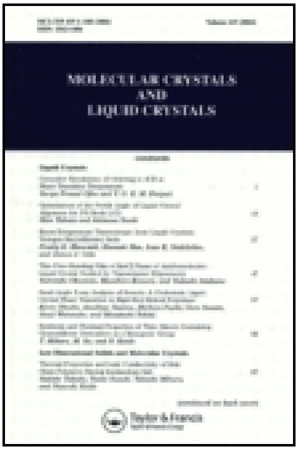

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Synthesis, Structure, and Magnetic Properties of Tetranuclear Copper(II) Complexes of Tridentate Dianionic Ligands with an *ONO* Donor Set

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Tetranuclear complexes $[CuL2H]_4$ (**1**), $[CuL2Me]_4$ (**2**), and $[CuL2Cl]_4$ (**3**) with a reduced Schiff base type tridentate ligand H_2L2H and its homologous with a substituent on the 2-hydroxymethylphenyl moiety (4-Me, H_2L2Me; 4-Cl, H_2L2Cl) were prepared and characterized by elemental analyses and magnetic measurements. The crystal structure of **1** was determined by X-ray crystallography. Tetracopper core is represented as a dimer-of-dimers structure by the stacking of two dicopper units bridged by alcoholic oxygens. One of the dicopper units contains square pyramidal (SP) Cu(II) ions, whereas the geometry of each Cu(II) ion in the other unit is described as essentially distorted trigonal bipyramid (TBP). Magnetic behaviors of the complexes are explained by modified equation based on the theoretical Spin Hamiltonian. The exchange integrals ($-2J$) are evaluated at 292 – 366 cm^{-1} for SP dicopper cores and 104 – 120 cm^{-1} for TBP, respectively, indicating the existence of different type of antiferromagnetic interaction-pathways corresponded to each copper geometry.

Keywords: Tridentate Ligand; Tetranuclear Copper(II) Complex; X-Ray Crystallography; Magnetic Susceptibility; Antiferromagnetic Interaction

INTRODUCTION

Transition metal complexes with *ONO*-tridentate ligand containing hydroxyl groups as terminal coordinating atoms have attracted much attention. The ligands can act as mono-, bi-, and tridentate so as to be suited to geometries of metal ions, and give various coordination structures.[1-3] According to the above mentioned point of view, the design of such ligands is considerably effective to obtain new metal-assembled complexes. The most of reported *ONO*-ligands are Schiff bases, such as salicylideneaminophenol. However, Schiff base ligands are fairly rigid, and the coordination aspect to the metal ion is rather standardized. In this study we have prepared reduced Schiff base ligands (H_2L2X: X = H, H_2L2H; 4-Me, H_2L2Me; 4-Cl, H_2L2Cl) of salicylaldehyde with aminobenzylalcohol, which are more flexible and not constrained to remaining planar. Here we report the X-ray structural characterization of the tetranuclear copper(II) complexes of the reduced ligands together with their magnetic properties.

EXPERIMENTAL

Preparation of Ligands

The Schiff base ligands H_2L1X (X = H, Me, and Cl) were prepared by condensation reaction of the appropriate *o*-aminobenzyl alcohol and salicylaldehyde in methanol.[3] The ligands H_2L2X (X = H, Me, and Cl) were isolated as boron complexes. The Schiff base ligand (10 mmol) in methanol (10 cm^3) was reduced with an excess of sodium borohydride (0.76 g, 20 mmol). The yellow color gradually discharged, and after 10 min the solution was acidified with acetic acid to a pH of 6. The resulting white precipitate was filtered off, washed with water and dried *in vacuo*. H_2L2H: yield, 77.5 %; (Found: C, 70.81; H, 5.24; N, 5.90 %. $C_{14}H_{14}BNO_2$ requires C, 70.33; H, 5.90; N, 5.86 %). H_2L2Me: yield, 68.3 %; (Found: C, 70.99; H, 5.72; N, 5.55 %. $C_{15}H_{16}BNO_2$ requires C, 71.18; H, 6.37; N, 5.53 %). H_2L2Cl: yield, 76.7 %; (Found: C, 61.74; H, 4.20; N, 5.17 %. $C_{14}H_{13}BClNO_2$ requires C, 61.48; H, 4.79; N, 5.12 %).

Preparation of Complexes

$[CuL2X]_4$. Copper(II) acetate monohydrate (0.199 g, 1.0 mmol) was dissolved in methanol (20 cm^3) and solution of appropriate H_2LX (1.0

mmol) was added. The mixture was stirred for 30 min with heating. The bright green precipitate was filtered off, washed with methanol and dried *in vacuo*. Crystallization from a dichloromethane–methanol (1:1) solution formed deep green crystals of **1** suitable for X-ray crystallography. $[CuL2H]_4$: yield, 74.1 %; (Found: C, 52.70; H, 4.66; N, 4.15; Cu, 20.42 %. $C_{56}H_{52}Cu_4N_4O_8 \cdot 3H_2O \cdot CH_2Cl_2$ requires C, 52.57; H, 4.64; N, 4.30; Cu, 19.52 %). *m/z* (FAB) 1163 $\{[CuL2H]_4H^+\}$. $[CuL2Me]_4$: yield, 65.1 %; (Found: C, 56.96; H, 5.45; N, 4.58; Cu, 19.87 %. $C_{60}H_{60}Cu_4N_4O_8 \cdot 2H_2O \cdot CH_3OH$ requires C, 56.91; H, 5.32; N, 4.35; Cu, 19.74 %). *m/z* (FAB) 1219 $\{[CuL2Me]_4H^+\}$. $[CuL2Cl]_4$: yield, 52.3 %; (Found: C, 50.52; H, 3.93; N, 4.27; Cu, 18.75 %. $C_{56}H_{48}Cl_4Cu_4N_4O_8 \cdot H_2O \cdot CH_3OH$ requires C, 50.67; H, 4.03; N, 4.15; Cu, 18.81 %). *m/z* (FAB) 1301 $\{[CuL2Cl]_4H^+\}$.

Physical Measurement

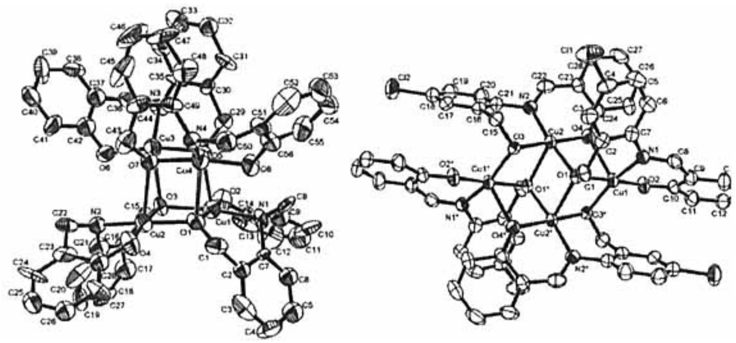
Elemental C, H, N analyses were obtained at the Service Center of Elemental Analysis at Kyushu University. Analysis of copper was made using a titrimetric method. FAB mass spectra were recorded on a JEOL JMS-HX110A high-resolution mass spectrometer. The magnetic susceptibilities were determined by the Faraday method. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[4]

X-Ray Crystal Structure Determination

The diffraction data were measured on a Rigaku AFC5S automated four-circle diffractometer. The data were collected using the ω–2θ scan technique to a maximum 2θ value of 55°. Crystal data and data collection parameters: **1**, $C_{59}H_{64}Cl_2Cu_4N_4O_{11}$, $M = 1330.26$, monoclinic, $a = 13.55(3)$, $b = 17.724(3)$, $c = 25.046(9)$ Å, $\beta = 99.2(1)$ °, $V = 5938(9)$ Å^3, space group $P2_1/n$ (#14), $Z = 4$, $T = 296 \pm 1$ K, μ(Mo-Kα) = 15.65 cm^{-1}, 14763 reflections measured, 4509 unique reflections with $I > 3.00\sigma(I)$, Final value for $R = 0.068$ / $R_W = 0.069$.

RESULT AND DISCUSSION

Analytical data of the complexes gave a 1:1 metal to ligand ratio. FAB mass spectral results indicated that tetranuclear structures have been formed for present complexes. The single crystals of **1** suitable for X-ray crystallography were obtained by a slow evaporation from



(a) (b)

FIGURE 1 (a) ORTEP drawing for **1**. (b) ORTEP drawing for Schiff base complex $[CuL1Cl]_4$.

dichloromethane-methanol solution. However, our attempts to obtain crystals of **2** and **3** were currently unsuccessful and single crystals of Schiff base complexes were obtained from the solution of **2** and **3**. Because oxidative dehydrogenation of a secondary amine in the ligands was occurred. The ORTEP drawing of **1** with the atom numbering scheme is illustrated in FIGURE 1 (a). The complex has a cubane-like tetranuclear core attributed to the dimer-of-dimers structure by the stacking of alkoxo-bridged dicopper units. The intra-unit Cu–Cu distances of Cu1–Cu2 and Cu3–Cu4 are 3.014(3) and 2.962(5) Å, respectively. The distances are much shorter than inter-unit Cu–Cu distances (3.144(2)–3.304(2) Å), which indicates the tetranuclear core is elongated from the ideal cubane structure. The coordination geometry of Cu1 and Cu2 ions is best described as a square pyramid. The apical positions are occupied by O5 and O7, where the distances are 2.351(9) and 2.349(9) Å, respectively. The basal coordination sites of each copper(II) ion are occupied by the NO_2 donor set of the tridentate ligand and an alkoxo-oxygen atom of the bridging ligand, where the bond distances are fall in the range 1.885(9)–1.99(1) Å. On the other hands, the geometry of Cu3 and Cu4 is best described as a distorted trigonal bipyramid with the trigonal-axes of O5–Cu3–O6 (169.1(4) °) and O7–Cu4–O8 (170.5(4) °), respectively. The phenyl rings in the ligands are fairly bending opposite to the cubane core to relax ring-strain caused by adjacent six-membered chelate rings. The single crystals of $[\mathrm{CuL1Cl}]_4$ were accidentally obtained in the process for recrystallization of $[\mathrm{CuL2Cl}]_4$. The crystal structure of $[\mathrm{CuL1Cl}]_4$ is shown in FIGURE 1 (b).[5] Four copper ions assume square pyramidal conformation, and the adjacent basal planes are nearly orthogonal with each other. It is apparent that the core structures in L1 and L2 complexes are depended on the planarity of a nitrogen atom in the ligand structure.

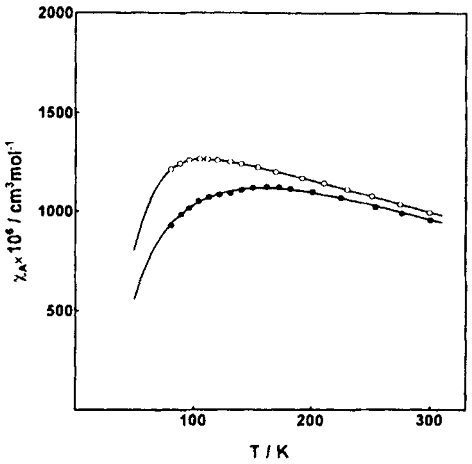


FIGURE 2. χ_A *vs.* T plots for **1** (○) and **2** (●). The solid lines were obtained as described in the text.

The magnetic properties of the present complexes were measured in the temperature range 80–300 K. Plots of the magnetic susceptibilities are shown in FIGURE 2. The analysis was carried using a modified equation (1) for the dimer-of-dimers stacking model based on the isotropic Heisenberg model, where J_1 and J_2 are spin-

$$\chi_A = \frac{1}{2}\frac{N\beta^2}{k(T-\theta)}\left(\frac{g_1^2}{3+\exp(-2J_1/kT)} + \frac{g_2^2}{3+\exp(-2J_2/kT)}\right) + N\alpha \qquad (1)$$

exchange integrals for Cu1(SP)–Cu2(SP) and Cu3(TBP)–Cu4(TBP), respectively, and θ is an inter-unit interaction parameter. The value of

TABLE 1. Magnetic Data for complexes **1** and **2**

Complexes	$-2J_1$ / cm^{-1}	$-2J_2$ / cm^{-1}	g_1	g_2	θ / K
1	-366	-120	2.10	2.08	18
2	-292	-104	2.15	2.00	-16

$N\alpha$ was fixed to 60×10^{-6} cm^{3}mol^{-1} in the present study. The best fitting parameters obtained by a Gauss-Newton non-linear least-square method are listed in TABLE 1. The values of $-2J_1$ are normal for the alkoxo-bridged square-pyramidal dicopper cores with the $d_{x^2-y^2}$ magnetic orbital. However, the magnetic orbital in the Cu3 and Cu4 is d_{z^2} which makes less overlap than that in the Cu1–Cu2 interaction.

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[5] Crystal data and data collection parameters: $[CuL1Cl]_4$, $C_{58}H_{44}Cl_8Cu_4N_4O_8$, M= 1462.82, triclinic, $a = 9.895(3)$, $b = 11.948(9)$, $c = 13.369(3)$ Å. $\alpha = 88.37(3)$. $\beta = 107.373(19)$, $\gamma = 106.00(3)$ °, $V = 1447.5(11)$ Å^3, space group $P\bar{1}$ (#2), $Z = 1$, $T = 296 \pm 1$ K, μ(Mo-Kα) = 18.77 cm^{-1}, 7020 reflections measured, 4213 unique reflections with I > 3.00σ(I). Final value for $R = 0.050$ / $R_W = 0.044$.