MAGNETIC INVESTIGATION OF AN UNUSUAL DISSYMMETRIC BINUCLEAR MANGANESE CARBOXYLATE COMPLEX

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Abstract: The magnetic susceptibility (χT) of an unusual dissymmetric binuclear manganese corboxylate complex has been measured from 2 to 300K. The magnetic data which have been fitted with help of the Heisenberg Dirac Van Vleck HDVV spin-exchange Hamiltonian $\hat{H} = -J\vec{S}_1\vec{S}_2$, indicate that an antiferromagnetic interaction equal to J = -0.90(1) cm^{-1} is present. A correlation between J values and Mn-H$_2$O-Mn angles has been tempted.

Keywords: manganese(II) carboxylates; magnetic properties

Introduction

The most important role in nature for manganese (Mn) is its involvement in water oxidation/oxygen evolution centre (WOC) within the photosynthetic apparatus of green plants and cyanobacteria.[1] A large variety of studies have shown manganese to be the site of binding and oxidation substrate (eq.1).

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \tag{1}$$

Nowadays special attention is focused on studying the cooperative action of binuclear or multinuclear Mn(II) compounds. Indeed, binuclear dimanganese(II) metal centers are present in several enzymes, including arginase, catalase, thiosulfate-oxidizing enzyme and glycohydrolase.[2]

Due to these facts, carboxylate-bridged di- or poly-manganese centers have attracted growing interest in both systematic modeling and physical characterization.

Results and discussion

We previously described the synthesis and X-ray analysis of an unexpected dissymmetric manganese (μ -aqua) dimer compound obtained with use of trichlorocetic acid and that corresponds to the following formula: $[Mn_2(\mu\text{-}H_2O)(\mu\text{-}CCl_3COO)_2(CCl_3COO)_2(H_2O)_4]H_2O$ (**I**).[3] The present paper reports on the magnetic investigation of this compound. A view of the X-ray structural determination is presented in Figure 1.

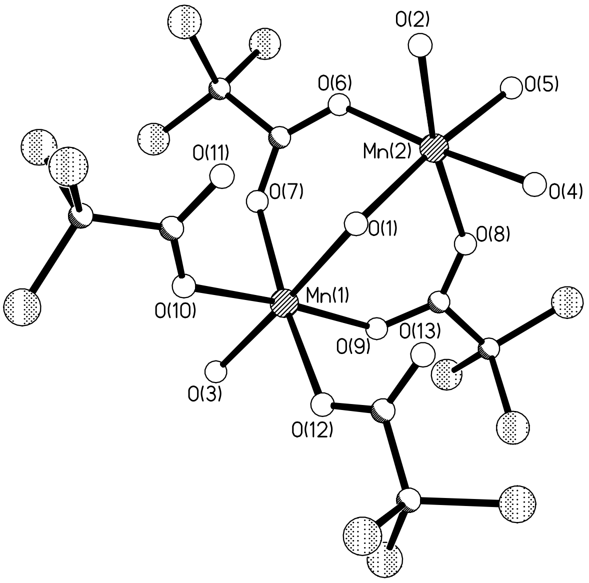

Figure 1. Structure of $[Mn_2(\mu\text{-}H_2O)(\mu\text{-}CCl_3COO)_2(CCl_3COO)_2(H_2O)_4]H_2O$.

The magnetic susceptibility (χT) of powdered samples has been measured from 2 to 300K with use of a SQUID magnetometer. At 297.8 K, the magnetic moment is equal to 8.39 BM, value that corresponds to two uncoupled high spin (S = 5/2) manganese(II) ions.[4a,b] (Fig. 2). The μ_{eff} value continuously decreases upon cooling and reaches

5.15 BM at 1.97 K, a value which is characteristic of an antiferromagnetic interaction between the two metal atoms through the double carboxylate and the water bridging molecule (Fig. 1). In order to evaluate the magnitude of the spin-exchange interaction, the magnetic data were fitted with help of the Heisenberg Dirac Van Vleck HDVV spin-exchange Hamiltonian [4c] (eqs. (2) and (3)).

$$\hat{H} = -J\vec{S}_1\vec{S}_2 \tag{2}$$

$$\chi = \frac{2Ng^2\beta^2}{k(T-\theta)} \cdot \frac{e^{J/kT} + 5e^{3J/kT} + 14e^{6J/kT} + 30e^{10J/kT} + 55e^{15J/kT}}{1 + 3e^{J/kT} + 5e^{3J/kT} + 7e^{6J/kT} + 9e^{10J/kT} + 11e^{15J/kT}} + N_\alpha \tag{3}$$

The coupling between the two paramagnetic $S=5/2$ spins generates states S having the following energies E: S(E) = 0(0), 1($-J$), 2($-3J$), 3($-6J$), 4($-10J$), 5($-15J$). The least-squares fit of the experimental data gives the following set of parameters: g = 2.002(1), θ = -1.28(2)K N_α = 0.002(6) J = -0.90(1) cm^{-1} The agreement factor $\sum(\chi T_{calc} - \chi T_{obs})^2 / \sum(\chi T_{obs})^2$ is then equal to $1.2 \cdot 10^{-4}$. The θ value has been obtained from the Curie-Weiss law (Fig. 3) (C = 2.49(2) cm^3·K·mol^{-1} θ = -1.28(2) K) and suggests the presence of second-order effects (such as intermolecular interactions, *etc.*).

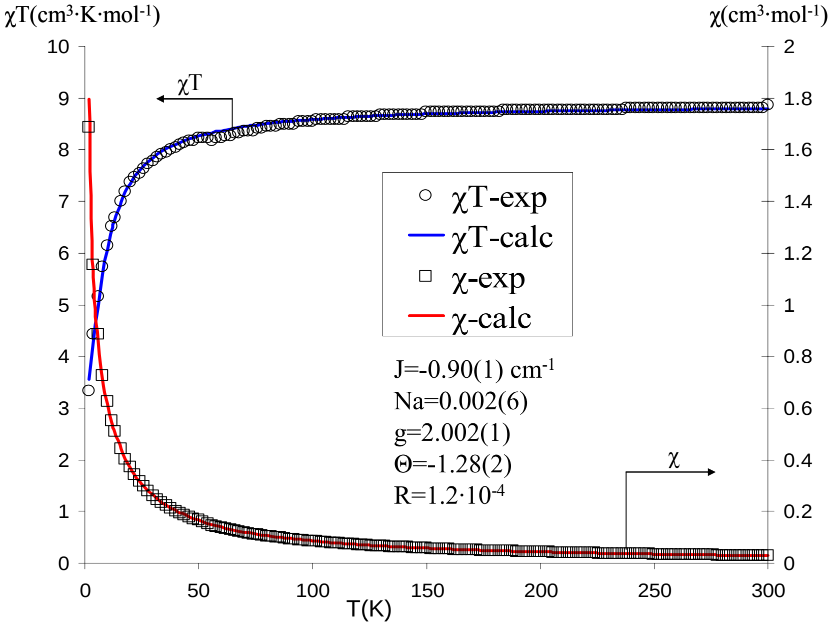

Figure 2. Temperature dependence of χ and χT for **I**. The solid line is the best fit for a pair of exchange-coupled $S = 5/2$ spins (eq. 3).

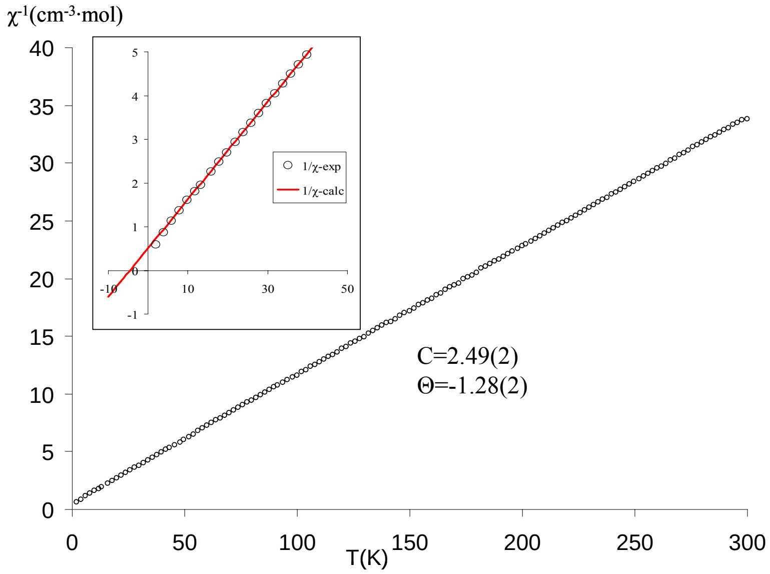

Figure 3. χ^{--1} versus temperature plot for **I** with the best fit plot according to the Curie-Weiss law.

The obtained J value, similar to the ones given in earlier published works, confirms the existence of an antiferromagnetic interaction (Table 1).[5] The bridging ligands control the metal-metal separations and provide an orbital overlapping through these ligand orbitals. Unfortunately the J value corresponds to the global behaviour, so that we are not able to differentiate the contributions from the carboxylate bridges and from the water bridge, as in the previously published results (Table 1). In order to compare our value with the literature data obtained with a different Hamiltonian ($H = -2JS_1S_2$), we have to take into account two factors. As the variations of the Mn-H_2O-Mn angles and of the Mn-Mn distances are very small, a correlation between these parameters and the J values is inappropriate. It is clear that these parameters are not the good ones to attempt a correlation. A comparison with the previously published symmetrical complexes indicates that the non symmetry of our complex could be considered as a factor responsible for the weakening of the antiferromagnetic interaction. Eventually, our data do confirm that the magnetic interaction through the μ-H_2O bridge is weak.

Table 1.
Structural and magnetic data for μ-aqua bridged manganese(II) carboxylate dimers.

Compound	Mn-Mn(Å)	Mn-H_2O-Mn(deg)	J(cm^{-1})	Ref
$Mn_2(\mu\text{-}H_2O)(H_2O)_4(Cl_3CCO_2)_4$	3.79	113.4	-0.9	This work
$Mn_2(\mu\text{-}H_2O)(imd)_4(OAc)_4$	3.777	114.4	-1.26	[5a]
$Mn_2(\mu\text{-}H_2O)(L)_2(C_2F_5CO_2)_4$	3.739	114.6	-1.65	[5b]
$Mn_2(\mu\text{-}H_2O)(Me_2bpy)_2(Piv)_4$	3.595	110.2	-2.73	[5c]
$Mn_2(\mu\text{-}H_2O)(tmeda)_2(OAc)_4$	3.621	110.0	-2.95	[5c]
Imd=imidazole; L=2-ethyl-4,4,5,5-tetramethyl-3-oxo-4,5-hydro-1H-imidazolyl-1-oxyl; tmeda=N,N,N',N'-tetramethylethylenediamine; Me_2bpy=4,4' dimethylbipyridil; OAc=acetato ion, piv=pivalato ion				

Experimental

Magnetic susceptibility data (2-300K) were collected on powdered samples with a Quantum Design MPMS SQUID susceptometer working in a 0.1T applied magnetic field. All data were corrected for diamagnetism of the ligands estimated from Pascal's constants.[6] The synthesis of the title compound was described before [3].

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