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Magnetic Properties of a Linear Trinuclear Manganese Compound $[Mn_3(PhCO_2)_6(Bipy)_2] \cdot H_2O$[1]

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Abstract—The reaction of the trinuclear oxo-centered mixed-valence complex $[Mn_3O(O_2CPh)_6(Py)_2(H_2O)]$ with 2,2'-bipyridyl (Bipy) and another potential tripodal ligand affords the title compound $[Mn_3(PhCO_2)_6(Bipy)_2] \cdot H_2O$ in good yield. The X-ray crystallographic diffraction study reveals that three manganese ions are arranged in a linear mode with Mn_{center}–$Mn_{terminal}$ and $Mn_{terminal}$–$Mn_{terminal}$ diatances of 3.588 and 7.176 Å, respectively. Molar magnetic susceptibility of the compound gradually decreases from 12.23 (300 K) to 4.45 cm^3 K mol^{-1} (2 K). Taking into account the structure of this compound, the data in the 2.0–300 K range were fit to the appropriate theoretical expression to give J = –2.73 cm^{-1}, ρ= 2.07%, N_a = –0.0004 cm^3 mol^{-1}, g = 1.992, and R^2 = 0.99996. The magnetization versus external magnetic field measurements at 2 K shows that the ground state is S_T = 5/2.

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INTRODUCTION

Polynuclear mangenese complexes are now receiving increased attention in various scientific areas, including chemistry, physics, and biology. Representative target molecules fascinating inorganic chemists are tetranuclear aggregates as models for the photosynthetic water oxidation centers [1] and "single-molecule magnets" potentially applicable to future molecular device [2, 3]. Most commonly, these complexes are synthesized by the self- or "serendipitous" assembly method [4]. Our approach to Mn–aggregated systems is using oxo-centered manganese triangles of general formula $[Mn_3O(O_2CR)_6(L)_3]$ as precursors by choosing suitable chelate ligands through the conventional synthetic method [5, 6]. This route toward the synthesis of high nuclearity clusters has been reported in the literature [7–9].

The work presented here continues this approach, and a new linear complex $[Mn_3(PhCO_2)_6(Bipy)_2] \cdot H_2O$ (**I**), where Bipy is 2,2'-bipyridyl, has been obtained by using $[Mn_3O(O_2CPh)_6(Py)_2(H_2O)]$ as the starting materials. The crystal structure of this compound has been communicated recently in preliminary form [10]. In this paper, the magnetic behavior of the title compound was investigated and variable-temperature solid-state magnetic susceptibility studies reveal that the data are consistent with the S_T = 5/2 ground state. The conclusion was confirmed by magnetization *vs*. field study in 0–70 kOe range (2.0 K). Fitting of the data to the appropriate theoretical expression gives J = –2.73 cm^{-1}. The obtained J value is consistent with that of previously published isostructural compounds.

EXPERIMENTAL

The precursor $[Mn_3O(O_2CPh)_6(Py)_2(H_2O)]$ was synthesized according to the literature method [11]. All the other starting materials were of reagent grade and obtained from commercial sources without further purification.

The elemental analysis was performed with a Flash EA 1112 elemental analyzer. IR spectra were recorded on a VECTOR 22 spectrometer in the spectral range 4000–400 cm^{-1} using the KBr disk method. Thermal analysis was performed in nitrogen with a heating rate of 10°C/min on a NETZSCH STA 409 PC instrument. Variable temperature magnetic susceptibility data were obtained on a polycrystalline sample (16.7 mg) from 2.0 to 300 K in a magnetic field of 2 kOe, using a Quantum Design MPMS-XL7 SQUID magnetometer. The data were corrected for the diamagnetic contributions of the compound obtained from Pascal's constants [12].

A suitable single crystal was chosen from the bulk sample and used for data collection on a Bruker SMART APEX CCD diffractometer using graphite monochromated MoK_α radiation (λ = 0.71073 Å) at room temperature. Crystallographic and refinement details have been reported [10].

[1] The article is published in the original.

BVS calculated assuming different oxidation state of manganese ions in the studied complex

Bonds	Bond length	Mn(II)	Mn(III)	Mn(IV)	Oxidation state
Mn(1)–O(1)	2.251(2)	0.26526	0.24593	0.25819	
Mn(1)–O(3)	2.139(2)	0.36392	0.33287	0.34946	
Mn(1)–O(6)	2.166(2)	0.33831	0.30944	0.32487	
Mn(1)–O(1a)	2.251(2)	0.26526	0.24593	0.25819	
Mn(1)–O(3a)	2.139(2)	0.36392	0.33287	0.34946	
Mn(1)–O(6a)	2.166(2)	0.33831	0.30944	0.32487	
		1.93498	1.77648	1.85246	Mn(II)
Mn(2)–O(1)	2.300(2)	0.23552	0.21542	0.22616	
Mn(2)–O(2)	2.282(2)	0.24726	0.22616	0.23744	
Mn(2)–O(4)	2.101(2)	0.40328	0.36887	0.38726	
Mn(2)–O(5)	2.075(2)	0.43264	0.39572	0.41545	
Mn(2)–N(1)	2.260(4)	0.32929	0.31878	0.30611	
Mn(2)–N(2)	2.271(4)	0.31964	0.30944	0.29715	
		1.96763	1.83439	1.86957	Mn(II)

The atomic coordinates and other parameters of structure I have been deposited with the Cambridge Crystallographic Data Centre (no. 690822; deposit@ ccdc.cam.ac.uk).

Synthesis of $[Mn_3(PhCO_2)_6(Bipy)_2] \cdot H_2O$ was carried out as described elsewhere [10].

RESULTS AND DISCUSSION

Treatment of a solution of $[Mn_3O(O_2CPh)_6(Py)_2(H_2O)]$ in CH_3CN with a mixture solution of 1,1,1-*tris*(hydroxymethyl)methylamine (**L**) and Bipy in CH_2Cl_2 gave a brown solution from which compound **I** was obtained in 46% yield by evaporating slowly at room temperature. The transformation is summarized as in Eq. 1:

$$2[Mn_3O(O_2CPh)_6(Py)_2(H_2O)] + 4Bipy \xrightarrow[CH_2Cl_2]{CH_3CN} 2[Mn_3(PhCO_2)_6(Bipy)_2] \cdot H_2O + 4Py + O_2. \quad (1)$$

Equation 1 is a short cut to represent the overall reaction occurred. This is reasonably deduced from that the $[Mn_2^{III}Mn^{II}O]^{6+}$ unit in the precursor has been reduced to a $[Mn_3^{II}]^{6+}$ species in the product. The oxidation states of manganase ions are assigned on the basis of charge balance. Bond valence sum (BVS) calculations [13] further confirm the assignment (table).

The ligand L, which is expected to display different bridging modes as other tripodal alcohols [14], was not included in the compound. This can clearly be seen from its crystallographic structure (Fig. 1). The results of elemental and thermal analyses further confirm the conclusion.

The structure consists of a $[Mn_3(PhCO_2)_6(Bipy)_2]$ species and one water molecule. The view of the structure is provided in Fig. 1. It shows that the linear complex includes a central octahedral Mn(1) ion located on a crystallographic inversion center. Its coordination sphere is composed of six oxygen atoms from six different benzoates. The central manganase ion is flanked by two octahedrally distorted (Mn(2) and Mn(2*A*)) ions. For the Mn(2) ion, four of its six coordination positions are occupied by the oxygen atoms O(1), O(2), O(4), and O(5) from the benzoate ligands. The remaining two positions are filled with the nitrogen atoms from the Bipy ligand. The Mn–N and Mn–O bond lengths are in a range of 2.075–2.300 Å, which could be compared with that in the similar complexes, $[Mn_3^{II}(CH_3CO_2)_6(Bipy)_2]$ [15], $Mn_3^{II}(AcO)_6(Pybim)_2$ [16], and $[Mn_3^{II}(ClCH_2COO)_6(Bipy)_2]$ [17]. The Mn(1)–Mn(2) distance of 3.588 Å. The Mn(1) and Mn(2) atoms are bridged by six benzoate ligands, four of which show the common μ_2-$\eta^1 : \eta^1$ coordination mode, while the other two adopt the μ_3-$\eta^2 : \eta^1$ coordination mode (Fig. 1).

Assignments manganase ions as Mn(II) are based on the following observations. The trinuclear molecules is neutral and composed of six monoanionic benzoate donors (*e.g.*, benzoates) and two neutral Bipy ligands. Additional support for this oxidation level is provided by the almost equal distances of the Mn–O and Mn–N bond lengths, which is typical of a d^5 system [15, 17]. BVS further confirm this assignments (table).

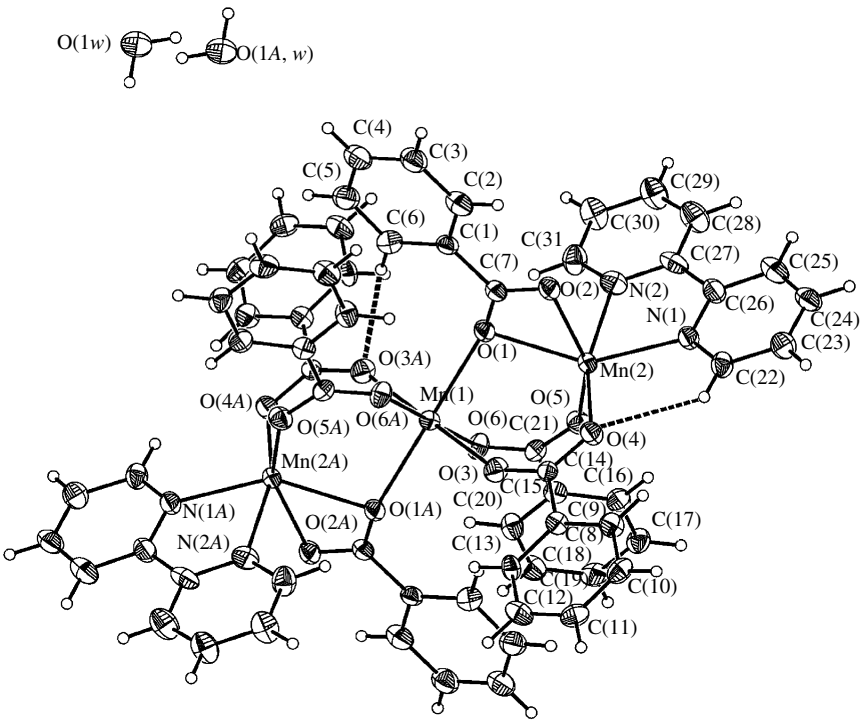


Fig. 1. View of the structure of the compound **I** with atom labeling scheme. The dashed lines represent the intramolecular hydrogen bonds.

There exists intramolecular hydrogen bonds in the trinuclear unit (dashed line in Fig. 1) and intermolecular hydrogen bonds between the units (dashed line in Fig. 2). These intra- and intermolecular hydrogen bond with C···O distance of 3.149(5)–3.458(5) Å and C–H···O angle of >115° are typical of C–H···O hydrogen bonds [18]. The compound then packed together *via* intermolecular C–H···O hydrogen bond, as well as van der Waals attractions (Fig. 2).

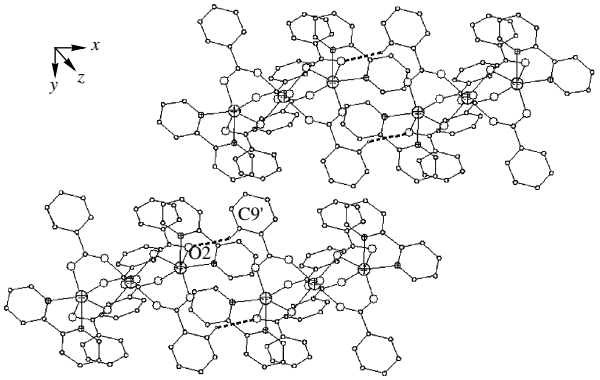
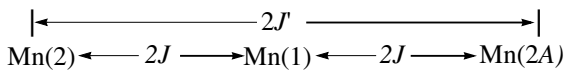


Fig. 2. Packing diagram of the title compound, showing one layer of molecules connected by intermolecular C–H···O hydrogen bonds (dashed lines). All H atoms not included in the intermolecular hydrogen bond were omitted for clarity.

The temperature-dependent dc magnetic susceptibility measurement was performed on the crystalline sample in the temperature range 2.0–300 K in a field of 2 kOe. The $\chi_m T$ value gradually decreases from 12.23 (300 K) to 10.72 cm^3 K mol^{-1} (80 K) before falling rapidly to 4.45 cm^3 K mol^{-1} at 2 K (Fig. 3). The $\chi_m T$ value at room temperature is smaller than the expected value of 13.125 cm^3 K mol^{-1} for three uncoupled Mn(II) ions with $S_i = 5/2$ ($g_j = 2$). This is indicative of an antiferromagnetic coupling, as confirmed by the decrease in $\chi_m T$ when T decreases. At low temperature the $\chi_m T$ value is indicative of an $S_T = 5/2$ spin ground state.

Taking into account the structure of this compound, two exchange pathways are considered. One pathway is between the central metal ion and the terminal metal ones with coupling constant 2J. The other is between two terminal ions with the coupling constant 2J' (Scheme).



Scheme.

We used the following Hamiltonian (Eq. 2) to describe the low-lying electronic states:

$$H = -2J(S_1S_2 + S_1S_{2A}) - 2J'\ S_2S_{2A}, \qquad (2)$$

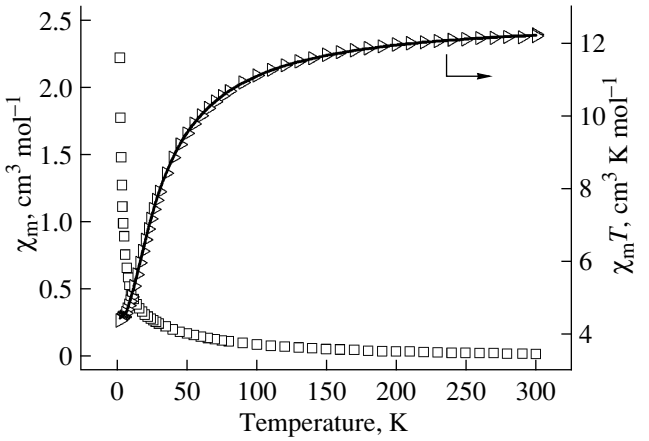


Fig. 3. Molar magnetic susceptibility χ_m and $\chi_m T$ *vs.* temperature.

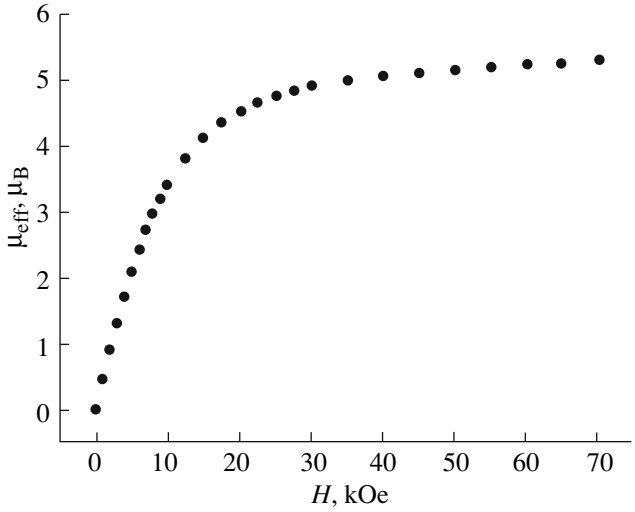


Fig. 4. Plot of isothermal (2 K) magnetization data *vs.* field H for the title compound.

where S_i is the spin of the manganase ion. The Kambe method gives the eigenvalue expression in Eq. 3:

$$E(S, S') = -JS(S+1) - (J'-J)S'(S'+1), \quad (3)$$

where S is the total spin of the molecule and S' is the spin quantum number associated with the spin $S' = S_2 + S_{2A}$ of the terminal Mn(II) ions. We have the conditions $0 \le S' \le 5$ and $|S'-5/2| \le S \le S'-5/2$. However, the magnetic interaction between the terminal manganese ions (Mn(2)···Mn(2A)) in a linear complex is negligible ($J' = 0$) [15, 16], and only the Mn(1)···Mn(2) interaction (J) is considered. Based on the energy of each $|S, S'\rangle$ state for $J' = 0$, the expression of the molar magnetic susceptibility of the trimer (Eq. 4) can easily be derived by applying the Van Vleck formula [12]

$$\chi_{M(Mn_3)} = \frac{Ng^2\beta^2}{3kT}\frac{A}{B}, \quad (4)$$

where $A = 52.5 + 1020x^{27.5} + 682.5x^{20} + 682.5x^{25} + 429x^{13.5} + 429x^{18.5} + 429x^{22.5} + 249x^{8} + 247.5x^{13} + 247.5x^{17} + 247.5x^{20} + 126x^{3.5} + 126x^{8.5} + 126x^{12.5} + 126x^{15.5} + 126x^{17.5} + 54x^{5} + 52.5x^{9} + 52.5x^{12} + 52.5x^{14} + 52.5x^{15} + 15x^{2.5} + 15x^{6.5} + 15x^{9.5} + 15x^{11.5}$;

$B = 6 + 16x^{27.5} + 14x^{20} + 14x^{25} + 12x^{13.5} + 12x^{18.5} + 12x^{22.5} + 12x^{8} + 10x^{13} + 10x^{17} + 10x^{20} + 8x^{3.5} + 8x^{8.5} + 8x^{12.5} + 8x^{15.5} + 8x^{17.5} + 8x^{5} + 6x^{9} + 6x^{12} + 6x^{14} + 6x^{15} + 4x^{2.5} + 4x^{6.5} + 4x^{9.5} + 4x^{11.5}$, and $x = \exp(-J/kT)$. The other symbols have their usual meanings.

Considering the affect of paramagnetic impurities and the contributions of both diamagnetism and temperature independent paramagnetism, the susceptibility expression becomes

$$\chi_m = \chi_{m(Mn_3)}(1-\rho) + 3\chi_{m(Mn)}\rho + N_\alpha,$$

where ρ is the molar ratio of the mononuclear impurities, $\chi_{M(Mn)}$ expresses the molar susceptibility of the impurities, and N_a represents the contributions of both diamagnetism and temperature independent paramagnetism. The $\chi_m T$–T fit in the temperature range 2.0–300 K, shown as the solid line in Fig. 3, gives parameters $J = -2.73$ cm^{-1}, $\rho = 2.07\%$, $N_a = -0.0004$ cm^3 mol^{-1}, $g = 1.992$, and R^2 (coefficient of determination) = 0.99996. The J and g values can be compared with those observed in $[Mn_3^{II}(CH_3CO_2)_6(Bipy)_2]$ [15] ($J = -4.4$ cm^{-1}, $g = 1.99$) and in $[Mn_3^{II}(\mu\text{-}ClCH_2COO)_6(Bipy)_2]$ ($J = -3.82$ cm^{-1}, $g = 2.01$) [17].

The spin ground state $S_T = 5/2$ obtained from the susceptibility data is further verified by the isothermal magnetization measurements as 2 K in applied fields up to 70 kOe (Fig. 4). The field dependence of the magnetization shows a rapid increase of the magnetization, reaching 4.99 μ_B (per Mn_3) at 35 kOe and at last5.31 μ_B (per Mn_3) at 70 kOe. These values are very close to the expected $S = 5/2$ value of 5 μ_B for antiparallel alignment of $Mn^{II}Mn^{II}Mn^{II}$ magnetic moments in a linear Mn_3 cluster.

In conclusion, the magnetic susceptibility data of the title compound were measured and further fitted using the conventional Kambe method. The fitting results explained satisfactorily the antiferromagnetic property of the title compound, as well as its total spin ground state.

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