cu2–Cl1, 2.6032(13); symmetry codes: (*) x, y, $-z + 1.5$; (′) $-x$, y, z; (″) $-x$, y, $-z + 1.5$.

Some trinuclear structures including pyrazolates or its derivatives as bridging ligands have been reported. Most of these complexes contain diamagnetic copper(I) and silver(I),[8] and few complexes involve magnetic metal ions.[9] Only one hexacopper(II) complex is known, although magnetic behavior of the complex was not reported.[9a]

The magnetic properties of **1** were investigated and are shown in Figure 2(a). The $\chi_m T$ value of **1** at 250 K is ca. 1.5 emu K mol^{-1}, which is much smaller than the spin only value of 2.25 emu K mol^{-1} for six dilute magnetic centers ($S = 1/2$ for copper(II)). This indicates the presence of a strong antiferromagnetic coupling between the copper(II) ions. The $\chi_m T$ value decreases as the temperature goes down and it shows a steeper decrease below 40 K, which suggests the magnetic interaction is rather strong. The magnetic data of **1** were analyzed using the HDvV model (eq 1) shown in Figure 2(b).[10]

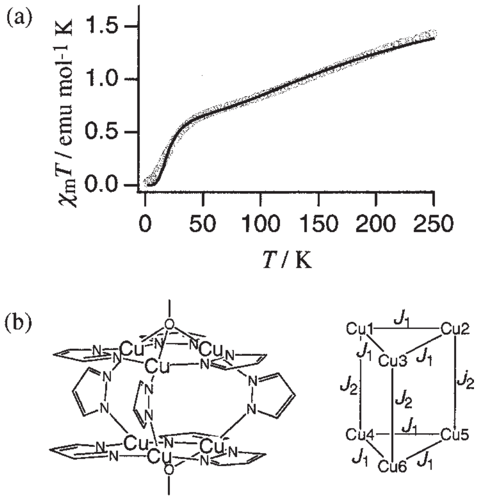

Figure 2. (a) Plots of χ_mT vs T for **1**. The solid line corresponds to the theoretical curve for which parameters are given in the text. (b) A schematic drawing of J_1 and J_2.

$$\begin{aligned} H = &-2J_1(S_{\mathrm{Cu1}} \cdot S_{\mathrm{Cu2}} + S_{\mathrm{Cu2}} \cdot S_{\mathrm{Cu3}} + S_{\mathrm{Cu3}} \cdot S_{\mathrm{Cu1}} \\ &+ S_{\mathrm{Cu4}} \cdot S_{\mathrm{Cu5}} + S_{\mathrm{Cu5}} \cdot S_{\mathrm{Cu6}} + S_{\mathrm{Cu6}} \cdot S_{\mathrm{Cu4}}) \\ &- 2J_2(S_{\mathrm{Cu1}} \cdot S_{\mathrm{Cu4}} + S_{\mathrm{Cu2}} \cdot S_{\mathrm{Cu5}} + S_{\mathrm{Cu3}} \cdot S_{\mathrm{Cu6}}) \qquad (1) \end{aligned}$$

In eq 1, J_1 represents an intra-unit interaction which operates between copper ions through the $\mathrm{pz}_{\parallel}^-$ and the OMe^-, and J_2 represents an inter-unit interaction mediated by the $\mathrm{pz}_{\perp}^-$. As mentioned above, the copper(II) ions are in a distorted square-pyramidal environment with Cl in the apical position, and each magnetic orbital lies in the basal plane. Therefore, magnetic interactions mediated by chloride (e.g., Cu1–Cu6 in Figure 2(b)) must be small and were omitted in eq 1. The least squares calculation yielded best fit parameters of $J_1 = -66.4(1)\,\mathrm{cm}^{-1}$ and $J_2 = -17.1(1)\,\mathrm{cm}^{-1}$ with $g = 2.00$ (fixed). The relation between the magnitude of the magnetic interaction and the structural parameters of the μ_3-hydroxy bridged tricopper(II) complex was reported previously.[9b] All interactions reported were antiferromagnetic and the magnitude of the interaction increases as the equatorial planes of the neighboring copper(II) ions become coplanar. In **1**, the dihedral angle of the basal planes for Cu1 (N1, N1*, N4, O1) and Cu2 (N2, N3, N5, O1) is 57°, and the dihedral angle for Cu2/Cu2* is 55°. Consequently, the obtained J_1 value, $-66.4(1)\,\mathrm{cm}^{-1}$, is roughly consistent with the expected value from the structure.

The same synthetic procedure using bromide or iodide instead of chloride did not lead to similar hexacopper(II) complexes. This indicates that the size of the cage is suitable only for the chloride ion. This result indicates that the size of a mono-atomic templating anion is essentially important in making the skeleton of the hexacopper(II) trigonal prism. The present synthetic method can be considered as a novel example of a one-pot metal ion assembly reaction.

This work was supported by a Grant-in Aid for Scientific Research (Nos. 10149102, 14340203, and 13740370) from the Ministry of Education Culture, Sports, Science, and Technology, Japan, as well as by JSPS Research Fellowships for Young Scientists (No. 12006281).

References and Notes

1 a) C. Boskovic, E. K. Brechin, W. E. Streib, K. Folting, J. C. Bollinger, D. N. Hendrickson, and G. Christou, *J. Am. Chem. Soc.*, **124**, 3725 (2002). b) E. C. Sañudo, V. A. Grillo, M. J. Knapp, J. C. Bollinger, J. C. Huffman, D. N. Hendrickson, and G. Christou, *Inorg. Chem.*, **41**, 2441 (2002).

2 K. D. Demadis, C. M. Hartshorn, and T. J. Meyer, *Chem. Rev.*, **101**, 2655 (2001).

3 a) G. Süss-Fink, M. Faure, and T. R. Ward, *Angew. Chem., Int. Ed.*, **41**, 99 (2002). b) M. Yagi and M. Kaneko, *Chem. Rev.*, **101**, 21 (2001).

4 a) V. Chandrasekhar and S. Kingsley, *Angew. Chem., Int. Ed.*, **39**, 2320 (2000). b) G. A. Ardizzoia, M. A. Angaroni, G. L. Monica, F. Cariati, S. Cenini, M. Moret, and N. Masciocchi, *Inorg. Chem.*, **30**, 4347 (1991).

5 a) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, **40**, 486 (2001). b) R. Vilar, D. M. P. Mingos, A. J. P. White, and D. J. Williams, *Angew. Chem., Int. Ed.*, **37**, 1258 (1998). c) B. Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. V. Dorsselaer, B. Kneisel, and D. Fenske, *J. Am. Chem. Soc.*, **119**, 10956 (1997).

6 An ESI-mass spectrometric study of the reaction solution of pyrazole, $\mathrm{Cu(ClO_4)_2{\cdot}6H_2O}$, and $\mathrm{Et_4NCl{\cdot}H_2O}$ in a 9 : 6 : x ratio ($x = 0$, 1, and 9) in the presence of $\mathrm{Et_3N}$ was performed. When the reaction ratio was the same as the hexacopper complex **1** ($x = 1$), an almost similar spectrum to that for $x = 0$ was obtained, but a quite different spectrum was obtained in the presence of chloride ion at the same molar ratio as the synthesis of **1** ($x = 9$). Although the peaks were not characterized, it clearly indicates that an excess chloride ion affects the formation of **1**.

7 Crystal data for **1**: $\mathrm{C_{29}H_{33}ClCu_6N_{18}O_2}$, $M = 1082.42$, orthorhombic, space group *Cmcm*, $a = 13.325(2)$ Å, $b = 18.092(3)$ Å, $c = 15.008(2)$ Å, $V = 3618.0(10)$ Å^3, $Z = 2$, $F(000) = 1080$, $D = 0.994\,\mathrm{g/cm^3}$, Mo K$\alpha$ radiation $\lambda = 0.71073$ Å, 2270 independent reflections, 1710 reflections were observed ($I > 2\sigma(I)$), $R1 = 0.0716$, $wR2 = 0.1283$ (observed), $R1 = 0.1015$, $wR2 = 0.1386$ (all data). The intensity data were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation. Data reductions were performed with the SAINT software, which corrects for Lorentz and polarization factors. Absorption corrections were applied with SADABS supplied by G. Sheldrick (Universität Göttingen). The structure was solved by the direct methods using SHELXS-97 and refined by least squares method on F^2, SHELXL-97, incorporated in SHELXTL-PC version 5.10. All non-hydrogen atoms were refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC 191408).

8 a) K. Singh, J. R. Long, and P. Stavropoulos, *J. Am. Chem. Soc.*, **119**, 2942 (1997). b) G. A. Ardizzoia, S. Cenini, G. L. Monica, N. Masciocchi, A. Maspero, and M. Moret, *Inorg. Chem.*, **37**, 4284 (1998).

9 a) K. Sakai, Y. Yamada, T. Tsubomura, M. Yabuki, and M. Yamaguchi, *Inorg. Chem.*, **35**, 542 (1996). b) M. Angaroni, G. A. Ardizzoia, T. Beringhelli, G. L. Monica, D. Gatteschi, N. Masciocchi, and M. Moret, *J. Chem. Soc., Dalton Trans.*, **1990**, 3305.

10 O. Kahn, "Molecular Magnetism," VCH Publishers, Weinheim (1993).