Bull. Chem. Soc. Jpn., ***74***, *2375–2376 (2001)* 2375

Structures of Dinuclear Copper(II) Complexes Bridged by One Oximato, One Methoxo and One Perchlorato Ligand, and One Oximato and Two Acetato Ligands

Sachiyo Sakamoto, Akihiro Yatani, Katsusi Kimura, Mie Fujii, Yasuo Nakao,* Setsuo Kashino,† Masashi Kinoshita,†† and Wasuke Mori††

Chemical Laboratory, Faculty of Education,
Okayama University, Okayama 700-8530

†Department of Chemistry, Faculty of Science,
Okayama University, Okayama 700-8530

††Department of Chemistry, Faculty of Science,
Kanagawa University, Hiratsuka, Kanagawa 259-1205

(Received June 26, 2001)

The cation of [Cu(L$_1$)(OMe)(ClO$_4$)Cu(bpy)] ClO$_4$ (**1**) consists of two coppers triply bridged by an oximato, a methoxo, and a perchlorato ligand, where L$_1$ is 3-[2-(2-pyridyl)ethyl]amino-2-butanone oxime. The geometry around each copper is distorted square-pyramidal. The cation of [Cu(L$_1$)(OAc)$_2$Cu(bpy)]ClO$_4$ (**2**), consists of two coppers triply bridged by an oximato, an unidentate and a bidentate acetato ligand. The geometry around the coppers is intermediate between a square pyramid and a trigonal bipyramid.

The dinuclear copper(II) complexes with oximato bridges have been investigated crystallographycally and magnetically.[1–9] We have reported on the synthesis, structures and properties of some mixed ligand dinuclear copper(II) complexes bridged by one deprotonated oximato and one or two simple ligands such as azido, hydroxo or acetato.[4,6,7] We report here the structures of two novel dinuclear copper(II) complexes 1 and 2.

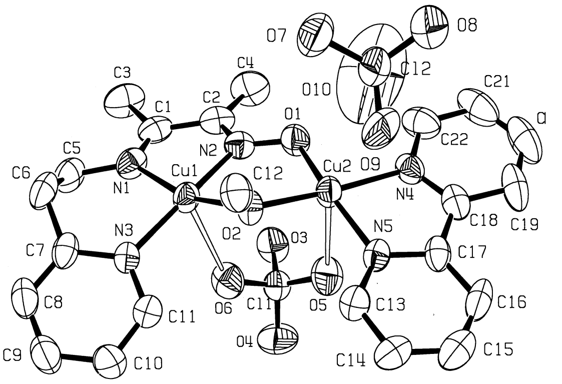

Fig. 1. Molecular structure of **1** showing the numbering scheme. Selected bond distances (Å) and angles (deg): Cu1–O2 1.918(3), Cu1–N1 1.984(4), Cu1–N2 1.980(4), Cu1–N3 2.006(4), Cu2–O1 1.930(3), Cu2–O2 1.921(3), Cu2–N4 1.997(4), Cu2–N5 1.976(4); O2–Cu1–N2 87.69(14), O2–Cu1–N3 98.04(13), N1–Cu1–N2 79.96(16), N1–Cu1–N3 95.39(15), O1–Cu2–O2 92.16(13), O1–Cu2–N4 89.71(15), O2–Cu2–N5 97.87(14), N4–Cu2–N5 81.57(16).

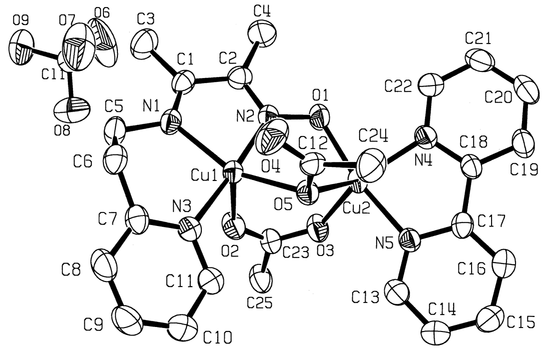

Fig. 2. Molecular structure of **2** showing the numbering scheme. Selected bond distances (Å) and angles (deg): Cu1–O2 2.163(3), Cu1–O5 2.030(3), Cu1–N1 1.994(3), Cu1–N2 1.976(3), Cu1–N3 1.992(3), Cu2–O1 1.921(3), Cu2–O3 1.989(3), Cu2–O5 2.210(3), Cu2–N4 2.030(3), Cu2–N5 1.990(3); O2–Cu1–O5 99.16(11), O2–Cu1–N3 88.62(13), O5–Cu1–N2 89.25(12), N1–Cu1–N2 79.79(14), N1–Cu1–N3 95.97(14), O1–Cu2–O3 97.74(13), O1–Cu2–O5 89.73(11), O1–Cu2–N4 89.43(13), O3–Cu2–O5 97.60(12), O3–Cu2–N5 90.42(13), O5–Cu2–N5 95.27(12), N4–Cu2–N5 80.39(14).

In the cation of **1**, a ligand L$_1$ coordinates to Cu1, and the N–O$^-$ portion of L$_1$ and OMe$^-$ bridge Cu1 and Cu2 (Fig. 1). The bpy chelates Cu2 (Fig. 1). The Cu1···Cu2 distance, 3.2327(11) Å, is close to that [3.295(4) Å] of the similar complex [Cu(L$_1$)(N$_3$)Cu(bpy)](ClO$_4$)$_2$.[6] The coordination around Cu1 exhibits distorted square pyramidal N$_3$O$_2$ coordination with three N atoms of L$_1$ and one O atom of OMe$^-$ in the basal plane and one oxygen (O6) of ClO$_4^-$ at the apical position. The geometry around Cu2 is also distorted square pyramidal N$_2$O$_3$ coordination with two N atoms of bpy and two O atoms of L$_1^-$ and OMe$^-$ in the basal plane and one oxygen (O5) of ClO$_4^-$ at the apical position. The Cu1–O6 and Cu2–O5 distances [2.495(4) and 2.712(4) Å] are in the range of the limit of semicoordination.[10] The dihedral angle between the two planes is 24.6°, being larger than those observed in two crystallographically independent [Cu(L$_1$)(N$_3$)Cu(bpy)](ClO$_4$)$_2$.[6] The Cu1–O2–Cu2 angle of 114.71(14)° is considerably smaller than those observed for the nearly diamagnetic mono-μ-hydroxo dinuclear copper(II) complexes.[11]

The cation in 2 consists of two Cu(II) ions bridged by the N−O$^-$ portion of L$_1$, one unidentate and one bidentate acetato ligand (Fig. 2). The distances Cu1–O5, Cu2–O5 and Cu1−O4 involving the unidentate bridging acetate are 2.030(3), 2.210(3), and 2.662(4) Å, respectively. These values are close to those in the complex $[Cu_2(OAc)_3(bpy)_2]$.[12] The geometry around Cu1 exhibits an intermediate feature between a square pyramid and a trigonal bipyramid. From the view point of the square pyramidal geometry, the N2, N1, N3 and O5 atoms form the equatorial plane and O2 occupies the apical position. From the view point of the trigonal bipyramidal geometry, N2 and N3 occupy the axial positions, and N1, O2, and O5 form the basal plane. The geometry around Cu2 is similar to that of Cu1. From the square pyramidal view point, O5 occupies the apical position, while from the trigonal bipyramidal view point, N5 and O1 occupy the axial positions. The τ values for $Cu(1)N_3O_2$ and $Cu(2)N_2O_3$ are 0.39 and 0.42, respectively, indicating the distortion towards a square pyramidal stereochemistry.[13] The Cu1···Cu2 distance is 3.2691(19) Å.[6]

The magnetic moment (μ_{eff}) of **1** at room temperature is 0.41 BM/Cu. The magnetic susceptibility per copper(II) ion is 70×10^{-6} emu mol^{-1} at 300 K and 88×10^{-6} emu mol^{-1} at 77 K, suggesting that the complex **1** is close to diamagnetic. The diamagnetism of **1** is explained as follows: (i) $N-O^-$ portion of L_1^- and OMe^- bridges lie in the equatorial planes of the tetragonal copper(II) centers; (ii) the $N-O^-$ group and OMe^- have good superexchange properties.

The complex **2** has a medium antiferromagnetic interaction ($2J = -260$ cm^{-1}).[7] This magnetic property is attributable to the geometry around the copper(II) ions; i.e., the intermediate structure between a trigonal bipyramid and a square pyramid for each copper ion. The complexes **1** and **2** showed a d–d transition peak at 545 nm and 671 nm with a shoulder at 830 nm, respectively, in solid state. The difference in the d–d band positions of these complexes can be ascribed to the geometry around copper(II) ions. That is, the energy of the copper(II) d–d transitions in **1** with a square pyramidal geometry near to square-planar is larger than that in **2** with an intermediate geometry between trigonal bipyramidal and square pyramidal.[14]

Experimental

Preparation of 1. To a methanol solution (15 cm^3) of HL_1 (0.21 g, 1.0 mmol) were added successively copper(II) perchlorate hexahydrate (0.74 g, 2.0 mmol), 2,2′-bipyridine (0.16 g, 1.0 mmol) and sodium hydroxide (0.08 g, 2.0 mmol). The reaction mixture was stirred at room temperature for several hours. After it had been filtered, crude complex was recrystallized from a methanol solution. Found: C,36.29; H,3.42; N,9.96%. Calcd for $C_{22}H_{25}N_5O_{10}Cl_2Cu_2$: C,36.83; H,3.51; N,9.76%.

Preparation of 2. The method of preparing complex **2** has been reported.[7] Crystals of **2** were grown on standing the filtrate.

Magnetic susceptibilities and UV-vis spectra were measured as described in the previous paper.[15]

X-ray Crystal Structure Analysis. The crystals of **1** and **2** were sealed respectively in glass capillaries. Intensity data were collected at 295±1 K on the Rigaku AFC-5R four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å, $2\theta_{\max} = 55°$). The intensity data were corrected for Lorentz-polarization effects and for absorption. Both structures were solved by PATTY in DIRDIF92,[16] and refined by the full-matrix least-squares method based on F^2 of all reflections with $I_o > 0$ using a teXsan program, package.[17] Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were fixed at calculated positions. Large displacement parameters of O9 and O10 in one of the perchlorate ions of **1** suggested that the ion would suffer from some disorder.

Crystallography. Crystal data for **1**: $C_{22}H_{25}N_5O_{10}Cl_2Cu_2$, Fw = 717.47, monoclinic, space group $P2_1/c$, $a = 14.714(3)$, $b = 13.191(3)$, $c = 14.331(5)$ Å, $\beta = 90.52(2)°$, $V = 2781.3(11)$ Å^3, $Z = 4$, $Dc = 1.713$ g cm^{-3}, $\mu = 1.784$ mm^{-1}, crystal size 0.50×0.25×0.25 mm, $R = 0.061$ for 3588 reflections with $I_o \geqq 2\sigma(I)$, $wR(F^2) = 0.108$ for 6371 reflections used in the refinements and GOF = 1.26 for 371 parameters. For **2**: $C_{25}H_{28}N_5O_9ClCu_2$, Fw = 705.07, triclinic, space group $P\bar{1}$, $a = 12.124(5)$, $b = 14.840(10)$, $c = 8.388(4)$ Å, $\alpha = 94.86(5)$, $\beta = 92.91(4)$, $\gamma = 69.52(4)°$, $V = 1408.3(13)$ Å^3, $Z = 2$, $Dc = 1.663$ g cm^{-3}, $\mu = 1.667$ mm^{-1}, crystal size 0.43×0.23× 0.18 mm, $R = 0.062$ for 4289 reflections with $I_o \geqq 2\sigma(I)$, $wR(F^2) = 0.119$ for 6468 reflections used in the refinements and GOF = 1.22 for 379 parameters. Crystallographic data have been deposited as Document No.74064 at the Office of the Editor of Bull. Chem. Soc. Jpn.

References

1 V. E. Uhlig and D. Schneider, *Z. Anorg. Allg. Chem.*, **333**, 90 (1964) .

2 J. A. Bertrand, J. H. Smith, and P. G. Eller, *Inorg, Chem.*, **13**, 1649 (1974) .

3 J. A. Bertrand, J. H. Smith and D. G. VanDerveer, *Inorg. Chem.*, **16**, 1477 (1977) .

4 Y. Nakao, W. Mori, and S. Suzuki, *Nippon Kagaku Kaishi*, **1988**, 413.

5 D. Luneau, H. Oshino, H. Okawa, M. Koikawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **63**,2212 (1990) .

6 K. Matsumoto, S. Ooi, W. Mori, and Y. Nakao, *J. Chem. Soc., Dalton Trans.*, **1990**, 3117.

7 W. Mori, S. Suzuki, Y. Nakao, T. Nishimura, and A. Ichimura, *Bull. Chem. Soc. Jpn.*, **65**, 3189 (1992) .

8 R. Ruiz, F. Lloret, M. Julve, J. Faus, M. C. Mnoz, and X. Solans, *Inorg. Chim. Acta*, **219**, 179 (1994) .

9 J. M. Dominguez-Vera, E. Colacio, A. Scuer, M. Klinga, R. Kivekas, and A. Romerasa, *Polyhedron*, **16**, 281 (1997) .

10 I. M. Procter, B. H. Hathaway, and P. Nicholls, *J. Chem. Soc., A*, **1968**, 1678.

11 M. G. B. Drew, J. Nelson, F. Esho, V. McKee, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, **1982**, 1837.

12 G. Christou, S. P. Perlepes, E. Libby, K. Folting, J. C. Huffman, R. J. Webb, and D. N. Hendrickson, *Inorg. Chem.*, **29**, 3657 (1990) .

13 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, **1984**, 1349.

14 B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, **1972**, 1196.

15 C. Li, N. Kanehisa, Y. Miyagi, Y. Nakao, S. Takamizawa, W. Mori, and Y. Kai, *Bull. Chem. Soc. Jpn.*, **70**, 2429 (1997) .

16 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granada, R. O. Gould, J. M. M. Smith, and C. Smykalla, "The DIRDIF program system (1992)," Technical Report of the Crystallographic Laboratory, University of Nijmegen, The Netherlands (1992).

17 "teXsan for Windows, Molecular Structure Corporation, Version 1.06," MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA (1997–1999).