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Antiferromagnetism induced by successive protonation of terminal phenol groups of a bis(μ-phenoxide)-bridged dicopper(II,II) complex

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Received 18th February 2002, Accepted 23rd July 2002
First published as an Advance Article on the web 2nd September 2002

The reaction of a tripodal ligand (H_2L = *N*,*N*-bis(2-hydroxybenzyl)-*N′*,*N′*-dimethylethylenediamine) with $Cu(NO_3)_2\cdot 3H_2O$ and $Cu(ClO_4)_2\cdot 6H_2O$ in methanol yielded $[Cu_2(HL)_2](NO_3)_2\cdot H_2O$ (**1**) and $[Cu_2(HL)_2](ClO_4)_2$ (**1′**), respectively. When H_2L was allowed to react with $CuSO_4\cdot 5H_2O$ in the presence of triethylamine (1 : 1 : 2) in methanol, the neutral dicopper(II,II) complex $[Cu_2(L)_2]$ (**2**) was obtained. The monopositive species $[Cu_2(L)(HL)]ClO_4\cdot CH_3OH\cdot H_2O$ (**3**) crystallized on mixing **1′** and **2** (1 : 1) in methanol–dichloromethane. The crystal structures of **1**, **2**, and **3** were determined by X-ray crystallography. All of the complexes consist of a discrete dinuclear molecule with bis(μ-phenoxide)-bridges. The tripodal ligand functions as a tetradentate ligand and one of the phenolic oxygen atoms serves as a bridging ligand. Protonation/deprotonation takes place at the terminal phenol moiety and as the phenol group is deprotonated the coordination geometry changes from a distorted square pyramid to a distorted trigonal bipyramid. The two copper ions in **1**–**3** are antiferromagnetically coupled with $2J = -714$ (**1**), -19.9 (**2**), and $-277\ \mathrm{cm^{-1}}$ (**3**). The results clearly demonstrate that protonation/deprotonation causes a change in coordination geometry, which in turn drastically affects magnetic exchange interactions.

Introduction

The chemistry of dicopper(II,II) complexes has been studied extensively because of the relevance to copper-containing enzymes such as tyrosinase, and because of their interesting magnetic properties.[1] Quite a few dicopper(II,II) complexes bridged by hydroxide, alkoxide, or phenoxide oxygen atoms have been prepared, most of them having a five-coordinate geometry around each copper ion.[2] Five-coordinate copper(II) complexes are stereochemically flexible and they can be square pyramidal or trigonal bipyramidal, or almost anything in between. A considerable body of experimental evidence has been accumulated to elucidate the magnetostructural relationship. It has been observed that the major factor controlling spin coupling between the metal centers in dicopper(II,II) complexes is the Cu–O–Cu bridging angle.[3,4] It would be informative to study the magnetism of dicopper(II,II) complexes with the same or closely related chemical compositions while having different geometries.

The diprotonated complex, $[Cu_2(HL)_2]^{2+}$ (H_2L = *N*,*N*-bis(2-hydroxybenzyl)-*N′*,*N′*-dimethylethylenediamine, Fig. 1) has a distorted square-pyramidal geometry around each copper(II) ion. The complex changes its coordination geometry upon deprotonation of the coordinated terminal phenolic oxygen atoms. In the monoprotonated $[Cu_2(L)(HL)]^+$ complex, one copper(II) ion is in a distorted square-pyramidal environment while the other in a distorted trigonal-bipyramidal environment. The completely deprotonated $[Cu_2(L)_2]$ complex has a distorted trigonal-bipyramidal geometry around each copper(II) ion. The present complexes seem to be ideal to study the magnetostructural correlations in dicopper(II,II) complexes bridged by two phenoxide groups. Here, we report the preparation, structures, and properties of these complexes with the emphasis on magnetostructural correlations.

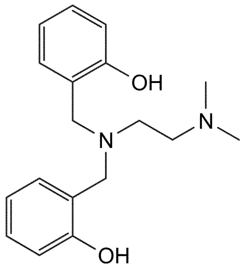

Fig. 1 The H_2L ligand, *N*,*N*-bis(2-hydroxybenzyl)-*N′*,*N′*-dimethylethylenediamine.

Experimental

Materials

All chemicals and solvents were of reagent grade and were used without further purification. *N*,*N*-Bis(2-hydroxybenzyl)-*N′*,*N′*-dimethylethylenediamine (H_2L) was prepared by using the same procedure as described in the literature.[5]

DOI: 10.1039/b201741e

Table 1 Crystallographic data and experimental details for $[Cu_2(HL)_2](NO_3)_2\cdot H_2O$ (**1**), $[Cu_2(L)_2]$ (**2**), and $[Cu_2(L)(HL)]ClO_4\cdot CH_3OH\cdot H_2O$ (**3**)

	1	**2**	**3**
Formula	$C_{36}H_{48}Cu_2N_6O_{11}$	$C_{36}H_{44}Cu_2N_4O_4$	$C_{37}H_{51}ClCu_2N_4O_{10}$
M	867.90	723.86	874.38
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$Pbca$ (no. 61)	$P\bar{1}$ (no. 2)	$P2_1/a$ (no. 14)
a/Å	22.44(1)	9.608(1)	17.012(1)
b/Å	19.62(1)	9.692(2)	17.596(1)
c/Å	17.30(1)	9.180(1)	26.692(2)
α/°		104.337(7)	
β/°		102.475(5)	101.7114(8)
γ/°		87.414(6)	
V/Å^3	7618(6)	808.6(2)	7824.0(8)
Z	8	1	8
μ(Mo Kα)/mm^{-1}	1.185	1.362	1.217
D_{calcd}/g cm^{-3}	1.514	1.486	1.484
T/K	298	298	113
No. of reflections measd	8362 (unique: 6983 $R_{int} = 0.030$)	4699 (unique: 3521, $R_{int} = 0.030$)	32734 (unique: 15708 $R_{int} = 0.059$)
No. of reflections obsd	4971 [$I > 0.70\sigma(I)$]	3110 [$I > 2\sigma(I)$]	15658 [$I > 2\sigma(I)$]
No. of parameters refined	496	208	973
R^a	0.102	0.058	0.080
$R_w{}^b$	0.105	0.085	0.197

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(F_o)$.

Syntheses

$[Cu_2(HL)_2](NO_3)_2\cdot H_2O$ (1). H_2L (0.5 mmol) was added to a methanol solution (10 cm^3) of $Cu(NO_3)_2\cdot 3H_2O$ (0.5 mmol) and the mixture was stirred for 1 h at room temperature. A green powder was collected by filtration and recrystallized from methanol–dichloromethane. Yield: 30%. Found: C, 49.86; H, 5.54; N, 9.80%. $C_{36}H_{48}Cu_2N_6O_{11} = [Cu_2(HL)_2](NO_3)_2\cdot H_2O$ requires C, 49.82; H, 5.57; N, 9.68%. Λ_M = 273 S cm^2 mol^{-1} in CH_3CN. UV-Vis (CH_3CN, λ_{max}/nm (ε/M^{-1} cm^{-1})): 420 (2200). IR (Nujol mull, cm^{-1}): $\nu(NO_3)$ 1380; ν(OH) 3400.

$[Cu_2(HL)_2](ClO_4)_2$ (1′). This complex was prepared by the same method as that for **1**, except that $Cu(ClO_4)_2\cdot 6H_2O$ was used instead of $Cu(NO_3)_2\cdot 3H_2O$. Yield: 50%. Found: C, 46.60; H, 5.01; N, 6.09%. $C_{36}H_{46}Cl_2Cu_2N_4O_{12}$ requires C, 46.76; H, 5.01; N, 6.06%. Λ_M = 303 S cm^2 mol^{-1} in CH_3CN. UV-Vis (CH_3CN, λ_{max}/nm (ε/M^{-1} cm^{-1})): 417 (1870). IR (Nujol mull, cm^{-1}): $\nu(ClO_4)$ 1090; ν(OH) 3400.

$[Cu_2(L)_2]$ (2). H_2L (0.5 mmol) and triethylamine (1 mmol) were added to a methanol solution (10 cm^3) of $CuSO_4\cdot 5H_2O$ (0.5 mmol) and the mixture was stirred for 1 h. A yellowish brown powder was collected by filtration and recrystallized from methanol–dichloromethane to yield dark green crystals. Yield: 41%. Found: C, 59.55; H, 6.15; N, 7.74%. $C_{36}H_{44}Cu_2N_4O_4$ requires C, 59.73; H, 6.13; N, 7.74%. Λ_M = 5.67 S cm^2 mol^{-1} in CH_3CN. UV-Vis (CH_3CN, λ_{max}/nm (ε/M^{-1} cm^{-1})): 390 (1770).

$[Cu_2(HL)(L)]ClO_4\cdot CH_3OH\cdot H_2O$ (3). This complex was obtained on mixing an equimolar amount of **1′** and **2** in methanol–dichloromethane (1 : 1). A dark green precipitate was recrystallized from methanol–dichloromethane. Yield: 64%. Found: C, 51.17; H, 5.76; N, 6.39%. $C_{37}H_{51}ClCu_2N_4O_{10} = [Cu_2(HL)(L)]ClO_4\cdot CH_3OH\cdot H_2O$ requires 50.83; H, 5.88; N, 6.41%. Λ_M = 108 S cm^2 mol^{-1} in CH_3CN. UV-Vis (CH_3CN, λ_{max}/nm (ε/M^{-1} cm^{-1})): 412 (2400). IR (Nujol mull, cm^{-1}): $\nu(ClO_4)$ 1091; ν(OH) 3600.

Physical measurements

UV-Visible absorption spectra were recorded with a JASCO Ubest-550 spectrophotometer. Infrared spectra were measured on a JASCO IR-810 spectrophotometer as Nujol mulls. Electrical conductivity measurements were carried out on a TOA CM30V conductometer in *ca.* 1×10^{-3} M acetonitrile solutions. Magnetic susceptibilities were measured with the Faraday method in the temperature range 80–300 K for **1** and **3**, and with a Quantum Design MPMS2 SQUID magnetometer operating with an applied magnetic field of 0.2 T in the temperature range 5–350 K for **2**. The effective magnetic moments per copper ion were calculated with eqn. (1), where χ_A is the molar magnetic susceptibility corrected for diamagnetism of the constituent atoms using Pascal's constants,[6] and N_α is the temperature-independent paramagnetism per mole of copper(II).

$$\mu_{eff} = 2.83 \times \sqrt{(\chi_A - N_\alpha)T} \qquad (1)$$

Elemental analyses were carried out on a Perkin-Elmer 2400II elemental analyzer.

X-Ray crystal structure determination

A summary of the crystallographic data and experimental details for complexes **1**–**3** is given in Table 1. Crystals of **1** and **3** were mounted in glass capillaries and a crystal of **2** was glued onto a glass fiber. For **1**, the diffraction measurements were made on a Rigaku AFC5R four-circle diffractometer at the X-ray Laboratory of Okayama University using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Unit cell dimensions were determined by a least-squares refinement of the angular settings of 25 reflections in the range of 21.2° < 2θ < 22.0°. During the data collection, the intensities of three standard reflections were measured after every 97 reflections and showed no significant reduction. For **2**, measurements were made on a Rigaku RAXIS-RAPID diffractometer at Aichi University of Education, and for **3**, on a Rigaku RAXIS-IV diffractometer at Okayama University of Science with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). A total of 44 (**2**) and 36 (**3**) images were collected. The camera radii were 127.40 and 100.00 mm for **2** and **3**, respectively. Exposure time was 3.00 and 4.00 min per degree for **2** and **3**, respectively. Readout was performed in the 0.100 mm pixel mode for both samples. Absorption correction was applied based on ψ scan data for **1**, while for **2** and **3** a numerical absorption correction using the programs NUMABS[7a] (for **2**) and Abscorr[7b] (for **3**) was applied. Calculations for **1** and **2**, and those for **3** were carried out using the teXsan[8a] and the CrystalStructure[8b] crystallographic package of Molecular Structure Corporation, respectively. The structures were solved by direct methods (SIR92 and 97)[9] and expanded using Fourier techniques (DIRDIF94).[10] All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2 for **3**, and on F for **1** and **2**. Most of the hydrogen atoms were placed at idealized positions and included in the refinement with fixed thermal parameters. The following hydrogen atoms were not included in the refinement; for **1**, hydrogen atoms attached to O(2), O(4), and O(11), and for **3**, hydrogen atoms attached to O(2), O(6), O(17), O(18), O(19), and O(20). In **3**, there are residual electron density peaks of greater than 3 e $Å^{-3}$ attributable to the disordered ClO_4^- ion and the disordered water molecule of crystallization. We could not solve the problem in site of our efforts.

CCDC reference numbers 179770–179772.

See http://www.rsc.org/suppdata/dt/b2/b201741e/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and characterization

The dipositive dicopper(II) complexes $[Cu_2(HL)_2]X_2$ (X = NO_3 (**1**) and ClO_4 (**1′**)) were prepared by mixing the tripodal tetradentate ligand H_2L with $Cu(NO_3)_2\cdot 3H_2O$ and $Cu(ClO_4)_2\cdot 6H_2O$, respectively, in a 1 : 1 molar ratio in methanol without the addition of a base. The neutral complex $[Cu_2(L)_2]$ (**2**) was prepared by the reaction of $CuSO_4\cdot 5H_2O$ with H_2L in the presence of triethylamine (1 : 1 : 2) in methanol. The monopositive species $[Cu_2(L)(HL)]ClO_4\cdot CH_3OH\cdot H_2O$ (**3**) crystallized on mixing **1′** and **2** (1 : 1) in methanol–dichloromethane. Complexes **1** and **1′**, **2**, and **3** differ only in the degree of protonation. The C, H, and N microanalyses agreed with the chemical formulas $[Cu_2(HL)_2](NO_3)_2\cdot H_2O$ (**1**), $[Cu_2(HL)_2](ClO_4)_2$ (**1′**), $[Cu_2(L)_2]$ (**2**), and $[Cu_2(HL)(L)]ClO_4\cdot CH_3OH\cdot H_2O$ (**3**). The infrared spectrum of complex **1** showed the characteristic absorption bands attributable to $\nu(NO_3)$ (1380 cm^{-1}) and ν(phenolic OH) (3400 cm^{-1}).[11] Complex **1′** showed $\nu(ClO_4)$ (1090 cm^{-1}) as the counteranion and ν(phenolic OH) (3400 cm^{-1}), and complex **3** showed such absorption bands at 1091 and 3600 cm^{-1}.

The molar conductivities of **1** and **3** in acetonitrile were in the expected range for 1 : 2 and 1 : 1 electrolytes, respectively.[12] The low molar conductivity for **2** supports the belief that the compound is a nonelectrolyte. The UV-visible spectrum of **1** in acetonitrile changes to that of **2** on the addition of triethylamine. The results suggest that the complexes retain their identities in acetonitrile.

Crystal structures

$[Cu_2(HL)_2](NO_3)_2\cdot H_2O$ (1). The crystal of **1** consists of a discrete dinuclear complex cation, two nitrate ions, and a water molecule of crystallization. Fig. 2 shows a molecular structure of **1** with the atomic labeling scheme. The selected bond distances and angles are listed in Table 2. Each copper ion is five coordinate and the two phenoxide oxygen atoms bridge the two copper atoms. The Cu(1)–O(2) (2.371(4) Å) and Cu(2)–O(4) (2.294(4) Å) bonds are significantly longer than any of the other Cu–N (2.01–2.09 Å) and Cu–O (1.93–1.98 Å) bonds, indicating that O(2) and O(4) occupy the apical positions of square pyramids. The basal positions are occupied by two nitrogen atoms (N(1), N(2), or N(3), N(4)) and two oxygen atoms (O(1), O(3)). The coordination geometry of a five-coordinate complex has been characterized by the angular structural parameter $\tau = (\beta - \alpha)/60$, where α and β are the two largest metal ligand bond angles in a five-coordinate system.[13] The τ value is 0 for a perfectly square-pyramidal geometry and 1 for a perfectly trigonal-bipyramidal geometry. Using this criterion ($\tau_1 = 0.20$ and $\tau_2 = 0.29$), the coordination geometry around each copper(II) ion for **1** is best described as a distorted square-pyramidal geometry. The copper basal coordination planes are distorted, with displacements of the donor atoms around Cu(1) in the range −0.18 to +0.19 Å, and around Cu(2) in the range −0.26 to +0.21 Å from their respective mean planes. The copper atoms themselves are displaced towards the apical oxygen atoms by 0.239 Å (Cu(1)) and 0.255 Å (Cu(2)) from the mean planes. The dihedral angle between the two basal planes is 141.1°. The Cu ··· Cu separation is 3.063(2) Å, and the Cu–O–Cu bridging angles are 102.8(3) (O(1)) and 103.1(3)° (O(3)). The Cu(1), Cu(2), O(1), and O(3) core is almost planar with an average deviation of 0.11 Å from the plane defined by these atoms. The sum of the angles at the bridging phenoxide oxygen is almost exactly 360° (O(1) 360(1)°; O(3) 360(1)°), indicating no pyramidal distortion.

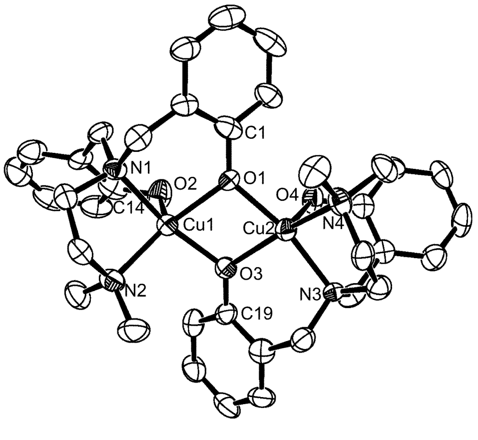

Fig. 2 ORTEP drawing of the complex cation of $[Cu_2(HL)_2](NO_3)_2\cdot H_2O$ (**1**) with the atom numbering scheme showing 50% probability ellipsoids.

The water molecule is hydrogen bonded to both a phenol oxygen atom and one oxygen atom of the NO_3^- anion with hydrogen bond distances of O(11) ··· O(4) = 2.59 Å and O(11) ··· O(9) = 2.62 Å. The angle of C(14)–O(2)–O(5) = 110.28° and the distance of O(2) ··· O(5) = 2.70 Å suggest that the phenol oxygen atom (O(2)) is hydrogen bonded to one oxygen atom of the NO_3^- anion.

$[Cu_2(L)_2]$ (2). The structure of **2** is illustrated in Fig. 3, and a detailed picture around the two copper ions is given in Fig. 4. Bond distances and angles relevant to the copper coordination spheres are listed in Table 2. Complex **2** has a crystallographic inversion center. This neutral dinuclear complex has two five-coordinate copper centers bridged by the two phenoxide oxygen atoms. The τ value for **2** is 0.40, and the coordination geometry

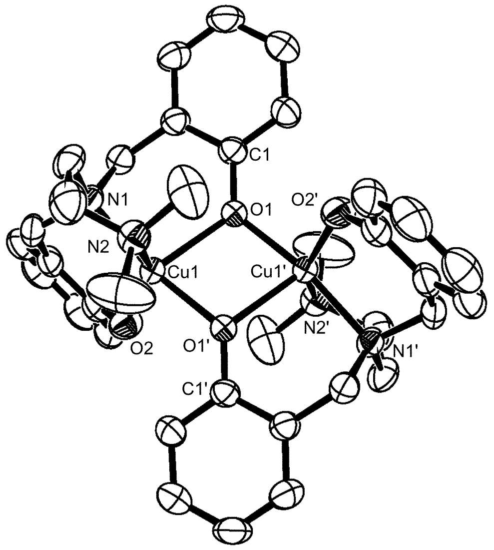

Fig. 3 ORTEP drawing of $[Cu_2(L)_2]$ (**2**) with the atom numbering scheme showing 50% probability ellipsoids.

Table 2 Selected bond distances (Å) and angles (°) for **1**, **2**, and **3**

1							
Cu(1)–O(1)	1.975(6)	Cu(1)–O(2)	2.371(4)	Cu(1)–O(3)	1.931(6)	Cu(1)–N(1)	2.009(7)
Cu(1)–N(2)	2.088(8)	Cu(2)–O(1)	1.943(6)	Cu(2)–O(3)	1.980(6)	Cu(2)–O(4)	2.294(4)
Cu(2)–N(3)	2.032(8)	Cu(2)–N(4)	2.053(8)	Cu(1) ··· Cu(2))	3.063(2)		
O(1)–Cu(1)–O(2)	96.5(3)	O(1)–Cu(1)–O(3)	75.8(3)	O(1)–Cu(1)–N(1)	92.3(3)	O(1)–Cu(1)–N(2)	156.1(3)
O(2)–Cu(1)–O(3)	94.2(3)	O(2)–Cu(1)–N(1)	89.1(3)	O(2)–Cu(1)–N(2)	107.3(3)	O(3)–Cu(1)–N(1)	167.9(3)
O(3)–Cu(1)–N(2)	101.9(3)	N(1)–Cu(1)–N(2)	88.2(3)	O(1)–Cu(2)–O(3)	75.4(2)	O(1)–Cu(2)–O(4)	93.4(2)
O(1)–Cu(2)–N(3)	169.6(3)	O(1)–Cu(2)–N(4)	101.7(3)	O(3)–Cu(2)–O(4)	93.9(3)	O(3)–Cu(2)–N(3)	94.3(3)
O(3)–Cu(2)–N(4)	152.1(3)	O(4)–Cu(2)–N(3)	88.5(3)	O(4)–Cu(2)–N(4)	114.0(3)	N(3)–Cu(2)–N(4)	86.8(3)
Cu(1)–O(1)–Cu(2)	102.8(3)	Cu(1)–O(3)–Cu(2)	103.1(3)	Cu(1)–O(1)–C(1)	128.1(6)	Cu(1)–O(3)–C(19)	130.5(6)
Cu(2)–O(1)–C(1)	128.8(6)	Cu(2)–O(3)–C(19)	126.3(6)				
2							
Cu(1)–O(1)	2.199(3)	Cu(1)–O(1′)	1.971(3)	Cu(1)–O(2)	1.932(3)	Cu(1)–N(1)	2.062(3)
Cu(1)–N(2)	2.096(3)	Cu(1) ··· Cu(1′)	3.190				
O(1)–Cu(1)–O(1′)	80.3(1)	O(1)–Cu(1)–O(2)	110.1(1)	O(1)–Cu(1)–N(1)	91.6(1)	O(1)–Cu(1)–N(2)	103.4(1)
O(2)–Cu(1)–O(1′)	94.8(1)	O(2)–Cu(1)–N(1)	92.7(1)	O(2)–Cu(1)–N(2)	146.4(2)	N(1)–Cu(1)–O(1′)	170.5(1)
N(1)–Cu(1)–N(2)	84.4(1)	N(2)–Cu(1)–O(1′)	92.5(1)	Cu(1)–O(1)–Cu(1′)	99.7(1)	Cu(1)–O(1)–C(1)	123.0(2)
Cu(1′)–O(1)–C(1)	129.3(3)						
3							
Cu(1)–O(1)	1.989(4)	Cu(1)–O(2)	2.261(4)	Cu(1)–O(3)	1.917(4)	Cu(1)–N(1)	2.038(5)
Cu(1)–N(2)	2.040(5)	Cu(2)–O(1)	1.980(5)	Cu(2)–O(3)	2.105(4)	Cu(2)–O(4)	1.985(4)
Cu(2)–N(3)	2.034(4)	Cu(2)–N(4)	2.094(5)	Cu(1) ··· Cu(2)	3.1239(9)	Cu(3)–O(5)	1.998(4)
Cu(3)–O(6)	2.232(4)	Cu(3)–O(7)	1.936(5)	Cu(3)–N(5)	2.030(6)	Cu(3)–N(6)	2.049(5)
Cu(4)–O(5)	1.972(4)	Cu(4)–O(7)	2.093(4)	Cu(4)–O(8)	1.989(4)	Cu(4)–N(7)	2.025(5)
Cu(4)–N(8)	2.059(5)	Cu(3) ··· Cu(4)	3.1141(11)				
O(1)–Cu(1)–O(2)	88.97(15)	O(1)–Cu(1)–O(3)	79.11(15)	O(1)–Cu(1)–N(1)	94.58(17)	O(1)–Cu(1)–N(2)	146.78(18)
O(2)–Cu(1)–O(3)	96.65(16)	O(2)–Cu(1)–N(1)	87.55(17)	O(2)–Cu(1)–N(2)	124.24(17)	O(3)–Cu(1)–N(1)	172.32(19)
O(3)–Cu(1)–N(2)	96.18(17)	N(1)–Cu(1)–N(2)	86.69(19)	O(1)–Cu(2)–O(3)	74.99(15)	O(1)–Cu(2)–O(4)	95.95(15)
O(1)–Cu(2)–N(3)	166.05(17)	O(1)–Cu(2)–N(4)	93.27(17)	O(3)–Cu(2)–O(4)	102.17(17)	O(3)–Cu(2)–N(3)	93.27(16)
O(3)–Cu(2)–N(4)	117.66(17)	O(4)–Cu(2)–N(3)	93.81(18)	O(4)–Cu(2)–N(4)	140.15(17)	N(3)–Cu(2)–N(4)	85.55(19)
Cu(1)–O(1)–Cu(2)	103.81(16)	Cu(1)–O(3)–Cu(2)	101.80(16)	Cu(1)–O(1)–C(1)	123.1(3)	Cu(1)–O(3)–C(19)	133.2(4)
Cu(2)–O(1)–C(1)	131.4(3)	Cu(2)–O(3)–C(19)	120.5(3)	O(5)–Cu(3)–O(6)	89.10(16)	O(5)–Cu(3)–O(7)	78.86(17)
O(5)–Cu(3)–N(5)	94.72(19)	O(5)–Cu(3)–N(6)	145.80(18)	O(6)–Cu(3)–O(7)	94.79(18)	O(6)–Cu(3)–N(5)	87.63(18)
O(6)–Cu(3)–N(6)	125.10(19)	O(7)–Cu(3)–N(5)	173.08(19)	O(7)–Cu(3)–N(6)	96.6(2)	N(5)–Cu(3)–N(6)	87.2(2)
O(5)–Cu(4)–O(7)	75.81(17)	O(5)–Cu(4)–O(8)	95.91(17)	O(5)–Cu(4)–N(7)	165.89(19)	O(5)–Cu(4)–N(8)	93.39(19)
O(7)–Cu(4)–O(8)	101.36(18)	O(7)–Cu(4)–N(7)	92.34(19)	O(7)–Cu(4)–N(8)	123.64(19)	O(8)–Cu(4)–N(7)	93.9(2)
O(8)–Cu(4)–N(8)	134.95(19)	N(7)–Cu(4)–N(8)	86.8(2)	Cu(3)–O(5)–Cu(4)	103.30(18)	Cu(3)–O(7)–Cu(4)	101.14(17)
Cu(3)–O(5)–C(37)	124.7(4)	Cu(3)–O(7)–C(55)	134.5(4)	Cu(4)–O(5)–C(37)	131.5(4)	Cu(4)–O(7)–C(55)	122.9(4)

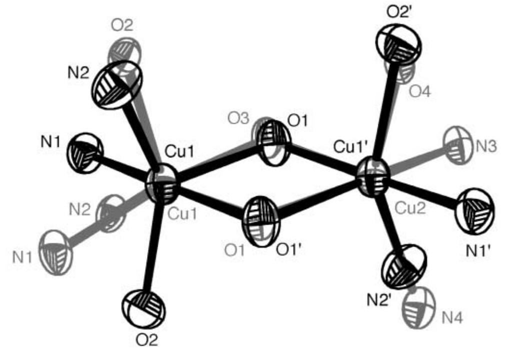

Fig. 4 Comparison of the inner coordination spheres about the Cu_2 core for **2** (black) and **3** (gray).

cannot be determined straightforwardly. The bond angles around Cu(1) suggest that the copper coordination sphere may be tentatively described as distorted trigonal bipyramidal. From this viewpoint, the axis of the bipyramid passes through N(1) and O(1′), and the equatorial plane comprises O(1), O(2), and N(2). From a viewpoint of the square pyramid, the apical position can be defined by O(1), since the Cu(1)–O(1) bond (2.199(3) Å) is longer than the other coordination bonds (1.93–2.10 Å). However, the basal plane defined by O(1′), O(2), N(1), and N(2) is severely distorted; the atoms lie between −0.43 and 0.81 Å. Thus, **2** is best described as a distorted trigonal-bipyramidal geometry. The Cu(1) ··· Cu(1′) separation of 3.190 Å is longer than that (3.063(2) Å) of **1**. The Cu–O–Cu bridge angle is 99.7(1)°. The sum of the angles at the bridging phenoxide oxygen (O(1) 352.0(6)°) is smaller than 360°, indicating pyramidal distortion.

[Cu_2(L)(HL)]ClO_4·CH_3OH·H_2O (3). The X-ray analysis of **3** revealed that two crystallographically independent dinuclear molecules, which are quite similar to each other, exist in the unit cell. Fig. 5 shows one of the molecular structures, and selected bond distances and angles are listed in Table 2. The Cu(1)–O(2)

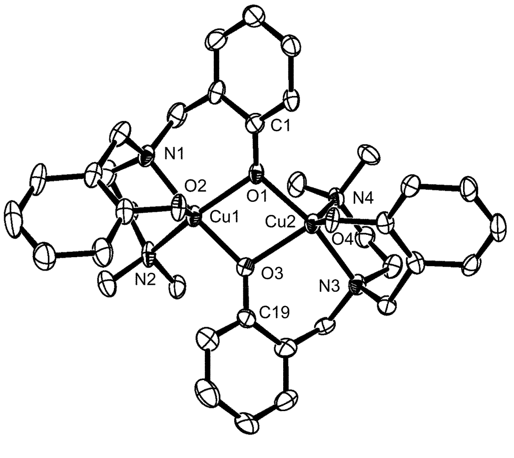

Fig. 5 ORTEP drawing of the complex cation of [Cu_2(HL)(L)]ClO_4·CH_3OH·H_2O (**3**) with the atom numbering scheme showing 50% probability ellipsoids.

Table 3 Magnetic susceptibility data for complexes **1**–**3**

Complex	$2J$/cm^{-1}	g	N_α/10^{-6} cm^3 mol^{-1}	p (%)	μ_{eff}/μ_B (T/K)
1	−714	2.20	60	0.7	0.66 (297.2)
2	−19.9	2.07	60	0.9	1.85 (299.7)
3	−277	2.10	60	0	1.38 (298.0)

bond (2.261(4) Å) is clearly longer than the corresponding Cu(2)–O(4) bond (1.985(4) Å), suggesting that the phenolic oxygen atom O(2) is protonated while O(4) is deprotonated. Each copper ion is five coordinate and the two phenoxide oxygen atoms bridge the two copper atoms. Fig. 4 compares the inner coordination spheres about the Cu$_2$ core for **2** and **3**. The coordination geometry around Cu(2) (τ_2 = 0.43) is similar to that in **2** (τ = 0.40), and is best described as distorted trigonal-bipyramidal. O(3), O(4), and N(4) lie in the equatorial plane of Cu(2), with the axial positions occupied by O(1) and N(3). The τ value for Cu(1) (τ_1 = 0.43) is the same as that for Cu(2). However, the coordination geometry around Cu(1) may be assigned to distorted square pyramidal on the basis of the overall structural features including the bond lengths. That the Cu(1)–O(2) bond (2.261(4) Å) is clearly longer than the other bonds (< 2.04 Å) is a strong indication that O(2) occupies the apical position of the distorted square-pyramidal structure. When a τ value is close to 0.5, care must be taken to assign the structure to either distorted trigonal bipyramidal or distorted square pyramidal, since the parameter is based only on the two largest angles (α and β). The basal plane defined by N(1), N(2), O(1), and O(3) is distorted with displacements of the donor atoms in the range −0.25 to +0.25 Å from the mean plane. The Cu(1) atom is displaced towards the apical oxygen atom by 0.339 Å from the mean plane. The Cu(1) ··· Cu(2) separation (3.1239(9) Å) is between those in **1** (3.063(2) Å) and **2** (3.190 Å), and the Cu(1)–O(1)–Cu(2) and Cu(1)–O(3)–Cu(2) bridge angles are 103.81(16) and 101.80(16)°, respectively. The Cu(1), Cu(2), O(1), and O(3) core is almost planar with an average deviation of 0.036 Å from the plane defined by these atoms. The sum of the angles at the bridging phenoxide oxygen is almost 360° (O(1) 358(1)°, O(3) 356(1)°) indicating only a small pyramidal distortion.

The methanol molecule is hydrogen bonded to phenol oxygen atoms with hydrogen bond distances of O(17) ··· O(2) = 2.53 Å and O(17) ··· O(4) = 2.60 Å.

Magnetic properties

The effective magnetic moments (μ_{eff}) of the present complexes **1**–**3** at room temperature are quite different from each other: 0.66 (**1**), 0.66 (**1′**), 1.85 (**2**), and 1.38 μ_B/Cu (**3**). A strong antiferromagnetic interaction is inferred in **1** and **1′**. **1**–**3** are dinuclear complexes bridged by two phenoxide oxygen atoms, and they differ only in the degree of protonation of the coordinated terminal phenolic oxygen atoms. In the doubly protonated complex, [Cu$_2$(HL)$_2$](NO$_3$)$_2$·H$_2$O (**1**), the copper ions assume distorted square-pyramidal geometries with protonated phenolic oxygen atoms at the apical positions. The coordination geometry changes from a distorted square pyramid to a distorted trigonal bipyramid as the terminal phenol group is deprotonated. These features create opportunities to investigate magnetostructural correlation and hence the mechanism of the antiferromagnetic interaction. Thus, variable-temperature magnetic susceptibility measurements were carried out on powdered samples in the temperature range 80–300 K for **1** and **3** by the Faraday method, and 5–350 K for **2** by the SQUID method. The plots of magnetic susceptibility (χ_A) *versus* temperature for **1**–**3** are shown in Fig. 6. The observed magnetic susceptibility data were fitted to the Bleaney–Bowers equation by allowing for the presence of monomer impurity.[14] The best-fit parameters $2J$ and g were obtained by a nonlinear least-squares fitting procedure. The magnetic data for **1**–**3** are well represented by the Bleaney–Bowers equation, indicating that an antiferromagnetic interaction is operative between the copper(II) ions in these complexes. A big difference in magnitude of magnetic interactions between the complexes, **1**–**3** (Table 3) should be related to the difference in their structures.

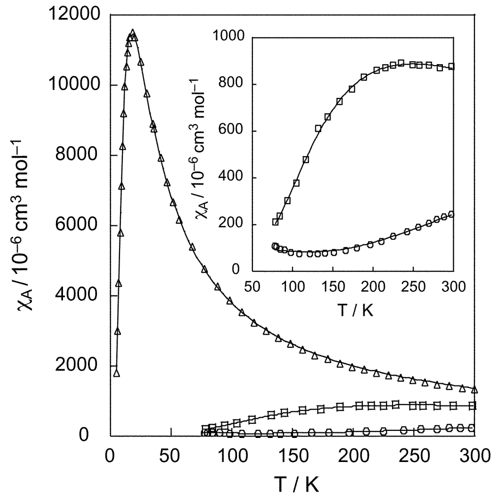

Fig. 6 Temperature dependence of χ_A for **1** (○), **2** (Δ), and **3** (□). Solid curves were obtained as described in the text.

Complex **1** exhibits strong antiferromagnetic coupling ($2J$ = −714 cm^{-1}) between the two copper ions. The coordination geometry around each copper ion of **1** is distorted square pyramidal, where the d$_{x^2-y^2}$ magnetic orbitals (containing the unpaired electron) point toward the bridging phenoxide oxygen atoms. This situation is favorable to strong magnetic interactions. The structures and magnetic properties for dicopper-(II,II) complexes bridged equatorially by pairs of hydroxide,[3a–c,15] alkoxide,[16] or phenoxide[4,17] oxygen atoms have been studied extensively. It has been established that the type (ferromagnetic or antiferromagnetic) and magnitude of the interaction are influenced by such factors as the Cu–O–Cu bridge angle, the Cu–O(bridge) distance, the Cu ··· Cu separation, the geometry around the copper(II) center, and the geometry around the bridging oxygen atom. The first magnetostructural correlation dealing with copper(II) dinuclear compounds was proposed by Hatfield and Hodgson.[3a,b] The correlation concerns planar di(μ-hydroxide)-bridged dicopper(II,II) complexes. The Cu–O–Cu bridging angle is the major factor controlling the magnetic interactions and a linear dependence of the bridging angle on the coupling parameter was deduced. A similar relationship also holds for the analogous di(μ-alkoxo)-bridged dicopper(II) complexes.[16] Recently, the magnetostructural correlations in bis(μ-phenoxide)-bridged macrocyclic dinuclear copper(II) complexes have been studied.[17j] The complexes adopt an essentially flat structure with the two square pyramidal copper centers. Again, a linear relationship between the exchange integral ($2J$) and the phenoxide bridging angle (θ) was observed; $2J = -31.95\theta + 2462$. If this relationship holds for complex **1** (θ = 103.0), a $2J$ value of *ca.* −830 cm^{-1} is anticipated. The relatively weak antiferromagnetic interaction ($2J$ = −714 cm^{-1}) with respect to the bridge angle is ascribed to the unfavorable overlaps of the magnetic orbitals for the distorted-square pyramidal geometry of this complex (τ_1 = 0.20 and τ_2 = 0.29). Distortion makes the magnetic interaction less effective.[18]

The magnitude of the exchange coupling in **2** ($2J = -19.9$ cm^{-1}) is much smaller than that in **1**. The weak antiferromagnetic interaction is accounted for by considering the symmetry of the magnetic orbitals of the interacting metallic fragments. The two copper ions are in distorted trigonal-bipyramidal environments. In a trigonal-bipyramidal structure the magnetic orbital is the d_{z^2} orbital. The trigonal-axes of N(1)–Cu(1)–O(1′) and N(1′)–Cu(1′)–O(1) are parallel to each other. The d_{z^2} magnetic orbital of Cu(1), for example, points toward the bridging O(1′) atom but does not interact strongly with O(1), which occupies an equatorial position. Thus, the two copper ions cannot interact effectively. Moreover, the small Cu–O–Cu bridging angle (99.7(1)°) and pyramidal distortion at the bridging phenoxide oxygen also make the magnetic interaction less effective.[17j]

In complex **3**, the two copper(II) ions have different coordination geometries; one is distorted square pyramidal and the other distorted trigonal bipyramidal. The magnitude of the magnetic coupling between the two copper(II) centers in **3** ($2J = -277$ cm^{-1}) is intermediate between those of **1** (-714 cm^{-1}) and **2** ($-$ 19.9 cm^{-1}). The intermediate magnetic interactions can be explained on the structural basis (*vide supra*). The $d_{x^2-y^2}$ magnetic orbital of Cu(1) interacts with the d_{z^2} magnetic orbital of Cu(2) at the bridging O(1) atom, but not at O(3). The overlaps of the magnetic orbitals will not be very favorable and we expect intermediate magnetic interactions. In addition to the overall structural features, local geometrical factors around the bridging oxygen atoms also contribute to stronger antiferromagnetic interactions for **3** than for **2**. The Cu–O–Cu bridging angles for **3** (103.81(16) and 101.80(16)°) are larger than that for **2** (99.7(1)°). The pyramidal distortion at the bridging oxygen atoms for **3** is less than that for **2**; the sums of the angles at the bridging phenoxide oxygen atoms for **3** (358(1) and 356(1)°) are closer to 360° than that for **2** (352.0(6)°). Both factors contribute favorably to strong antiferromagnetic interactions for **3**.

Conclusions

A series of dicopper(II,II) complexes with bis(μ-phenoxide) bridges was prepared by successive deprotonation of the terminal phenol groups. Deprotonation caused a change in coordination geometry from a distorted square pyramid to a distorted trigonal bipyramid. The electron density of the oxygen atom increases on deprotonation, which in turn strengthens the Cu–O bond. The shortening of the Cu–O bond must be the driving force of the geometrical transformation. This geometrical change from a distorted square pyramid to a distorted trigonal bipyramid drastically reduced the antiferromagnetic interaction. Thus, the magnetic interactions between the two copper(II) centers have been discussed on the structural basis.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area (No. 12023236 "Metal-assembled Complexes") from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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