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Complexed bridging ligand, {Cu(bptap)$_2$}, as a ferromagnetic coupler

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A novel complexed bridging ligand [Cu(bptap)$_2$] which acts as a ferromagnetic coupler forms one dimensional chain consisting of tri-copper(II) [Cu$_2${Cu(bptap)$_2$}]$^{4+}$ units in which adjoining copper(II) ions are ferromagnetically coupled.

The design and synthesis of novel metal complexes with a large ground spin state is a challenging and important research theme in modern chemistry. Several mechanisms have been proposed to produce ferromagnetic interactions between metal centers[1] such as magnetic orbital orthogonality,[2] spin polarization,[3] double exchange,[4] and so on. Kahn *et al*. and Okawa and coworkers first reported the idea of strict orthogonality between two magnetic orbitals with different symmetries in a VO (d_{xy})–Cu ($d_{x^2-y^2}$) system.[2] Using this idea in designing molecules, high ground state spin multiplicities along with ferromagnetic behavior have been achieved. In homometallic systems, ferromagnetic and antiferromagnetic can both occur depending on the bridging ligand shape, bridging angles,[5] and so on.[1]

Recently we reported, for the first time, the bridging ability of bpca$^-$ (Hbpca = bis(2-pyridylcarbonyl)amine) as an O_2N_3 pentadentate ligand[6,7] and also reported metal complexes having weak ferromagnetic interactions due to the peculiar bridging geometry of bpca$^-$, *i.e.* κ^2O:κ^3N mode with local C_2 symmetry.[7] We report here the synthesis of a novel tri-copper(II) complex consisting of 2,4-bis(2-pyridyl)-1,3,5-triazapentandienate (bptap$^-$), a Schiff base derivative of bpca$^-$, in which a ferromagnetic interaction operates through the controlled bridging geometry. In addition, a novel complex ligand [Cu(bptap)$_2$], which can be regarded as a general ferromagnetic coupler, is reported.

It is well-known that tris(2-pyridyl)triazine (tptz) can be hydrolyzed in the presence of metal ions to form mononuclear bpca$^-$ complexes.[7,8] When non-substituted triazine is allowed to react with copper(II) perchlorate in ethanol, triazine decomposes to form 1,3,5-triazapentandiene which was isolated as its copper complex.[9] In the same manner, a novel tri-copper(II) complex *catena*-[Cu$_3$(bptap)$_2$(OAc)$_2$](ClO$_4$)$_2$ (**1**) was synthesized by the reaction of copper(II) acetate anhydride and tptz in absolute methanol followed by addition of excess of sodium perchlorate (Scheme 1).†

Complex **1** has a one-dimensional chain structure consisting of a tri-copper(II) moiety {Cu$_3$(bptap)$_2$}$^{4+}$ and two bridging acetates (Fig. 1).‡ The tri-copper(II) moieties can be divided into two parts: two terminal copper ions (Cu2 and Cu2′) and a complex ligand {Cu(bptap)$_2$} including Cu1. The two organic bptap$^-$ ligands in {Cu(bptap)$_2$} coordinate to the central copper(II) ion in a κ^2N mode (Scheme 2) forming a moderately strong N$_{C=NH}$–Cu bond with distances of 1.948(3) and 1.958(4) Å. The complex ligand bridges two terminal copper(II) ions in a bis-tridentate fashion with short N$_{amide}$–Cu distances of 1.930(3) Å and longer N$_{py}$–Cu separations of 1.989(3) and 1.994(3) Å.

The central Cu1 is located on a crystallographic inversion center. The terminal Cu2 is doubly bridged by two oxygen atoms each from two different acetates (Fig. 1(b)). Cu2 is in a square pyramidal coordination environment with a short O$_{basal}$–Cu2 bond length of 1.940(2) Å and a long O$_{apical}$–Cu2 bond length of 2.480(2) Å, hence the magnetic orbital of Cu2, mainly $d_{x^2-y^2}$, lies in the N$_3$O$_{basal}$ plane towards the four basal donors. Cu1 is in an extremely elongated octahedral environment having a long contact distance with axial perchlorate ions (O$_{perchlorate}$–Cu1 = 2.777(5) Å). Thus the magnetic orbital of this ion is regarded as $d_{x^2-y^2}$ which directs towards the four N atoms from two bptap$^-$ (Scheme 2).

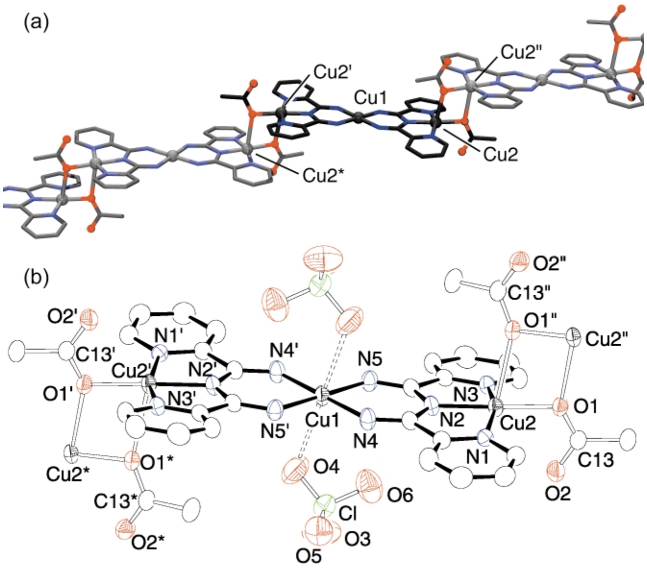
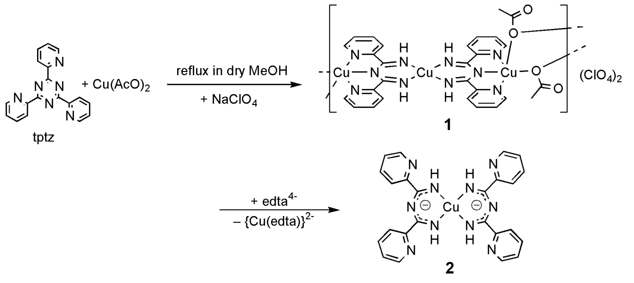
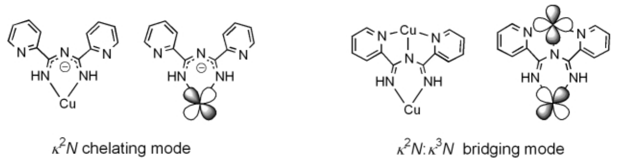


Fig. 1 (a) Chain structure and (b) repeating unit of **1** with thermal ellipsoids at 40% probability for the ORTEP drawing. Hydrogen atoms and perchlorate anions are omitted. Selected atom–atom distances (Å): Cu2···Cu2′ 3.431(1), Cu1–N4 1.958(3), Cu1–N5 1.948(3), Cu1···O4 2.777(5), Cu2–N1 1.994(3), Cu2–N2 1.930(3), Cu2–N3 1.989(3), Cu2–O1 1.940(2), Cu2···O1′ 2.480(2). Symmetry transformations used to generate equivalent atoms: (′) $-x + 1/2$, $-y + 3/2$, $-z + 1$: (″) $-x + 1$, y, $-z + 1/2$: (*) $x - 1/2$, $-y + 3/2$, $z + 1/2$.



Scheme 1



Scheme 2

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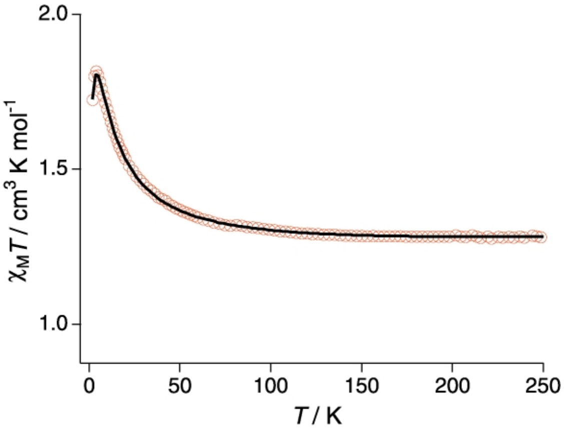

Fig. 2 Plots of $\chi_M T$ *vs.* T for **1**. The $\chi_M T$ values were calculated for the tri-copper(II) units. The solid line represents a theoretical fit.

Fig. 2 shows the magnetic behavior of **1** which shows continuous increase of $\chi_M T$ values on lowering the temperature indicating the presence of ferromagnetic interactions among copper(II) ions. From the structural analysis, **1** is considered to consist of well-separated tri-copper(II) units connected by acetates with the closest Cu2···Cu2′ distance of 3.431(1). The temperature dependence of $\chi_M T$ was analyzed by an isolated three-spin model ($H = -2J(\boldsymbol{S}_{\mathrm{Cu2}}\cdot\boldsymbol{S}_{\mathrm{Cu1}} + \boldsymbol{S}_{\mathrm{Cu1}}\cdot\boldsymbol{S}_{\mathrm{Cu2'}})$)[1] with the interaction between trinuclear units, θ, which also includes inter-chain interactions, packing effects, and so on. The best fit parameters were $J = 7.2(1)$ cm^{-1} and $\theta = -0.3(1)$ K with an averaged g value of 2.076(1). The three copper(II) ions are ferromagnetically coupled and each tri-copper(II) unit has a ground spin multiplicity of 3/2, which is supported by the field dependence of the magnetization. The existence of the ferromagnetic interaction can be understood by the spin orbital orthogonality which is reminiscent of the VO (d_{xy})–Cu ($d_{x^2-y^2}$) system. In **1**, the magnetic interactions are mediated by the triazapentanedienate moiety of bptap$^-$ which bridges Cu(II) ions in a κ^1N:κ^2N mode with local C_2 symmetry along the Cu$_{\mathrm{central}}$–Cu$_{\mathrm{terminal}}$ axis. All of the copper(II) ions have a dσ spin in the $d_{x^2-y^2}$ orbital directed towards the donor N-atoms from this bridging ligand. Two neighboring magnetic orbitals have different symmetry about a two-fold rotation axis, *i.e.*, the Cu$_{\mathrm{central}}$ is antisymmetric whereas the Cu$_{\mathrm{terminal}}$ is symmetric, and hence these two $d_{x^2-y^2}$ orbitals are orthogonal to each other. This orthogonality is advantageous to ferromagnetic coupling. The ONO$^-$ anion is expected to bridge two metal ions in a similar bridging fashion,[10] and one example was reported by Kahn *et al*. in which nickel(II) and manganese(II) ions were bridged by ONO$^-$ in κ^1N:κ^2O mode.[10] This system also showed ferromagnetic behavior.

In this bridging system, the magnetic interactions between dσ spin(s) and dπ spin(s) are antiferromagnetic due to through space overlap. However, the interaction will be weak or negligible compared to the ferromagnetic dσ–dσ interaction *via* bonding. The orthogonality will be expected for other combinations of metal ions containing dσ spin(s), and the complex ligand [Cu(bptap)$_2$] has possibility to be a highly useful ferromagnetic coupler. Free complex ligand, [Cu(bptap)$_2$] (**2**, Fig. 3), was obtained by removing the terminal copper(II) ions from **1**,†‡ and such investigations are now in progress.[11]

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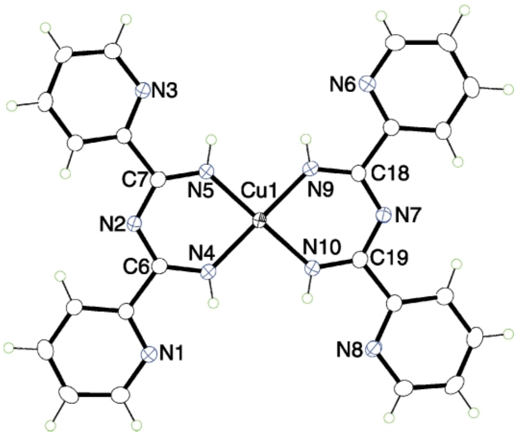

Fig. 3 ORTEP drawing of **2** with thermal ellipsoids at 40% probability. Selected bond distances (Å): Cu1–N4 1.943(2), Cu1–N5 1.944(2), Cu1–N9 1.942(2), Cu1–N10 1.941(2), N2–C6 1.339(3), N2–C7 1.340(3), N4–C6 1.313(3), N5–C7 1.314(3), N7–C18 1.338(3), N7–C19 1.346(3), N9–C18 1.305(3), N10–C19 1.306(3).

Notes and references

† *Synthesis* of **1**: 0.33 g (2 mmol) of copper(II) acetate anhydride and 0.31 g (1 mmol) of 2,4,6-tris(2-pyridyl)-1,3,5-triazine were mixed and refluxed in 20 ml of absolute methanol for 3 h during which the color turned from greenish blue to deep blue. The solution was cooled to room temperature and the addition of excess of sodium perchlorate afforded blue–green microcrystals. To the microcrystals collected by filtration was added methanol to give a greenish blue suspended solution. After standing overnight, the microcrystals disappeared and deep blue crystals of **1**·2CH$_3$OH·2H$_2$O formed. Yield, 80%.

Synthesis of **2**: 72 mg (0.07 mmol) of **1** and 114 mg of Na$_4$edta (0.3 mmol) were vigorously stirred for 2 h in a water (7 ml)/chloroform (10 ml) mixture at room temperature. The orange organic layer was separated and was evaporated to dryness. Orange prisms of **2**·CHCl$_3$ were obtained by recrystallization from hot chloroform. Yield, 80%.

‡ *Crystal data* for **1**·2CH$_3$OH·2H$_2$O: $C_{30}H_{38}Cl_2Cu_3N_{10}O_{16}$, M = 1056.22, monoclinic, space group $C2/c$, a = 15.4718(8), b = 13.2535(6), c = 19.2782(10) Å, β = 93.773(2)°, U = 3944.5(3) Å^3, T = 223 K, Z = 4, μ(Mo–Kα) = 1.823 mm^{-1}, 4539 independent measured reflections, 2807 were observed reflections ($I > 2\sigma(I)$, $2\theta_{\max}$ = 55°), 339 parameters, F^2 refinement, R_1 = 0.0441 (observed), wR_2 = 0.1186 (all data).

Crystal data for **2**·CHCl$_3$: $C_{25}H_{21}Cl_3CuN_{10}$, M = 631.41, monoclinic, space group $P2_1/c$, a = 11.6906(4), b = 23.6124(8), c = 10.7435(3) Å, β = 116.1580(10)°, U = 2661.93(15) Å^3, T = 200 K, Z = 4, μ(Mo-Kα) = 1.159 mm^{-1}, 6127 independent measured reflections, 4436 independent observed reflections ($I > 2\sigma(I)$, $2\theta_{\max}$ = 55°), 436 parameters, F^2 refinement, R_1 = 0.0394 (observed), wR_2 = 0.1037 (all data).

CCDC reference numbers 176944 and 176946. See http://www.rsc.org/suppdata/cc/b2/b202967g/ for crystallographic data in CIF or other electronic format.

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