Ferromagnetic and Antiferromagnetic Polymeric Complexes with the Macrocyclic Ligand 1,4,7-Triazacyclononane

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Three novel copper polymers, $\{[Cu_4(tacn)_4(o\text{-bda})_2](ClO_4)_4(H_2O)_2\}_n$ (**1**), $\{[Cu(tacn)(m\text{-bda})](CH_3OH)_{0.5}(H_2O)_{0.5}\}_n$ (**2**), and $\{[Cu_2(tacn)_2(p\text{-bda})](ClO_4)_2\}_n$ (**3**) (tacn = 1,4,7-triazacyclononane, bda = benzenedicarboxylic acid) have been synthesized and structurally characterized. Compound **1** belongs to the monoclinic space group *C*2, while **2** and **3** crystallize in the orthorhombic space group *Pmc*2(1) and the monoclinic space group $P2_1/n$, respectively. They are all 1D zigzag polymers, which can be considered as $Cu(tacn)^{2+}$ building units linked by isomers of benzenedicarboxylic acid. The variable-temperature (2–300 K) magnetic behavior revealed the existence of ferromagnetic interactions in **1** and **2**. The best fittings of the experimental magnetic susceptibilities gave $J = 4.0$ cm^{-1} and $g = 2.04$ for **1**, $J = 1.2$ cm^{-1}, $zJ' = -0.18$ cm^{-1} and $g = 2.07$ for **2**, whereas the exchange coupling between Cu^{II} ions in **3** is antiferromagnetic with $J = -13.1$ cm^{-1} and $g = 2.05$. The transformation of interactions between copper ions from ferromagnetic to antiferromagnetic is closely related to the variations in the isomeric benzenedicarboxylic acids.

Introduction

The development of metal-based coordination polymers constructed by self-assembly processes has developed at a tremendous rate recently.[1−7] This expansion, which has been driven by potential magnetic, optical, electronic and catalytic applications,[8−11] may ultimately lead to new functional materials. Although the design and construction of coordination polymers is still a great challenge due to the difficulties in selecting proper metal ions and polydentate ligands,[12] many such coordination polymers with novel topological structures and fascinating properties constructed from polycarboxylic acids have been described.[13−16] Surprisingly, however, 1D or multi-dimensional polymers with tacn (tacn = 1,4,7-triazacyclononane) as the terminal ligand have seldom been reported so far, which can probably be attributed to the fact that tacn is such a strong tridentate chelating 6-electron donor, that it can effectively prevent building blocks from forming an effectively infinite aggregation. In principle, half-sandwich complexes containing tacn can be extended into infinite structures through proper bridging ligands, but controlling the ratio of reagents and the selection of bridging ligands is critical to the formation of polymers. With this goal in mind, we have investigated the bridging bda (bda = benzenedicarboxylic acid) ligands and employed the strategy of an equal stoichiometry of reagents. We report herein, the preparation of three novel copper polymers, $\{[Cu_4(tacn)_4(o\text{-bda})_2](ClO_4)_4(H_2O)_2\}_n$ (**1**), $\{[Cu(tacn)(m\text{-bda})](CH_3OH)_{0.5}(H_2O)_{0.5}\}_n$ (**2**), and $\{[Cu_2(tacn)_2(p\text{-bda})](ClO_4)_2\}_n$ (**3**).

In order to design and synthesize complexes with expected magnetic behavior, it is extremely important to probe the essential magneto-structural relationship. Hoffmann et al.[17] and Kahn et al.[18] have described investigations of the effects on magnetic exchange interactions of the metal−ligand−metal bridge angle, the bridging atom electronegativity, and the geometrical environment around the central metal ion. In contrast, and to the best of our knowledge, systematic studies of the influence of various isomers of some dicarboxylic acids on magnetic properties have not been reported to date. In this study we have used three isomers of bda as bridging ligands to obtain complexes **1**−**3**. Furthermore, we have investigated the relationship between their structures and magnetic properties.

Results and Discussion

X-ray crystal structure analyses revealed 1D zigzag polymeric structures for **1**, **2** and **3**. The ORTEP diagrams are shown in Figures 1−3, respectively. Notably, in these polymers, the copper(II) ions are all five-coordinate: three nitrogen atoms of tacn and two oxygen atoms of the bda ligand

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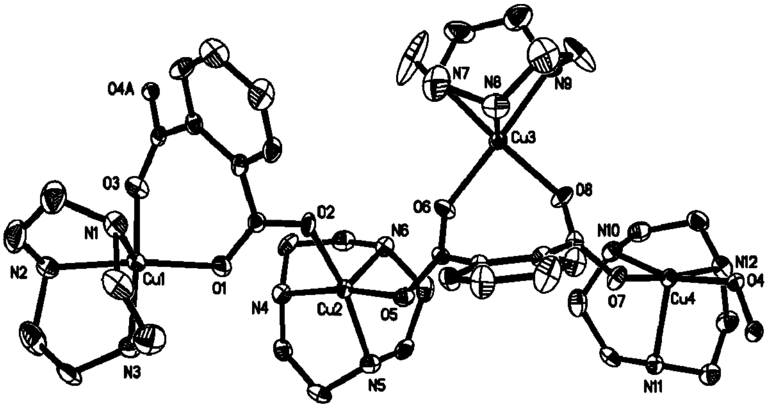


Figure 1. ORTEP diagram of **1**; H atoms, perchloric acid anions and solvent molecules are omitted for clarity

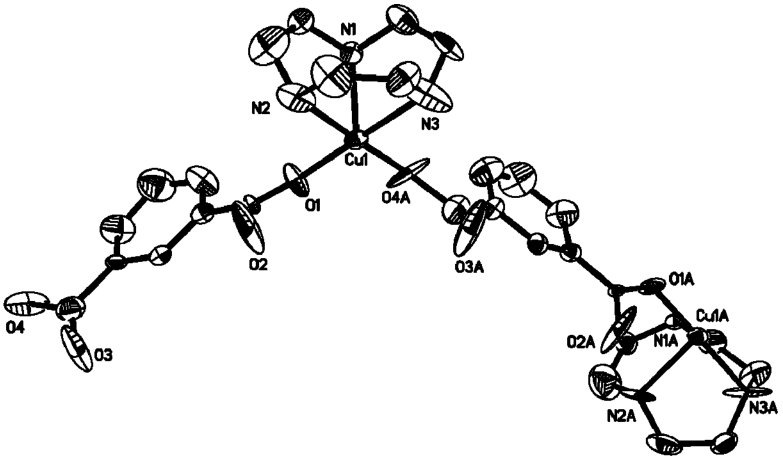


Figure 2. ORTEP diagram of **2**; H atoms and solvent molecules are omitted for clarity

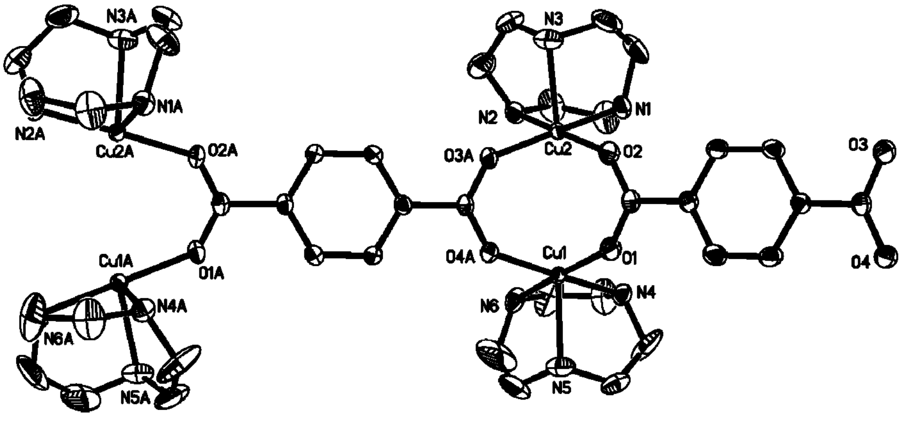


Figure 3. ORTEP diagram of **3**; H atoms and perchloric acid anions are omitted for clarity

complete the square-based pyramidal coordination geometry.

Crystal Structure of {[Cu_4(tacn)$_4$(*o*-bda)$_2$](ClO_4)$_4$(H_2O)$_2$}$_n$ (1)

The structure of **1** contains the cation [Cu_4(tacn)$_4$(*o*-bda)$_2$]$^{4+}$, the anion ClO_4^- as well as solvated water molecules. The cation exhibits a zigzag chain-like structure as shown in Figure 1. The copper atom is in a distorted square-pyramidal environment. Interestingly, there are two types of copper atoms according to the copper−oxygen coordination modes, namely chelating (Cu1) and bridging (Cu2). Two carboxylate oxygen atoms from the same *o*-bda ligand are chelated to Cu1 [Cu1−O1 1.974(6), Cu1−O3 1.955(7) Å], and three nitrogen atoms of the tacn ligand complete the configuration. The apical site of the distorted square pyramid is occupied by N1. The axial copper−nitrogen bond [Cu1−N1 2.322(6) Å] is somewhat longer than the equatorial ones [Cu1−N2 2.022(8), Cu1−N3 2.013(9) Å]. The largest deviation from the mean N2N3O1O3 basal plane is 0.132(5) Å for N2. The Cu1 atom is displaced toward the apical site by 0.097(2) Å. The angles O1−Cu1−N2 and O3−Cu1−N3 are 170.5(3) and 173.7(3)°, respectively. For Cu2, there are two carboxylate oxygen atoms from two *o*-bda ligands as well as three coordinated nitrogen atoms from tacn. The basal plane consists of N4N5O2O5 with the largest deviation of 0.087(5) Å for N5. The Cu2 atom is displaced toward the apical site by 0.162(8) Å. The average Cu2−O bond length is slightly longer than that of Cu1−O, whereas the average Cu2−N bond length is shorter than that of Cu1−N. Similar differences were also observed for the N−Cu−N and N−Cu−O angles. These features may result from the Cu2−O2(O5) bridging coordination mode. The dihedral angle between the mean coordination planes of Cu1 and Cu2 is 85.0°. These two types of copper centers are alternately arrayed in **1**, which leads to the zigzag chain-like structure (Figure 4, a). The shortest Cu−Cu distance is 5.010 Å along the chain.

In **1**, all Cu−N bond lengths ranging from 2.013(9) to 2.322(6) Å, are similar to those in other (tacn)Cu^{II} complexes.[19,20] The Cu−O distances, ranging from 1.954(6) to 1.990(6) Å, are also in line with the corresponding values in phthalato complexes.[21] It is noteworthy that the coordination geometry of *o*-bda bridged complexes largely relies on the terminal ligands. In our published report,[22] the cyclic tetranuclear complex $[Mn_4(\mu\text{-}o\text{-bda})_2(bpy)_8](ClO_4)_2\cdot 3H_2O$ was constructed from an *o*-bda bridge, the metal center is six-coordinate with four nitrogen atoms and two oxygen atoms. Once the terminal ligand is replaced by tridentate tacn, complex **1** was obtained as a 1D coordination polymer.

$\{[Cu(tacn)(m\text{-bda})](CH_3OH)_{0.5}(H_2O)_{0.5}\}_n$ (2)

In **2** (Figure 2), the apical site of the distorted square pyramid is occupied by N1 [Cu1−N1 2.184(8) Å]. The Cu−N bond lengths vary slightly from 2.124(8) to 2.184(8) Å. Compared with those in the *m*-bda bridged complexes, the Cu−O bonds (Cu1−O1 1.906(9) Å, Cu1−O4A 1.870(14) Å] are somewhat shorter,[23,24] which may be due to the distorted square-pyramidal structure caused by the

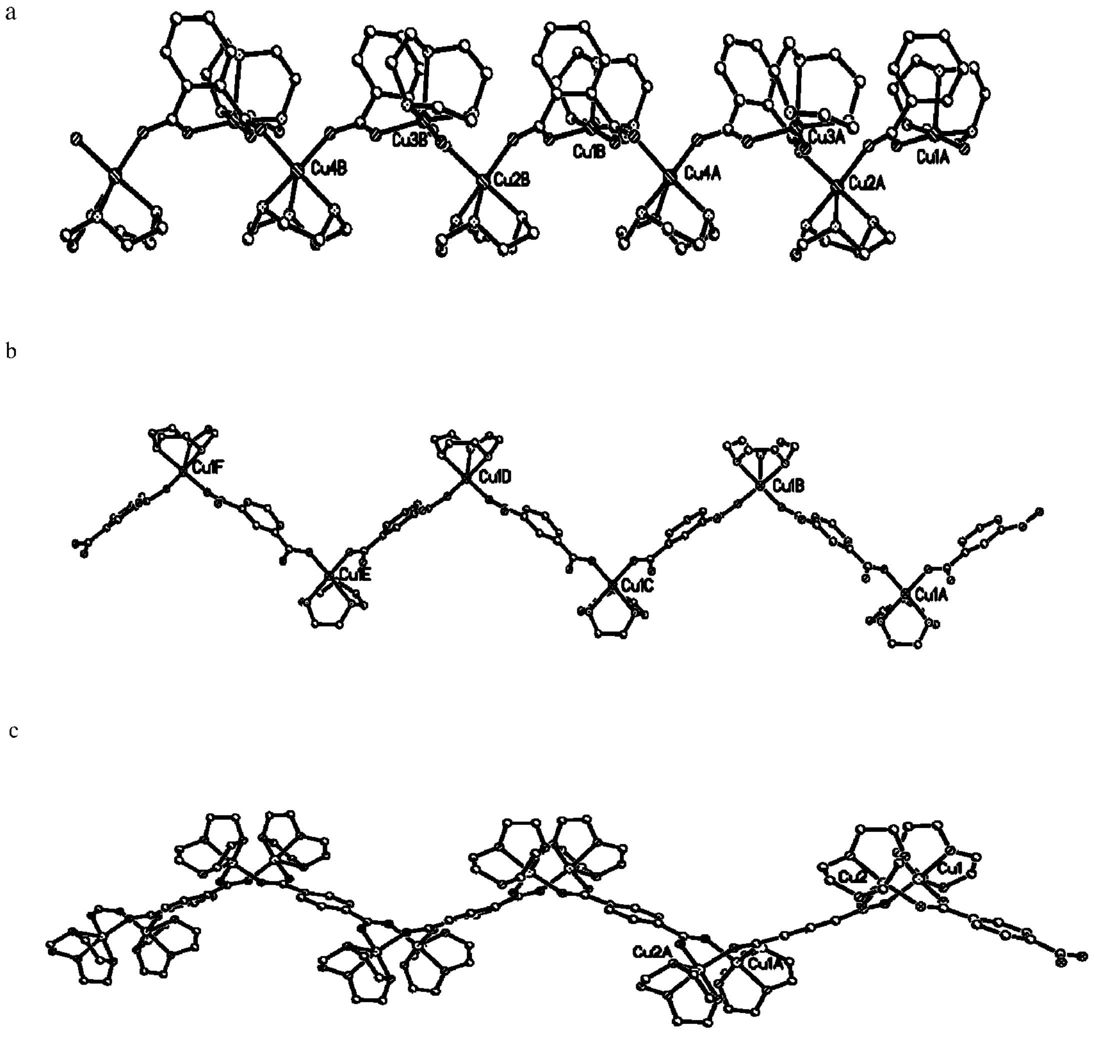


Figure 4. Zigzag chain structure for **1** (a), **2** (b), and **3** (c)

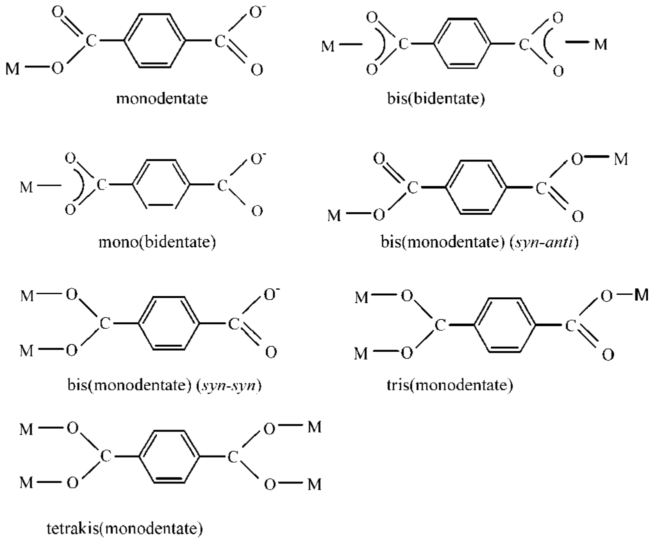
coordination of the rigid tridentate tacn ligand. The best equatorial plane can be defined by N2, N3, O1 and O4A. The largest deviation from the mean plane is 0.0641(7) Å for O4A and the Cu1 atom is 0.0276(4) Å from this plane. The dihedral angle between the benzene ring of the *m*-bda ligand and the equatorial plane of the Cu1 square pyramid is 72.7(5)°.

The *m*-bda group acts as a bis(monodentate) ligand, which bridges copper(II) ions to form a 1D zigzag chain-like motif as shown in Figure 4 (b). The distance between the copper(II) ions along the chain is 10.783 Å, which is much longer than the shortest distance between copper centers (7.171 Å) in neighboring chains. It is worth noting that examples of structurally characterized polymers with bridging *m*-bda groups[25] are relatively rare.

$\{[Cu_2(tacn)_2(p\text{-}bda)](ClO_4)_2\}_n$ (3)

The polymeric cationic $[Cu_2(p\text{-}bda)(tacn)_2]^{2+}$ unit of **3** is shown in Figure 3. The carboxylic groups of *p*-bda make it behave as a tetrakis(monodentate) ligand, which is bound on each side to two copper(II) ions through the oxygen atoms of the carboxylic groups in a *syn-syn* conformation[26] yielding a zigzag chain, which runs parallel to the *z* axis (Figure 4, c). The copper environments are distorted square-pyramidal. The equatorial plane includes O1 and O4A from the carboxylic groups as well as N4 and N6 from one of the tacn ligands. N5 of tacn occupies the apical position [Cu−N 2.011(4)−2.235(4), Cu−O 1.954(3)−1.961(3) Å; all angles of the square pyramid range from 83.36(17) to 100.55(15)°]. The Cu−O bond lengths are in the normal range.[27−29] The largest deviation from the mean plane is 0.0517(8) Å for N4, and the Cu1 atom is 0.0525(4) Å from this plane. Two copper(II) ions linked by two carboxylic groups form an eight-membered ring, $Cu_2C_2O_4$, and the crystallographic inversion center is located at the center of the eight-membered ring.

Recent reports of *p*-bda-bridged Cu^{II} centers include descriptions of seven kinds of coordination modes of *p*-bda, which are listed in Scheme 1.[27−32] Materials containing both short and long bridges have been reported based on *p*-bda-bridged Mn^{II} and Cu^{II} complexes.[29,33] Long *p*-bda bridges typically produce M···M separations of about 11 Å. With respect to the *p*-bda ligand, the most remarkable structural feature of **3** is its rare tetrakis(monodentate) coordinating character used in the assembly of its chain-like structure. In the complex its eight carbon atoms are strictly coplanar. The shortest Cu1···Cu2 separation is 3.486 Å. The intra-chain separations are 10.496 and 11.044 Å for Cu1···Cu1A and Cu1···Cu2A, respectively.



Scheme 1

Comparing the crystal structures of **1**, **2**, and **3**, the distortion of the square pyramid decreases on varying the bridging ligand from *o*-bda to *p*-bda. The differences in the bond angles and bond lengths decrease upon changing the bridging ligand. A summary of the main structural features of **1**, **2**, and **3** is listed in Table 1.

Magnetic Properties

The molar magnetic susceptibilities χ_M of **1**, **2**, and **3** were measured in the temperature range of 2−300 K in a field of 5 KOe. The plots of χ_M and μ_{eff} versus T for **1−3** are shown in Figures 5−7, respectively.

The bridging modes of bda and the chain structures of **1**, **2**, and **3** exhibit subtle differences, however, which lead to significantly different magnetic interactions between copper(II) ions. Initial magnetic studies of the three coordination polymers indicate interesting magnetic behavior.

The effective magnetic moment of **1** is 1.766 μ_B at 300 K. This is smaller than the spin-only value for the isolated cop-

Table 1. Summary of structural features of **1**, **2** and **3**

Compound	1	2	3
Length of chain motif	11.709 Å	16.175 Å	15.744 Å
Coordination mode of bridgng ligand (bda)	mono(bidentate), bis(monodentate) (*syn-anti*)	bis(monodentate) (*syn-anti*)	tetrakis(monodentate)
Ratio metal ion/bridging ligand/terminal ligand	4:2:4	1:1:1	2:1:2
Coordination number	5	5	5
Metal ion numbers coordinated to bridging ligand	3	2	4
Square pyramid angles	82.3(3)−108.0(3)°	79.9(5)−101.3(5)°	83.36(17)−100.55(15)°
Average bond length difference	0.368 Å	0.314 Å	0.281 Å
Shortest Cu···Cu distance	5.010 Å	7.171 Å	3.486 Å

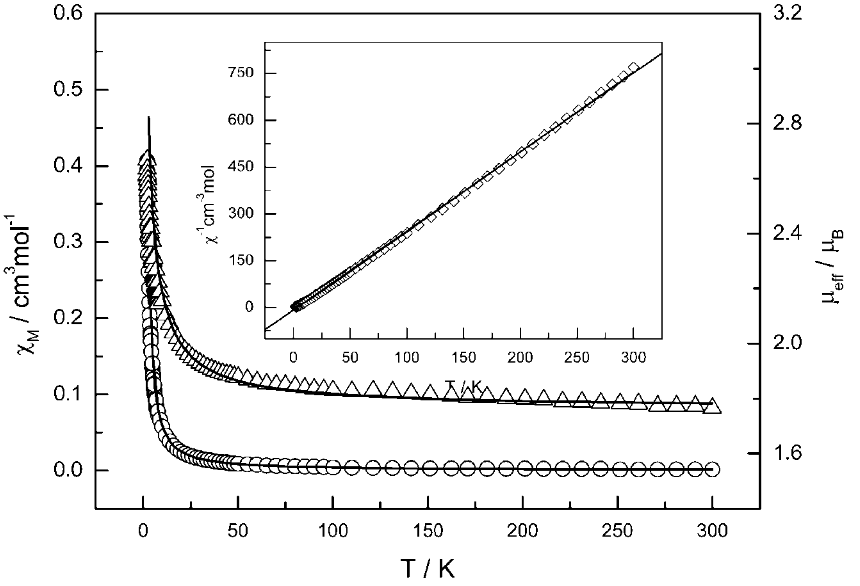


Figure 5. Plots of χ_M vs. T (open circles) and μ_{eff} vs. T (open triangles) and χ_M^{-1} vs. T (open squares) (inset) for **1**; the solid line represents the theoretical curve with the best fit parameters

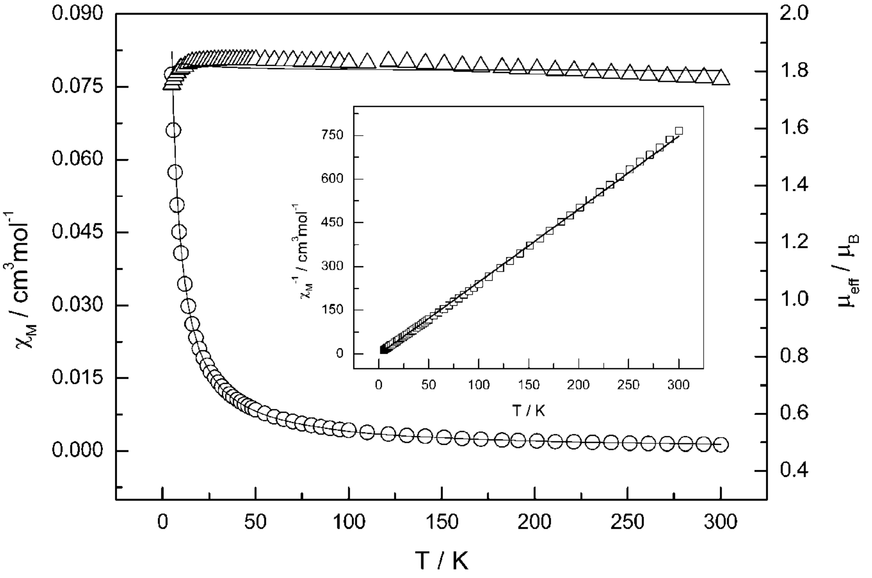


Figure 6. Plots of χ_M vs. T (open circles) and μ_{eff} vs. T (open triangles) for **2** and χ_M^{-1} vs. T (open squares) (inset); the solid line represents the theoretical curve with the best fit parameters

per(II) ion (1.73 μ_B, $g = 2.0$). With decreasing temperature, the μ_{eff} value for **1** increases smoothly down to ca. 20 K, and then sharply reaches a maximum value of 2.67 μ_B at 2.2 K (as shown in Figure 5). This behavior suggests the existence of a ferromagnetic interaction between the metal centers, and we know that the bridging group *o*-bda usually transmits a ferromagnetic exchange interaction between copper(II) ions.[23] The χ^{-1} data for **2** obey the Curie–Weiss law with a Curie–Weiss temperature $\theta = 3.18$ K, and a Curie constant $C = 0.39$ emu K·mol^{-1} (inset of Figure 5). The Curie constant is close to the expected value for one uncoupled Cu^{2+} spin ($S = 1/2$, $C_{theor.} = 0.375$ emu·K·mol^{-1}). The positive sign of the Weiss constant suggests ferromagnetic interactions between copper centers. Upon examining the crystal structure of **1**, we found that the neighboring Cu···Cu distances are almost equal, and only one kind of exchange pathway is available, namely Cu–O–C–O–Cu. The magnetic susceptibility data were, therefore, fitted by Equation (1) incorporating ferromagnetic chain properties with $S = 1/2$[34] and $H = -2JS_1S_2$

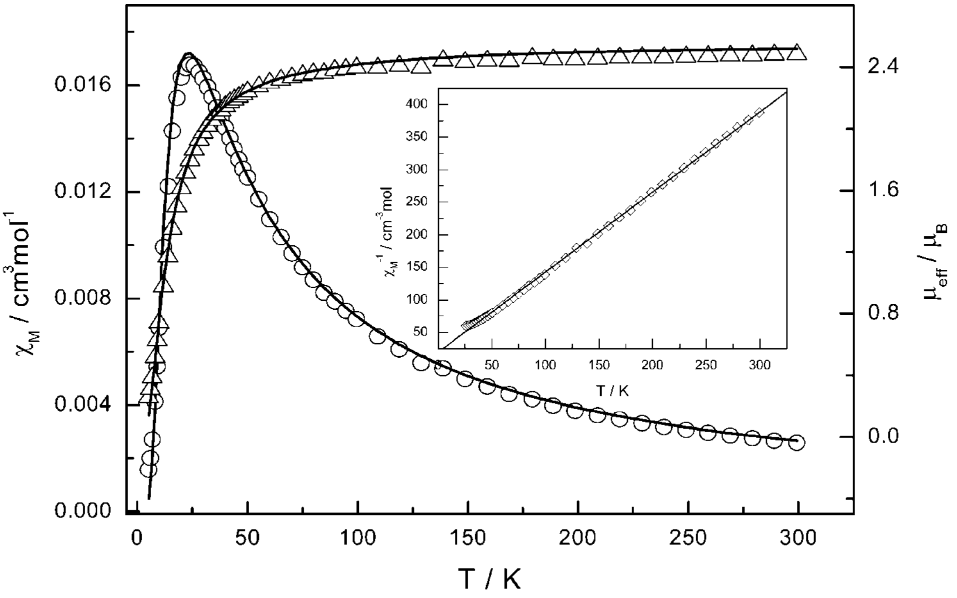


Figure 7. Plots of χ_M vs. T (open circles) and μ_{eff} vs. T (open triangles) for **3** and χ_M^{-1} vs. T (open squares) (inset); the solid line represents the theoretical curve fitted by Equation (3)

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 $x = J/2kT$.

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

A temperature-independent susceptibility term ($N\alpha$) was also included, and was set as 60 × 10^{-6} cm^3·mol^{-1}. Other symbols have their usual meanings. The best fit of the magnetic susceptibility data yielded J = 4.0 cm^{-1}, g = 2.04, and R = 3.2 × 10^{-3} [agreement factor, defined as $\Sigma(\chi_M^{obsd.} - \chi_M^{calcd.})^2/\Sigma(\chi_M^{obsd.})^2$]. These results confirm the ferromagnetic coupling between adjacent copper(II) ions through the bridging *o*-bda ligand.

For compound **2** the effective magnetic moment is 1.77 μ_B at room temperature. This value is close to that of the isolated Cu^{II} ion (1.73 μ_B). As the temperature is lowered, μ_{eff} of **2** smoothly increases to a maxmium value of 1.84 μ_B at 36 K, and then decreases to 1.75 μ_B at 2 K. The increase in μ_{eff} is due to the intra-chain ferromagnetic coupling, while the inter-chain antiferromagnetic coupling results in a decrease of μ_{eff} below 36 K. We used the same theoretical susceptibility equation for **1** to obtain a fit of the data. As a consequence of the decrease of μ_{eff} below 36 K, a molecular field correction was applied [Equation (2)].

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

The fit (as shown in Figure 6) was obtained with values of J = 1.2 cm^{-1}, zJ' = −0.18 cm^{-1}, g = 2.07, and R = 1.6 × 10^{-3}. The fitting parameters indicate the weak ferromagnetic coupling between adjacent copper ions along the chain, while $zJ' < 0$ indicates the weak antiferromagnetic interaction between the chains. The χ^{-1} data for **2** obey the Curie−Weiss law with a Curie−Weiss temperature θ = 2.54 K and a Curie constant C = 0.395 emu·K·mol^{-1} (inset of Figure 6). The Curie constant is close to the expected value for one uncoupled Cu^{2+} spin (S = 1/2, $C_{theor.}$ = 0.375 emu·K·mol^{-1}). The positive sign of the Weiss constant suggests that ferromagnetic interactions are dominant.

For **3**, μ_{eff} is 2.48 μ_B at 299 K. This is similar to the spin-only value of 2.45 μ_B for two uncoupled copper(II) ions (Figure 7). The value of μ_{eff} decreases gradually as the temperature decreases, indicating the presence of antiferromagnetic interactions. The occurrence of a sharp susceptibility maximum around 24 K is characteristic of an antiferromagnetic interaction with a singlet ground state. The χ^{-1} data for **3** obey the Curie−Weiss law above 24 K with a Curie−Weiss temperature θ = −16.0 K and a Curie constant C = 0.81 emu·K·mol^{-1} (inset of Figure 7). The negative sign of the Weiss constant suggests antiferromagnetic interactions between the copper centers.

The magnetic parameters were estimated from a least-squares fitting of the susceptibility data by the equation given in the literature for dinuclear Cu^{II} complexes [Equation (3)].[35]

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

Table 2. Selected structural and magnetic parameters of terephthalato-bridged dinuclear and 1D copper(II) complexes

Complex[a]	Bridged mode	Shortest Cu···Cu separation [Å]	d_{inter} [Å]	J [cm^{-1}]	Ref.
$[Cu_2(bipy)_4(p\text{-bda})](ClO_4)_2$	bis(monodentate) *syn-anti*	7.638	11.004	−2.20	[30]
$[Cu_2(terpy)_2(H_2O)_2(p\text{-bda})](ClO_4)_2$	bis(monodentate) *syn-anti*	7.272	10.913	−0.01	[30]
$[Cu_2(SalNEt_2)_2(p\text{-bda})](H_2O)(CH_3OH)$	bis(monodentate) *syn-anti*	8.8179	11.0348	+0.6	[32]
$[\{Cu(pmedien)(H_2O)\}_2(p\text{-bda})]$	bis(monodentate) *syn-anti*	7.840	11.129	−2.70	[36]
$[\{Cu(petdien)(H_2O)\}_2(p\text{-bda})](ClO_4)_2(H_2O)$	bis(bidentate)	8.215, 8.140	10.710	0	[36]
$[Cu_2(dien)_2(p\text{-bda})](ClO_4)_2$	bis(monodentate) *syn-anti*	4.179	11.006	−3.66	[37]
$[Cu(en)(H_2O)_2(p\text{-bda})]_n$	bis(monodentate) *syn-anti*	5.7263	11.1673	+4[b]	[37]
$[Cu(p\text{-bda})(H_2O)_2](H_2O)$	bis(monodentate) *syn-syn*	3.150	12.002	−12.72	[27]
$\{[CuL(\mu_2\text{-}p\text{-bda})](CH_3OH)_2\}_n$	bis(monodentate) *syn-anti*	6.034	11.284	0.02	[38]
$[Cu_2(p\text{-bda})(tacn)_2](ClO_4)_2$	tetrakis(monodentate)	3.486	10.496, 11.044	−13.1	this work
$[L'_2Cu_2(H_2O)_2(p\text{-bda})](ClO_4)_2$	bis(monodentate) *syn-anti*	7.587	11.252	−140	[39]

[a] *p*-bda = terephthalato, bipy = 2,2′-bipyridine, terpy = 2,2′:6′,2′′-terpyridine, $SalNEt_2$ = *N*-[2-(diethylamino)ethylsalicylidenaminate], pmdien = *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine, pedien = *N*,*N*,*N*′,*N*′′,*N*′′-pentaethyldiethylenetriamine, dien = diethylenetriamine, en = ethylenediamine, L = *N*,*N*-dimethyl-*N*′-(pyrid-2-ylmethyl)ethylenediamine, L′ = 1,4,7-trimethyl-1,4,7-triazacyclononane. [b] The intra-chain exchange interaction was ferromagnetic with $J = +4$ cm^{-1} and the inter-chain exchange interaction was antiferromagnetic with $zJ = -7$ cm^{-1}.

A temperature-independent susceptibility term ($N\alpha$) was also included and was set as 1.2×10^{-4} cm^3·mol^{-1}. The best fit was obtained for $J = -13.1$ cm^{-1}, $g = 2.05$, and $R = 6.5 \times 10^{-4}$. The above results confirmed the antiferromagnetic coupling between copper atoms in the dinuclear unit.

The relatively strong antiferromagnetic interactions in **3** can be explained by the short bridge, via one carboxylate end, between two copper atoms. Due to the special tetrakis(monodentate) coordination mode of *p*-bda, longer bridges through the benzene ring exist at the same time, but they are too weak to be taken into account. Some related (*p*-bda)Cu complexes are listed in Table 2 together with selected magneto-structural data. The *J* values of the complexes listed in Table 2 do not follow a simple trend. In spite of the large variation of the nearest metal−metal separation (from 3.150 to 8.818 Å), the values of *J* are insensitive to this. It can be seen that the magnetic interaction is very weak except in the last example. The weak coupling observed is not surprising in the light of the large intramolecular metal−metal separation. The *J* value reported for the last compound is anomalously large in comparison with the others. Bürger et al. attributed this strong antiferromagnetic coupling to the formation of an intramolecular O−H···O hydrogen bond between the H_2O molecule and the carbonyl oxygen atom of the coordinated carboxylate. In Table 2, the *J* value of $[Cu(p\text{-bda})(H_2O)_2](H_2O)$ is similar to that of **3**. For the former, the coordination mode of *p*-bda [bis(monodentate), as shown in Scheme 1], and the H_2O bridges result in the close intramolecular Cu···Cu separation, which leads to the correspondingly large antiferromagnetic coupling. In our work, however, the effective antiferromagnetic exchange pathway was achieved by the unusual tetrakis(monodentate) coordination mode of *p*-bda. From Table 2 we can see, that (*p*-bda)Cu complexes with the tetrakis(monodentate) coordination mode have rarely been reported. Samuel et. al prepared $[Cu_4(p\text{-bda})_3(4,4'\text{-bipy})_2]_n$, containing tetrakis(monodentate) coordinated *p*-bda, by a hydrothermal synthesis,[40] but they did not further investigate its magnetic properties. Our study provides some useful structural and magnetic information about this type of complex.

The transformation of interactions between copper ions from ferromagnetic to antiferromagnetic is closely related to changes in the bridging ligands. In compound **2**, the Cu···Cu distance is somewhat longer than that in **1**, and the exchange pathway passes across the benzene ring, which greatly weakens the ferromagnetic interactions. In consideration of the comparatively large antiferromagnetic interactions in the dinuclear unit of **3**, the weak interaction through the benzene ring can be ignored.

Conclusion

Three novel zigzag chain copper coordination polymers containing the tacn ligand were successfully constructed by deliberate selection of the bridging bda ligand. Among the previously reported complexes with tacn, coordination polymers with infinite structures are rather rare. Systematic investigations of the structures and magnetic properties of coordination polymers with a series of isomers of dicarboxylic bridging ligands have not been reported so far. Most importantly, the structural differences caused by the bridging ligands lead to unexpected magnetic behavior including changes from ferromagnetic to antiferromagnetic coupling. The present work provides another possible direction for exploring the magneto-structural relationship.

Experimental Section

Physical Measurements: C, H, and N analyses were obtained at the Institute of Elemental Organic Chemistry, Nankai University.

Variable-temperature magnetic susceptibilities were measured with a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

Preparation of {[Cu_4(tacn)$_4$(*o*-bda)$_2$](ClO_4)$_4$(H_2O)$_2$}$_n$ (1): A methanol solution (30 mL) of *o*-bda (0.4 mmol, 66.45 mg), and freshly prepared $Cu(OH)_2$ (0.4 mmol, 39.0 mg) was heated to reflux for 2 h, then filtered; tacn (0.4 mmol, 51.6 mg), dissolved in methanol (10 mL), and an aqueous solution of $NaClO_4$ (0.4 mmol, 49.0 mg) were added to the filtrate. The resultant mixture was heated to reflux for 2 h, and then filtered. Several weeks later, blue crystals were obtained by concentration of the filtrate at room temperature. Yield: 76.7 mg (50%). $C_{40}H_{72}Cl_4Cu_4N_{12}O_{26}$ (1533.06): calcd. C 31.3, H 4.63, N 11.0; found C 31.7, H 4.88, N 10.8.

{[Cu(tacn)(*m*-bda)](CH_3OH)$_{0.5}$(H_2O)$_{0.5}$}$_n$ (2): An acetonitrile/methanol (1:1) mixture (30 mL) was added to a mixture of *m*-bda (0.4 mmol, 66.45 mg), and freshly prepared $Cu(OH)_2$ (0.4 mmol, 39.0 mg). After heating to reflux for 1 h, methanol (10 mL), tacn (0.4 mmol, 51.6 mg), and water (1 mL) were added. The resultant mixture was heated to reflux for a further 2 h, and then filtered. The filtrate was concentrated slowly at room temperature. Blue crystals were obtained after one month. Yield: 106.9 mg (70%). $C_{14.5}H_{22}CuN_3O_5$ (381.89): calcd. C 45.6, H 5.76, N 11.0; found C 45.9, H 5.89, N 10.7.

{[Cu_2(tacn)$_2$(*p*-bda)](ClO_4)$_2$}$_n$ (3): Ligand *p*-bda (42 mg, 0.25 mmol) and a few drops of piperidine were added to an aqueous solution (30 mL) of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.186 g, 0.5 mmol), and tacn (0.065 g, 0.5 mmol). The resultant mixture was stirred at room temperature for 15 h. The solution was then filtered, and the filtrate was allowed to stand for several days resulting in the formation of well-formed light blue crystals. Yield: 104.8 mg (56%). $C_{20}H_{34}Cl_2Cu_2N_6O_{12}$ (748.51): calcd. C 32.06, H 4.54, N 11.22; found C 31.79, H 4.88, N 10.71.

Crystallographic Studies: Crystals, having the approximate dimensions 0.30 mm × 0.25 mm × 0.20 mm for **1** and **2**, and 0.35 mm × 0.30 mm × 0.20 mm for **3**, were mounted on glass fibers. Determination of the unit cells and data collection were performed with Mo-K_α radiation (λ = 0.71073 Å) with a Bruker Smart 1000 diffractometer equipped with a CCD camera. Cell parameters were determined from least-squares refinements on the setting angles in the range $0.99° < \theta < 25.03°$ (**1**), $2.29° < \theta < 25.03°$ (**2**), and $1.66° < \theta < 26.40°$ (**3**) at 293(2) K. The ω-2θ scan technique was employed. Crystal parameters and structural refinements for **1**, **2**, and **3** are summarized in Table 3; selected bond lengths and angles are listed in Table 4. The structures were solved primarily by direct methods and secondly by Fourier difference techniques, and refined by the full-matrix least-squares method. The computations were performed with the SHELXL-97 program.[41,42] 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. CCDC-196813 to -196815 (**1**−**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk].

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

	1	**2**	**3**
Empirical formula	$C_{40}H_{72}Cl_4Cu_4N_{12}O_{26}$	$C_{14.5}H_{22}CuN_3O_5$	$C_{20}H_{34}Cl_2Cu_2N_6O_{12}$
Formula mass	1533.06	381.89	748.51
T [K]	293(2)	293(2)	293(2)
Space group	$C2$	$Pmc2(1)$	$P2_1/n$
a [Å]	41.327(19)	7.1711(14)	11.1165(7)
b [Å]	9.984(5)	7.5961(15)	24.5625(17)
c [Å]	14.460(7)	17.751(4)	11.4332(8)
β [°]	96.217(9)	90.10(3)	111.6840(10)
V [Å^3]	5931(5)	967.0(3)	2900.9(3)
Z	4	2	4
ρ [g·cm^{-3}]	1.717	1.312	1.714
μ [mm^{-1}]	1.687	1.154	1.720
θ [°]	0.99−25.03	2.29−25.03	1.66−26.40
Index ranges	$-48 \le h \le 49$	$-7 \le h \le 8$	$-13 \le h \le 13$
	$-11 \le k \le 8$	$-9 \le k \le 5$	$-30 \le k \le 30$
	$-17 \le l \le 16$	$-20 \le l \le 21$	$-14 \le l \le 7$
Refl. collected	12419	3343	13519
Independent refl.	7713 (R_{int} = 0.0403)	2839 (R_{int} = 0.0865)	5940 (R_{int} = 0.0270)
Max./min. transmission	0.7290/0.6315	0.8020/0.7233	0.9664/0.5843
Data/restraints/parameter	7713/13/787	2839/20/227	5940/8/412
Goodness-of-fit on F^2	0.908	0.972	1.035
R_1, wR_2 [$I > 2\sigma(I)$]	0.0486, 0.1218	0.0820, 0.1658	0.0492, 0.1342
R_1, wR_2 (all data)	0.0664, 0.1332	0.1478, 0.1919	0.0672, 0.1477
Largest diff. peak/hole [e·Å^{-3}]	0.894/−0.435	0.573/−0.488	1.070/−0.436

Table 4. Selected bond lengths [Å] and angles [°] for **1**, **2**, and **3**

Complex **1**			
Cu1−O3	1.955(7)	Cu1−O1	1.974(6)
Cu1−N2	2.022(8)	Cu1−N3	2.013(9)
Cu1−N1	2.322(6)	Cu2−O5	1.974(6)
Cu2−O2	1.990(6)	Cu2−N4	2.021(7)
Cu2−N5	2.046(8)	Cu2−N6	2.202(8)
Cu3−O6	1.954(6)	Cu3−O8	1.959(6)
Cu4−O7	1.964(6)	Cu4−O4	1.970(5)
O3−Cu1−O1	89.5(3)	O3−Cu1−N2	91.6(3)
O3−Cu1−O1	89.5(3)	O3−Cu1−N2	91.6(3)
O1−Cu1−N2	170.5(3)	O3−Cu1−N3	173.7(3)
O1−Cu1−N3	93.1(3)	N2−Cu1−N3	84.9(4)
O3−Cu1−N1	103.7(3)	O1−Cu1−N1	106.5(3)
N2−Cu1−N1	82.3(3)	N3−Cu1−N1	81.0(3)
O5−Cu2−O2	88.4(2)	O5−Cu2−N4	170.1(3)
O2−Cu2−N4	93.5(3)	O5−Cu2−N5	91.5(3)
O2−Cu2−N5	168.1(3)	N4−Cu2−N5	84.7(3)
O5−Cu2−N6	104.7(3)	O2−Cu2−N6	108.0(3)
N4−Cu2−N6	83.9(3)	N5−Cu2−N6	83.6(3)
Complex **2**[a]			
Cu1−O3	1.955(7)	Cu1−O1	1.974(6)
Cu1−O4#1	1.870(14)	Cu1−O1	1.906(9)
Cu1−N2	2.124(8)	Cu1−N3	2.129(9)
Cu1−N1	2.184(8)		
O4#1−Cu1−O1	88.9(5)	O4#1−Cu1−N2	176.9(6)
O1−Cu1−N2	94.2(5)	O4#1−Cu1−N3	92.8(7)
O1−Cu1−N3	177.7(4)	N2−Cu1−N3	84.1(5)
O4#1−Cu1−N1	98.0(5)	O1−Cu1−N1	101.3(5)
N2−Cu1−N1	81.1(4)	N3−Cu1−N1	79.9(5)
C1−O1−Cu1	135.6(9)		
Complex **3**[b]			
Cu1−O1	1.954(3)	Cu1−O4#1	1.961(3)
Cu1−N6	2.011(4)	Cu1−N4	2.014(4)
Cu1−N5	2.230(4)	Cu2−O3#1	1.957(3)
Cu2−O2	1.959(3)	Cu2−N1	2.012(4)
Cu2−N2	2.018(4)	Cu2−N3	2.235(4)
O1−Cu1−O4#1	95.05(14)	O1−Cu1−N6	172.65(17)
O4#1−Cu1−N6	91.56(15)	O1−Cu1−N4	89.26(15)
O4#1−Cu1−N4	173.69(15)	N6−Cu1−N4	83.90(17)
O1−Cu1−N5	97.74(17)	O4#1−Cu1−N5	100.55(15)
N6−Cu1−N5	84.18(19)	N4−Cu1−N5	83.38(16)
O3#1−Cu2−O2	95.15(13)	O3#1−Cu2−N1	174.15(15)
O2−Cu2−N1	89.42(15)	O3#1−Cu2−N2	90.74(15)
O2−Cu2−N2	172.76(16)	N1−Cu2−N2	84.43(16)
O3#1−Cu2−N3	98.72(15)	O2−Cu2−N3	99.84(16)
N1−Cu2−N3	84.04(17)	N2−Cu2−N3	83.36(17)
C1−O1−Cu1	136.7(3)	C1−O2−Cu2	130.6(3)

[a] # 1: x, $-y + 1$, $z + 1/2$. [b] #1: $x + 1/2$, $-y + 1/2$, $z - 1/2$.

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