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Synthesis, X-ray Structure, and Magnetic Properties of Ferromagnetically Coupled Binuclear Copper(II) Complexes Having a (μ-Hydroxo/methoxo)bis(μ-benzoato)dicopper(II) Core

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Binuclear copper(II) complexes of composition $[Cu_2(OH/OMe)(O_2CPh)_2(tmen)_2](PF_6)$ (**1**) are prepared by reacting copper(II) benzoate with *N,N,N′,N′*-tetramethylethane-1,2-diamine (tmen) in methanol followed by an addition of NH_4PF_6. The crystalline product **1** is a 1:1 mixture of two complexes *viz.* $[Cu_2(OH)(O_2CPh)_2(tmen)_2](PF_6)$ (**1a**) and $[Cu_2(OMe)(O_2CPh)_2(tmen)_2](PF_6)$ (**1b**) but the homogeneous crystalline mass **2,** obtained from a similar reaction in ethanol, has a composition of $\mathbf{1a}\cdot\mathbf{1a}\cdot H_2O\cdot 0.5NH_4PF_6$, i.e. two **1a** molecules in the crystallographic asymmetric unit. The formulation of the products **1** and **2** has been made from the X-ray structural studies and analytical data. Crystal data are as follows: **1**, orthorhombic, $P2_12_12_1$, $a = 12.364(3)$ Å, $b = 19.560(4)$ Å, $c = 29.071(3)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$; **2**, rhombohedral, $R\bar{3}$, $a = b = 27.083(10)$, $c = 56.096(9)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $Z = 18$. The complexes have a $[Cu_2(\mu\text{-}OH/OMe)(\mu\text{-}O_2CPh)_2(tmen)_2]^+$ core with bidentate chelating tmen as terminal ligands. The geometry at the copper ion is essentially square-pyramidal with one carboxylate bridge occupying the apical sites giving much longer Cu−O bond distances compared to those at the basal planes. The Cu···Cu distances and Cu−O−Cu angles in the core lie in the range 3.229(1)−3.259(3) Å and 112.6(2)−115.7(8)°. The dihedral angles between two copper planes are 38.31, and 44.20° for **1** and 39.70 and 41.68° for **2**. The complexes display axial X-band EPR spectral features in the polycrystalline state at 77 K giving $g_{11} = 2.28$ ($A_{11} = 150 \times 10^{-4}$ cm^{-1}), $g_\perp = 2.08$ for **1** ($\mathbf{1a}\cdot\mathbf{1b}\cdot H_2O$) and $g_{11} = 2.25$ ($A_{11} = 150 \times 10^{-4}$ cm^{-1}), $g_\perp = 2.07$ for **2** ($\mathbf{1a}\cdot\mathbf{1a}\cdot H_2O\cdot 0.5NH_4PF_6$). In addition, both the complexes display a $|\Delta M_S| = 2$ transition at $g = 4.42$ indicating the presence of spin-exchange coupling. The complexes are ferromagnetic and the theoretical fit of the susceptibility data in the temperature range 300−20 K gives $2J = 35.4$ cm^{-1}, $\Theta = 8.4$ K, $g = 2.0$ for **1** and $2J = 45.1$ cm^{-1}, $\Theta = 9.7$ K, $g = 2.0$ for **2**. The sum of the angles at oxygen of OH and OMe in $\mathbf{1a}\cdot\mathbf{1b}\cdot H_2O$ is 333° (average). The ferromagnetism of **1** has been found to be related to the pyramidal geometry at oxygen. The magnetostructural properties of this emerging class of tribridged dicopper(II) complexes presenting a new spin system have been discussed.

Introduction

Binuclear copper(II) complexes are useful models to study the intramolecular magnetic-exchange interactions. The systems that have drawn considerable interests to magnetostructural chemists are as follows: (i) copper(II) carboxylates with a "paddle-wheel" structure showing antiferromagnetic spin−spin coupling,[2] (ii) symmetrically dibridged binuclear copper(II) complexes containing hydroxo, alkoxo, or chloro bridging ligands and exhibiting magnetic-exchange interactions whose nature depends on various factors including the type of bridging atom and the monoatomic bridge angle,[3] and (iii) asymmetrically dibridged dicopper(II) complexes having a (μ-hydroxo/alkoxo)-(μ-carboxylato)dicopper(II) core in which the magnitude of the magnetic-exchange interaction parameter J is usually small possibly due to the counter-complimentary nature of the overlap of magnetic orbitals involving the monoatomic and three-atom bridging ligands.[4]

In this paper, we report the synthesis, X-ray structure and magnetic properties of dicopper(II) complexes having a (μ-hydroxo/methoxo)bis(μ-benzoato)dicopper(II) core in $[Cu_2(OR)(O_2CPh)_2(tmen)_2](PF_6)$ (R = H, Me), where tmen is bidentate chelating *N,N,N′,N′*-tetramethylethane-1,2-diamine. While the crystalline product obtained from a reaction in

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methanol is a 1:1 mixture of hydroxy and methoxy complexes, *viz.* **1a** and **1b**, complex **1a** has been isolated as a single product from a similar reaction in ethanol. Isolation of complexes with a $[Cu_2(\mu\text{-OH/OR})(\mu\text{-}O_2CPh)_2]^+$ core is of significance as the chemistry of other 3d and 4d metal complexes with an analogous core structure is well developed[5] following the discovery[6] of such a core in several non-heme iron- and manganese-containing metalloproteins. The copper(II) complexes **1a** and **1b** are ferromagnetic and this work makes significant contribution to the emerging chemistry of the virtually unexplored class of tribridged dicopper(II) complexes, presenting a new magnetic system.[7−10]

Experimental Section

Preparation of $[Cu_2(OR)(O_2CPh)_2(tmen)_2](PF_6)$ (R = H, 1a; Me, 1b). The synthesis of the crystalline species **1**, consisting of two dimeric complexes **1a** and **1b** in a 1:1 molar ratio along with 1 mol of H_2O, was achieved by reacting a methanol solution (20 mL) of copper(II) benzoate (0.33 g, 0.5 mmol) with *N,N,N′,N′*-tetramethylethane-1,2-diamine (tmen) (0.15 mL, 1.0 mmol) at 25 °C for 20 min with stirring, followed by an addition of an aqueous solution (5 mL) of ammonium hexafluorophosphate (0.16 g, 1.0 mmol) to the reaction mixture. The resulting solution was cooled at 5 °C to initiate crystallization upon slow evaporation of the solvent. Blue square-shaped uniform crystalline blocks of composition **1a·1b·**H_2O (**1**) were obtained in ~70% yield. Anal. Calcd for $C_{53}H_{90}N_8O_{11}F_{12}P_2Cu_4$: C, 40.78; H, 5.77; N, 7.18. Found: C, 40.64; H, 5.60; N, 7.28. Visible electronic spectral data in MeCN, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 676 (260).

Preparation of $[Cu_2(OH)(O_2CPh)_2(tmen)_2](PF_6)$ (1a). This complex was prepared by following a similar procedure as adopted for **1** except the reaction was carried out in ethanol. The uniform crystalline mass was obtained in ~65% yield. The analysis was in agreement with a composition of 2 mol of **1a** with 1 mol of water and 0.5 mol of NH_4PF_6 as observed from the X-ray structure (*vide infra*).[11] Anal. Calcd for $C_{52}H_{90}N_{8.5}O_{11}F_{15}P_{2.5}Cu_4$: C, 38.38; H, 5.53; N, 7.32. Found: C, 38.88; H, 5.47; N, 7.00.Visible electronic spectral data in MeCN, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 678 (280).

Table 1. Crystallographic Data for Complexes **1** and **2**

complex	**1**	**2**
chem. formula	$C_{53}H_{90}N_8O_{11}F_{12}P_2Cu_4$	$C_{52}H_{90}N_{8.5}O_{11}F_{15}P_{2.5}Cu_4$
fw	1559.5	1626.9
cryst size, mm	0.2 × 0.3 × 0.3	0.1 × 0.2 × 0.1
a, Å	12.364(3)	27.083(10)
b, Å	19.560(4)	27.083(10)
c, Å	29.071(3)	56.096(9)
α, deg	90.0	90.0
β, deg	90.0	90.0
γ, deg	90.0	120.0
V, Å^3	7030(2)	35634(20)
Z	4	18
space group (No.)	$P2_12_12_1$ (19)	$R\bar{3}$ (148)
T, K	294	294
λ, Å	0.7107	0.7107
ρ_{calc}, g cm^{-3}	1.47	1.37[a]
μ (Mo Kα) cm^{-1}	13.28	11.78
$R(F_o)$[b]	0.0446	0.0919
$R_w(F_o)$[c]	0.0455	0.0930

[a] ρ_{obs}, g cm^{-3} = 1.39. [b] $R(F_o) = (\sum||F_o| - |F_c||)/(\sum|F_o|)$. [c] $R_w(F_o) = [(\sum w^{1/2}||F_o| - |F_c||)/(\sum w^{1/2}|F_o|)]$; $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. $g = 0.000494$ for **1** and $g = 0.002652$ for **2**.

Measurements. The elemental analyses were done using a Heraeus CHN-O Rapid instrument. The electronic and EPR spectra were recorded on Hitachi U 3400 and Varian E-109 X-band spectrometers respectively. Variable-temperature magnetic susceptibility data were obtained on polycrystalline samples from a George Associates Model 300 Lewis-coil-force magnetometer using $Hg[Co(NCS)_4]$ as calibrant. The X-ray intensity data were collected at 294 K using an Enraf-Nonius CAD4 diffractometer fitted with a graphite-monochromated Mo Kα radiation.

X-ray Crystallographic Procedures. The crystal structures of **1** (**1a·1b·**H_2O) and that of pure **1a** crystallizing as **1a·1a·**H_2O·0.5NH_4PF_6 (**2**) were determined using procedures reported earlier.[12] The crystallographic data are presented in Table 1. The positional coordinates with isotropic equivalent thermal parameters for selected atoms in the cationic complexes of **1** and **2** are given in Table 2. The intensity data were corrected for Lorentz, polarization, and absorption effects. The structures were solved by the Patterson method and refined by full-matrix least-squares techniques. All calculations were carried out using a VAX88 computer and SHELX[13] system of programs with scattering factors taken from ref 14. All non-hydrogen atoms were refined anisotropically except C(47) of **2** which became non-positive definite on anisotropic refinement, and this atom was left at an isotropic stage. The hydrogen atoms in their calculated positions were used for structure factor calculations except H(1) of the hydroxy bridge in **1** as it was located in the difference Fourier map and refined for one cycle. The hydrogen atoms of OH in **1a** molecules of **2** could not be located from the difference Fourier map. The final difference Fourier maps for both the structures were featureless. The crystal structure of **1a·1b·**H_2O (**1**) refined well. The structure determination of **2** (**1a·1a·**H_2O·0.5NH_4PF_6) gave minor crystallographic problems. For this crystal, the intensity data collection was restricted to only $2\theta \le 44°$ due to poor quality of data at higher angles (θ) because of the small size of the crystals. Attempts to crystallize the complex from other solvents in absence of NH_4PF_6 were not successful. In **2,** the complex cations, the PF_6 anions, and the lattice water were refined to our satisfaction. However, the ammonium ion present in the crystal lattice showed problems related to the site occupancy factor (sof) as well as the expected electron density of the associated peaks in the

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(11) The formulation of **2** showing two **1a** moieties has been tentatively made from the crystal structure showing two complexes differing marginally in bond distances and bond angles, presumably due to packing effects. Spectroscopically, **1a** molecules in **2** are identical to each other. Hence, product **2** can as well be formulated as **1a**·0.5H_2O·0.25NH_4PF_6 from the analytical and EPR spectral data.

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Table 2. Positional Coordinates and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for the Core atoms in Complexes **1** and **2**

	1				2			
atom	x	y	z	$U_{eq}{}^a$	x	y	z	$U_{eq}{}^a$
Cu(1)	−0.00518(7)	0.26781(4)	0.67165(3)	44(0.3)	0.6231(1)	0.8684(1)	0.6755(1)	46(2)
Cu(2)	−0.21770(7)	0.27340(5)	0.60723(3)	45(0.3)	0.7101(1)	0.8690(1)	0.6352(1)	58(2)
O(1)	−0.0616(4)	0.2776(3)	0.6103(2)	49(2)	0.6931(6)	0.9133(5)	0.6575(2)	53(7)
O(11)	−0.1006(5)	0.1839(3)	0.6945(2)	69(2)	0.6365(6)	0.7997(6)	0.6856(3)	58(9)
O(12)	−0.0934(5)	0.3443(3)	0.6968(2)	65(2)	0.5756(5)	0.8323(6)	0.6457(2)	53(8)
O(21)	−0.2495(5)	0.1893(3)	0.6520(2)	75(3)	0.6889(7)	0.7933(6)	0.6566(3)	70(10)
O(22)	−0.2369(5)	0.3503(3)	0.6512(2)	62(2)	0.6381(7)	0.8387(7)	0.6182(2)	65(8)
N(11)	0.0769(6)	0.2690(4)	0.7329(2)	65(3)	0.5478(7)	0.8350(8)	0.6938(3)	48(10)
N(12)	0.1298(6)	0.2129(4)	0.6474(2)	64(3)	0.6587(8)	0.9230(8)	0.7047(3)	60(12)
N(21)	−0.3776(6)	0.2865(4)	0.5906(3)	77(3)	0.7389(9)	0.8434(10)	0.6055(3)	72(14)
N(22)	−0.2121(7)	0.2159(4)	0.5460(2)	64(3)	0.7967(8)	0.9123(10)	0.6438(4)	82(12)
Cu(3)	0.17713(8)	0.33268(4)	0.92258(3)	42(0.3)	0.7883(1)	0.9902(1)	0.7937(1)	50(2)
Cu(4)	0.17137(8)	0.16770(4)	0.91743(3)	43(0.3)	0.8100(1)	0.8879(1)	0.7773(1)	54(2)
O(2)	0.1953(4)	0.2470(2)	0.9559(1)	48(2)	0.8232(6)	0.9457(6)	0.8004(2)	55(9)
O(31)	0.2567(5)	0.3090(3)	0.8584(2)	63(2)	0.7041(6)	0.9202(7)	0.7866(3)	68(9)
O(32)	0.0259(4)	0.3115(3)	0.9067(2)	56(2)	0.8197(6)	1.0092(6)	0.7603(2)	62(9)
O(41)	0.2580(4)	0.1955(3)	0.8572(2)	56(2)	0.7230(6)	0.8554(7)	0.7718(3)	70(9)
O(42)	0.0222(4)	0.1973(3)	0.9013(2)	52(2)	0.8444(6)	0.9445(7)	0.7509(3)	73(10)
N(31)	0.1436(5)	0.4308(3)	0.8996(2)	50(2)	0.7636(8)	1.0501(8)	0.7895(3)	56(10)
N(32)	0.3095(7)	0.3768(3)	0.9556(3)	67(3)	0.7793(9)	1.0012(10)	0.8297(3)	71(13)
N(41)	0.1295(6)	0.0738(3)	0.8906(2)	57(3)	0.8060(10)	0.8307(10)	0.7530(5)	85(13)
N(42)	0.3010(7)	0.1145(3)	0.9480(3)	67(3)	0.8034(12)	0.8277(12)	0.8018(5)	113(17)
H(1)	−0.019(5)	0.332(3)	0.597(2)	27(15)				
C(27)	0.1229(10)	0.2467(6)	0.9955(3)	100(5)				

[a] $U_{eq} = {}^1/_3\,[\sum_i\sum_j U_{ij}\mathbf{a}_i{}^*\mathbf{a}_j{}^*\mathbf{a}_i\mathbf{a}_j]$.

difference Fourier map. Some of the atoms were in special positions. The atoms P(3) and N(33) had sof values of 0.3333 each and P(4) had 0.1667. The atom N(44) of the ammonium ion was expected to have a sof of 0.3333 but on refinement it showed a very high thermal parameter. To balance the overall charge, it was modeled with a sof of 0.1667 to get an acceptable thermal parameter. Such an assumption was made as the atoms were present along a channel and the possibilty of having alternate voids could not be ruled out. Overall, there were 0.5 NH_4PF_6 per asymmetric unit. The composition was verified from the elemental analysis data. The relatively high value of the residuals for this structure could be due to the inherent disorder in the crystal. However, the complex cation and the PF_6 anions did not show any unusual structural features.

Magnetic Measurement. The magnetic susceptibility data were recorded over a temperature range from 300 to 20 K. The data were corrected with a diamagnetic correction ($\chi_{dia} = -216.4 \times 10^{-6}$ cm^3 mol^{-1} for **1** and -220.3×10^{-6} cm^3 mol^{-1} for **2**) and for temperature independent paramagnetism, TIP ($N_\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1} per copper). The molar magnetic susceptibility per mole of copper was fitted to the Bleaney−Bowers expression,[2d] $\chi_{Cu} = [Ng^2\beta^2/k(T - \Theta)][3 + \exp(-2J/kT)]^{-1}(1 - \rho) + (Ng^2\beta^2/4kT)\rho + N_\alpha$, where ρ was the fraction of monomeric impurity. The best fit gave the lowest value of the index defined as $R = [\sum(\chi_{obsd} - \chi_{calcd})^2/\sum\chi_{obsd}{}^2]^{1/2}$ with $\rho = 0$.

Results and Discussion

The reaction of copper(II) acetate with tmen in an alcoholic medium is known[4i] to form the dibridged dicopper(II) complex $[Cu_2(OH)(O_2CMe)(tmen)_2]^{2+}$ in high yield. A similar reaction of tmen with copper(II) benzoate has led to the formation of tribridged dicopper(II) complexes with a $[Cu_2(\mu\text{-}OH/OMe)(\mu\text{-}O_2CPh)_2]^+$ core. The blue crystalline complexes are 1:1 electrolytes and display a visible band near 677 nm. The molecular and crystal structures of the complexes are determined by X-ray diffraction studies.

The crystals obtained from the reaction in methanol on X-ray structural analysis show the presence of two discrete binuclear copper(II) complexes $[Cu_2(OH)(O_2CPh)_2(tmen)_2](PF_6)$ (**1a**) and $[Cu_2(OMe)(O_2CPh)_2(tmen)_2](PF_6)$ (**1b**). The complexes are in a 1:1 molar ratio along with 1 mol of lattice water giving the composition of **1** as **1a·1b·**H_2O. The ORTEP[15] diagrams for the cationic species are shown in Figure 1. Selected bond distances and angles are presented in Table 3. The complexes have a $[Cu_2(\mu\text{-}OH/OMe)(\mu\text{-}O_2CPh)_2]^+$ core. The hydroxy

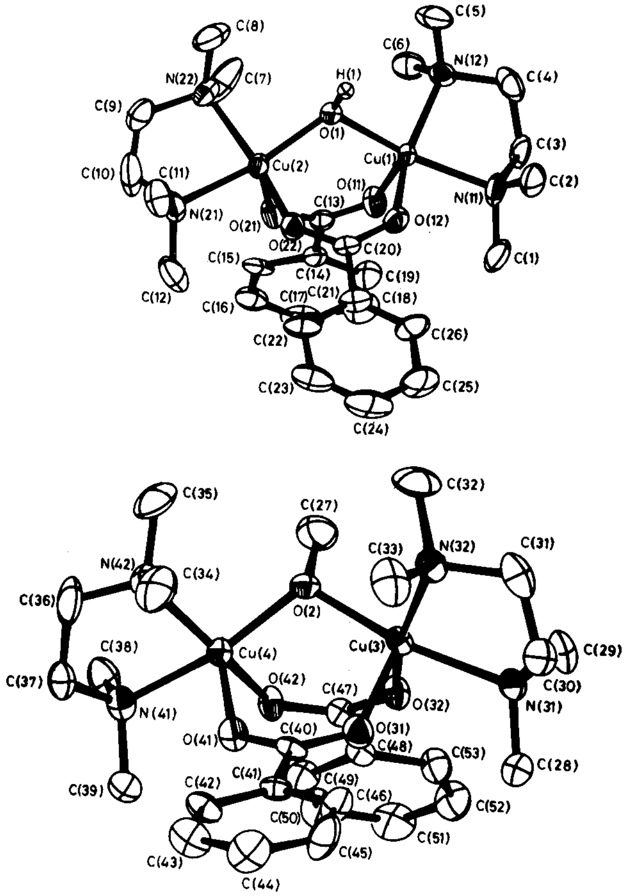

Figure 1. ORTEP views of the cationic complexes in **1a·1b·**H_2O with atom labelling scheme showing 50% probability thermal ellipsoids.

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(15) Johnson, C. K. *ORTEP II: A Program for Thermal Ellipsoid Plotting*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) in **1** (**1a**·**1b**·H_2O) and **2** (**1a**·**1a**·H_2O·0.5NH_4PF_6)

	1	2		1	2
			Bond Distances (Å)		
Cu(1)···Cu(2)	3.229(1)	3.259(3)	Cu(3)···Cu(4)	3.231(1)	3.240(4)
Cu(1)−O(1)	1.925(6)	1.946(13)	Cu(3)−O(2)	1.949(4)	1.90(2)
Cu(1)−O(11)	2.128(6)	2.14(2)	Cu(3)−O(31)	2.160(6)	2.15(12)
Cu(1)−O(12)	1.991(6)	2.037(11)	Cu(3)−O(32)	1.970(5)	2.015(11)
Cu(1)−N(11)	2.050(6)	2.05(2)	Cu(3)−N(31)	2.074(6)	2.15(3)
Cu(1)−N(12)	2.106(7)	2.09(2)	Cu(3)−N(32)	2.084(8)	2.02(2)
Cu(2)−O(1)	1.934(5)	1.941(15)	Cu(4)−O(2)	1.935(4)	1.923(15)
Cu(2)−O(21)	2.134(6)	2.19(2)	Cu(4)−O(41)	2.123(6)	2.09(2)
Cu(2)−O(22)	1.988(6)	1.95(2)	Cu(4)−O(42)	1.989(5)	2.00(2)
Cu(2)−N(21)	2.051(8)	2.10(2)	Cu(4)−N(41)	2.061(6)	2.03(3)
Cu(2)−N(22)	2.107(7)	2.09(2)	Cu(4)−N(42)	2.107(8)	2.07(3)
O(1)−H(1)	1.25(6)		O(2)−C(27)	1.458(11)	
			Bond Angles (deg)		
Cu(1)-O(1)-Cu(2)	113.6(3)	114.0(6)	Cu(3)-O(2)-Cu(4)	112.6(2)	115.7(8)
O(1)-Cu(1)-O(11)	99.5(2)	98.3(6)	O(2)-Cu(1)-O(31)	101.1(2)	97.0(6)
O(1)-Cu(1)-O(12)	93.8(2)	93.3(5)	O(2)-Cu(1)-O(32)	92.6(2)	93.8(6)
O(1)-Cu(1)-N(11)	169.5(3)	168.8(7)	O(2)-Cu(3)-N(31)	168.2(2)	169.5(7)
O(1)-Cu(1)-N(12)	91.6(2)	90.2(6)	O(2)-Cu(3)-N(32)	92.1(3)	91.7(6)
O(11)-Cu(1)-O(12)	99.3(2)	98.1(6)	O(31)-Cu(3)-O(32)	100.7(2)	100.3(6)
O(11)-Cu(1)-N(11)	90.7(2)	92.7(7)	O(31)-Cu(3)-N(31)	90.6(2)	93.1(8)
O(11)-Cu(1)-N(12)	98.7(3)	100.9(7)	O(31)-Cu(3)-N(32)	97.4(3)	99.1(8)
O(12)-Cu(1)-N(11)	86.8(3)	87.1(7)	O(32)-Cu(3)-N(31)	86.0(2)	87.4(7)
O(12)-Cu(1)-N(12)	160.1(3)	160.0(8)	O(32)-Cu(3)-N(32)	160.1(3)	159.0(8)
N(11)-Cu(1)-N(12)	84.5(3)	85.79(7)	N(31)-Cu(3)-N(32)	85.5(2)	83.7(8)
O(1)-Cu(2)-O(21)	100.9(2)	101.1(6)	O(2)-Cu(4)-O(41)	101.2(2)	98.9(7)
O(1)-Cu(2)-O(22)	93.3(3)	94.5(8)	O(2)-Cu(4)-O(42)	92.6(2)	92.8(6)
O(1)-Cu(2)-N(21)	165.3(3)	163.3(7)	O(2)-Cu(4)-N(41)	166.2(2)	173.4(10)
O(1)-Cu(2)-N(22)	91.7(3)	92.9(8)	O(2)-Cu(4)-N(42)	92.1(3)	95.8(9)
O(21)-Cu(2)-O(22)	99.7(2)	97.8(7)	O(41)-Cu(4)-O(42)	101.5(2)	102.1(7)
O(21)-Cu(2)-N(21)	93.6(3)	95.3(8)	O(41)-Cu(4)-N(41)	92.5(2)	87.7(9)
O(21)-Cu(2)-N(22)	96.3(3)	95.4(8)	O(41)-Cu(4)-N(42)	95.2(3)	97.6(10)
O(22)-Cu(2)-N(21)	86.7(3)	86.1(6)	O(42)-Cu(4)-N(41)	86.4(3)	85.1(9)
O(22)-Cu(2)-N(22)	162.0(3)	163.3(7)	O(42)-Cu(4)-N(42)	161.5(3)	157.0(11)
N(21)-Cu(2)-N(22)	84.2(3)	82.6(10)	N(41)-Cu(4)-N(42)	84.9(3)	83.9(11)
Cu(1)−O(1)−H(1)	103(3)		Cu(3)-O(2)-C(27)	109.0(5)	
Cu(2)−O(1)−H(1)	116(3)		Cu(4)-O(2)-C(27)	111.1(5)	

proton which has been located from the difference Fourier map has been refined isotropically. The product obtained from a similar reaction in ethanol gives a uniform crystalline mass belonging to a different crystal system compared to that of **1**. The crystals on structural analysis show the presence of two molecules of $[Cu_2(OH)(O_2CPh)_2(tmen)_2](PF_6)$ along with one water and 0.5 NH_4PF_6 in the crystallographic asymmetric unit. The product **2** thus has a composition of **1a**·**1a**·H_2O·0.5NH_4PF_6 in which two identical **1a** moieties differ crystallographically due to packing and related effects.[11] Selected bond distances and angles for **2** are given in Table 3.

The copper atoms in **1a** and **1b** are bridged by one monodentate hydroxo or methoxo and two three-atom bridging benzoate ligands. The terminal ligands are bidentate chelating tmen. The coordination environment of copper is O_3N_2 showing a distorted square-pyramidal geometry. Interestingly, one benzoate bridging ligand occupies the apical sites giving much longer Cu−O bond distances compared to those in the basal planes. The tribridged core structure in the present dicopper(II) complexes thus differs considerably from the (μ-hydroxo)bis(μ-carboxylato)dimetal cores reported[5] for analogous 3d- and 4d- metal complexes showing an essentially similar M-O(O_2CR) distances. The Cu···Cu distances and Cu−O−Cu angles in the $[Cu_2(\mu\text{-OH/OMe})(\mu\text{-}O_2CPh)_2]^+$ core lie in the range 3.229(1)−3.259(3) Å and 112.6(2)−115.7(8)°. The unit cell packing diagrams and the structural data do not show any interdimer bonding features. The Cu(1) to Cu(4) atoms deviate by 0.251(1), 0.274(1), 0.245(1), and 0.261(1) Å in **1** and 0.265(3), 0.267(2), 0.220(3), and 0.251(3) Å in **2** from the least-squares planes made by basal coordinating ligand atoms. The dihedral angles between two copper containing square planes are 38.31, 44.20° for the first and 39.70, 41.68° for the second structure. The extent of distortion for the Cu(1) to Cu(4) atoms from the square-pyramidal to the trigonal bipyramidal geometry can be estimated[16] from the τ values that are 0.16, 0.06, 0.14, and 0.08 for **1** and 0.23,0.10, 0.15, and 0.0 for **2**.

The complexes in the polycrystalline state at 77 K exhibit axial X-band EPR spectra giving $g_{11} = 2.28$ ($A_{11} = 150 \times 10^{-4}$ cm^{-1}), $g_\perp = 2.08$ in **1** and $g_{11} = 2.25$ ($A_{11} = 150 \times 10^{-4}$ cm^{-1}), $g_\perp = 2.07$ for **1a** in **2**. In addition, both the complexes display a $|\Delta M_S| = 2$ transition at $g = 4.42$ indicating the presence of spin-exchange coupling.[17] The spectral data suggests that the core structures are essentially same for both the species. The magnetic susceptibilities of these complexes have been measured in the temperature range 300−20 K. The least-squares fitting of the experimental data using Bleaney−Bowers equation for coupled d^9−d^9 systems have given $2J = 35.4$ cm^{-1}, $\Theta = 8.4$ K, and $g = 2.0$ for **1** and $2J = 45.1$ cm^{-1}, $\Theta = 9.7$ K, and $g = 2.0$ for **2** (Figure 2). The positive value of $2J$ indicates the ferromagnetic nature of the spin coupling.

The magnetostructural data on (μ-hydroxo/alkoxo)bis(μ-carboxylato)dicoppper(II) complexes are compared in Table 4. The number of copper(II) complexes belonging to this class of spin-system is very small.[7−10] The paucity of data makes it difficult to draw any definite magnetostructural correlation. The Cu···Cu distance ranges between 3.0 and 3.4 Å and the Cu−O−Cu angle varies between 106 and 116° in this class of complexes. The geometry at the copper site is either square-

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(16) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Vershcoor, G. C. *J. Chem. Soc., Dalton. Trans.* **1984**, 1349.

(17) Tolman, W. B.; Rardin, R. L.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111,* 4532.

Table 4. Comparison of the Magnetostructural Data for Complexes Having a $[Cu_2(\mu\text{-}X)(\mu\text{-}O_2CR)_2]^+$ Core (X = OH^-, RO^-, or RCO_2^-)

no	complex	Cu···Cu, Å	Cu−O−Cu, deg	δ, deg	$2J$ cm^{-1}	ref
1	$[Cu_2(O_2CMe)_3(bpy)_2](ClO_4)$	3.392(1)	109.8(1)		7.2	7
2	$[Cu_2(L^1)(O_2CPh)_2](PF_6)^a$	3.297(3)	112.0(3)	90	−126.4	8
3	$[Cu_2(L^2)(O_2CMe)_2](ClO_4).H_2O^b$	3.263(2)	113.7(3)	91.5	−72.0	9
4	$[Cu_2(OMe)(O_2CMe)_2(bpy)_2](PF_6)^c$	3.093(1)	106.8(1)	107.5	*d*	10
5	$[Cu_2(OEt)(O_2CMe)_2(bpy)_2](PF_6)^c$	3.230(1)	112.1(1)	34.5	*d*	10
6	$[Cu_2(OH/OMe)(O_2CPh)_2(tmen)_2](PF_6)^{e,f}$	3.230[1]	113.1[2]	41.5	35.4	this work
7	$[Cu_2(OH)(O_2CPh)_2(tmen)_2](PF_6)^{f,g}$	3.250[3]	114.9[7]	40.7	45.1	this work

[a] HL^1, 2,6-bis[(*N*-(2-(diethylamino)ethyl)-*N*-ethylamino)methyl]-4-methylphenol. [b] HL^2, 2,6-bis((*N*-methylpiperazino)methyl)-4-chlorophenol. [c] bpy, 2,2′-bipyridine. [d] Not reported. [e] Complex formulation **1a**·**1b**·H_2O. [f] Structural data present average values. [g] Complex formulation **1a**·**1a**·H_2O·$0.5NH_4PF_6$ (*vide text*, ref 11b).

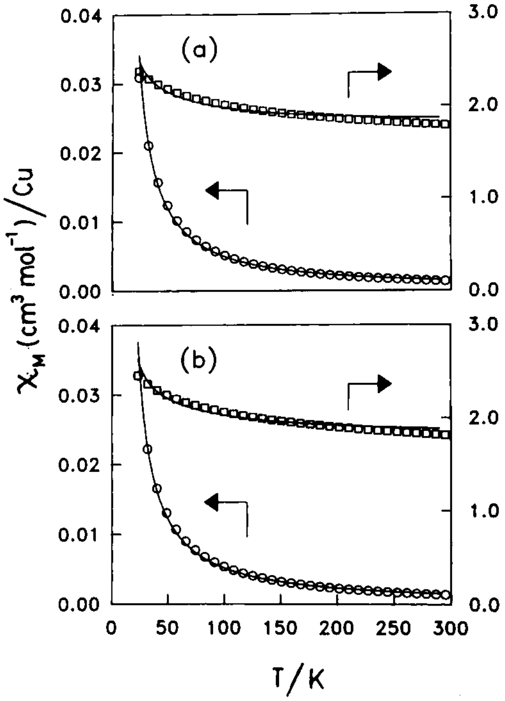

Figure 2. Plots of molar magnetic susceptibility per copper (χ_M/Cu) and the effective magnetic moment per copper (μ_{eff}/Cu) vs temperature for the crystalline products **1** (a) and **2** (b). The theoretical fit of the susceptibility data is shown by the solid line.

pyramidal or trigonal bipyramidal (tbp). In $[Cu_2(O_2CMe)_3(bpy)_2]^+$, the metal centers are known[7] to have square-pyramidal and tbp geometries. The complexes with multidentate ligands providing the endogenous alkoxo bridge are antiferromagnetic although the dihedral angles (δ) between two copper planes are 90°.[8,9] The present complexes with δ values ∼42° are ferromagnetic in nature.

It has been observed by Murray and co-workers[4a] for dibridged binuclear copper(II) complexes that a distortion from the trigonal-planar to a pyramidal geometry at the endogenous bridging oxygen atom of OH or OR reduces the extent of antiferromagnetism (negative *J*) and they have shown in a specific case where it leads to net ferromagnetism. The rationalization has been made on the ground that a π-type overlap between copper out-of-plane orbitals with the nonbonding electron pair on monoatomic bridging oxygen is expected to be more significant for promoting antiferromagnetism for a trigonal-planar (sp^2) oxygen and reducing antiferromagnetism for a pyramidal (sp^3) oxygen. Although the core structures in dibridged and tribridged dicopper(II) systems are different, they resemble each other in the magnetochemical sense in presence of a carboxylate ligand at the elongated apical sites in the square-pyramidal geometry. A perusal of the structural data reveals that the sum of angles at the monoatomic bridging oxygen in $[Cu_2(O_2CMe)_3(bpy)_2]^+$ is 345.5° and the complex is ferromagnetic. The antiferromagnetic complexes have a trigonal-planar oxygen atom. The sum of the angles at oxygen of OH and OMe in **1a**·**1b**·H_2O is 333° (average). The ferromagnetism in this complex may be related to the pyramidal geometry at oxygen. The product **2** is also ferromagnetic and that could be due to a pyramidal geometry at the hydroxo oxygen in **1a** as observed in **1**. The bipyridine complexes are reported[10] to have a pyramidal oxygen, but the magnetic data are not available for comparison.

In conclusion, it has been observed that the geometry at the monoatomic bridging oxygen proves to be an important indicator in predicting the major pathway for the spin−spin coupling in this emerging class of tribridged dicopper(II) complexes. Crystal structures of **1** and **2** provide the first structural evidence for a (μ-hydroxo)bis(μ-carboxylato)dicopper(II) core.[10]

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Supporting Information Available: Full lists of crystal data, positional parameters, bond distances, bond angles, anisotropic thermal parameters, and susceptibility data in the range 300−20 K for **1** and **2** and ORTEP diagrams for two **1a** molecules in **2** and unit cell packing diagrams for **1** and **2** (45 pages). Ordering and Internet access information is given on any current masthead page.

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