

Dinuclear Copper(II) Complexes of a Macrocyclic Compartmental Ligand in Two Isomeric Forms. Exogenous Ion Effect upon Ligand Isomerism

Noboru Sekine, Takuya Shiga, Masaaki Ohba,† and Hisashi Ōkawa*

Department of Chemistry, Faculty of Science, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581

Received October 28, 2005; E-mail: okawascc@mbox.nc.kyushu-u.ac.jp

A dinucleating compartmental ligand derived from the cyclic [2:1:1] condensation of 2,6-diformyl-4-methylphenol, 1,3-propanediamine, and diethylenetriamine (dien) assumes two isomeric forms in the dinuclear copper(II) complexes, $[Cu_2(L^a)](ClO_4)_2 \cdot 2H_2O$ (**1**) and $[Cu_2(L^b)(AcO)]BPh_4$ (**2**). Complex **1** has the ligand in the usual condensation with a trimethylene chain ($-(CH_2)_3-$) and a 3-azapentamethylene chain ($-(CH_2)_2NH(CH_2)_2-$) between two azomethine nitrogen atoms; the nitrogen atom of the 3-azapentamethylene chain is free from coordination. Complex **2** has the ligand in an unusual condensation with dien: The central amino nitrogen of dien is further involved in the condensation with one C=N linkage to form an imidazolidine ring. An acetate ion bridges two copper ions to form a μ-acetato-di(μ-phenolato) dinuclear core with a saddle-like shape. The origin for the unusual condensation in **2** is considered and the physicochemical properties of **1** and **2** are examined.

Many bimetallic biosites are asymmetric with respect to two metal atoms (metal asymmetry), the nature of donor atoms about each metal (donor asymmetry), geometric arrangement of donor atoms about each metal (geometric asymmetry), or the number of donor atoms about each metal (coordination number asymmetry).[1] Such asymmetric dinuclear complexes are also of interest in bimetallic catalysis by the conjunction of the distinct roles of two metal ions. In order to produce asymmetric dinuclear complexes, dinucleating compartmental ligands possessing two dissimilar metal-binding sites have been developed.[2] The macrocyclic dinucleating ligand derived from the cyclic [2:1:1] condensation of 2,6-diformyl-4-methylphenol, ethylenediamine, and diethylenetriamine (dien) (Fig. 1a, $m = 2$) has been extensively used in this laboratory for the study of asymmetric dinuclear metal complexes.[3] In this work, an analogous macrocyclic ligand with trimethylene chain instead of the ethylene chain (Fig. 1a, $m = 3$; abbreviated as H_2L) has been used for providing two dinuclear copper(II) complexes: $[Cu_2(L^a)](ClO_4)_2 \cdot 2H_2O$ (**1**) and $[Cu_2(L^b)(AcO)]BPh_4$ (**2**). It is shown that complex **1** has the ligand in the usual condensation (Fig. 1a), whereas complex **2** has the ligand in an isomeric form produced by an unusual condensation with diene (Fig. 1b). The origin for the unusual condensation in **2** is considered and the physicochemical properties of **1** and **2** are studied.

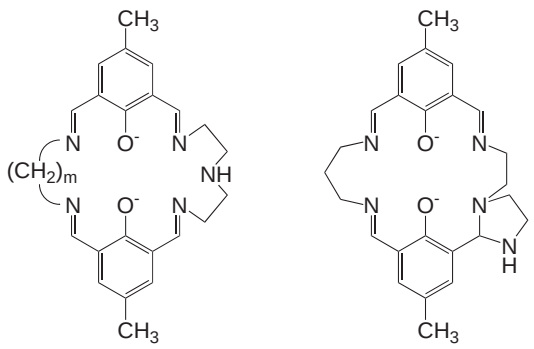

Fig. 1. (a) Macrocyclic compartmental ligands: The ligand of $m = 3$ is abbreviated as H_2L^a. (b) An isomeric form H_2L^b produced by unusual condensation with dien.

Experimental

Preparation. 2,6-Diformyl-4-methyphenol was prepared by the literature method.[4] The synthesis of *N*,*N*′-1,3-propylene-bis(5-methyl-3-formylsalicylideneaminato)copper(II) has been described in our previous paper.[5]

$[Cu_2(L^a)](ClO_4)_2 \cdot 2H_2O$ (**1**). *N*,*N*′-1,3-Propylene-bis(5-methyl-3-formylsalicylideneaminato)copper(II) (214 mg, 0.5 mmol) and copper(II) perchlorate hexahydrate (185 mg, 0.5 mmol) were dissolved in acetonitrile (30 cm^3). To this was dropwise added a solution of diethylenetriamine (52 mg, 0.5 mmol) in acetonitrile (10 cm^3) with stirring at room temperature to give green microcrystals. They were separated by filtration and dried in vacuo. The yield was 97 mg (24%). Anal. Found: C, 38.02; H, 3.91; N, 8.66; Cu, 16.10%. Calcd for $C_{25}H_{33}N_5O_{12}Cl_2Cu_2$: C, 37.84; H, 4.19; N, 8.83; Cu, 16.02%. Selected IR data [ν/cm^{-1}] on KBr: 1640, 1121, 1108, 1093. UV–vis [λ/nm (ε/M^{-1} cm^{-1})]: 360 (11900) and 615 (165) in DMF. Molar conductance [Λ_M/S cm^2 mol^{-1}]: 145 in DMF.

$[Cu_2(L^b)(AcO)]BPh_4$ (**2**). A suspension of *N*,*N*′-1,3-propylene-bis(5-methyl-3-formylsalicylideneaminato)copper(II) (214 mg, 0.5 mmol) in acetonitrile (40 cm^3) and a solution of copper(II) acetate

† Present address: Graduate School of Engineering, Department of Synthetic Chemistry and Biological Chemistry, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510

Published on the web June 6, 2006; doi:10.1246/bcsj.79.881

monohydrate (100 mg, 0.5 mmol) and sodium tetraphenylborate (376 mg, 1.1 mmol) in acetonitrile (20 cm^3) were mixed, and the mixture was stirred at room temperature to give a green solution. To this was dropwise added a solution of diethylenetriamine (52 mg, 0.5 mmol) in acetonitrile (10 cm^3) at room temperature, and the reaction mixture was stirred for a couple of hours. The reaction solution was diffused with diethyl ether to give green crystals. They were separated by filtration and dried in vacuo. The yield was 105 mg (22%). Anal. Found: C, 65.26; H, 5.59; N, 7.47; Cu, 13.42%. Calcd for $C_{51}H_{52}N_5O_4BCu_2$: C, 65.38; H, 5.59; N, 7.48; Cu, 13.57%. Selected IR data [ν/cm^{-1}] on KBr: 1648, 1631, 1568, 1454, 734, 708. UV–vis [λ/nm (ε/M^{-1} cm^{-1})]: 360 (9150) and 660 (250) in DMF. Molar conductance [Λ_M/S cm^2 mol^{-1}]: 60 in DMF.

Physical Measurements. Elemental analyses of C, H, and N were obtained at The Service Center of Elemental Analysis, Kyushu University. Analyses of copper were obtained using a Shimadzu AA-680 Atomic Absorption/Flame Emission Spectrophotometer. Infrared spectra were measured using KBr disks on a Perkin-Elmer Spectrum BX FT-IR system. Molar conductances in DMF were measured using a DKK AOL-10 conductivity meter at 25 °C. Electronic absorption spectra in *N*,*N*-dimethylformamide (DMF) were recorded on a Shimadzu UV-3100PC spectrophotometer. Magnetic susceptibilities of powdered samples were measured on a Quantum Design MPMS XL SQUID susceptometer in the temperature range of 2–300 K. Diamagnetic corrections were made using Pascal's constant.[6]

X-ray Crystallography. A single crystal of **2** was mounted on a glass fiber and coated with epoxy resin. Crystallographic measurements were carried out at −95 °C on a Rigaku/MSC Mercury diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71070 Å). A symmetry-related absorption correction using the program ABSCOR and an empirical absorption correction based on azimuthal scans of several reflections were applied. Pertinent crystallographic parameters are summarized in Table 1.

The structure was solved by the direct method and expanded using the Fourier technique. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure analysis but not refined. All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation.[7]

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC), 12, Union Road, Cambridge, CB2 1EZ, UK. Copies of the data can be obtained by quoting the publication citation and deposition number CCDC-281936 via http://www.ccdc.cam.ac.uk/conts/retrieving.html (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Crystal Structure of $[Cu_2(L^b)(AcO)]BPh_4$ (2). ORTEP[8] views of **2** are shown in Fig. 2 together with the atom numbering scheme. The selected bond distances and angles are summarized in Table 2.

The X-ray crystallographic result indicates that the ligand has a rare structure as the result of an unusual condensation with dien. That is, the central nitrogen atom of dien is also involved in the condensation with one C=N linkage to form an

Table 1. Crystallographic Parameters for $[Cu_2(L^b)(AcO)]$-BPh_4 (**2**)

Formula	$BC_{51}Cu_2H_{52}N_5O_4$
Formula weight	936.90
Color	green
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
a/Å	14.207(4)
b/Å	10.996(3)
c/Å	28.683(8)
β/°	104.964(4)
V/$Å^3$	4328.82(1)
Z value	4
D_{calcd}/g cm^{-3}	1.437
μ(Mo Kα)/cm^{-1}	10.36
No. observations	9818
R (all data)	0.087
$R1$ ($>2.0\sigma(I)$)	0.059
Rw	0.153
G.O.F.	1.00

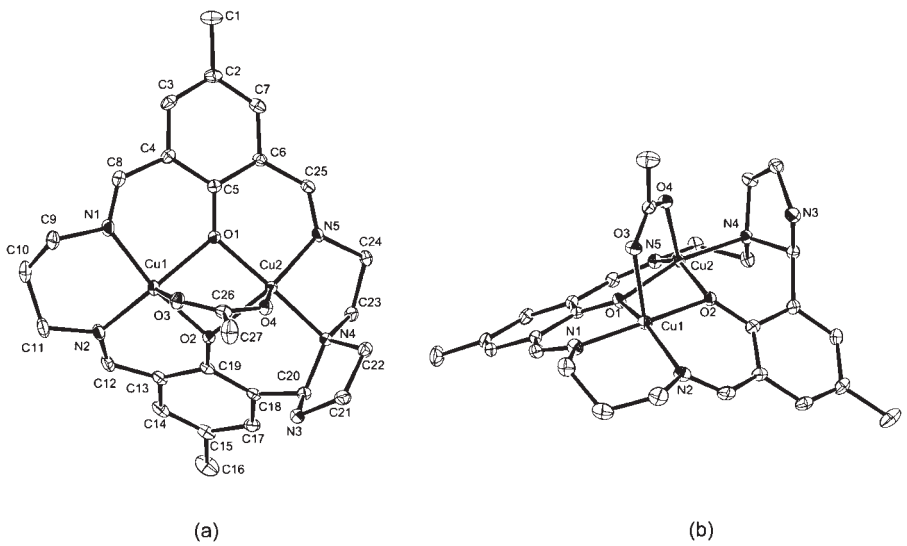

Fig. 2. ORTEP views of $[Cu_2(L^b)(AcO)]BPh_4$ (**2**): (a) a top view with the atom numbering scheme and (b) a side view indicating a saddle-shape of the dinuclear core.

Table 2. Selected Bond Distances and Angles of $[Cu_2(L^b)(AcO)]BPh_4$ (**2**)

Bond distances/Å			
Cu(1)–O(1)	2.026(2)	Cu(1)–O(2)	1.956(3)
Cu(1)–O(3)	2.109(3)	Cu(1)–N(1)	1.962(3)
Cu(1)–N(2)	1.969(3)	Cu(2)–O(1)	1.931(3)
Cu(2)–O(2)	2.033(2)	Cu(2)–O(4)	2.129(3)
Cu(2)–N(4)	2.003(3)	Cu(2)–N(5)	1.951(3)
Cu(1)···Cu(2)	2.991(1)		
Bond angles/degree			
O(1)–Cu(1)–O(2)	80.1(1)	O(1)–Cu(1)–O(3)	91.4(1)
O(1)–Cu(1)–N(1)	88.6(1)	O(1)–Cu(1)–N(2)	146.7(1)
O(2)–Cu(1)–O(3)	88.6(1)	O(2)–Cu(1)–N(1)	168.0(1)
O(2)–Cu(1)–N(2)	90.6(1)	O(3)–Cu(1)–N(1)	95.8(1)
O(2)–Cu(1)–N(2)	120.5(1)	N(1)–Cu(1)–N(2)	96.8(1)
O(1)–Cu(2)–O(2)	80.6(1)	O(1)–Cu(2)–O(4)	94.5(1)
O(1)–Cu(2)–N(4)	164.5(1)	O(1)–Cu(2)–N(5)	90.3(1)
O(2)–Cu(2)–O(4)	84.3(1)	O(2)–Cu(2)–N(4)	95.6(1)
O(2)–Cu(2)–N(5)	148.8(1)	O(4)–Cu(2)–N(4)	100.1(1)
O(4)–Cu(2)–N(5)	126.4(1)	N(4)–Cu(2)–N(5)	85.3(1)
Cu(1)–O(1)–Cu(2)	98.2(1)	Cu(1)–O(2)–Cu(2)	97.2(1)

imidazolidine ring. The resulting ligand has two four-coordinate cavities of the N_2O_2 donor set sharing two phenolic oxygen atoms. An acetate group bridges two Cu(II) ions in the *syn–syn* mode affording a five-coordinate geometry about each metal ion.

The geometry around the Cu(1) bound to the site with the trimethylene chain can be regarded as a square-pyramid: the parameter τ[9] discriminating between square-pyramid ($\tau = 0$) and trigonal-bipyramid ($\tau = 1$) is 0.355. The equatorial Cu(1)-to-donor bond distances range from 1.956(3) to 2.026(2) Å. The axial Cu(1)–O(3) bond is slightly elongated (2.109(3) Å). The Cu(1) is displaced by 0.338 Å from the N_2O_2 least-squares plane toward O(3). The geometry around Cu(2) bound to the site formed with dien is also square-pyramidal with the acetate oxygen O(4) at the apical site (τ: 0.262). The equatorial Cu(2)-to-donor distances range from 1.931(3) to 2.033(2) Å. The axial Cu(2)–O(4) bond length is 2.129(3) Å. The Cu(2) is displaced by 0.394 Å from the basal N_2O_2 least-squares plane toward O(4).

The $\{Cu_2(L)\}$ entity assumes a saddle-like shape with the bridging acetate group on the saddle (Fig. 2b). The O(1)–C(5) bond and the O(2)–C(19) bond make an angle of 118.67°. The N_2O_2 least-squares plane of Cu(1) and that of Cu(2) are bent at the O···O edge with a dihedral angle of 14.89°. The dihedral angle between the least-squares plane defined by Cu(1), O(1), and O(2) and the least-squares plane defined by Cu(2), O(1), and O(2) is 19.72°. The bridging oxygen atom O(1) has a planar configuration: The sum of the Cu(1)–O(1)–Cu(2), Cu(1)–O(1)–C(5), and Cu(2)–O(1)–C(5) angles is 360°. On the other hand, the oxygen atom O(2) has a non-planar configuration: The sum of the Cu(1)–O(2)–Cu(2), Cu(1)–O(2)–C(19), and Cu(2)–O(2)–C(19) angles is 342.2°. The Cu(1)···Cu(2) separation is 2.991(1) Å. The Cu(1)–O(1)–Cu(2) and Cu(1)–O(2)–Cu(2) angles are 98.2(1) and 97.2(1)°, respectively.

A similar unusual condensation between a dicarbonyl compound and a linear polyamine in template reaction affording macrocyclic compounds containing a five-membered imidazolidine ring or a six-membered hexahydro-pyrimidine ring has been reported.[3i,10–14] It is considered that the unusual condensation is preferred to usual condensation when the unusual condensation product gives rise to a large thermodynamic stability in complexation relative to the usual condensation product.

Di(μ-phenolato) dinuclear copper(II) complexes of diphenol-based macrocyclic ligands generally have a Cu···Cu separation of ca. 3.1 Å.[15,16] On the other hand, μ-acetato-di(μ-phenolato) dinuclear complexes have a short Cu···Cu separation (<3.0 Å) as a result of the acetate bridge.[17,18] We may conclude that the unusual condensation in **2** results from the acetate bridge, which requires a short Cu···Cu separation (2.991(1) Å).

Complex **1** has the ligand in the usual condensation (Fig. 1a) judging from its physicochemical properties discussed below. In this complex, the perchlorate group has no effect on the Cu···Cu separation.

Properties. Infrared Spectra: The IR spectrum of **1** has one ν(C=N) stretching mode at 1640 cm^{-1}. It appears that the C=N linkage in the cavity with the trimethylene chain and that in the cavity with the 3-azapentamethylene chain are practically equivalent. On the other hand, the IR spectrum of **2** shows two ν(C=N) modes at 1648 and 1631 cm^{-1}, indicating that two distinct C=N linkages exist in the molecule. The X-ray crystallographic study indicates that N(1)–C(8), N(2)–C(12), and N(5)–C(25) bonds are 1.290(5), 1.290(5), and 1.278(5) Å, respectively. Thus, the IR band at 1631 cm^{-1} is associated with the C=N linkages formed with the trimethylene chain (N(1)=C(8) and N(2)=C(12)), and the IR band at 1648 cm^{-1} is associated with the C=N linkage formed with diene (N(5)=C(25)). The antisymmetric and symmetric ν(COO) vibrations of the acetate group are observed at 1568 and 1454 cm^{-1}, respectively. The small separation between the two vibration modes (<150 cm^{-1}) is in accord with the bridging function of the acetate group.[19] In the IR spectrum of **1**, the ν_3 band of the perchlorate group is split into three: 1121, 1108, and 1093 cm^{-1}. This fact implies that the perchlorate ion weakly interacts with the dinuclear core in the solid state.[20] The two bands at 734 and 708 cm^{-1} of **2** are associated with the phenyl group of the tetraphenylborate ion.

Molar Conductances and Electronic Absorption Spectra: The molar conductance of **1** and **2** in DMF is 145 and 60 $S\,cm^2\,mol^{-1}$, respectively, indicating that **1** behaves as a 2:1 electrolyte and **2** behaves as a 1:1 electrolyte in this solvent.[21] The molar conductance of **2** demonstrates that the acetate-bridged dinuclear structure is maintained in DMF.

Electronic absorption spectra of **1** and **2** in DMF have an intense band at 360 nm that is attributed to the π–π^* transition associated with the azomethine linkage of the macrocyclic ligands.[22,23] The molar extinction coefficient of the π–π^* band (**1**, 11900 $M^{-1}\,cm^{-1}$; **2**, 9150 $M^{-1}\,cm^{-1}$) seems to reflect the number of C=N linkages within the complex molecule: four C=N linkages in **1** and three C=N linkages in **2**. An extinction coefficient of ca. 3000 $M^{-1}\,cm^{-1}$ per one C=N linkage can be deduced from these data. In fact, the azomethine π–π^* band of the related tetra-imine macrocyclic complexes[24] have an intensity of ca. 12000 $M^{-1}\,cm^{-1}$, and that of the related di-imine macrocyclic complexes[25] have an intensity of ca. 6000

$M^{-1}\,cm^{-1}$ in DMF. However, it must be mentioned that the intensity of the azomethine π–π^* band varies by a molecular distortion or by the change of solvent.[3d,18]

In the visible region, **1** shows a weak band at 615 nm (ε: $165\,M^{-1}\,cm^{-1}$ per molecule); this is a superposition of the d–d bands of two Cu(II) ions. The band maximum is compared to that of the dinuclear copper(II) complex of the symmetric ligand with two trimethylene chains.[26] This fact supports that the nitrogen atom of the 3-azapentamethylene chain is free from coordination in solution. Complex **2** has a d–d band maximum at 660 nm (ε: $250\,M^{-1}\,cm^{-1}$). The d–d band maximum of **2** is located at a longer wavelength relative to that of **1** due to the distinct square-pyramidal geometry about each copper with an acetate oxygen atom at the apical site.

Magnetic Properties: The magnetic susceptibilities of **1** and **2** were measured on a powdered sample in the temperature range of 2–300 K. The temperature-dependences of effective magnetic moments are given in Fig. 3.

The magnetic moment of **1** at room temperature is subnormal (0.71 μ_B per Cu) and the moment decreases with decreasing temperature to reach a near plateau value of ca. 0.6 μ_B below 100 K. The μ_{eff} vs T curve suggests the operation of a strong antiferromagnetic interaction within the molecule and the presence of a significant amount of paramagnetic impurity. A paramagnetic contaminant of ca. 8–9% is evaluated from the magnetic moment of $\approx$0.6 μ_B at low temperature. The magnetic behavior can be simulated by the Bleaney–Bowers equation including a correction term for paramagnetic impurity,[27]

$$\chi_A = (1-\rho)\{Ng^2\beta^2/kT\} \times [3+\exp(-2J/kT)]^{-1} + \rho \times \{Ng^2\beta^2/4kT\} + N\alpha, \quad (1)$$

where χ_A is the magnetic susceptibility per Cu, N is Avogadro's number, g is the Lande g factor, β is the Bohr magneton, k is the Boltzmann constant, J is the exchange integral, T is the absolute temperature, $N\alpha$ is the temperature-independent paramagnetism, and ρ is the fraction of paramagnetic impurity. The best-fit parameters for **1** are $g = 2.12$, $J = -470\,cm^{-1}$, $\rho = 0.085$, and $N\alpha = 60 \times 10^{-6}\,cm^3\,mol^{-1}$.

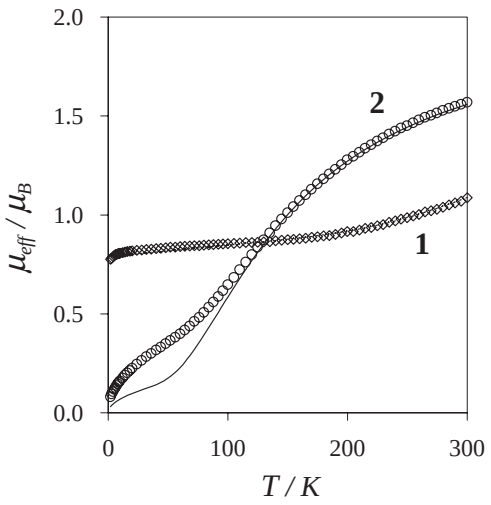

Fig. 3. Temperature-variations of the magnetic moments of **1** and **2**. The solid line for **1** is drawn based on the Bleaney–Bowers equation using $g = 2.12$, $J = -470$ cm^{-1}, $N\alpha = 60 \times 10^{-6}\,cm^3\,mol^{-1}$, and $\rho = 0.085$, and the solid line for **2** is drawn using $g = 2.12$, $J = -115$ cm^{-1}, and $N\alpha = 60 \times 10^{-6}\,cm^3\,mol^{-1}$.

The significant paramagnetic impurity in **1** must be noted. In the complexes of analogous macrocyclic ligands having a 3-hydroxypentamethylene chain (–$(CH_2)_2CH(OH)(CH_2)_2$–) or 3-thiapentamethylene chain (–$(CH_2)_2S(CH_2)_2$–), the metal ion in the cavity of the chain is readily released in solution affording mononuclear $[Cu(H_2L)](ClO_4)_2$.[28,29] We suppose that $[Cu(H_2L^a)](ClO_4)_2$ is a paramagnetic contaminant in **1**.

Complex **2** has a magnetic moment of 1.56 μ_B (per Cu) at room temperature and the moment decreased with decreasing temperature in a two-step manner to reach 0.12 μ_B at 2 K. The magnetic behavior in the range of 120–300 K can be simulated by the Bleaney–Bowers equation, using the best-fit parameters of $g = 2.12$, $J = -115\,cm^{-1}$, and $N\alpha = 60 \times 10^{-6}$ $cm^3\,mol^{-1}$. The magnetic behavior in the range of 2–120 K suggests a magnetic phase-transition occurring at low temperature. We presume that a geometrical change in the dinuclear core can be a likely cause for the magnetic phase transition.

The relation between dinuclear structure and magnetic interaction of oxo-bridged dinuclear copper(II) complexes has been reviewed.[30] A good magnetostructural correlation has been established for di(μ-hydroxo) dinuclear copper(II) complexes of nearly coplanar structure: A strong antiferromagnetic interaction occurs when the Cu–O–Cu angle is large, whereas a ferromagnetic interaction appears when the Cu–O–Cu angle is smaller than 97.7°.[31] Geometrical distortion of the dinuclear core, such as a tetrahedral distortion of the equatorial base of each copper, a displacement of copper from each equatorial base, a bend of two equatorial bases at the O···O edge, or a non-planar distortion about the bridging oxygen atom gives rise to a reduction in antiferromagnetic interaction.[32] Di(μ-phenolato) dinuclear copper(II) complexes generally show a strong antiferromagnetic interaction when the Cu···Cu separation is short,[30] but a definite magnetostructural correlation has not been established for the complexes because of their diverse dinuclear structures. The strong antiferromagnetic interaction of **1** ($J = -470\,cm^{-1}$) means a good co-planarity of its dinuclear core, supporting that the nitrogen atom of the 3-azapentamethylene chain is free from coordination. The antiferromagnetic interaction of **2** ($-115\,cm^{-1}$) is unexpectedly weak in spite of its short Cu···Cu separation (2.99 Å). We suppose that the weak antiferromagnetic interaction in **2** results from the molecular distortions in the saddle-like shape: a large displacement of Cu from the equatorial base (0.338 Å for Cu(1) and 0.394 Å for Cu(2)), a large dihedral angle between the two equatorial bases at the O···O edge (14.92°) and a tetrahedral distortion about O(2).

Conclusion

The dinucleating compartmental ligand, derived from the cyclic [2:1:1] condensation of 2,6-diformyl-4-methylphenol, 1,3-propanediamine, and diethylenetriamine, assumes two isomeric forms in the dinuclear copper(II) complexes, $[Cu_2(L^a)](ClO_4)_2 \cdot 2H_2O$ (**1**) and $[Cu_2(L^b)(AcO)]BPh_4$ (**2**). In complex **1**, the ligand has the normal structure with one trimethylene chain (–$(CH_2)_3$–) and one 3-azapentamethylene chain (–$(CH_2)_2NH(CH_2)_2$–) between two azomethine nitrogen atoms. The nitro-

gen atom of the 3-azapentamethylene chain is free from coordination. In complex **2**, the ligand is in an isomeric form with the ligand in **1**; the central nitrogen atom of dien is also involved in the condensation with one C=N bond to form an imidazolidine ring. An acetate group bridges two copper ions affording a μ-acetato-di(μ-phenolato) dicopper(II) core in a Cu···Cu separation of 2.991(1) Å. The unusual condensation of the ligand in **2** is concerned with the acetate bridge that necessitates a short Cu···Cu separation. The perchlorate ion has no effect upon the Cu···Cu separation, giving rise to the usual condensation of the ligand in **1**.

References

1 J. H. Satcher, Jr., M. W. Droege, T. J. R. Weakley, R. T. Taylor, *Inorg. Chem.* **1995**, *34*, 3317.

2 a) S. E. Groh, *Isr. J. Chem.* **1977**, *15*, 277. b) D. E. Fenton, U. Casellato, P. A. Vigato, M. Vidali, *Inorg. Chim. Acta* **1982**, *62*, 57. c) D. E. Fenton, H. Ōkawa, *Chem. Rev./Recl.* **1997**, *130*, 433. d) H. Ōkawa, H. Furutachi, D. E. Fenton, *Coord. Chem. Rev.* **1998**, *174*, 51.

3 a) H. Ōkawa, J. Nishio, M. Ohba, M. Tadokoro, N. Matsumoto, M. Koikawa, S. Kida, D. E. Fenton, *Inorg. Chem.* **1993**, *32*, 2949. b) J. Nishio, H. Ōkawa, S. Ohtsuka, M. Tomono, *Inorg. Chim. Acta* **1994**, *218*, 27. c) S. Ohtsuka, M. Kodera, K. Motoda, M. Ohba, H. Ōkawa, *J. Chem. Soc., Dalton Trans.* **1995**, 2599. d) H. Furutachi, H. Ōkawa, *Inorg. Chem.* **1997**, *36*, 3911. e) M. Yamami, H. Furutachi, T. Yokoyama, H. Ōkawa, *Chem. Lett.* **1998**, 211. f) H. Furutachi, H. Ōkawa, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 671. g) H. Furutachi, S. Fujinami, M. Suzuki, H. Ōkawa, *Chem. Lett.* **1998**, 779. h) M. Yamami, H. Furutachi, T. Yokoyama, H. Ōkawa, *Inorg. Chem.* **1998**, *37*, 6832. i) H. Furutachi, A. Ishida, H. Miyasaka, N. Fukita, M. Ohba, H. Ōkawa, M. Koikawa, *J. Chem. Soc., Dalton Trans.* **1999**, 367. j) H. Furutachi, S. Fujinami, M. Suzuki, H. Ōkawa, *J. Chem. Soc., Dalton Trans.* **1999**, 2197. k) H. Furutachi, S. Fujinami, M. Suzuki, H. Ōkawa, *Chem. Lett.* **1999**, 763.

4 D. A. Denton, H. Suschitzly, *J. Chem. Soc.* **1963**, 4741.

5 a) H. Ōkawa, S. Kida, *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 751. b) H. Ōkawa, S. Kida, *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1759.

6 *Landolt-Börnstein, Neue Series II/11*, Springer-Verlag, Berlin, **1981**.

7 teXsan: *Crystal Structure Analysis Package*, Molecular Structure Corporation, Houston, TX, **1985** and **1999**.

8 C. K. Johnson, *Report 3794*, Oak Ridge National Laboratory, Oak Ridge, TN, **1965**.

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

10 S. Tamburini, P. A. Vigato, D. Chiarello, P. Traldi, *Inorg. Chim. Acta* **1989**, *156*, 271.

11 M. G. B. Drew, J. Nelson, S. Nelson, *J. Chem. Soc., Dalton Trans.* **1981**, 1678.

12 a) R. Menif, A. E. Martell, *J. Chem. Soc., Chem. Commun.* **1989**, 1521. b) R. Menif, A. E. Martell, P. J. Squattrito, A. Clearfield, *Inorg. Chem.* **1990**, *29*, 4723.

13 M. P. Ngwenya, D. Chen, A. E. Martell, J. Reibenspies, *Inorg. Chem.* **1991**, *30*, 2732.

14 K. Motoda, H. Sakiyama, N. Matsumoto, H. Ōkawa, S. Kida, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1176.

15 F. Hoskins, N. J. McLeod, H. A. Schaap, *Aust. J. Chem.* **1976**, *29*, 515.

16 K. Matsumoto, K. Arimura, M. Ohba, H. Ōkawa, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1589.

17 A. J. Atkins, D. Black, A. J. Blake, A. Matin-Becerra, S. Parsons, L. Ruiz-Ramirez, M. Schröder, *J. Chem. Soc., Chem. Commun.* **1996**, 457.

18 M. Yonemura, Y. Matsumura, H. Furutachi, M. Ohba, H. Ōkawa, D. E. Fenton, *Inorg. Chem.* **1997**, *36*, 2711.

19 G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **1980**, *33*, 227.

20 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, **1970**, pp. 175–176.

21 W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81.

22 B. Bosnich, *J. Am. Chem. Soc.* **1968**, *90*, 627.

23 R. S. Downing, F. L. Urbach, *J. Am. Chem. Soc.* **1969**, *91*, 5977.

24 S. Kita, H. Furutachi, H. Ōkawa, *Inorg. Chem.* **1999**, *38*, 4038.

25 K. Inoue, M. Ohba, H. Ōkawa, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 99.

26 a) R. Robson, *Aust. J. Chem.* **1970**, *23*, 2217. b) N. H. Pilkington, R. Robson, *Aust. J. Chem.* **1970**, *23*, 2225.

27 B. Bleaney, K. D. Bowers, *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

28 M. Tadokoro, H. Sakiyama, N. Matsumoto, M. Kodera, H. Ōkawa, S. Kida, *J. Chem. Soc., Dalton Trans.* **1992**, 313.

29 S. Ohtsuka, M. Kodera, K. Motoda, M. Ohba, H. Ōkawa, *J. Chem. Soc., Dalton Trans.* **1995**, 2599.

30 M. Melník, *Coord. Chem. Rev.* **1982**, *42*, 259.

31 V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, W. E. Hatfield, *Inorg. Chem.* **1976**, *15*, 2107.

32 M. Handa, N. Koga, S. Kida, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3853.