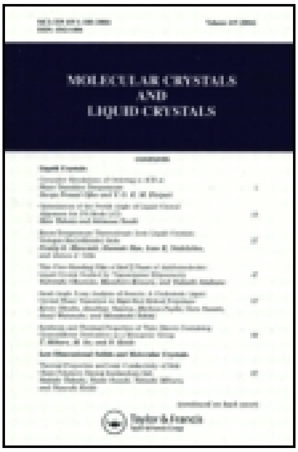

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Syntheses and Magnetic Properties of Tetranuclear Copper(II) Complexes Consisting of Two Bis(μ-carboxylato)dicopper Cores

Naoko Mishima [a], Chiaki Matsuo [a], Masayuki Koikawa [a] & Tadashi Tokii [a]

[a] Department of Chemistry, Faculty of Science and Engineering, Saga University, Honjo 1, Saga, 840-8502, Japan

To cite this article: Naoko Mishima, Chiaki Matsuo, Masayuki Koikawa & Tadashi Tokii (2002): Syntheses and Magnetic Properties of Tetranuclear Copper(II) Complexes Consisting of Two Bis(μ-carboxylato)dicopper Cores, Molecular Crystals and Liquid Crystals, 376:1, 359-364

To link to this article: http://dx.doi.org/10.1080/10587250210719

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 359-364
Copyright © 2002 Taylor & Francis
1058-725X/02 \$12.00 + .00

Syntheses and Magnetic Properties of Tetranuclear Copper(II) Complexes Consisting of Two Bis(μ-carboxylato)dicopper Cores

NAOKO MISHIMA, CHIAKI MATSUO,
MASAYUKI KOIKAWA and TADASHI TOKII

*Department of Chemistry, Faculty of Science and Engineering,
Saga University, Honjo 1, Saga, 840-8502, Japan*

Novel bis(μ-carboxylato)-bridged tetranuclear copper(II) complexes $[Cu_2(NO_3)(suc)(phen)_2(MeOH)]_2(NO_3)_2$ (**1**), and $[Cu_2(NO_3)(glu)(phen)_2(H_2O)]_2(NO_3)_2$ (**2**), where suc = succinato, glu = glutarato, and phen = 1,10-phenanthroline were prepared and characterized by magnetic susceptibility and X-ray crystallography. Complexes **1** and **2** have a distorted square-pyramidal configuration around each copper(II) ion with end-to-end carboxylato-bridges of a syn-syn mode. The angular structural parameters (τ) for **1** and **2,** which are applicable to five coordinate structueres as an index of degree of trigonality, are in the 0.11–0.25 range. The magnetic susceptibility data for **1** and **2** conform to the usual dimer equation with $-2J$ values of 44 cm^{-1} for **1** and 84 cm^{-1} for **2**, indicating an antiferromagnetic interaction is operative between copper(II) ions.

Keywords tetranuclear copper(II) complex; bis(μ-carboxylato)-bridge; syn-syn bridging mode; antiferromagnetic interaction

INTRODUCTION

A large number of binuclear copper(II) carboxylate adducts have been isolated and their magneto-structural correlations have extensively been studied.[1-5] Their magnetic properties depend on metal-metal distances, bonding angles of bridging atoms, dihedral angles between planes including metal centers and bond distances and coordination environments around metal centers.[4] Here, we report syntheses, crystal structures and magnetic properties of novel tetranuclear copper(II) complexes with dicarboxylate ligands.

EXPERIMENTAL

Preparations

$[Cu_2(NO_3)(suc)(phen)_2(MeOH)]_2(NO_3)_2$ **1.** A solution (5 ml) of $Cu(NO_3)_2 \cdot 3H_2O$ (2 mmol) in methanol was added to a mixture of H_2suc (1 mmol) and phen (2 mmol) in methanol (5 ml). To the resulting solution triethylamine (0.5 mmol) was added under stirring. Blue precipitates were filtered off, and the filtrate was allowed to stand overnight at room temperature. The deep blue crystals were collected. Yield: 0.30 g (Found: C, 45.28; H, 3.24; N, 11.06; Cu, 16.50. $C_{58}H_{48}Cu_4N_{12}O_{22}$ requires C, 45.85; H, 3.18; N, 11.06; Cu, 16.73%)

$[Cu_2(NO_3)(glu)(phen)_2(H_2O)]_2(NO_3)_2$ **2.** This complex was prepared by the same method as complex **1**, except replacing H_2suc with H_2glu. Recrystallization from a methanol solution formed deep blue crystals of **2** suitable for X-ray crystallography. Yield: 0.25 g (Found: C, 45.75; H, 3.19; N, 11.04; Cu, 16.69. $C_{58}H_{48}Cu_4N_{12}O_{22}$ requires C, 45.85; H, 3.18; N. 11.06; Cu, 16.73 %)

Physical measurements

Elemental analyses were obtained at the Service Center of Elemental Analysis at Kyushu University. Analysis of copper was made using a titrimetric method. The magnetic susceptibilities were determined by the Faraday method. The susceptibilities were collected for diamagnetism of the constituent atoms using Pascal's constant.

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**, $C_{58}H_{48}Cu_4N_{12}O_{22}$, $M = 1519.27$, orthorhombic, $a = 22.11(2)$, $b = 16.524(4)$, $c = 16.26(8)$ Å, $V = 5941(18)$ Å^3, space group *Pbca*, $Z = 4$, $Dc = 1.699$ g / cm^3, μ (Mo-Kα) = 15.06 cm^{-1}, 7542 reflections measured, 3288 unique reflections with $I > 1.50\sigma(I)$. Final value for $R = 0.076$ / $R_w = 0.051$: **2**, $C_{58}H_{48}Cu_4N_{12}O_{22}$, $M =$

1519.27, triclinic, $a = 10.446(3)$, $b = 11.061(4)$, $c = 14.648(3)$ Å, $\alpha = 80.30(4)°$, $\beta = 98.83(3)°$, $\gamma = 117.01(2)°$, $V = 1480.6(9)$ Å^3, space group $P\overline{1}$, $Z = 1$, $Dc = 1.704$ g / cm^3, μ (Mo-Kα) = 15.10 cm^{-1}, 7206 reflections measured, 3933 unique reflections with $I > 1.50\sigma(I)$. Final value for $R = 0.083$ / $R_w = 0.121$.

RESULTS AND DISCUSSION

The crystal structures of **1** and **2** are shown in Figures 1 and 2, respectively. The structures of **1** and **2** consist of two bis(μ-carboxylato)dicopper cores in a syn-syn form at both ends of dicarboxylato anions. Each complex cation in **1** and **2** has an inversion center in a molecule. The coordination environment around each copper ion is square pyramidal with nitrogen donors of a phenanthroline, two oxygen donors of two carboxylates occupying basal sites, and an axial coordination of a nitrate ion, a methanol, or a water molecule. The Cu1...Cu2 distances are 3.032(2) Å in **1** and 3.044(3) Å in **2**. The structure of the $Cu_2(OCO)_2(phen)_2$ moiety is essentially the same as that in the $[Cu_2(RCOO)_2(phen)_2(H_2O)_2]^{2+}$ complexes (where R = H[4], CH_3[4], or PhC_2H_4[5]).

Addison *et al.* have proposed an angular structural parameter, τ,[6] is applicable to five-coordinate structures as an index of the degree of trigonality. The τ value is equal to zero for a perfectly tetragonal geometry, while it becomes unity for a perfectly trigonal bipyramidal geometry. Judging from this criterion, the coordination geometry for **1** (τ = 0.25 for Cu1 and τ = 0.11 for Cu2) and **2** (τ = 0.17 for Cu1 and τ = 0.13 for Cu2) is better described as a distorted square pyramidal configuration. The degree of distortion toward a trigonal bipyramidal geometry for Cu1 in **1** is greater than that for the others. The dihedral angles between the basal coordination planes around the copper atoms are 22.1° in **1** and 23.1° in **2**. This tilting of the basal plane is reflected on the Cu-O-C angles of the carboxylates. The angles have average values of 123° (Cu1-O-C) and 134° (Cu2-O-C) in **1**, 130°(Cu1-O-C) and 127° (Cu2-O-C) in **2**. Compared with analogous di-μ-carboxylate dicopper(II) complexes $[Cu(RCOO)(phen)(H_2O)]_2^{2+}$ (R = H, CH_3; Cu1-O-C 129°, Cu2-O-C 127°), the Cu2-O-C angle in **1** is larger than the corresponding angles in the other complexes.

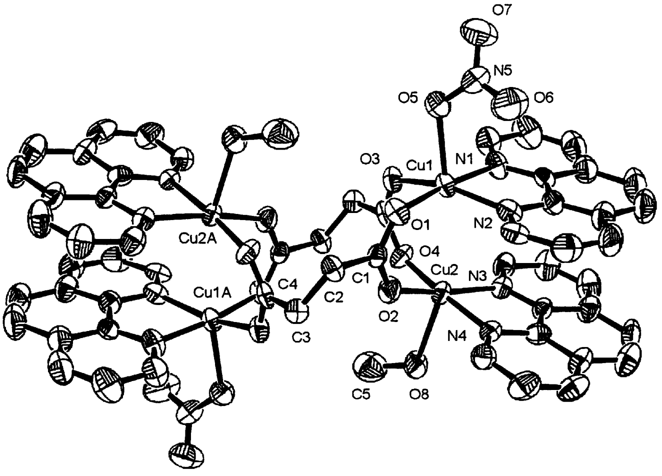

FIGURE 1 An ORTEP drawing for **1**. Selected bond lengths (Å) and angles (°): Cu1-O1 1.936(6), Cu1-O3 1.959(6), Cu1-O5 2.175(6), Cu1-N1 2.011(7), Cu1-N2 1.986(7), Cu2-O2 1.932(6), Cu2-O4 1.912(6), Cu2-O8 2.198(6), Cu2-N3 2.020(7), Cu2-N4 1.997(7); Cu1-O1-C1 124.9(6), Cu1-O3-C4A 121.3(6), Cu2-O2-C1 131.8(6), Cu2-O4-C4A 135.5(6)

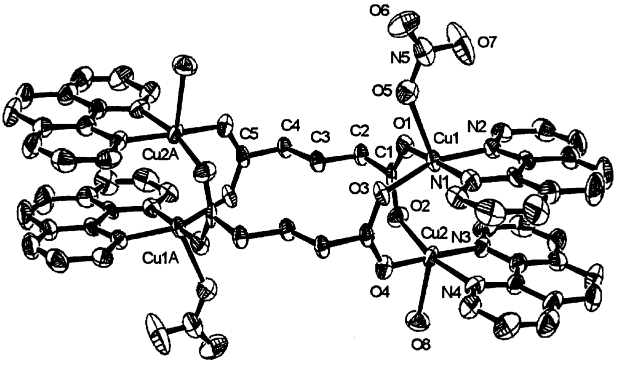

FIGURE 2 An ORTEP drawing for **2**. Selected bond lengths (Å) and angles (°): Cu1-O1 1.93(1), Cu1-O3 1.96(1), Cu1-O5 2.21(1), Cu1-N1 2.01(1), Cu1-N2 2.02(1), Cu2-O2 1.93(1), Cu2-O4 1.91(1), Cu2-O8 2.21(1), Cu2-N3 2.01(1), Cu2-N4 2.01(1); Cu1-O1-C1 128(1), Cu1-O3-C5A 132(1), Cu2-O2-C1 128(1), Cu2-O4-C5A 126(1)

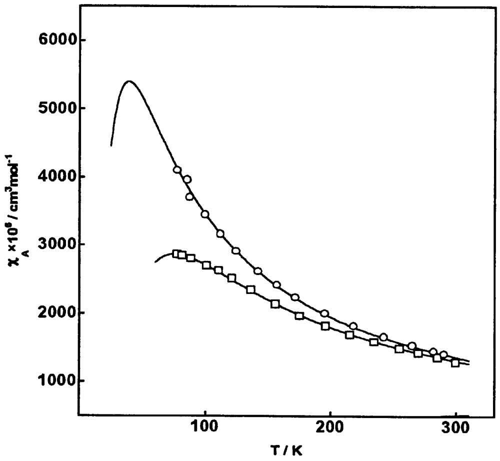

FIGURE 3. χ_A vs. T plots for **1** (O) and for **2** (□). The solid lines were obtained as described in the text.

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

Complex	$-2J$ / cm^{-1}	g	σ_{dis} / %	μ_{eff} / B.M. (T / K)
1	44	2.10	1.43	1.77 (290.0)
2	84	2.12	0.49	1.72 (299.0)

The magnetic properties of the present complexes were measured in the temperature rang 80-300 K. Plots of the magnetic susceptibilities are shown in Figure 3. The best fitting parameters obtained by the Bleaney-Bowers equation[7] for a dimer model of S = 1/2 are listed in Table 1. Since metal-metal distances between bis(μ-carboxylato) dicopper cores, Cu1...Cu1A (more than 7.4 Å in **1** and 8.9 Å in **2**) and Cu1...Cu2A (more than 6.2 Å in **1** and 8.4 Å in **2**) are too long, the magnetic interactions between these copper ions are not operative. The value of $N\alpha$ was fixed to 60×10^{-6} cm^{3}mol^{-1}. The spin-exchange coupling constant $-2J = 44$ cm^{-1} for **1** and 84 cm^{-1} for **2** indicate that an antiferromagnetic interaction is operative between the copper(II) ions in these complexes. Comparing the $-2J$ values for **1**, **2** and the related complexes, $[Cu(RCOO)_2(phen)_2(H_2O)]_2^{2+}$ ($-2J$ =

86–125 cm^{-1}), the spin-exchange coupling in **1** is very weak. The strength of antiferromagnetic interaction may be accounted for by the coordination geometry. The Cu2-O-C angle in **1** (134°) is larger than The corresponding angles in another complexes. The dihedral angle between the basal planes in **1** is slightly opened (22.1°) depends on Cu-O-C angles of carboxylates, although the dihedral angle between the phen planes is almost parallel (7.3°) and the non-bonding ring-ring interaction are dominated by a π–π stack between the phen ligands. This structural distortion brings small overlap of the magnetic $d_{x^2-y^2}$ orbital with the carboxylato ligand orbital, and then an antiferromagmetic interaction in **1** becomes weak.

ACKNOWLEDGMENT

This work was supported by Grants-in-Aid for Scientific Research (No. 10440196) and for Scientific Research on Priority Area 'Metal-assembled Complexes' (No. 12023241) from the Ministry of Education, Science, Sports and Culture, Japan.

REFERENCES

1. R. W. Jotham, S. F. A. Kettle, and J. A. Marks, J.Chem. Soc., Dalton trans., 428 (1972).
2. R. J. Doedens, Prog. Inorg. Chem., **21**, 209 (1976).
3. M. Kato and Y. Muto, Coord. Chem. Rev., **92**, 45 (1988), and references therein.
4. T. Tokii, N. Watanabe, M. Nakashima, Y. Muto, M. Morooka, S. Ohba, and Y. Saito, Bull. Chem. Soc. Jpn., **63**, 364 (1990).
5. E. dubler, U. K. Häring, K. H. Scheller, P. Baltzer, and H. Sigel, Inorg. Chem., **23**, 3785 (1984).
6. A. W. Addison, T. N. Rao, J. Reedijk, J. Rijn, and G. C. Verschoor, J. Chem. Soc., Dalton Trans., 2649 (1995).
7. B. Bleaney and K. D. Bowers, Prog. R. Soc. London Ser. A, **214**, 451 (1952).