# Linear Trinuclear Copper(II) Complexes Bridged by Oximato and Azido or Hydroxo Groups

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The linear trinuclear copper(II) complexes $Cu_3(L_1)_2(N_3)_2(NO_3)_2 \cdot 2H_2O \cdot 2CH_3OH$ **1** and $Cu_3(L_1)_2(OH)_2(ClO_4)_2$ **2** containing 3-[{2-(2-pyridinyl)ethyl}imino]-2-butanone oximato ligand ($L_1$) were prepared; the crystal structure of **1** was determined by X-ray crystallography. Magnetic susceptibility measurements from liquid helium temperature to room temperature showed a very strong antiferromagnetic exchange coupling between copper(II) ions($J$ = -266 $cm^{-1}$ and -245 $cm^{-1}$ for **1** and **2**, respectively, $H = -2JS_1 \cdot S_2$).

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Studies on di- and trinuclear copper(II) complexes have been focused in two areas; i.e. (i) the magnetostructural relationships and (ii) characterization of active sites in type 3 copper and multicopper proteins. The linear and triangular trinuclear copper(II) complexes with the oximato group ($C{=}N{-}O^-$) have been structurally and magnetically characterized from the viewpoint of their magnetostructural relationships.[1-8] In particular, Luneau *et al.* have reported some linear trinuclear copper(II) complexes with double oximato bridges, such as $[Cu(dimethylglyoximato)\{Cu(2,2'\text{-}bipyridine)(CH_3OH)\}_2](NO_3)_2$.[6,7] However, no linear type of trinuclear copper(II) complex bridged by an oximato and a simple bridging ligand such as $N_3^-$ or $OH^-$ has been reported so far. We describe here preparation and characterization of two novel linear trinuclear copper(II) complexes $Cu_3(L_1)_2(N_3)_2(NO_3)_2 \cdot 2H_2O \cdot 2CH_3OH$ **1** and $Cu_3(L_1)_2(OH)_2(ClO_4)_2$ **2** containing bridging oximato and azido or hydroxo species.

$Cu_3(L_1)_2(N_3)_2(NO_3)_2 \cdot 2H_2O \cdot 2CH_3OH$ **1** was prepared by a reaction between $HL_1$ (0.41 g, 2.0 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (0.72 g, 3.0 mmol), $NaN_3$ (0.13 g, 2.0 mmol), and NaOH (0.08 g, 2.0 mmol) in a mixture of $H_2O$ and $CH_3OH$ (4 : 1). The dark-brown crystals suitable for X-ray study were obtained by keeping the reaction mixture in air at room temperature for several days (0.81 g, 90% yield). Anal. Calcd for $C_{24}H_{40}N_{14}O_{12}Cu_3$ **1**: C, 31.76; H, 4.45; N, 21.61. Found: C, 30.96; H, 4.37; N, 21.29. $Cu_3(L_1)_2(OH)_2(ClO_4)_2$ **2** was prepared analogously [$HL_1$ (0.41 g, 2.0 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (1.11 g, 3.0 mmol), NaOH (0.16 g, 4.0 mmol)] (0.70 g, 84% yield). Anal. Calcd for $C_{22}H_{30}N_6O_{12}Cu_3$ **2**: C, 31.75; H, 3.64; N, 10.10. Found: C, 31.32; H, 3.78; N, 9.89.

Crystal data for **1**: $F_w$ = 907.30, monoclinic, space group $P2_1/c$, $a$ = 9.778(2), $b$ = 10.122(2), $c$ = 18.623(2) Å, $\beta$ = 101.64(1)°, $V$ = 1805.3(5) $Å^3$, $Z$ = 2, $D_m$ = 1.66, $D_c$ = 1.67g $cm^{-3}$, $\mu(MoK\alpha)$ = 18.3 $cm^{-1}$. A total of 4640 reflections with $2\theta \leq 50°$ were collected on a RIGAKU AFC7S diffractometer using Mo$K\alpha$ radiation ( $\lambda$ = 0.71069 Å). Empirical absorption correction was applied. The structure was solved by SHELXS 86[9] and refined by full-matrix least-squares {refinement on F for 2995 observed reflections [$I \geq 3\sigma(I)$] with TEXSAN}.[10] $R$ and $R_w$ were 0.040 and 0.037 for 241 parameters with $w = 1/\sigma^2(F_o)$. The maximum and minimum electron densities on the final Fourier difference synthesis were 0.41 and -0.46 e $Å^{-3}$.

ORTEP[11] view of $[Cu_3(L_1)_2(N_3)_2(H_2O)_2(CH_3OH)_2]^{2+}$ in **1** is shown in Figure 1 with selected bond lengths and angles. The cation has an inversion center at the central copper atom Cu(1). The coordination around Cu(1) is square planar with $N_2O_2$ donor set from two nitrogens of bridging azido ligands and two oximato oxygens. The Cu(1)—N(4) and Cu(1)—O(1) bond lengths are 1.993(3) and 1.909(2) Å, respectively. Each terminal copper atom Cu(2) exhibits an elongated octahedral $N_4O_2$ coordination with three nitrogen atoms of $L_1$ and one nitrogen atom of azido in the basal plane and each oxygen of water and methanol molecules at the axial position. The plane defined by N(1), N(2), N(3), and N(4) atoms is nearly planar: maximum deviation is 0.141 Å (N(1)). The O(2) and O(3) atoms are at 2.430 and 2.583 Å below and above the plane. The Cu(2)—N(1,2,3,4) bond lengths are in the range 1.985(3)–2.020(3) Å. The Cu(2)—O(2) and Cu(2)—O(3) bond lengths are 2.434(3) and 2.600(3) Å. The terminal copper and central copper are linked through one oximato and one azido ligands, and the Cu(1)···Cu(2) separation is 3.4008(5) Å. The dihedral angle between planes [Cu(1), O(1), N(4), O(1'), N(4') (-x, -y, -z)] and [Cu(2), N(1), N(2), N(3), N(4)] is 6.6°.

The magnetic moments of 1 and 2 at room temperature are 1.19 and 1.12 BM, respectively, which are fairly smaller than the spin-only value. The magnetic susceptibilities of **1** and **2** were measured over the range from liquid helium temperature to room

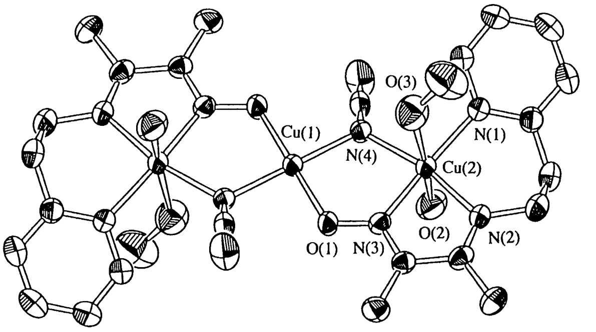

**Figure 1.** ORTEP view of $[Cu_3(L_1)_2(N_3)_2(H_2O)_2(CH_3OH)_2]^{2+}$ in **1**. Selected bond lengths (Å) and angles (°): Cu(1)—O(1) 1.909(2), Cu(1)—N(4) 1.993(3), Cu(2)—N(1) 2.020(3), Cu(2)—N(2) 1.990(3), Cu(2)—N(3) 1.985(3), Cu(2)—N(4) 1.996(3), Cu(2)—O(2) 2.434(3), Cu(2)—O(3) 2.600(3) Å; O(1)—Cu(1)—N(4) 91.7(1), N(4)—Cu(1)—O(1') 88.3(1), Cu(1)—N(4)—Cu(2) 117.0(1), Cu(1)—O(1)—N(3) 118.6(2), Cu(2)—N(3)—O(1) 126.0(2), N(1)—Cu(2)—N(2) 94.1(1), N(2)—Cu(2)—N(3) 79.9(1), N(3)—Cu(2)—N(4) 86.6(1), N(1)—Cu(2)—N(4) 99.5(1)°.

temperature with a SQUID magnetometer (Quantum design MPMS-5S). The molar susceptibilities, $\chi_A$, were fitted to the theoretical equation (1)[12]

$$\chi_A = \frac{Ng^2\mu_B^2}{12kT} \times \frac{1+\exp(-2J/kT)+10\exp(J/k)}{1+\exp(-2J/kT)+2\exp(J/k)} + N\alpha \quad (1)$$

where $J$, $g$, and $N\alpha$ denote the exchange integral, $g$ value and T.I.P., respectively. The magnetic parameters can be estimated as $g = 2.10$, $J = -266$ cm$^{-1}$, and $N\alpha = 60\times10^{-6}$ cgs emu mol$^{-1}$ for **1** and $g = 2.09$, $J = -245$ cm$^{-1}$, and $N\alpha = 60\times10^{-6}$ cgs emu mol$^{-1}$ for **2**. An example of the data is given in Figure 2. These results show that a very strong antiferromagnetic spin-coupling occurs in both **1** and **2**. In addition, these complexes are ESR silent in the solid phase and in a methanol solution. These strong antiferromagnetic interactions in **1** are probably due to two reasons; (i) the geometry of the complex is such that the planes [Cu(2), N(1), N(2), N(3), N(4)], [Cu(1), O(1), N(4), O(1'), N(4')], and [Cu(2'), N(1'), N(2'), N(3'), N(4')] are coplanar and (ii) the Cu(1)–N(4)–Cu(2) angle of 117.0° are greater than 103°.[13] The molar conductivities, Λ, of these complexes in a methanol solution are 173 S·cm$^2$·mol$^{-1}$ for **1** and 182 S·cm$^2$·mol$^{-1}$ for **2**, characteristic for 1 : 2 electrolytes. Accordingly, the solid state structures of **1** and **2** are supposed to be maintained in methanol. The electronic absorption spectra of **1** and **2** in methanol solutions exhibit the d-d band at 626 nm (ε, 241(sh)) for **1**, and those at 614 nm (ε, 176(sh)) and 521 nm (ε, 246(sh)) for **2**. The X-ray analysis of **2** is now in progress.

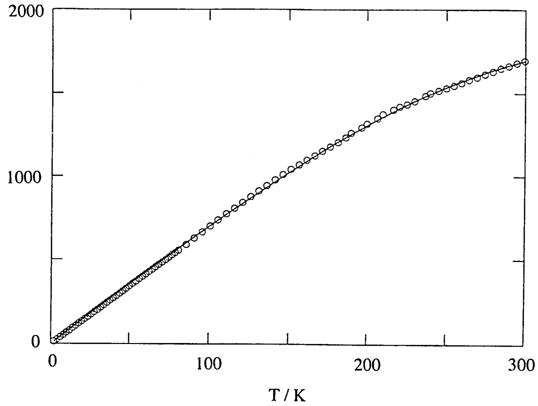

**Figure 2.** Temperature dependence of the inverse magnetic susceptibility of **1**. The open circles indicate observed susceptibility. The solid line shows the theoretical susceptibility calculated by the equation (1).

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