A $Mn^{II}Cu^{II}Mn^{II}$ Trinuclear Species with an $S = 9/2$ Ground State

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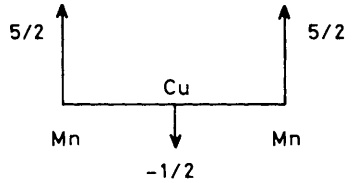
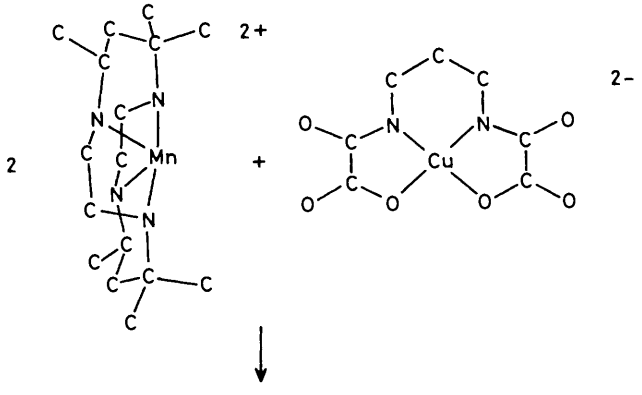
The $S = 9/2$ ground state of a linear $Mn^{II}Cu^{II}Mn^{II}$ trinuclear complex arises from the parallel alignment of the local spins (5/2) of the two terminal Mn^{II} ions through antiferromagnetic interactions with the local spin (1/2) of the central Cu^{II} ion.

One of the main challenges in the field of molecular materials is the design of molecular ferromagnets.[1] A step toward this goal is to find a strategy leading to molecular systems with a high-spin multiplicity in their ground state. The most obvious strategy is to achieve a ferromagnetic interaction between the nearest neighbour ions of a polymetallic system.[2] However the symmetry requirements for such an interaction are difficult to realize. It is well known that in most cases the interaction between nearest neighbour ions is antiferromagnetic. An alternative strategy[3] involves the polarization of local spins (5/2, Mn^{II} or Fe^{III}) along the same direction through an antiferromagnetic interaction with a local spin (1/2, Cu^{II}) according to Scheme 1, valid for a trinuclear species, which leads to an $S = 9/2$ ground state. We report here on the first $Mn^{II}Cu^{II}Mn^{II}$ complex of this kind, with the formula $\{[Mn(Me_6\text{-}[14]ane\text{-}N_4)]_2Cu(pba)\}(CF_3SO_3)_2\cdot 2H_2O$, (**1**); $[Me_6\text{-}[14]ane\text{-}N_4]$ = (±)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane,[4,5] pba = propylene-1,3-bisoxamato.[6]

Compound (**1**) was synthesized by reaction of 10^{-4} mol of $Na_2[Cu(pba)]\cdot 2H_2O$[6] with 2×10^{-4} mol of $[Mn(Me_6\text{-}[14]ane\text{-}N_4)](CF_3SO_3)_2$[7] in a 40—60 mixture of methanol–water under nitrogen according to Scheme 2. Me_6-[14]ane-N_4 is known to give a folded co-ordination in the presence of a bidentate anion.[8] Satisfactory chemical analyses of the C, H, N, Cu, and Mn elements for $C_{41}H_{82}N_{10}O_{14}F_6S_2CuMn_2$, (**1**), were obtained.



Scheme 1



$[Mn(Me_6\text{-}[14]ane\text{-}N_4)]_2Cu(pba)^{2+}$

(**1**)

Scheme 2

The skeleton of the trinuclear unit is depicted in Figure 1. The oxamato bridging ligands are known for their remarkable efficiency in propagating strong antiferromagnetic interaction between two metal centres relatively far away from each other.[2] The $\chi_M T$ *vs.* T plot for (**1**) in the temperature range $2 < T < 300$ K is shown in Figure 2, χ_M being the molar magnetic susceptibility.† The high temperature limit of $\chi_M T$ is equal to that expected for two Mn^{II} and a Cu^{II}. Upon cooling down, $\chi_M T$ decreases, reaches a minimum around 170 K, then increases

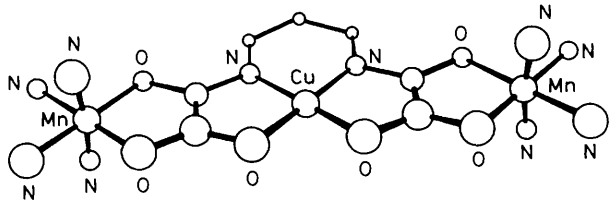


Figure 1. Schematic representation of the skeleton of the $Mn^{II}Cu^{II}Mn^{II}$ trinuclear species.

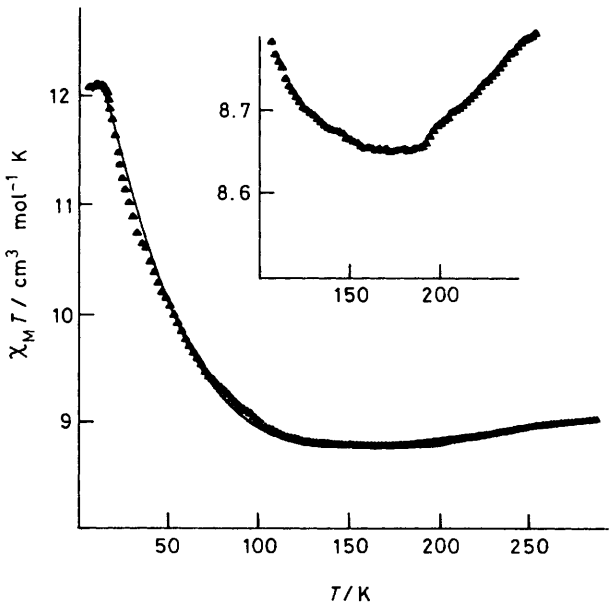


Figure 2. Experimental (▲) and calculated (—) $\chi_M T$ *vs.* T plot for (**1**). In the insert, an expansion of the $\chi_M T$ axis in the 100—250 K temperature range is shown to give evidence of the minimum of $\chi_M T$. The minimum is the signature of this kind of antiferromagnetically coupled polymetallic system where the spin multiplicity of the low lying states does not vary monotonically with the energy.

† In the derivation of χ_M, we explicitly calculated the g-factors for each of the eleven low-lying states as a function of their local g-factors g_{Mn} and g_{Cu}.

rapidly and finally reaches a plateau in the 2—10 K range with $\chi_M T$ = 12.1 cm^3 mol^{-1} K. This plateau corresponds to the temperature range where only the S = 9/2 ground state is thermally populated, with $\chi_M T = 33\ N\beta^2 g^2/8k$. The g-factor value for this state, deduced from the magnetic data, is then 1.98. In the whole temperature range, the magnetic data closely follow the theoretical expression of the magnetic susceptibility arising from the spin Hamiltonian:

$$\mathcal{H} = -J(\hat{S}_{Mn1}.\hat{S}_{Cu} + \hat{S}_{Mn2}.\hat{S}_{Cu}) + \beta[g_{Mn}(\hat{S}_{Mn1} + \hat{S}_{Mn2}) + g_{Cu}\hat{S}_{Cu}].H$$

where the interaction between the terminal Mn^{II} ions is assumed to be negligible. The parameters‡ are; J = −36.6 cm^{-1}, g_{Mn} = 2.03 and g_{Cu} = 2.10.

The increase of $\chi_M T$ upon cooling down below 170 K is reminiscent of a ferromagnetic interaction whereas actually the $Mn^{II}Cu^{II}$ interaction is strongly antiferromagnetic. This is due to the spin multiplicity of the ground state being higher than those of the first excited states.[9]

The X-band powder e.s.r. spectrum of (**1**) at 4.2 K exhibits the $\Delta M_s = \pm 1$ allowed transition within the S = 9/2 ground state at g = 1.991 and features of decreasing intensity at $g \sim 4$, 6, and 8, which could be assigned to the $\Delta M_s = \pm 2, \pm 3$, and ± 4 forbidden transitions respectively.

The ground state of (**1**) exhibits quite an unusual high-spin multiplicity and is well separated from the first excited states. This strategy could lead to the formation of the first genuine molecular ferromagnet.

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‡ In the fitting, a Weiss constant θ was introduced to account for intermolecular interactions and found as −0.31 K. The agreement factor defined by $\Sigma[(\chi_M T)_{calc.} - (\chi_M T)_{obs.}]^2/\Sigma[(\chi_M T)_{obs.}]^2$ was then equal to 3.9×10^{-5} for 160 experimental points.

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