A Structural and Magnetic Investigation of Ferromagnetically Coupled Copper(II) Isophthalates

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Dinuclear and one-dimensional copper complexes $[Cu_2(tpa)_2(m\text{-bda})](ClO_4)_2$ (**1**), $[\{Cu_2(tpm)_2(m\text{-bda})_2\}\cdot 2\,CH_3OH\cdot 4\,H_2O]_n$ (**2**), and $[\{Cu_2(bpm)_2(m\text{-bda})_2(H_2O)\}\cdot CH_3CN\cdot H_2O]_n$ (**3**) [tpa: tris(2-pyridylmethyl)amine; tpm: tris(pyrazolyl)methane; bpm: bis(pyrazolyl)methane; *m*-bda: isophthalate dianion] have been prepared from various polydentate terminal ligands. Complex **1** crystallizes in the monoclinic $P2_1/c$ space group with a = 14.003(6), b = 17.201(7), c = 20.654(9) Å, Z = 4, R_1 = 0.0678, wR_2 = 0.1751. Complex **2** crystallizes in the triclinic $P\bar{1}$ space group with a = 10.250(7), b = 15.078(10), c = 15.190(10) Å, Z = 2, R_1 = 0.0571, wR_2 = 0.1288. Complex **3** crystallizes in the orthorhombic *Pnma* space group with a = 17.956(6), b = 17.615(5), c = 10.776(4) Å, Z = 4, R_1 = 0.0554, wR_2 = 0.0845. In these complexes the isophthalate anion acts as a bis(monodentate) ligand bridging copper(II) centers. The variable temperature magnetic behavior reveals the existence of ferromagnetic interactions in **1**–**3**. The best fittings to the experimental magnetic susceptibilities give J = 1.02 cm^{-1} (**1**), 2.58 cm^{-1} (**2**), and 35.5 cm^{-1} (**3**). In light of the structural data it can be concluded that the magnetic coupling via the isophthalate bridging ligand is negligibly small, and the abnormally large ferromagnetic interaction in complex **3** may be due to the hydrogen bonding between copper centers via carboxylic groups through a spin-polarization mechanism.

Introduction

The study of superexchange interactions between paramagnetic ions in a variety of magnetic systems has been a vital field in inorganic chemistry in the last decades driven by the need to understand the fundamental science associated with magnetic interactions between metal centers and develop structure-function relationships that enable the rational design of new magnetic materials.[1] Owing to its fundamental importance, the study of long-range magnetic interactions has also been an active field of research,[2] in which phenyldicarboxylate ligands have been extensively studied.[3–6] Alhough magnetic interactions transmitted through phenyldicarboxylate bridges are usually weak,[2,6–8] the magnitude and nature of the coupling interactions can be influenced by a series of factors, such as the separation of the metal centers, bridging modes, degree of coplanarity between the coordination basal planes and the ligand, the dihedral angles between the carboxylato planes and the phenyl ring, and the angle between the planes of the two carboxylato groups of each phthalato bridge.[9–12]

In copper phthalates, magnetic systems with terephthalate as bridges are the most abundant, whereas those with isophthalate have been less widely reported.[5,6,13,14] In fact, compounds of phenyldicarboxylates are mostly dinuclear and oligonuclear, while those with polymeric structures and transition metal varieties are still relatively limited, especially for isophthalic acid. In a previous report,[14] we systematically investigated the influence of various isomers of phthalic acids on magnetic properties, and found that the structural differences caused by the bridging ligands lead to unexpected magnetic behavior, including changes from ferromagnetic to antiferromagnetic couplings. As a continuation of this magneto-structural relationship study, we initiated a systematic experimental approach in an attempt to design μ-isophthalato-Cu^{II} magnetic systems to investigate the factors that influence the isophthalate-bridged complexes. Three ferromagnetically coupled complexes $[Cu_2(tpa)_2(m\text{-bda})](ClO_4)_2$ (**1**), $[\{Cu_2(tpm)_2(m\text{-bda})_2\}\cdot 2\,CH_3OH\cdot 4\,H_2O]_n$ (**2**), and $[\{Cu_2(bpm)_2(m\text{-bda})_2(H_2O)\}\cdot CH_3CN\cdot H_2O]_n$ (**3**) [tpa: tris(2-pyridylmethyl)amine; tpm: tris(pyrazolyl)methane; bpm: bis(pyrazolyl)methane; *m*-bda: isophthalate dianion] were prepared. The coordination geometries of the Cu^{II} centers are tuned by the various polydentate terminal ligands, which ultimately leads to the different crystal structures and magnetic properties.

Results and Discussion

Complexes **1**–**3** were prepared with the same bridging ligand, the isophthalate dianion, and three different terminal

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ligands, tris(pyrazolyl)methane, tris(2-pyridylmethyl)amine and bis(pyrazolyl)methane. Since tris(pyrazolyl)methane is a tridentate ligand, it reacts very easily with 0.5 equiv. of the metal ion to form the sandwich complex M(tpm)$_2$. On the other hand, the isophthalate dianion is not an active bridging ligand in neutral environments. In this paper, we successfully obtained a half-sandwich structure by making the pH basic. This solution also works when we change the terminal ligand into tris(2-pyridylmethyl)amine or bis(pyrazolyl)methane.

The X-ray crystal structure analyses reveal a dinuclear unit for **1** and one-dimensional zigzag chain motifs for **2** and **3**. The copper(II) ions in **1** and **2** are all five-coordinate, whereas there are two types of crystallographically different copper atoms – four-coordinate and five-coordinate – in **3**.

Crystal Structure of [Cu$_2$(tpa)$_2$(*m*-bda)](ClO$_4$)$_2$ (1)

The structure of **1** contains a [Cu$_2$(tpa)$_2$(*m*-bda)]$^{2+}$ cation and a ClO$_4^-$ anion. The [Cu$_2$(tpa)$_2$(*m*-bda)]$^{2+}$ unit is shown in Figure 1. The tpa ligand acts as a quadridentate terminal ligand with four nitrogen atoms ligated at the copper center. The *m*-bda group acts as a bis(monodentate) ligand, and bridges copper(II) ions to form a dinuclear complex. The coordination geometry around the copper atom is distorted trigonal-bipyramidal. The apical sites of the trigonal bipyramid are occupied by the N4 and O1 atoms [Cu1–N4 = 2.033(6) Å; Cu1–O1 = 1.901(5) Å]. The best equatorial plane is defined by atoms N1, N2, and N3, with an average Cu–N bond length and N–Cu–N bond angle of 2.085(7) Å and 117.3(3)°, respectively. The Cu1 atom is 0.091(6) Å out of this plane. The distance between two copper(II) ions is 10.557(5) Å.

[{Cu2(tpm)2(*m*-bda)2}·2 CH$_3$OH·4 H$_2$O]$_n$ (2)

In the structure of **2**, tpm is a tridentate terminal ligand. The isoelectronic tris(pyrazolyl)methane ligand is formally derived from tris(pyrazolyl)borate ligands by replacing the central boron anion with a carbon atom, and has received considerably less attention.[15–17] Surprisingly, 1D or multidimensional polymers with tpm as terminal ligand have seldom been reported so far, which is probably due to the fact that tpm is such a strong tridentate, chelating, six-electron donor that it can effectively prevent building blocks from constructing infinite aggregates. In principle, the half-sandwich complexes containing tpm can be extended into infinite structures through appropriate bridging ligands. Here, the *m*-bda anion, as a bis(monodentate) ligand, bridges copper(II) ions to form a one-dimensional zigzag chain-like structure, as shown in Figure 2. The coordination geometry around the copper atom is distorted square pyramidal. The apical site of the square pyramid around the Cu1 atom is occupied by N3 [Cu1–N3 = 2.414(5) Å]. Other Cu–N bond lengths vary slightly, from 1.984(5) to 1.991(4) Å. The Cu–O bond lengths [Cu1–O1 = 1.899(4) Å, Cu1–O5 = 1.905(14) Å] are somewhat shorter than in other *m*-bda-bridged complexes,[5,6,13] which may be due to the distorted square pyramid geometry caused by the rigid tridentate tpm ligand. The best equatorial plane is defined by N1, N5, O1, and O5. The largest deviation from the mean plane is 0.2261 Å for O5, and the Cu1 atom is 0.0023 Å out of this plane. The distance between copper(II) ions along the chain is 10.403 Å, which is much longer than the shortest interchain distance (6.644 Å) between copper ions.

[{Cu$_2$(bpm)$_2$(*m*-bda)$_2$(H$_2$O)}·CH$_3$CN·H$_2$O]$_n$ (3)

The polymeric [Cu$_2$(bpm)$_2$(*m*-bda)$_2$(H$_2$O)} unit of **3** is shown in Figure 3. The bpm ligand acts as a bidentate terminal ligand. There are two kinds of crystallographically different Cu^{II} ions in **3**: Cu1 (five-coordinate) and Cu2 (four-coordinate). The coordination geometry around Cu1 is perfectly square pyramidal, with two nitrogen atoms from bpm [Cu1–N1(N1A) = 2.081(3) Å] and two oxygen atoms from *m*-bda [Cu1–O1(O1A) = 1.937(3) Å] composing the equatorial plane. The Cu1 atom is 0.0541(4) Å out of this plane. The apical site of this square pyramid is occupied by the oxygen atom from the coordinated water molecule [Cu1–O5 = 2.394(4) Å]. The coordination geometry around Cu2 is a distorted square plane with two nitrogen atoms from bpm [Cu2–N3(N3B) = 2.009(3) Å] and two oxygen

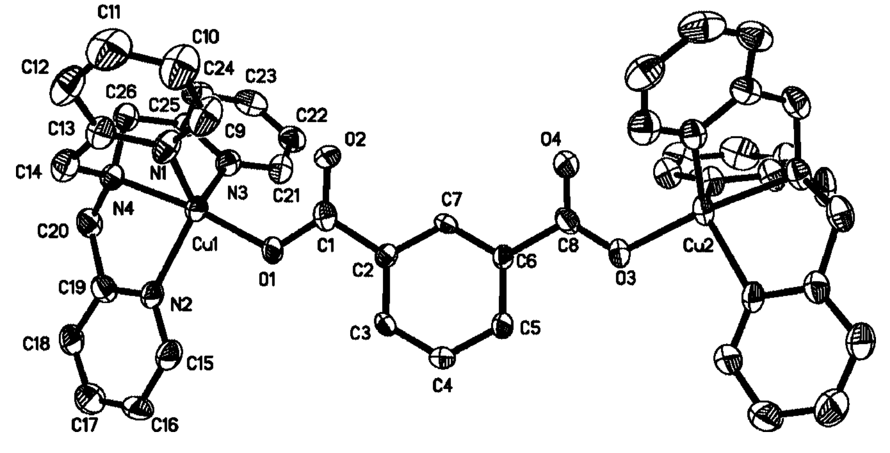


Figure 1. ORTEP drawing of [Cu$_2$(tpa)$_2$(*m*-bda)](ClO$_4$)$_2$ (**1**); ClO$_4^-$ and H atoms have been omitted for clarity.

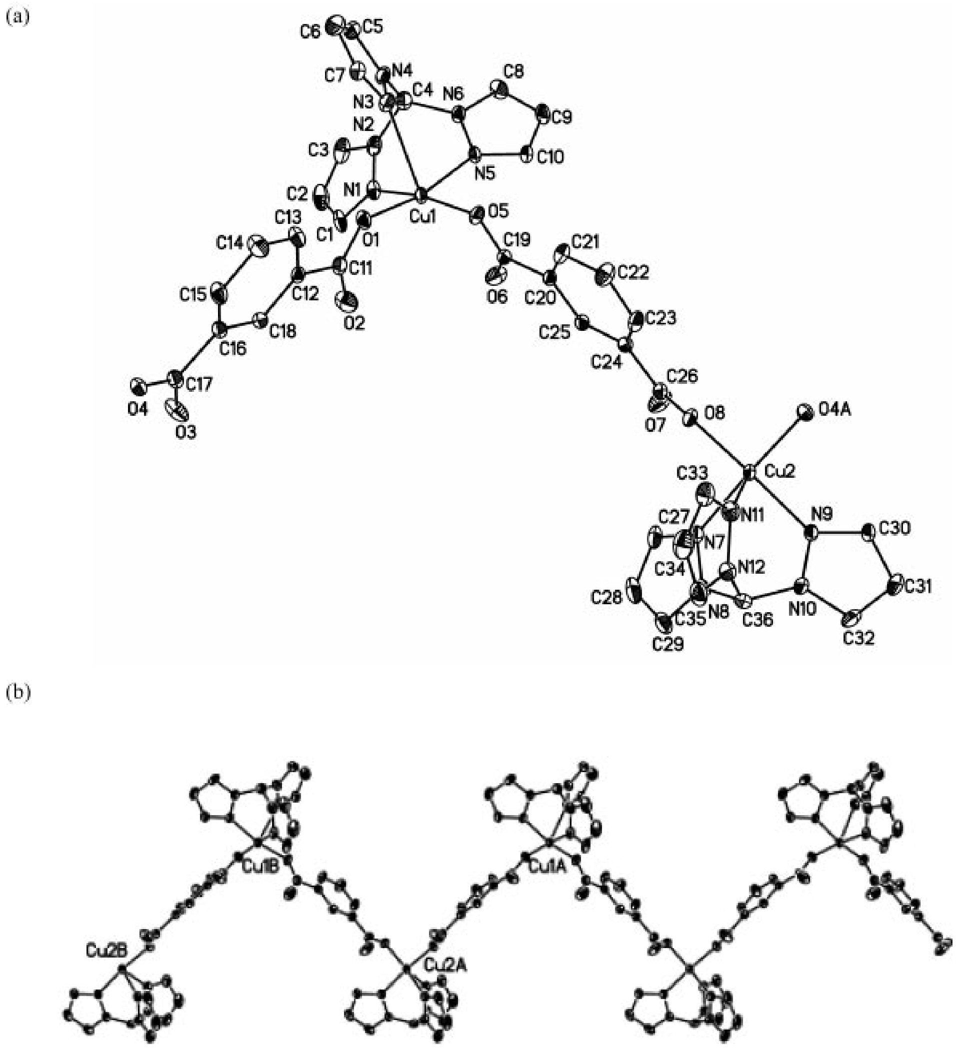


Figure 2. (a) ORTEP drawing of [{$Cu_2(tpm)_2(m\text{-bda})_2$}·2 CH_3OH·4 H_2O]$_n$ (**2**); solvent molecules and H atoms have been omitted for clarity. (b) Zigzag chain structure of **2**.

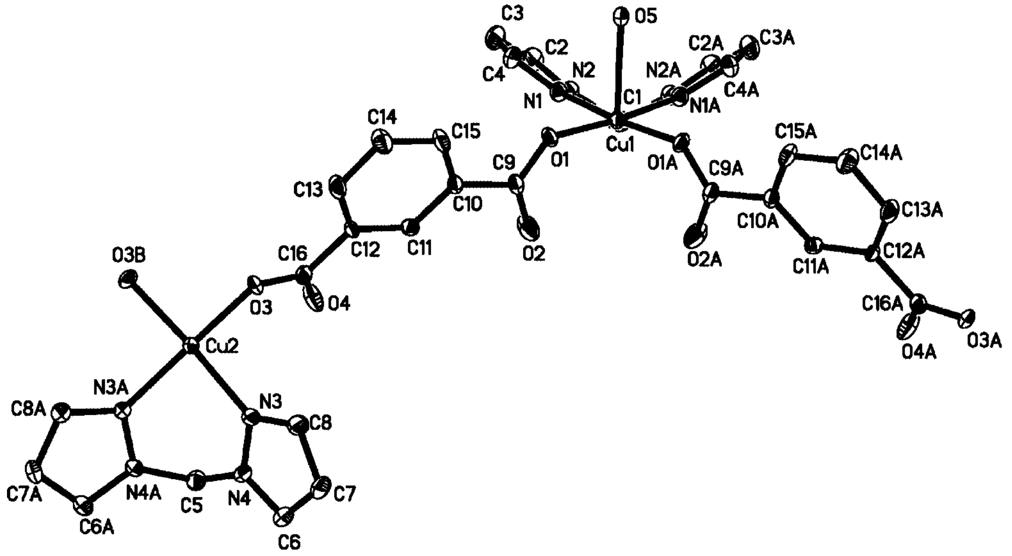


Figure 3. ORTEP drawing of [{$Cu_2(bpm)(m\text{-bda})_2(H_2O)$}·$CH_3CN$·$H_2O$]$_n$ (**3**); solvent molecules and H atoms have been omitted for clarity.

atoms from *m*-bda [Cu2–O3(O3B) = 1.939(9) Å]. The Cu2 atom is 0.1514 Å out of the plane. The *m*-bda group acts as a bis(monodentate) ligand and bridges two crystallographically different copper(II) ions alternately to form a one-dimensional zigzag chain (Figure 3). The distance between copper(II) ions along the chain is 10.643 Å, which is much longer than the shortest interchain distance [4.936(4) Å] between copper ions.

There are two kinds of weak interactions between neighboring copper chains: (i) Cu–O···Cu weak coordination bonds, where the oxygen atom from the coordinated water molecule of the five-coordinate Cu atom forms a weak coordination bond with the four-coordinate Cu atom of the neighboring chain [Cu···O 2.552(7) Å, bold dashed line in Figure 4]. The Cu···Cu distance is 4.936(4) Å, and the Cu–O···Cu angle is 172.7(8)°; (ii) hydrogen bonds, with a distance of 2.692(3) Å between the oxygen atom of the H_2O coordinated to one Cu and the nonbonded carboxylate oxygen atoms of the adjacent Cu center. Such a distance strongly suggests the occurrence of H-bonding between these units (thin dashed line in Figure 4).

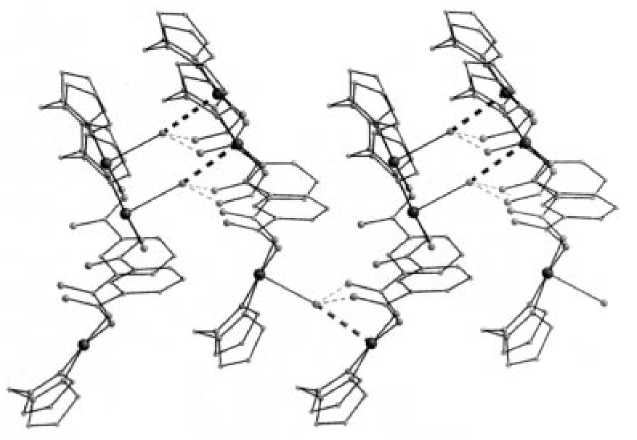


Figure 4. Packing arrangement of **3** along the *ac* plane.

The terminal ligands play an important role during the structure formation. For **1**, the terminal ligand is tetradentate tpa, and the large steric hindrance prevents the formation of infinite chainlike polymer; a dinuclear complex **1** is therefore obtained. For complex **2**, tpm is a tridentate ligand, and the steric hindrance is smaller than tpa. The copper centers are five-coordinate, with two oxygen atoms from an *m*-bda ligand which bridges copper centers into a 1D chain. We have previously published a series of phthalic acid bridged complexes – $[\{Cu_4(tacn)_4(o\text{-}bda)_2\}(ClO_4)_4(H_2O)_2]_n$, $[\{Cu(tacn)(m\text{-}bda)\}(CH_3OH)_{0.5}(H_2O)_{0.5}]_n$, and $[\{Cu_2(tacn)_2(p\text{-}bda)\}(ClO_4)_2]_n$ (tacn = 1,4,7-triazacyclononane, bda = benzenedicarboxylic acid)[14] – in which the terminal ligand tacn is also a tridentate ligand and leads to the formation of one-dimensional chains. For complex **3**, bpm is a bidentate ligand, and the steric hindrance is the smallest, which allows a water molecule to coordinate to Cu1 while Cu2 is square planar. In general, tetradentate tpa ligands create a binuclear complex, whereas tridentate tpm and tacn ligands favor the formation of 1D chains, and the bidentate bpm ligand permits the formation of a 2D layer composed of weak interactions.

Magnetic Properties

The molar magnetic susceptibilities, χ_M, were measured in a field of 5000 G for **2** and 10000 G for **1** and **3**; plots of χ_M and μ_{eff} vs. T are shown below.

For **1**, the μ_{eff} is 2.55 μ_B at room temperature, which is similar to the spin-only value of 2.45 μ_B for two uncoupled copper(II) ions (Figure 5). It increases slightly on cooling to 18 K, and then decreases to 2.45 μ_B at 6 K. Intermolecular antiferromagnetic coupling results in the decrease of μ_{eff} be-

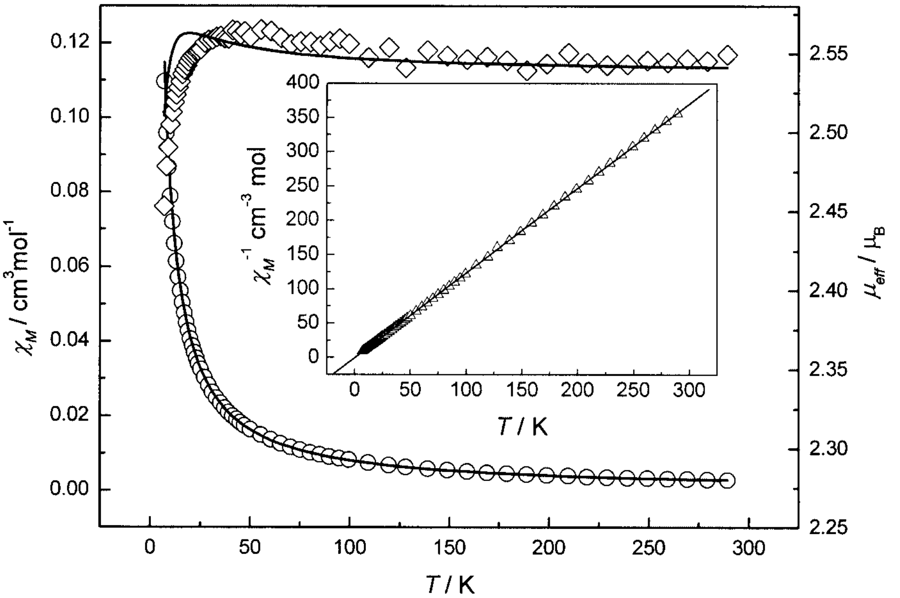


Figure 5. Plots of χ_M (O) and μ_{eff} (◊) vs. T and χ_M^{-1} vs. T (Δ) (inset) for **1**. The solid line represents the theoretical curve with the best-fit parameters.

low 18 K. The χ^{-1} data for **1** obey the Curie–Weiss law with a Curie–Weiss temperature, θ, of 0.2 K and a Curie constant, C, of 0.81 emu K mol^{-1} (see inset of Figure 5). The Curie constant is larger than the expected value for two uncoupled Cu^{2+} spins (C_{theor} = 0.75 emu K mol^{-1}). The positive sign of the Weiss constant suggests the presence of ferromagnetic interactions between two copper centers. The magnetic parameters were estimated from a least-squares fitting of the susceptibility data by the equation for dinuclear Cu^{II} complexes [Equation (1)],[18] considering the decrease of μ_{eff} below 18 K, a temperature independent susceptibility term ($N\alpha$) was applied and set as 1.2×10^{-4} cm^3 mol^{-1}. A molecular field approximation [Equation (2)] was also used. The best fit was obtained for J = 1.02 cm^{-1}, zJ' = –0.05 cm^{-1}, g = 2.08, and $R = 3.6\times10^{-3}$ [agreement factor, defined as $\Sigma(\chi_M^{\text{obs}} - \chi_M^{\text{calc}})^2/\Sigma(\chi_M^{\text{obs}})^2$].

$$\chi_M = \frac{2Ng^2\beta^2}{kT}\left[3+\exp(-2J/kT)\right]^{-1} + N\alpha \qquad (1)$$

$$\chi_M = \chi_{\text{chain}}/(1 - zJ'\chi_{\text{chain}}/NG^2\beta^2)$$
$$H = -2JS_1S_2 \qquad (2)$$

For **2**, the effective magnetic moment is 1.83 μ$_B$ at room temperature, which is close to that of an isolated Cu^{II} ion (1.73 μ$_B$). As the temperature is lowered, μ_{eff} of **2** smoothly increases to the maximum value of 1.91 μ$_B$ at 24 K, and then decreases to 1.84 μ$_B$ at 5.2 K (Figure 6). The increase of μ_{eff} is due to intrachain ferromagnetic coupling, while the interchain antiferromagnetic coupling results in the decrease of μ_{eff} below 24 K. The χ^{-1} data above 24 K for **2** obey the Curie–Weiss law, with a Curie–Weiss temperature of 1.4 K and a Curie constant of 0.42 emu K mol^{-1} (see inset of Figure 6). The Curie constant is larger than the expected value for one uncoupled Cu^{2+} spin (S = 1/2, C_{theor} = 0.375 emu K mol^{-1}), and the positive sign of the Weiss constant suggests ferromagnetic interactions between copper centers.

The magnetic susceptibility data of **2** were fitted approximately by the equation for a ferromagnetic chain [Equation (3)] with S = 1/2 and a molecular field correction equation [Equation (4)][19] in which A = 5.7979916, B = 16.902653, C = 29.376885, D = 29.832959, E = 14.036918, A' = 2.7979916, B' = 7.0086780, C' = 8.6538644, D' = 4.5743114, and $x = 2|J|/KT$. A temperature-independent susceptibility term (Nα) was also included and set as 60×10^{-6} cm^3 mol^{-1}. The other symbols have their usual meanings.

$$\chi_{chain} = \frac{Ng^2\beta^2}{4KT}\left[\frac{1+Ax+Bx^2+Cx^3+Dx^4+Ex^5}{1+A'x+B'x^2+C'x^3+D'x^4}\right]^{2/3} + N\alpha \qquad (3)$$

$$\chi_M = \chi_{\text{chain}}/(1 - zJ'\chi_{\text{chain}}/NG^2\beta^2) \qquad (4)$$

The best fit to the magnetic susceptibility data yielded J = 2.58 cm^{-1}, zJ' = –0.9 cm^{-1}, g = 2.13, and $R = 9.8\times10^{-4}$. These results confirmed the weak ferromagnetic coupling between adjacent copper(II) ions through the bridging isophthalate ligand, while $zJ' < 0$ indicates the weaker antiferromagnetic interaction between the chains.

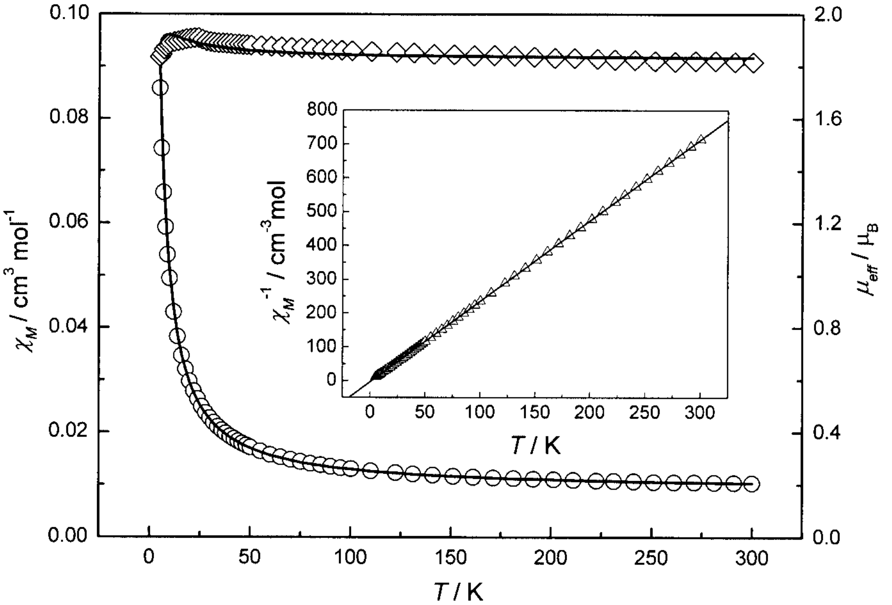


Figure 6. Plots of χ_M (O) and μ_{eff} (◊) vs. T and χ_M^{-1} vs. T (Δ) (inset) for **2**. The solid line represents the theoretical curve with the best-fit parameters.

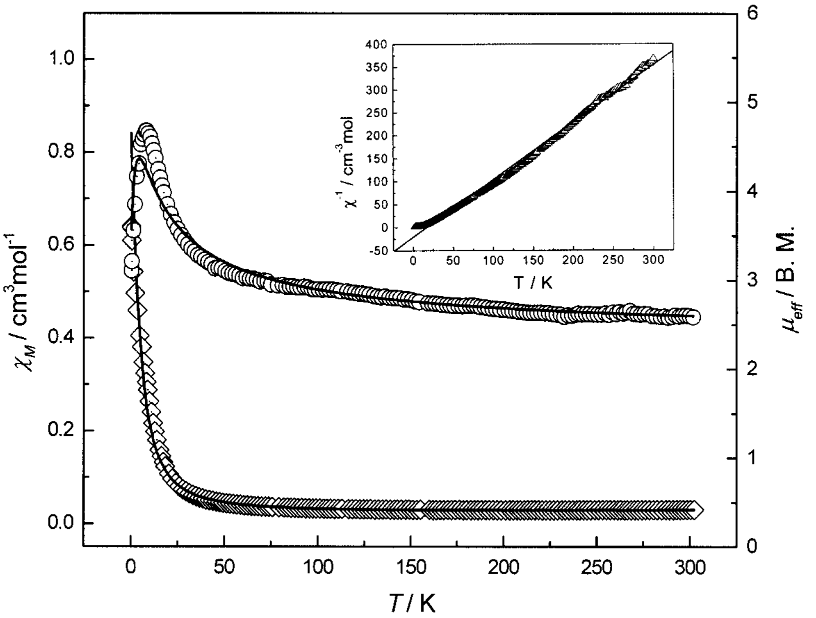
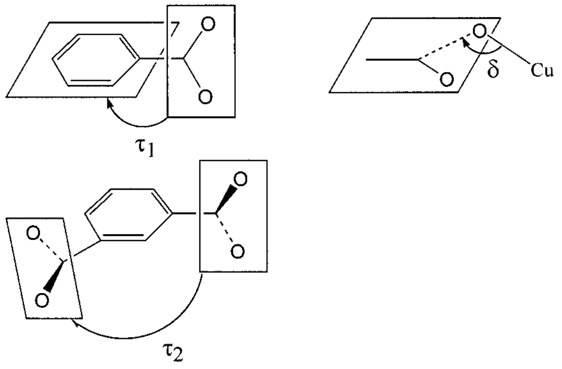


Figure 7. Plots of χ_M (O) and μ_{eff} (◊) vs. T and χ_M^{-1} vs. T (Δ) (inset) for **3** from Equation (1). The solid line represents the theoretical curve with the best-fit parameters.

The effective magnetic moment of **3** is 2.56 μ_B at room temperature, which is close to the value of two isolated Cu^{II} ions (2.45 μ_B). As the temperature is lowered, μ_{eff} of **3** increases to a maximum value of 4.79 μ_B at 9.5 K, and then decreases to 3.15 μ_B at 2 K (Figure 7). The increase of μ_{eff} indicates a ferromagnetic coupling between the copper centers. The χ^{-1} data obey the Curie–Weiss law, with a Curie–Weiss temperature of 16.2 K and a Curie constant of 0.42 emu K mol^{-1}. The positive sign of the Weiss constant also suggests the presence of ferromagnetic interactions between copper centers. Although the one-dimensional zigzag chain structure of **3** is similar to that of **2**, and the neighboring Cu···Cu distances are almost equal, the magnetic behavior is significantly different from that of **2**. First, we attempted to analyze the susceptibilities by the same equation as for complex **2** with the best-fit parameters of J = 33.9 cm^{-1}, zJ' = –2.73 cm^{-1}, g = 2.00, and $R = 9.38 \times 10^{-3}$. In our previous published results, we obtained an *m*-bda-bridged complex $[\{Cu(tacn)(m\text{-bda})\}(CH_3OH)_{0.5}(H_2O)_{0.5}]_n$ (**4**) (tacn = 1,4,7-triazacyclononane).[14] Like tpm, tacn is a tridentate ligand, and the crystal structure of complex **4** is similar to that of **2**. Consequently, J was found to be 1.2 cm^{-1}, which is also close to that of **2**. The selected magnetostructural data of **1**–**4** are listed in Table 1; τ_1, τ_2, and δ are defined in Scheme 1. Comparing the terminal ligands, we can see that although the steric hindrance of the tetradentate ligand tpa prevents the formation of infinite aggregates for **1**, a long bridge through the benzene ring exists at the same time for **1**–**4**, which leads to a similar intramolecular metal–metal separation; in **1**, **2**, and **4** it is the only exchange pathway.

Table 1. Selected structural and magnetic parameters of *m*-bda-bridged copper(II) complexes.

	1	**2**	**3**	**4**
Bridging mode	bis(monodentate)	bis(monodentate)	bis(monodentate)	bis(monodentate)
Terminal ligand	tetradentate	tridentate	bidentate	tridentate
Cu:*m*-bda:terminal ligand	2:2:1	1:1:1	1:1:1	1:1:1
Coordination number	5	5	4, 5	5
Coordination geometry	trigonal-bipyramid	square pyramid	square pyramid, square plane	square pyramid
Cu–O(*m*-bda)$_{av}$ [Å]	1.912(5)	1.898(4)	1.937(3)	1.888(9)
τ_1 [°]	2.9(7), 4.1(2)	1.8(4), 17.9(8)	12.8(5), 17.9(3)	17.8(3), 26.3(8)
τ_2 [°]	7.3(8)	16.3(6)	27.7(3)	43.8(5)
δ [°]	119.9(5), 120.4(5)	129.4(4), 110.1(4)	123.4(3), 123.6(3)	135.6(9), 128.5(15)
d_{intra} [Å]	10.557	10.403	10.643	10.783
d_{inter} [Å]	–	6.644	4.936	7.171
J [cm^{-1}]	1.02	2.58	33.9/38.5	1.2
zJ' [cm^{-1}]	–0.05	–0.9	–2.37/–2.25	–0.18
g	2.08	2.13	2.00/2.06	2.07



Scheme 1.

Despite the anomalously different τ_1, τ_2, and δ angles, the J values of **1**, **2** and **4** are similar. This implies that the coordination geometry of the metal centers and *m*-bda bridging configuration has no effect on the magnitude of the exchange coupling via the *m*-bda ligand. Accordingly, isophthalic acid is not an efficient bridging ligand for the transmission of electronic effects. The presence of weak ferromagnetic interactions in **1**, **2**, and **4** could be the result of the accidental orthogonality of the magnetic orbitals, while the unusually strong ferromagnetic interaction observed for complex **3** is not possible for the simple exchange pathway through the *m*-bda bridge. A similar condition has been observed by Bakalbassis et al.[20] By calculating the energies of the frontier MOs of $[Cu_2(\mu\text{-TPHA})(bpy)_2(OH_2)_2](ClO_4)_2$ (TPHA = terephthalato and bpy = 2,2′-bipyridine) on the basis of the EHMO method, they ascribed the unexpectedly strong antiferromagnetic interaction ($2J = -51.8\ \mathrm{cm^{-1}}$) to the orbital interactions located on the intermolecular Cu–O···Cu moieties and came to the conclusion that the terephthalato bridging unit has an unfavorable character to transmit electronic effects over long distances owing to the very low electron density delocalization on the bridging unit of each magnetic orbital. As for our complex **3**, in the Cu–O···Cu weak coordination bonds the bridging oxygen atom occupies an axial coordination site on both Cu^{II} ions, but the magnetic orbital for Cu^{II} is not located along the z axis, and therefore only a very weak exchange interaction can be expected. The contribution of intrachian interactions via the *m*-bda bridge is insignificant to the overall magnetic behavior of **3**. Thus, the hydrogen bonding between copper centers via carboxylic groups may account for the ferromagnetic interactions through a spin-polarization mechanism. Accordingly, the magnetic data of **3** were fitted again by the same equation as for complex **1** for dinuclear Cu^{II} complexes.[18] Considering the decrease of μ_{eff} in the low-temperature region, a molecular field correction was applied. A fit of the data gave $J = 35.5\ \mathrm{cm^{-1}}$, $zJ' = -2.0\ \mathrm{cm^{-1}}$, $g = 2.08$, and $R = 3.0\times10^{-3}$.

Cano et al. have also proposed that the relatively strong antiferromagnetic coupling observed for terephthalate-bridged Cu^{II} complexes is due to the carboxylate-assisted loss of the coordinated water molecule and subsequent carboxylate dimerization.[8] In light of the peculiar coordination geometry of Cu^{II} in **3** (four- and five-coordinate), the presence of hydrogen bonds between copper centers via carboxylic groups through a spin-polarization mechanism is feasible.

Conclusions

In summary, three copper isophthalates have been prepared and characterized by variable-temperature susceptibility measurements. The above discussion shows that isophthalic acid can be used as an appropriate bridging unit to design magnetic systems with a separation of about 11 Å between the two paramagnetic centers. However the magnetic interactions are, as with the terephthalate-bridged systems, negligibly small. The small steric hindrance of the terminal ligand bpm leads to hydrogen bonding between Cu^{II} centers, which accounts for the abnormally large ferromagnetic coupling of complex **3**.

Experimental Section

General Remarks: Copper(II) perchlorate hexahydrate, tpm, bpm, and tpa were obtained by literature methods.[21–24] These ligands were analyzed by elemental analysis and NMR spectroscopy. Isophthalic acid and other reagents were obtained from commercial sources and used without further purification. Analyses for C, H, and N were carried out on a Perkin–Elmer analyzer at the Institute of Elemento-Organic Chemistry, Nankai University. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

Synthesis of $[Cu_2(tpa)_2(m\text{-bda})](ClO_4)_2$ (1): $Tpa\cdot3HClO_4$ (0.059 g, 0.1 mmol) was dissolved in 10 mL of methanol and triethylamine (1.572 g, 1.55 mmol) was added. $Cu(ClO_4)_2\cdot6H_2O$ (0.0371 g, 0.1 mmol) and dipotassium isophthalate (0.0105 g, 0.05 mmol) were added to the resulting solution. The mixture was stirred for 30 min and then filtered. After several weeks, green crystals suitable for X-ray analysis were obtained. Yield: 0.012 g (32% based on Cu). IR (KBr): ṽ = 1603 (s) cm⁻¹, 1560 (m), 1475 (w), 1435 (m), 1356 (s), 1315 (w), 1280 (w), 1085 (s), 1010 (m), 815 (w), 760 (s). $C_{44}H_{40}C_{12}Cu_2N_8O_{12}$ (1070.8): calcd. C 49.35, H 3.74, N 10.46; found C49.10, H 3.71, N 10.48.

Synthesis of $[\{Cu_2(tpm)_2(m\text{-bda})_2\}\cdot2CH_3OH\cdot4H_2O]_n$ (2): An aqueous solution of $CuCl_2\cdot2H_2O$ (0.171 g, 1.0 mmol) was added to NaOH (0.040 g, 2.0 mmol) in H_2O (5 mL), then isophthalic acid (0.166 g, 1.0 mmol) was added. After stirring for 2 h at room temperature, tpm (0.214 g, 1.0 mmol) in MeOH (15 mL) was added dropwise and stirred for 1 h. The mixture was then filtered. Blue crystals suitable for X-ray structure analysis were obtained by slow evaporation of the filtrate. Yield: 0.066 g (39% based on Cu). IR (KBr): ṽ = 1600 (s) cm⁻¹, 1568 (m), 1440 (w), 1400 (s), 1360 (w), 1290 (s), 1240 (w), 1080 (m), 850 (s). $C_{37}H_{40}Cu_2N_{12}O_{13}$ (987.89): calcd. C 44.94, H 4.05, N 17.65; found C 44.48, H 4.04, N 17.50.

Synthesis of $[\{Cu_2(bpm)_2(H_2O)(m\text{-bda})_2\}\cdot CH_3CN\cdot H_2O]_n$ (3): A solution of $Cu(ClO_4)_2\cdot6H_2O$ (0.0742 g, 0.2 mmol) in CH_3CN (5 mL) was added to bpm (0.214 g, 1.0 mmol) in CH_3CN (5 mL), then an aqueous solution of isophthalic acid (0.166 g, 1.0 mmol) was added. After stirring for 15 min, NaOH (0.1 M) was added to adjust the pH value to 7. The mixture was stirred for 2 h at room temperature and the precipitates were filtered off. Blue crystals suitable for X-ray structure analysis were obtained by slow evaporation of the filtrate. Yield: 0.030g (40% based on Cu). IR (KBr): $\tilde{\nu}$ = 1620 (s) cm^{-1}, 1572 (m), 1460 (w), 1410 (s), 1350 (w), 1300 (s), 1250 (w), 1100 (m), 850 (s). $C_{32}H_{31}Cu_2N_9O_{10}$ (828.74): calcd. C 44.34, H 3.74, N 15.20; found C 44.56, H 3.35, N 15.32.

Crystallographic Studies: Crystals of complexes **1**, **2**, and **3** were mounted on a Bruker Smart 1000 diffractometer equipped with a CCD camera. The determination of unit-cell parameters and data collection were performed with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved primarily by direct methods and secondly by Fourier difference techniques and refined by the full-ma-

Table 2. Data collection and processing parameters for **1, 2** and **3**.

	1	**2**	**3**
Empirical formula	$C_{44}H_{40}Cl_2Cu_2N_8O_{12}$	$C_{37}H_{40}Cu_2N_{12}O_{13}$	$C_{32}H_{31}Cu_2N_9O_{10}$
Formula mass	1070.82	987.89	828.74
Temperature (K)	298(2)	273(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	orthorhombic
Space group	*P*21/*c*	$P\bar{1}$	*Pnma*
a [Å]	14.003(6)	10.250(7)	17.956(6)
b [Å]	17.201(7)	15.078(10)	17.615(5)
c [Å]	20.654(9)	16.2328(6)	10.776(4)
α [°]	90	114.241(12)	90
β [°]	90.637(9)	90.212(13)	90
γ [°]	90	108.389(11)	90
V [Å^3]	4975(4)	2007(2)	3408.5(18)
Z	4	2	4
$D_{calcd.}$ [mg m^{-3}]	1.430	1.635	1.615
Crystal size (mm^3)	0.25 × 0.10 × 0.20	0.35 × 0.25 × 0.10	0.24 × 0.20 × 0.08
θ	1.45–25.03	1.49–25.03	2.20–26.48
Reflections collected	20495	7529	15588
Independent reflections	8652 [*R*(int.) = 0.3379]	6809 [*R*(int.) = 0.0326]	3632 [*R*(int.) = 0.1157]
Max. and min. transmission	0.9797 and 0.7830	0.8943 and 0.6905	1.0000 and 0.8112
Data/restraints/parameters	8652/0/613	6809/0/595	3632/0/256
Goodness-of-fit on F^2	0.997	0.975	1.009
R_1, wR_2 [$I > 2\sigma(I)$]	0.0678, 0.1751	0.0571, 0.1288	0.0554, 0.0845
R_1, wR_2 (all data)	0.1851, 0.2138	0.1135, 0.1543	0.1208, 0.1011
Largest diff. peak and hole (e Å^{-3})	0.823 and –0.455	0.513 and –0.422	0.420 and –0.556

[a] $R_1 = \Sigma||F_o| - |F_C||/\Sigma|F_o|$, $wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0880P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$ for **1**; $w = 1/[\sigma^2(F_o^2) + (0.0728P)^2 + 0.0000P]$, $P = (F_o^2 + 2F_c^2)/3$ for **2**; $w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 0.0000P]$, $P = (F_o^2 + 2F_c^2)/3$ for **3**.

Table 3. Selected bond lengths [Å] and angles [°] for **1**, **2** and **3**.

1		**2**[a]		**3**[b]	
Cu(1)–O(1)	1.901(5)	Cu(1)–O(1)	1.899(4)	Cu(1)–O(1)	1.937(3)
Cu(1)–N(4)	2.033(6)	Cu(1)–O(5)	1.905(4)	Cu(1)–N(1)	2.018(3)
Cu(1)–N(2)	2.068(6)	Cu(1)–N(1)	1.984(5)	Cu(1)–O(5)	2.394(4)
Cu(1)–N(3)	2.086(7)	Cu(1)–N(5)	1.991(4)	Cu(2)–O(3)	1.937(3)
Cu(1)–N(1)	2.101(7)	Cu(1)–N(3)	2.414(5)	Cu(2)–N(3)	2.018(3)
Cu(2)–O(3)	1.922(5)	Cu(2)–O(8)	1.891(4)		
Cu(2)–N(8)	2.040(6)	Cu(2)–O(4)#1	1.897(4)		
Cu(2)–N(6)	2.073(7)	Cu(2)–N(9)	1.976(4)		
Cu(2)–N(5)	2.081(7)	Cu(2)–N(7)	1.981(5)		
Cu(2)–N(7)	2.085(7)	Cu(2)–N(11)	2.434(5)		
O(1)–Cu(1)–N(4)	172.8(2)	O(1)–Cu(1)–O(5)	89.97(17)	O(1)–Cu(1)–N(1)	88.80(13)
O(1)–Cu(1)–N(2)	92.3(2)	O(1)–Cu(1)–N(1)	95.33(18)	O(1)#1–Cu(1)–O(1)	94.99(16)
N(4)–Cu(1)–N(2)	80.5(3)	O(5)–Cu(1)–N(1)	166.53(19)	O(1)#1–Cu(1)–N(1)	175.01(13)
O(1)–Cu(1)–N(3)	102.2(3)	O(1)–Cu(1)–N(5)	166.82(19)	N(1)–Cu(1)–N(1)#1	87.2(2)
N(4)–Cu(1)–N(3)	80.7(3)	O(5)–Cu(1)–N(5)	91.04(18)	O(1)–Cu(1)–O(5)	89.41(11)
N(2)–Cu(1)–N(3)	115.2(3)	N(1)–Cu(1)–N(5)	86.62(19)	N(1)–Cu(1)–O(5)	87.39(12)
O(1)–Cu(1)–N(1)	104.3(3)	O(1)–Cu(1)–N(3)	86.31(18)	O(3)#2–Cu(2)–O(3)	90.29(17)
N(4)–Cu(1)–N(1)	80.2(3)	O(5)–Cu(1)–N(3)	110.42(18)	O(3)#2–Cu(2)–N(3)	171.07(14)
N(2)–Cu(1)–N(1)	121.8(3)	N(1)–Cu(1)–N(3)	82.3(2)	O(3)–Cu(2)–N(3)	90.48(12)
N(3)–Cu(1)–N(1)	114.8(3)	N(5)–Cu(1)–N(3)	81.02(19)	N(3)–Cu(2)–N(3)#2	87.40(19)
O(3)–Cu(2)–N(8)	173.1(3)	O(8)–Cu(2)–O(4)#1	89.95(18)	C(4)–N(1)–Cu(1)	128.4(3)
O(3)–Cu(2)–N(6)	102.2(3)	O(8)–Cu(2)–N(9)	165.91(19)	N(2)–N(1)–Cu(1)	123.9(3)
N(8)–Cu(2)–N(6)	79.8(3)	O(4)#1-Cu(2)–N(9)	91.56(18)	C(8)–N(3)–Cu(2)	130.7(3)
O(3)–Cu(2)–N(5)	91.7(3)	O(8)–Cu(2)–N(7)	95.05(18)	N(4)–N(3)–Cu(2)	123.5(3)
N(8)–Cu(2)–N(5)	81.5(3)	O(4)#1–Cu(2)–N(7)	166.64(19)	C(16)–O(3)–Cu(2)	123.6(3)
N(6)–Cu(2)–N(5)	116.3(3)	N(9)–Cu(2)–N(7)	86.61(19)		

[a] #1 *x*, *y*, *z* + 1; #2 *x*, *y*, *z* – 1. [b] #1 *x*, –*y* + 1/2, *z*; #2 *x*, –*y* + 3/2, *z*.

trix least-squares method. The computations were performed with the SHELXL-97 program.[25,26] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. The crystal parameters and details of the data collections and refinement for the complexes are listed in Table 2. Selected bond lengths are listed in Table 3.

CCDC-257849 (for **1**), -196145 (for **2**), and -196147 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) D. Gatteschi, O. Kahn, J. Miller, F. Palacio, *Molecular Magnetic Materials*, Kluwer, Dordrecht, **1991**; b) J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortés, L. Lezama, T. Rojo, *Coord. Chem. Rev.* **1999**, *193–195*, 1027–1068.

[2] a) L. Deakin, A. M. Arif, J. S. Miller, *Inorg. Chem.* **1999**, *38*, 5072–5077; b) R. H. Groeneman, L. R. MacGillivray, J. L. Atwood, *Inorg. Chem.* **1999**, *38*, 208–209; c) N. Ohata, H. Masuda, Y. Osamu, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 531–532; d) M. Eddaoudi, H. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391–1397.

[3] a) O. M. Yaghi, C. E. Davis, G. Li, H. Li, *J. Am. Chem. Soc.* **1997**, *119*, 2861–2868; b) H. J. Choi, M. P. Suh, *J. Am. Chem. Soc.* **1998**, *120*, 10 622–10 628; c) O. M. Yaghi, H. L. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474–484; d) E. G. Bakalbassis, D. G. Paschalidis, *Inorg. Chem.* **1998**, *37*, 4735–4737.

[4] a) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148–1150; b) R. H. Groeneman, L. R. MacGillivray, J. L. Atwood, *Chem. Commun.* **1998**, 2735–2736.

[5] a) H. X. Zhang, B. S. Kang, A. W. Xu, Z. N. Chen. Z. Y. Zhou, A. S. C. Chan, K. B. Yu, C. Ren, *J. Chem. Soc. Dalton Trans.* **2001**, 2559–2566; b) X. M. Chen, G. F. Liu, *Chem. Eur. J.* **2002**, *8*, 4811–4817; c) C. B. Ma, C. N. Chen, Q. T. Liu, D. Z. Liao, L. C. Li, L. C. Sun, *New J. Chem.* **2003**, *27*, 890–894.

[6] X.-S. Tan, J. Sun, D.-F. Xiang, W.-X. Tang, *Inorg. Chim. Acta* **1997**, *255*, 157–161.

[7] L. C. Francesconi, D. R. Corbin, A. W. Clauss, D. N. Hendrickson, G. D. Stucky, *Inorg. Chem.* **1981**, *20*, 2078–2083.

[8] J. Cano, G. D. Munno, J. L. Sanz, R. Ruiz, J. Faus, F. Lloret, M. Julve, A. Caneschi, *J. Chem. Soc. Dalton Trans.* **1997**, 1915–1924.

[9] C. E. Xanthopulos, M. P. Sigalas, G. A. Katsoulos, C. A. Tsipis, A. Terzis, M. Mentzafos, A. Hountas, *Inorg. Chem.* **1993**, *32*, 5433–5436.

[10] E. G. Bakalbassis, J. Mrozinski, C. A. Tsipis, *Inorg. Chem.* **1986**, *25*, 3684–3690.

[11] C. S. Hong, S.-K. Son, Y. S. Lee, M.-J. Jun, Y. Do, *Inorg. Chem.* **1999**, *38*, 5602–5610.

[12] S. K. Shakhatreh, E. G. Bakalbassis, I. Brüdgam, H. Hartl, J. Mrozinski, C. A. Tsipis, *Inorg. Chem.* **1991**, *30*, 2801–2806.

[13] Y. T. Li, D. Z. Liao, Z. H. Jiang, G. L. Wang, *Synth. React. Inorg. Met.-Org. Chem.* **1995**, *25*, 319–326.

[14] P. Cheng, S. P. Yan, C. Z. Xie, B. Zhao, X. Y. Chen, X. W. Liu, C. H. Li, D. Z. Liao, Z. H. Jiang, G. L. Wang, *Eur. J. Inorg. Chem.* **2004**, 2369–2378.

[15] N. Kitajima, Y. Moro-oka, *Chem. Rev.* **1994**, *94*, 737–757.

[16] D. L. Reger, C. A. Little, V. G. Young, P. Maren, *Inorg. Chem.* **2001**, *40*, 2870–2874.

[17] D. L. Reger, R. F. Semeniuc, V. Rassolov, M. D. Smith, *Inorg. Chem.* **2004**, *43*, 537–554.

[18] O. Kahn, *Molecular Magnetism*, Wiley-VCH, New York, **1993**.

[19] D. D. Swank, C. P. Landee, R. D. Willet, *Phys. Rev. B: Condens. Matter* **1979**, *20*, 2154–2162.

[20] E. G. Bakalbassis, C. A. Tsipis, J. Mrozinski, *Inorg. Chem.* **1985**, *24*, 4231–4233.

[21] J. R. Bethrendt, S. K. Madan, *J. Inorg. Nucl. Chem.* **1950**, *20*, 195–202.

[22] J. E. Richman, T. J. Atkins, *J. Am. Chem. Soc.* **1974**, *96*, 2268–2270.

[23] D. L. Reger, T. C. Grattan, *J. Organomet. Chem.* **2000**, *607*, 120–128.

[24] B. G. Gafford, R. A. Holwerda, *Inorg. Chem.* **1989**, *28*, 60–66.

[25] G. M. Sheldrick, *SHELXS 97, Program for the Solution of Crystal Structures*, University of Göttingen, Germany, **1997**.

[26] G. M. Sheldrick, *SHELXL 97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

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