Novel Dinuclear Copper(II) Complexes with *syn–syn* and *syn–anti* Coordination Modes of Bis(μ-phosphinato)-bridges: Structures and Magnetic Properties

Koichi Koga, Miki Ohtsubo, Yasunori Yamada, Masayuki Koikawa, and Tadashi Tokii*
Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, Saga 840-8502

(Received October 7, 2004; CL-041183)

Novel dinuclear copper(II) complexes with phosphinato bridging ligands, $[Cu_2(NO_3)(bmp)_2(5\text{-dmbpy})_2]NO_3{\cdot}H_2O$ (**1**), $[Cu_2(bmp)_2(5\text{-dmbpy})_2(MeOH)_2](BF_4)_2$ (**2**) (Hbmp = bis(4-methoxyphenyl)phosphinic acid, 5-dmbpy = 5,5′-dimethyl-2,2′-bipyridine), have been prepared and characterized. Crystal structures of **1** and **2** have revealed that two copper(II) ions in **1** are linked by two *syn–syn* bridging phosphinates, whereas **2** has two *syn–anti* bridging phosphinates. Magnetic susceptibility data for the present complexes are well represented by the dimer equation with the $2J$ values of $-19.1\,\mathrm{cm^{-1}}$ for **1** and $-0.7\,\mathrm{cm^{-1}}$ for **2**, indicating that weak antiferromagnetic interactions are operative.

In recent years, the reaction between a transition metal ion and a phosphorus acid or ester in the phosphate metabolism systems has attracted attentions of bioinorganic chemistry and inorganic chemistry.[1,2] There has been a growing interest in correlations between structures and magnetic properties of binuclear complexes having bridging ligands such as alkoxo, carboxylato, or oxo. However, the syntheses and magnetic properties of the polynuclear complexes with phosphate were still rare.[3–6] Especially, no reports on the correlation between structures and magnetic properties in the dinuclear copper(II) complexes with phosphinato (R_2POO^-) bridges are known. In this paper, we report the crystal structures and magnetic properties of $[Cu_2(NO_3)(bmp)_2(5\text{-dmbpy})_2]NO_3{\cdot}H_2O$ (**1**), which is the first example of dinuclear copper(II) complexes with *syn–syn* phosphinato bridges, and $[Cu_2(bmp)_2(5\text{-dmbpy})_2(MeOH)_2](BF_4)_2$ (**2**) with *syn–anti* coordination modes.

A typical synthetic procedure is as follows. Complex **1**: A solution of Hbmp (1 mmol) and 5-dmbpy (1 mmol) in $10\,\mathrm{cm^3}$ of methanol was added to a solution of Cu $(NO_3)_2{\cdot}3H_2O$ (1 mmol) in $5\,\mathrm{cm^3}$ of methanol under stirring for 10 min. To the resulting solution ca. 1 mmol of Et_3N was added under stirring. The blue green solution was filtered and the filtrate was allowed to stand for several weeks at room temperature. The blue green crystals were collected, washed with methanol, and dried under air (yield 0.19 g, 16.0%). Anal. Calcd for $C_{52}H_{54}Cu_2N_6O_{15}P_2$: C, 52.39; H, 4.57; N, 7.05; Found: C, 52.05; H, 4.52; N, 7.00%. Complex **2**: The complex was prepared as blue green crystals in a manner similar to that of **1**, except that Cu $(BF_4)_2$ 45% aq was used instead of Cu $(NO_3)_2{\cdot}3H_2O$ (yield 0.77 g, 29.8%). Anal. Calcd for $C_{54}H_{60}B_2Cu_2F_8N_4O_{10}P_2$: C, 50.37; H, 4.70; N, 4.35; Found: C, 50.08; H, 4.61; N, 4.37%.

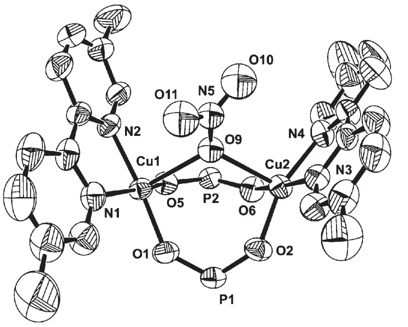


Figure 1. An ORTEP drawing at 50% probability level of the complex cation of **1**. Phenyl groups of phosphinato bridges are omitted for clarity. Selected bond distances (Å) and angles (°): Cu1···Cu2 3.933(8), Cu1–O1 1.941(8), Cu1–O5 1.941(8), Cu1–O9 2.353(1), Cu1–N1 2.008(2), Cu1–N2 2.007(1), Cu2–O2 1.937(4), Cu2–O6 1.938(9), Cu2–O9 2.322(4), Cu2–N3 1.988(2), Cu2–N4 1.999(1), O1–Cu1–O5 94.1(8), Cu1–O9–Cu2 94.1(8), O2–Cu2–O6 95.2(5).

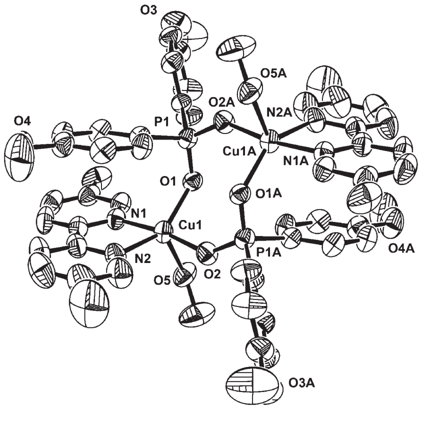
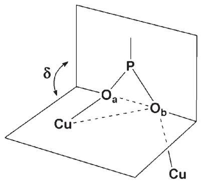


Figure 2. An ORTEP drawing at 50% probability level of the complex cation of **2**. Selected bond distances (Å) and angles (°): Cu1···Cu1A 4.811(1), Cu1–O1 1.961(2), Cu1–O2 1.915(3), Cu1–O5 2.243(3), Cu1–N1 1.990(3), Cu1–N2 2.021(3), O2–Cu1–N2 92.9(1), O5–Cu1–N1 87.3(1), O2–Cu1–N1 171.0(1), Cu1–O1–P1 125.5(2), O1–P1–O2A 116.16(2).

The crystal structures of **1** and **2** are shown in Figures 1 and 2, respectively.[7] The complex cation of **1** consists of a dicopper core with two phosphinates, one bridging nitrate, and two terminal ligands of 5-dmbpy. The geometry of each copper(II) ion is a distorted square-pyramidal configuration with the basal plane comprised of two 5-dmbpy nitrogen and two bmp oxygen atoms. According to the procedure described by Addison et al.,[8] the τ value of Cu1 and Cu2 is 0.21 and 0.16, respectively. Each apical site is occupied by an oxygen atom of an exogenous bridging nitrate ion. The most unusual feature of the structure in **1** is the dihedral angle (δ) observed between the least-squares planes through the bridging phosphinates, $[O_a, P, O_b]$ and $[O_a, O_b, Cu]$. The definition of coordination modes is based on the bridging modes of carboxylates.[9] The values of δ are 164.3° and 150.1° for [the O1, P1, O2 plane/the O2, O1, Cu1 plane and the O1, O2, Cu2 plane], respectively, and for the other O5–P2–O6 bridge corresponding the δ values are 168.6° and 157.0°, respectively. While the δ values are less than 180°, the phosphinate groups can be classified into the *syn-syn* bridging modes.



The complex cation of **2** consists of a dicopper core with two phosphinates, two terminal ligands of 5-dmbpy, and two methanol molecules. Especially, there are major differences in the coordination modes between **1** and **2**. The coordination around each copper(II) ion is a distorted trigonal-bipyrimidal geometry ($\tau = 0.45$) with the equatorial plane comprising of a 5-dmbpy nitrogen (N2), a bmp oxygen (O1), and a methanol oxygen atom (O5). Each axial site is occupied by a 5-dmbpy nitrogen (N1) and a bmp oxygen atom (O2). The δ values was 82.7° for [the O1, P1, O2A plane/the O2A, O1, Cu1 plane]. On the other hands, the δ values is 158.5° for [the O1, P1, O2A plane/the O1, O2A, Cu1A plane]. The phosphinato bridges can be assigned to *syn–anti* coordination modes. The difference of bridging modes between **1** and **2** has affected the Cu···Cu separation lengths of 3.993(8) and 4.811(1) Å, respectively.

The temperature dependence of the magnetic susceptibilities (χ_A) and the effective magnetic moments (μ_{eff}) per Cu(II) ion for **1** and **2** are shown in Figures 3 and 4. The μ_{eff} values for **1** (1.87 μ_B) and **2** (1.82 μ_B) at room temperature decrease to 0.28 and 1.72 μ_B at 2 K, respectively. A nonlinear least-squares fitting procedure of the magnetic data to the Bleaney–Bowers equation gave the following spin exchange coupling parameters: $2J = -19.1\,\mathrm{cm}^{-1}$ and $g = 2.19$ for **1**; $2J = -0.7\,\mathrm{cm}^{-1}$ and $g = 2.12$ for **2**. These results indicate that a weak antiferromagnetic interaction is operative in the present complexes. The difference in the strength of the antiferromagnetic interaction may be accounted for by the coordination geometry. The antiferromagnetic interaction in **1** and **2** can be operative primarily via the phosphinates directed toward the $d_{x^2-y^2}$ for **1** and d_{z^2} magnetic orbitals for **2** with unpaired spin density on the two copper(II) ions. The antiferromagnetic interaction for **1** could be mainly attributed to the exchange couplings between the copper ions through phosphinates, since the oxygen atom of an exogenous bridging nitrate ion locates in apical site of each copper(II) ion. The overlap of d_{z^2} magnetic orbital is expected to be weaker than that in **1** with the $d_{x^2-y^2}$ magnetic orbital.[10] The correlation between $2J$ values and coordination modes were in agreement with the $2J$ values of dinuclear copper(II) complexes with *syn–syn* and *syn–anti* bridging carboxylates.[11]

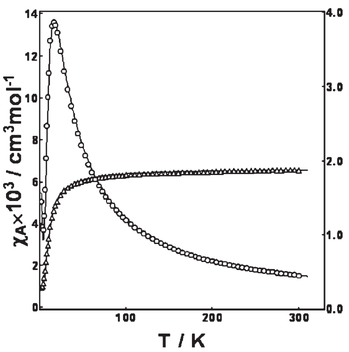


Figure 3. Magnetic susceptibilities χ_A and effective magnetic moments μ_{eff} for **1**.

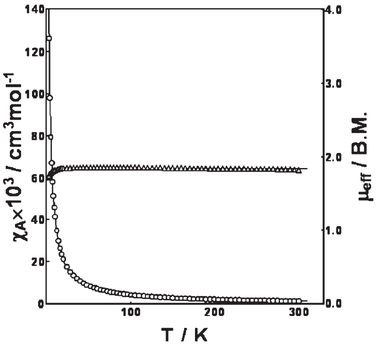


Figure 4. Magnetic susceptibilities χ_A and effective magnetic moments μ_{eff} for **2**.

A part of this work was supported by "Nanotechnology Support Project" of the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 N. H. Williams, B. Takasaki, M. Wall, and J. Chin, *Acc. Chem. Res.*, **32**, 485 (1999).
2 P. E. Jurek and A. E. Martell, *Inorg. Chem.*, **38**, 6003 (1999).
3 R. P. Doyle, P. E. Kruger, B. Moubaraki, K. S. Murray, and M. Nieuwenhuyzen, *J. Chem. Soc., Dalton Trans.*, **2003**, 4230.
4 L. Spiccia, B. Graham, M. T. W. Hearn, G. Lazarev, B. Moubaraki, K. S. Murray, and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, **1997**, 4089.
5 K. Aoki, *J. Am. Chem. Soc.*, **100**, 7106 (1978).
6 O. J. Parker, R. M. Harvey, and G. L. Breneman, *Acta Crystallogr., Sect. C*, **C52**, 871 (1996).
7 Crystallographic data for **1•MeOH**: $C_{53}H_{58}Cu_2N_6O_{16}P_2$, $M = 1224.11$, triclinic, space group $P_{\bar{1}}$, $a = 12.322(2)$ Å, $b = 14.485(2)$ Å, $c = 17.962(2)$ Å, $\alpha = 105.690(9)°$, $\beta = 92.01(1)°$, $\gamma = 99.30(1)°$, $V = 3035.6(7)$ Å^3, $Z = 2$, $D_{calcd} = 1.339\,\mathrm{g/cm^3}$, μ(Mo Kα) $= 8.21\,\mathrm{cm}^{-1}$, $T = 298$ K, $R_1 = 0.066$ and $wR_2 = 0.113$ for 14383 observed reflections with $I > 2.0\sigma(I)$. Crystallographic data for **2**: $C_{54}H_{60}B_2Cu_2F_8N_4O_{10}P_2$, $M = 1287.74$, triclinic, space group $P_{\bar{1}}$, $a = 10.961(2)$ Å, $b = 12.062(4)$ Å, $c = 12.738(1)$ Å, $\alpha = 87.82(1)°$, $\beta = 70.175(8)°$, $\gamma = 70.98(2)°$, $V = 1502.9(6)$ Å^3, $Z = 1$, $D_{calcd} = 1.423\,\mathrm{g/cm^3}$, μ(Mo Kα) $= 8.43\,\mathrm{cm}^{-1}$, $T = 298$ K, $R1 = 0.039$ and $wR2 = 0.118$ for 5069 observed reflections with $I > 3.0\sigma(I)$. All measurements were made on a Rigaku AFC5S diffractometer with graphite monochromated Mo Kα radiation. Crystallographics data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-235365, 235366.
8 A. W. Addison, T. N. Rao, T. Reedijk, J. van Riju, and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, **1984**, 1349.
9 H. Matsushima, E. Ishiwa, M. Koikawa, M. Nakashima, and T. Tokii, *Chem. Lett.*, **1995**, 129.
10 H. Matsushima, H. Hamada, K. Watanabe, M. Koikawa, and T. Tokii, *J. Chem. Soc., Dalton Trans.*, **1999**, 971.
11 G. Psomas, C. P. Raptopulou, L. Iordanidis, C. D.-Samara, V. Tangoulis, and D. P. Kessissoglou, *Inorg. Chem.*, **39**, 3042 (2000).

Published on the web (Advance View) November 13, 2004; DOI 10.1246/cl.2004.1606