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Ferromagnetic Coupling through Spin Polarization in the Hexanuclear $[\mathrm{Mn^{II}}_3\mathrm{Cu^{II}}_3]$ Complex

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A novel Cu(II)–Mn(II) hexanuclear complex of formula $[\{\mathrm{MnCuL}\}_3(\mathrm{tma})](\mathrm{ClO_4})_3\cdot8\mathrm{H_2O}$ [$\mathrm{H_2L}$ = macrocyclic Robson proligand; $\mathrm{H_3tma}$ = trimesic acid] has been obtained by connecting three heterobinuclear $[\mathrm{Cu^{II}Mn^{II}L}]^{2+}$ cationic species through the trimesate anion. The complex exhibits a C_3 rotational symmetry, imposed by the geometry of the bridging ligand. The interaction within each Mn(II)–Cu(II) pair is antiferromagnetic (J = –16.7 $\mathrm{cm^{-1}}$). A weak ferromagnetic coupling among the three $S = 2$ resulting spins through the tricarboxylato bridge leads to a $S = 6$ ground spin state, for which the spin polarization mechanism is responsible.

The search for new synthetic routes leading to multimetallic complexes is of current interest in modern inorganic chemistry.(1) The building block approach was particularly developed in order to obtain heterometallic complexes with interesting magnetic, optical, or electric properties. It consists of the use of anionic complexes, with potentially bridging ligands, which may interact with wide variety of assembling cations. An extremely rich chemistry has been developed, particularly with the families of oxamido-,(2) cyano-,(3) and oxalato-bridged systems.(4) Paralleling the rational method of metal assembly, serendipitous assembly also affords compounds with spectacular structures and properties.(5) The retrospective analysis of the compounds obtained by accident provides the necessary information in the attempt to design complexes with pre-established nuclearities and dimensionalities.

We are currently developing a synthetic approach aiming at obtaining multimetallic complexes by using homo- and heterobinuclear complexes as building blocks. The following types of cationic species are employed: (i) binuclear copper(II) species with end-off compartmental Schiff-base ligands;(6) (ii) alkoxo-bridged copper(II) species;(7) (iii) heterobinuclear 3d−4f species with side-off Schiff-base ligands.(8,9)

Heterobinuclear complexes with two different 3d metal ions, combining the electronic and stereochemical peculiarities of two metal ions, are very attractive as building blocks in designing heterometallic complexes. For example, the reaction between a $[\mathrm{Cu^{II}Zn^{II}}]$ complex and bis(4-pyridyl)ethylene afforded a heterometallic molecular rectangle.(10) More exciting from the magnetic point of view are binuclear species with two different paramagnetic ions. Here we report on such a complex, which has been obtained starting from

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10.1021/ic0493651 CCC: $27.50

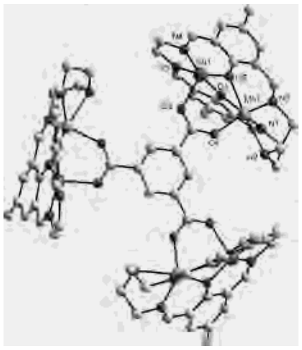
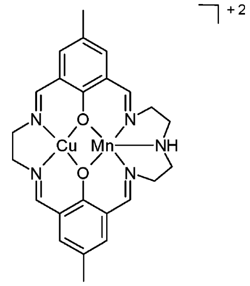


Figure 1. Perspective view of the hexanuclear cation in **1**.

a binuclear cation, $[Mn^{II}Cu^{II}L]^{2+}$ [H_2L is a dissymmetric macrocyclic Robson proligand resulting from 2,6-diformyl-4-methyl-phenol, ethylenediamine, and diethylenetriamine (see Scheme 1)]. In order to obtain a hexanuclear complex,

Scheme 1



we used the anion of the trimesic acid, tma^{3-}, as a linker. This anion has been chosen as a bridge not only because of its potential ability to bridge 3 × 2 metal ions, but also since it fulfils the necessary conditions to mediate a ferromagnetic coupling through a spin polarization mechanism:[11] the whole bridging molecule can be planar, and the metallic centers are separated by an odd number of atoms.

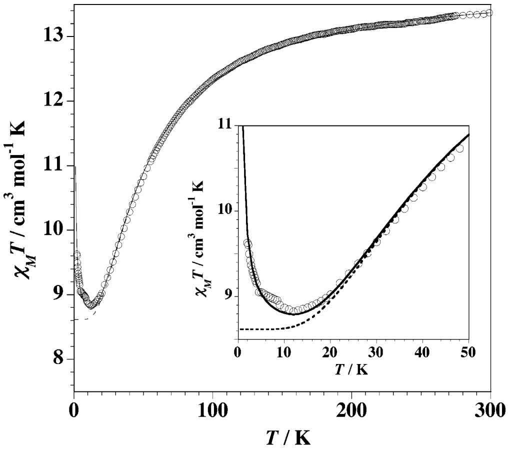


Figure 2. $\chi_M T$ versus T plot for compound **1**: (○) experimetal data; (—) best fit using eq 2; (- - -) best fit considering three magnetically isolated $Cu^{II}-Mn^{II}$ pairs (see text). The inset shows the low-temperature region.

The self-assembly process between $[Mn^{II}Cu^{II}L]^{2+}$ cations and the trimesate ion leads to a hexanuclear complex with the formula $[\{MnCuL\}_3(tma)](ClO_4)_3 \cdot 8H_2O$, **1**.[12,13] The crystal structure of **1** has been solved.[14] It consists of hexanuclear cationic entities, perchlorate anions and crystallization water molecules. As expected, three [MnCu] entities are connected through the tma^{3-} anion, resulting in a complex entity with a 3-fold axis (Figure 1). The Mn(II) and Cu(II) ions within each pair are bridged by two phenoxo oxygen atoms and by a carboxylato group (*syn*−*syn* bridging mode) arising from the tma^{3-} spacer. The copper(II) ions are pentacoordinated with a square planar geometry, in which the apical position is occupied by the oxygen atom arising from the carboxylato bridge [Cu(1)−O(3) = 2.238(10) Å]. The basal plane is formed by two nitrogen atoms from the Schiff-base ligand, and two phenoxo oxygen atoms, with the Cu−O and Cu−N distances falling in the range 1.890(12)−1.939(7) Å. The manganese ions are coordinated by two imino nitrogen atoms from the Schiff-base [Mn(1)−N(1) = 2.208(11) Å; Mn(1)−N(3) = 2.216(13) Å], one secondary amine nitrogen [Mn−N(2) = 2.382(10) Å], two phenoxo oxygens [Mn(1)−O(1) = 2.215(9) Å; Mn(1)−O(2) = 2.230(7) Å], and one oxygen atom from the carboxylato bridge [Mn(1)−O(4) = 2.053(7) Å]. The three short Mn···Cu distances are 3.109(2) Å. The intramolecular Mn···Mn and Cu···Cu distances are, respectively, 9.847 and 10.179 Å. The tma^{3-} bridge is planar.

The magnetic properties of **1** are quite interesting. The $\chi_M T$ versus T plot is shown in Figure 2. At room temperature, $\chi_M T$ is equal to 13.5 cm^3 mol^{-1} K, a value which roughly corresponds to three Mn^{2+} and three Cu^{2+} magnetically isolated metal ions (the calculated value is 14.2 cm^3 mol^{-1} K). Upon cooling, $\chi_M T$ continuously decreases, reaches a minimum at 12 K ($\chi_M T$ = 8.8 cm^3 mol^{-1} K), and further increases to 9.6 cm^3 mol^{-1} K at 1.9 K.

In light of the structure of **1**, four intramolecular exchange coupling parameters (J_1−J_4) are involved (see Scheme 2), the corresponding Hamiltonian being defined by eq 1:

$$\mathbf{H} = -J_1(\mathbf{S_1S_2} + \mathbf{S_3S_4} + \mathbf{S_5S_6}) - J_2(\mathbf{S_1S_6} + \mathbf{S_2S_3} + \mathbf{S_4S_5}) - J_3(\mathbf{S_1S_3} + \mathbf{S_3S_5} + \mathbf{S_1S_5}) - J_4(\mathbf{S_2S_4} + \mathbf{S_2S_6} + \mathbf{S_4S_6}) \quad (1)$$

The analysis of the magnetic data of **1** through eq 1 would lead to overparametrization due to an important correlation

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(12) The binuclear precursor $[CuMnL](ClO_4)_2 \cdot H_2O \cdot CH_3OH$ was prepared according to a previously described procedure.[13] Complex $[(CuMnL)_3(TMA)](ClO_4)_3 \cdot 8H_2O$: To the methanolic solution (10 mL) of the binuclear precursor, $[CuMnL](ClO_4)_2 \cdot H_2O \cdot CH_3OH$ (0.039 g, 0.05 mmol), was added a methanolic solution (5 mL) of trimesic acid (0.01 g, 0.05 mmol) and triethylamine (0.015 g, 0.15 mmol). The slow evaporation of the resulted solution gave after 2 days green crystals suitable for X-ray diffraction. Yield: 55%. Anal. Calcd (%): C, 44.9; H, 4.2; N, 9.7; Cu, 8.7; Mn, 7.6. Found (%): C, 44.4; H, 4.2; N, 9.5; Cu, 8.4; Mn, 7.3. IR bands (KBr, cm^{-1}): 3416 (br), 3300 (br), 2921 (m), 2858 (m), 1648 (vs), 1566 (s), 1443 (s), 1404 (m), 1374 (s), 1327 (s), 1276 (w), 1235 (m), 1192 (w), 1099 (s), 998 (w), 934 (w), 876 (w), 807 (m), 769 (m), 717 (m), 621 (m), 501 (m).

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(14) Crystal data for **1**: fw, 2238.40; hexagonal, space group $P\bar{6}2c$. Unit cell dimensions: a = 16.474(2) Å, c = 20.244(4) Å; cell volume 4758.1(13) Å^3; Z = 2; D_c = 1.562 g/cm^3; μ = 1.217 mm^{-1}; T = 293(2) K. Final R indices: R1 = 0.0546 for 1417 reflections [$I > 2\sigma(I)$, and 0.1468 for all 3132 data].

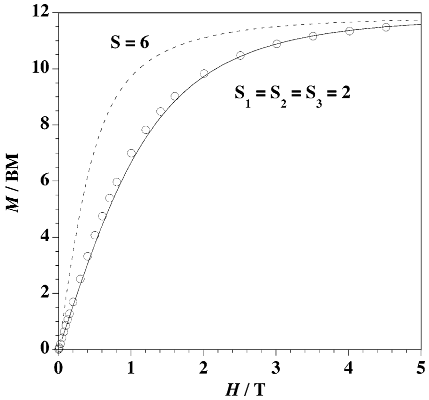
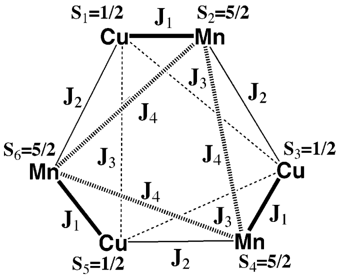
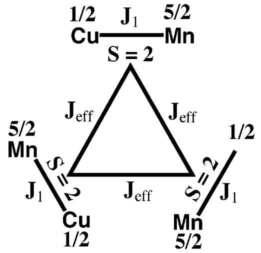


Figure 3. Magnetization versus **H** at 2.0 K for **1**: (○) experimental data; Brillouin functions for (- - -) an $S = 6$ spin state and for (—) three magnetically isolated $S = 2$ units with $g = 1.98$ ($g_{Mn} = 1.99$ and $g_{Cu} = 2.08$).

Scheme 2



Scheme 3



among the different coupling parameters. The exchangeinteraction within each Mn(II)−Cu(II) pair (J_1) is much stronger than the other ones. Indeed, the magnetic coupling between Cu(II) and Mn(II) in other three binuclear species with the same compartmental ligand is antiferromagnetic (J_1 values varying between −40 and −27 cm^{-1})[13] while the exchange interaction mediated by the tma^{3-} ions was always found to be very weak.[15] The magnetic behavior of **1** between room temperature and slightly above 12 K can be described considering only three magnetically isolated Cu^{II}−Mn^{II} binuclear units with $J_1 = -16.7$ cm^{-1} (see dashed line in Figure 2). At $T < 12$ K, the ferromagnetic coupling among the three $S = 2$ spin units through the spin polarization mechanism causes the observed increase of $\chi_M T$. Having in mind the spin topology depicted in Scheme 3, the simulation of the magnetic properties of **1** were performed through eq 2, which is valid for $|J_{eff}| \ll |J|$:[16]

$$\chi_M = \frac{N\beta^2}{2kT} F_D \cdot F_T \qquad (2)$$

F_D describes the exchange interaction within each Mn−Cu pair (J_1), and F_T describes the one between the three $S = 2$ spins (J_{eff}):

$$F_D = \frac{5{g_2}^2 + 14{g_3}^2 \exp(x)}{5 + 7\exp(x)} \quad x = \frac{3J}{kT} \qquad (3)$$

$$F_T = {g_2}^2 \frac{A}{B} \qquad (4)$$

$$A = 3\exp(y) + 25\exp(3y) + 56\exp(6y) + 90\exp(10y) + 110\exp(15y) + 91\exp(21y) \qquad (5)$$

$$B = 1 + 9\exp(y) + 25\exp(3y) + 28\exp(6y) + 27\exp(10y) + 22\exp(15y) + 13\exp(21y) \qquad (6)$$

$$y = J_{eff}/kT \quad g_2 = (7g_{Mn} - g_{Cu})/6 \quad g_3 = (5g_{Mn} + g_{Cu})/6$$

The best-fit parameters are $J_1 = -16.7$ cm^{-1}; $J_{eff} = +0.05$ cm^{-1}; $g_{Cu} = 2.08$; $g_{Mn} = 1.99$; $R = 2 \times 10^{-5}$ (R is the agreement factor defined as $\sum_i[(\chi_M T)_{obs}(i) - (\chi_M T)_{calc}(i)]^2/\sum_i[(\chi_M T)_{obs}(i)]^2$).

The low-temperature limit of the $\chi_M T$ product (9.6 cm^3 mol^{-1} K) is far from that expected for a $S = 6$ ground state (21 cm^3 mol^{-1} K with $g = 2.0$). This is because even at 2.0 K ($kT = 1.4$ cm^{-1}), spin states other than the low-lying $S = 6$ one are thermally populated.

The magnetization versus the applied magnetic field at 2.0 K is shown in Figure 3. The magnetization data are placed slightly above the Brillouin curve of three magnetically isolated $S = 2$ spins indicating the occurrence of weak ferromagnetic interaction between the three $S = 2$ states ($J_{eff} = +0.05$ cm^{-1}).

Two interesting examples of homonuclear trigonal complexes, where the three metal ions are bridged by a tris(semiquinone) ligand, with three ferromagnetically coupled semiquinone units, have been described by Dei and Shultz et al.[17]

Here we reported on the first example of ferromagnetic coupling between paramagnetic centers across the trianion of the trimesic acid through the spin polarization mechanism. This compound could be useful as a model for the study of the spin polarization by means of alternative methods (e.g., polarized neutron diffraction or NMR techniques).

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Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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