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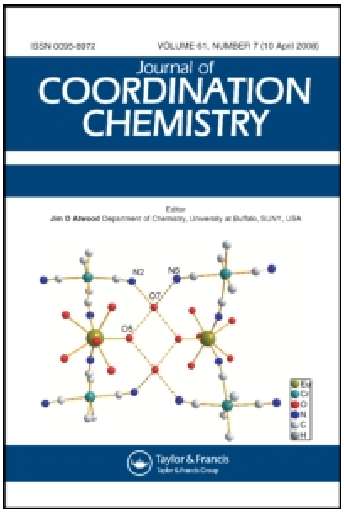

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Structure and magnetism of a linear trimanganese (III, II, III) complex based on benzoate and Schiff-base ligands

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Structure and magnetism of a linear trimanganese (III, II, III) complex based on benzoate and Schiff-base ligands

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Reaction of $[Mn_3O(PhCO_2)_6(py)_2(H_2O)]$ with a tridentate Schiff-base 2-salicylideneaminoethanol (H_2sae) affords a trinuclear manganese complex $[Mn_3(PhCO_2)_4(sae)_2]$ (**1**). X-ray structural analysis of **1** reveals that three manganese ions are linear with each pair bridged by two benzoate groups and one μ-alkoxo oxygen of the sae^{2-} ligand. The central manganese has an octahedral $\{Mn^{II}O_6\}$ configuration and the terminal ones are five-coordinate $\{Mn^{III}NO_4\}$ with a Jahn-Teller elongation axis. The trinuclear complex shows small antiferromagnetic exchange J coupling. The magnetic susceptibility data in the temperature range 2–300 K give the best fitting parameters with $J = -8.44\,cm^{-1}$, $g = 2.02$, $zJ' = -0.34\,cm^{-1}$, and $R^2 = 0.99942$. The magnetization *versus* external magnetic field measurements at 2 K proved that the ground state is $S = 3/2$.

Keywords: Manganese complex; Schiff-base; Antiferromagnetism

1. Introduction

The chemistry of manganese in various states and various nuclearities has received much attention since the discovery of their utility as models for the photosynthetic water oxidation centers [1] and their potential as single-domain nanoscale magnetic particles [2]. The simple manganese triangles of general formula $[Mn_3O(O_2CR)_6(L)_3]$ have been used as precursors to manganese complexes by choosing suitable chelate ligands through conventional synthetic [3–6] or solvothermal method [7]. Among the ligands for assembling these compounds, polydentate Schiff-base ligands based on H_2sae or its derivatives [8–11] can chelate and bridge Mn_3 and Mn_4 centers.

In this article, we report the reaction between $[Mn_3O(PhCO_2)_6(py)_2(H_2O)]$ and the potential chelating ligand H_2sae affording the linear $Mn^{III}Mn^{II}Mn^{III}$ complex $[Mn_3(O_2CPh)_4(sae)_2]$ (**1**). Although several linear $Mn^{III}Mn^{II}Mn^{III}$ compounds have been structurally and magnetically characterized [12–17], **1** is rare in view of the Schiff-base ligand as well as the square pyramidal geometry of the terminal Mn^{III} ions.

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We describe here the preparation, crystal structure and magnetic behavior of new linear trinuclear compound featuring sae^{2-}.

2. Experimental

2.1. *Materials and methods*

The ligand H_2sae was prepared according to the procedure reported by Boskovic [9]. $[Mn_3O(O_2CPh)_6(py)_2(H_2O)]$ was synthesized according to the literature method [18]. All the other starting materials were of reagent grade obtained from commercial sources without further purification.

Elemental analysis was performed in a Flash EA 1112 elemental analyzer. IR spectra were recorded on a VECTOR 22 spectrometer in the range 4000–400 cm^{-1} using KBr disks. Thermal analysis was performed in nitrogen with a heating rate of 10°C min^{-1} on a NETZSCH TG 209 instrument. Variable temperature magnetic susceptibility data were obtained on polycrystalline sample (25.05 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 diamagnetic contributions of the compound from Pascal's constants [19]. Magnetization *versus* external magnetic field measurements were performed on polycrystalline sample (57.4 mg) from 0 to 70 kOe at 2 K to prove the $S = 3/2$ ground state.

2.2. *Synthesis of $[Mn_3(O_2CPh)_4(sae)_2]$ (1)*

The solution of H_2sae (1.0 mmol) in CH_3OH (10 mL) was added dropwise to a solution of $[Mn_3O(O_2CPh)_6(py)_2(H_2O)]$ (0.5 mmol) in CH_3CN (20 mL). After the mixture was stirred for 30 min, the deep-brown filtrate was allowed to evaporate slowly in air. Black crystals of **1** appeared after a few days. Yield: 36% based on Mn. Anal. Calcd for $C_{46}H_{38}Mn_3N_2O_{12}$: C, 56.63; H, 3.93; N, 2.87%. Found: C, 56.94; H, 4.01; N, 3.20%. IR (cm^{-1}, KBr pellets): 3423 m, 3058 w, 3026 w, 2939 w, 2870 w, 1600 s, 1568 s, 1543 m, 1448 m, 1396 s, 1302 m, 1205 w, 1151 w, 1130 w, 1066 w, 1045 w, 1026 w, 941 w, 902 w, 862 w, 835 w, 800 w, 758 m, 719 s, 675 w, 632 m, 586 m, 461 m. Thermogravimetric analysis of **1** shows no weight loss in the temperature range 30–260°C, consistent with no solvent in the structure. The total weight loss (73.3%) is slightly lower than the calculated value of 76.5% for the final product Mn_3O_4.

2.3. *Crystallographic study*

Single crystal of dimension $0.20 \times 0.18 \times 0.18$ mm^3 was affixed to a glass capillary with mother liquid and used for data collection on a Rigaku RAXIS-IV X-ray diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Numbers of collected and observed independent $[I > 2\sigma(I)]$ reflections were 3321 and 2473. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and allowed to ride on their

Table 1. Crystallographic data and refinement parameters for **1**.

Empirical formula	$C_{46}H_{38}Mn_3N_2O_{12}$
Formula weight	975.60
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.230(18)
b (Å)	10.898(2)
c (Å)	11.985(2)
α (°)	88.05(3)
β (°)	75.18(3)
γ (°)	72.37(3)
Volume (Å^3)	1109.5(4)
Z	1
D_{Calcd} (g. cm^3)	1.460
μ(Mo-Kα) (mm^{-1})	0.905
F(000)	499
Total, unique data, R_{int}	3321, 3321, 0.000
Observed data [$I > 2.0\sigma(I)$]	2473
R_1[a], wR_2[b], Goodness-of-fit[c]	0.0738, 0.1946, 1.09
$(\Delta\rho)_{\max}$, $(\Delta\rho)_{\min}$ (e Å^{-3})	−1.30, 0.79

[a] $R_1 = \Sigma || F_o| - |F_c|| / \Sigma |F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$. [c] Goodness-of-fit $= [\Sigma[w(F_o^2 - F_c^2)^2]/(N_{\mathrm{observation}} - N_{\mathrm{parameter}})]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Mn1–O1	1.865(5)	Mn2–O2	2.147(5)
Mn1–O2	1.864(5)	Mn2–O3	2.149(5)
Mn1–O4	2.061(6)	Mn2–O5	2.176(4)
Mn1–O6	1.939(5)	Mn2–O2a	2.147(5)
Mn1–N1	1.981(7)	Mn2–O3a	2.149(5)
Mn1–Mn2	3.439	Mn2–O5a	2.176(4)
O1–Mn1–O2	170.5(3)	O2–Mn2–O3	91.5(2)
O1–Mn1–O4	91.2(2)	O2–Mn2–O5	89.47(19)
O1–Mn1–O6	87.9(2)	O2–Mn2–O2a	180.00
O1–Mn1–N1	90.2(2)	O2–Mn2–O3a	88.5(2)
O2–Mn1–O4	96.7(2)	O2–Mn2–O5a	90.53(19)
O2–Mn1–O6	95.6(2)	O3–Mn2–O5	89.59(19)
O2–Mn1–N1	82.6(2)	O2a–Mn2–O3	88.5(2)
O4–Mn1–O6	101.8(2)	O3–Mn2–O3a	180.00
O4–Mn1–N1	105.6(2)	O3–Mn2–O5a	90.41(19)
O6–Mn1–N1	152.6(3)	O5–Mn2–O5a	180.00

Symmetry code: a = 1 − x, 1 − y, −z.

respective parent atoms. Crystallographic and refinement details of **1** are listed in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Synthesis*

Treatment of an CH_3CN solution of $[Mn_3O(O_2CPh)_6(py)_2(H_2O)]$ with 2 equiv. of H_2sae in CH_3OH gave a brown solution from which a linear trinuclear manganese complex

Table 3. Bond valence sums of **1**.

	Mn(II)	Mn(III)	Mn(IV)	Oxidation
Mn1	3.30251	3.05811	3.14986	Mn(III)
Mn2	2.07282	1.90186	1.99669	Mn(II)

was obtained in 36% yield by slow evaporation at room temperature. The transformation is summarized in equation (1):

$$\begin{aligned}&[\mathrm{Mn_3O(O_2CPh)_6(py)_2(H_2O)}]\\&\quad + 2\mathrm{H_2sae} \xrightarrow{\mathrm{CH_3OH/CH_3CN}} [\mathrm{Mn_3(O_2CPh)_4(sae)_2}]\\&\quad + 2\mathrm{PhCOOH} + 2\mathrm{py} + 2\mathrm{H_2O}\end{aligned} \tag{1}$$

The product is mixed-valence $2\mathrm{Mn^{III}}$ and $\mathrm{Mn^{II}}$, as is the precursor; thus, the formation of **1** appears not to involve redox but just fragmentation and structural rearrangement.

The oxidation states of Mn ions are assigned on the basis of charge balance, bond lengths and the presence of Jahn-Teller elongation axis on Mn1 and Mn1A ions. Bond valence sum calculations [20] further confirm the assignment (table 3). In addition, the $S = 3/2$ ground state, as shown below, was also proved by the oxidation states of Mn ions.

3.2. *Description of crystal structure*

Compound **1** crystallized in the triclinic space group $P\bar{1}$; the molecular geometry and the atom-labeling scheme are shown in figure 1. The core of **1** includes three linear manganese ions. The Mn1 ⋯ Mn2 distance of 3.439 Å and the intramolecular Mn1 ⋯ Mn1A separation of 6.878 Å have been found. The central metal Mn2, which is located on a crystallographic inversion center, is coordinated octahedrally by four oxygen atoms (O3, O3A, O5 and O5A) from four benzoate and two μ–alkoxo oxygens (O2 and O2A) of the Schiff-base ligand. The Mn–O distances are in the narrow range of 2.147(5)–2.176(4) Å, comparable to those in other $\mathrm{Mn^{II}O_6}$ octahedra [13, 21] and Mn2 is accordingly determined as Mn(II). The terminal manganese ions, Mn1 and Mn1A, have a distorted square-pyramidal geometry. The basal plane is occupied by an {O N O} donor set of $\mathrm{sae^{2-}}$ and one benzoate oxygen (O6) with Mn–N bond distance 1.981(7) Å and Mn–O bond distances in the range 1.864(5)–1.939(5) Å; the apical position is benzoate oxygen (O4) with bond distance 2.061(6) Å. The axial bond length is distinctly longer than those in the equatorial plane. Such marked axial elongation is typical for a high-spin d^4 system [11]; the Mn1 and Mn1A are thus regarded as Mn(III). The most reasonable valence is thus assigned as $\mathrm{Mn^{III}Mn^{II}Mn^{III}}$ considering bond distances, Jahn-Teller elongation axis as well as calculation of charge balance.

As in other manganese clusters [8, 9], the $\mathrm{sae^{2-}}$ ligands in **1** coordinate in a bis-chelating fashion, with the ethoxo-type O atom serving in a bridging capacity between Mn centers. The adjacent Mn ions are connected by the ethoxo oxygen and two benzoate ligands, thus forming a $\mathrm{Mn_3}$ unit. The $\mathrm{Mn_3}$ units are held together by van der Waals attractions in the three-dimensional space; there is no solvent molecule between the units (figure 2).

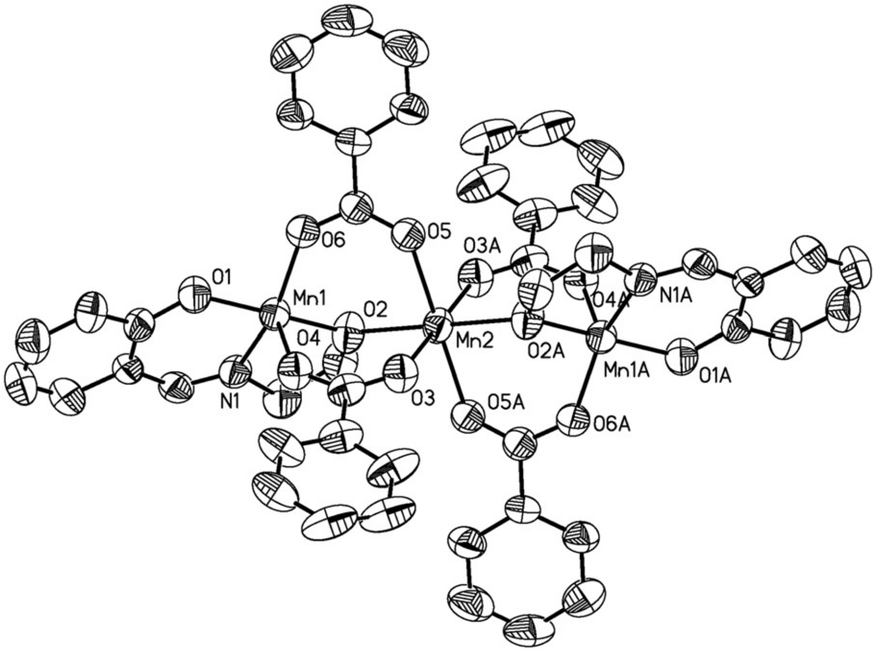


Figure 1. ORTEP drawing of **1** with atomic numbering scheme for selected atoms (50% probability level), where symmetry operation (A): $1-x$, $1-y$, $-z$. Hydrogen atoms are omitted for clarity.

The structure of **1**, which has strictly 180° $Mn^{III}{-}Mn^{II}{-}Mn^{III}$ angles as required by the crystallographic inversion symmetry, is very similar to other trimers reported by Kessissoglou, such as $Mn^{III}Mn^{II}Mn^{III}$(5-Cl-Hsaladhp)$_2$(OAc)$_4$(CH$_3$OH)$_2 \cdot 4$CH$_3$OH [12] and $Mn^{III}Mn^{II}Mn^{III}$(Hsaladhp)$_2$(Sal)$_4 \cdot 2$CH$_3$CN [22] but is distinguished from the bent mixed-valence compound, $Mn^{III}Mn^{II}Mn^{III}$(saladhp)$_2$(OAc)$_4$(CH$_3$OH)$_2$ [23].

3.3. *Magnetic property*

Temperature-dependent dc magnetic susceptibility measurement was performed on polycrystalline **1** in the temperature range 2.0–300 K in a field of 2 kOe. The $\chi_m T$ value gradually decreases from 7.76 cm^3 K mol^{-1} at 300 K to 1.77 cm^3 K mol^{-1} at 10 K before falling rapidly to 1.11 cm^3 K mol^{-1} at 2 K (figure 3). The profile is characteristic of an antiferromagnetic system. This is verified by the fact that $\chi_m T$ at 300 K (7.76 cm^3 K mol^{-1}) is lower than the expected $\chi_m T$ value of 10.375 cm^3 K mol^{-1} for uncoupled Mn(III) ions with $S_i = 2$ and one Mn(II) ion with $S_i = 5/2$ ($g_i = 2$).

From the structure of this compound, two exchange passways are considered. One is between the central Mn^{2+} and the terminal ones with coupling constant $2J$. The other is between two terminal ions with coupling constant $2J'$ (scheme 1). We used the following Hamiltonian (equation (2)) to describe the low-lying electronic states

$$H = -2J(S_1 \cdot S_2 + S_2 \cdot S_1\mathrm{A}) - 2J' S_1 \cdot S_1\mathrm{A} \qquad (2)$$

where S_i is the spin of the Mn ion number i in figure 1.

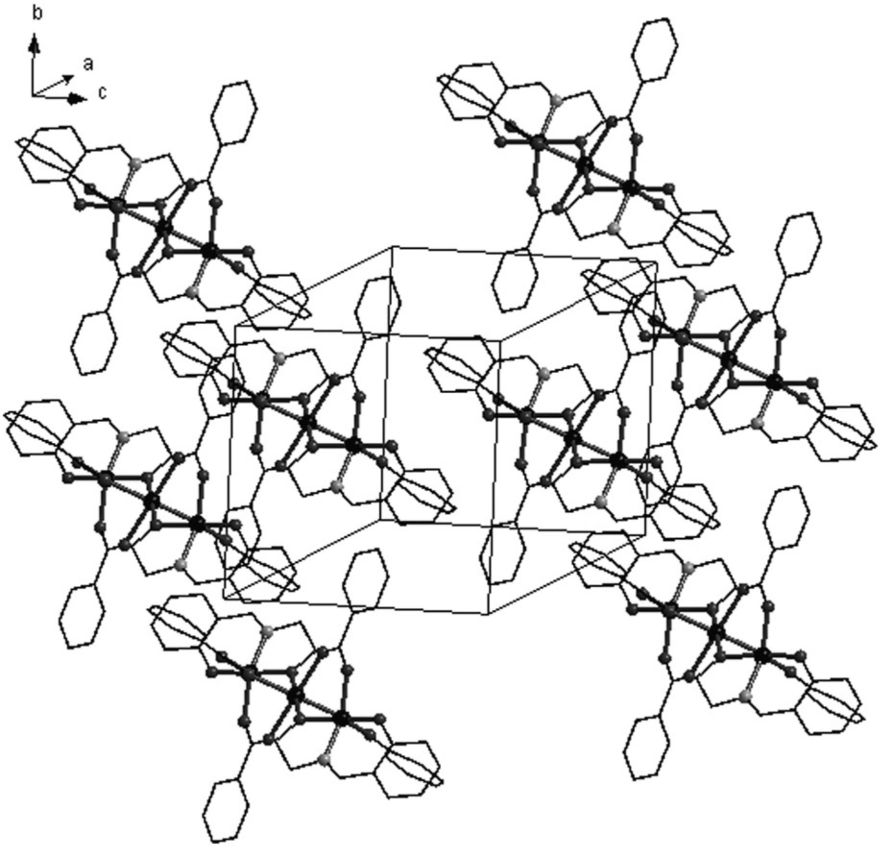
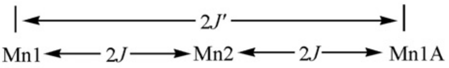


Figure 2. Perspective view of the three-dimensional framework of **1**. All H atoms are omitted for clarity.



Scheme 1.

The Kambe method gives the eigenvalue expression in equation (3):

$$E(S, S') = -JS(S+1) - (J' - J)S'(S'+1) \tag{3}$$

where S is the total spin of the molecule and S' is the spin quantum number associated with the spin $S' = S_1 + S_{1A}$ of the terminal Mn ions. We have the conditions $0 \leq S' \leq 4$ and $|S' - 5/2| \leq S \leq S' + 5/2$. The possible values for S and S' can be obtained together with the energy of each spin state in the case of $J' = 0$ (table 4). Based on the energy of each $|S, S'|$ state for $J' = 0$, the expression of the molar magnetic susceptibility of the trimer (equation (4)) can be easily derived by applying the Van Vleck formula [19].

$$\chi_{\mathrm{M}} = \frac{Ng^2\beta^2}{3kT}\frac{A}{B} \tag{4}$$

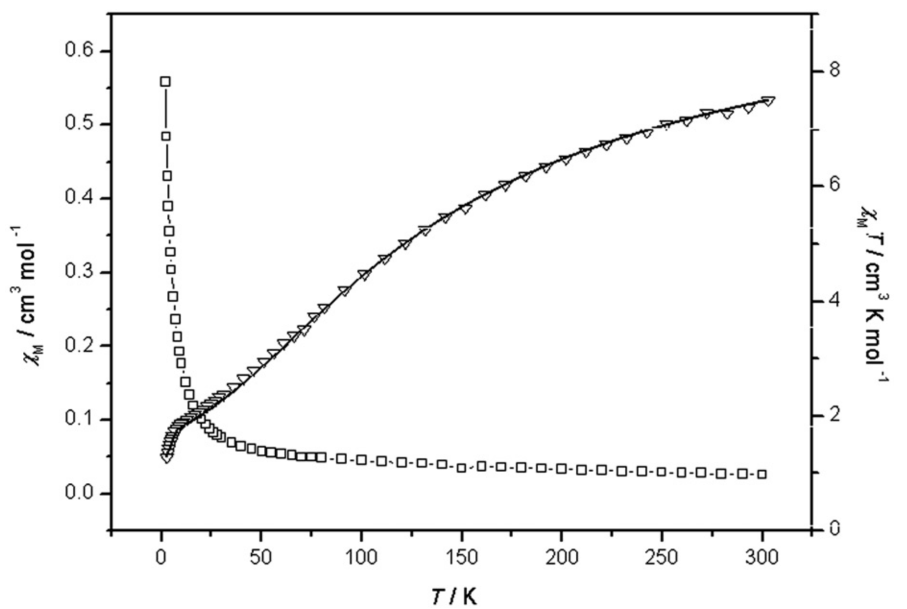


Figure 3. Magnetic susceptibility of **1** plotted as χ_M *vs.* T (left axis) and $\chi_M T$ *vs.* T (right axis) with the fit to equation (5) (solid line).

Table 4. Values of the total spin S, the subspin S', and the energy of each $|S, S'|$ state in **1** for $J' = 0$.

S	S'	$E(S, S')$ (J)	S	S'	$E(S, S')$ (J)
1/2	3	40	7/2	4	33
	2	34		3	25
	1	30		2	19
3/2	4	45		1	15
	3	37	9/2	4	24
	2	31		3	16
	1	27		2	10
5/2	4	40	11/2	4	13
	3	32		3	5
	2	10	13/2	4	0
	1	22			
	0	20			

where $A = 682.5 + 429x^{13} + 429x^5 + 247.5x^{24} + 247.5x^{16} + 247.5x^{10} + 126x^{33} + 126x^{25} + 126x^{19} + 126x^{25} + 52.5x^{40} + 52.5x^{32} + 52.5x^{10} + 52.5x^{22} + 52.5x^{20} + 15x^{45} + 15x^{37} + 15x^{31} + 15x^{27} + 1.5x^{40} + 1.5x^{34} + 1.5x^{30}$, $B = 14 + 12x^{13} + 12x^5 + 10x^{24} + 10x^{16} + 10x^{10} + 8x^{33} + 8x^{25} + 8x^{19} + 8x^{25} + 6x^{40} + 6x^{32} + 6x^{10} + 6x^{22} + 6x^{20} + 4x^{45} + 4x^{37} + 4x^{31} + 4x^{27} + 2x^{40} + 2x^{34} + 2x^{30}$, and $x = \exp(-J/kT)$. The other symbols have their usual meanings.

Because of the van der Waals attractions a mean field correction was added and the final expression of the susceptibility is given by equation (5):

$$\chi_{MFC} = \frac{\chi_M}{1 - (2zJ'\chi_M/N\beta^2 g^2)} \tag{5}$$

where zJ' is the inter-cluster coupling constant.

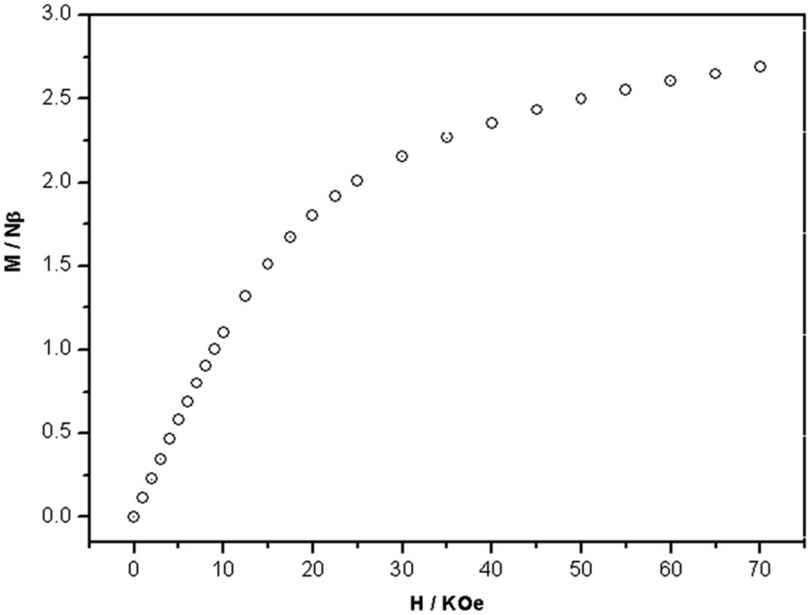


Figure 4. Plot of isothermal (2 K) magnetization data *vs.* field, *H*, for **1**.

The magnetic susceptibility data for **1** are fit by equation (5) in the temperature range 2–300 K (figure 3). The best fitting parameters are: $J = -8.44\,\mathrm{cm}^{-1}$, $g = 2.02$, $zJ' = -0.34\,\mathrm{cm}^{-1}$, and R^2 (coefficient of determination) = 0.99942. The fitting values approximate to that observed in $\mathrm{Mn_3(Hsaladhp)_2(AcO)_2(5\text{-}Cl\text{-}sal)_2(thf)_2}$ ($J = -5.6\,\mathrm{cm}^{-1}$, $g = 1.95$, $zJ' = -0.25\,\mathrm{cm}^{-1}$) [12] and can also be compared with that observed in $\mathrm{[Mn_3(O_2CCH_3)_4(sae)_2(Him)_2]}$ ($J/k = -10.61\,\mathrm{K}$, $g = 2.00$) [11] and in $\mathrm{[Mn_3(SALADHP)_2(OAc)_4(CH_3OH)_2]}$ ($J/k = -10.22\,\mathrm{K}$, $g = 2.04$) [13]. The negative value of J and zJ' imply an antiferromagnetic exchange interaction within the trimers and a weak antiferromagnetic exchange interaction among the trimers, respectively.

The field dependence of the magnetization (0–70 kOe) measured at 2.0 K shows a rapid increase of magnetization, reaching 2.69 $N\beta$ per $\mathrm{Mn_3}$ at 70 kOe, very close to the Brillouin function with $S = 3\,N\beta$ for anti-parallel alignment of $\mathrm{Mn^{III}Mn^{II}Mn^{III}}$ magnetic moments in a linear $\mathrm{Mn_3}$ (figure 4). This clearly shows that the lowest state was $S_\mathrm{T} = 3/2$. The same ground state is also designated to the mixed-valence tirmanganese complex $\mathrm{Mn^{III}Mn^{II}Mn^{III}(Hsaladhp)_2(Sal)_4 \cdot 2CH_3CN}$ [22] and the homologous series of complexes $\mathrm{Mn^{III}Mn^{II}Mn^{III}(SALADHP)_2(acetate)_4(x)_2}$ ($\mathrm{x{=}CH_3OH, H_2O}$, Hpyro) [14].

Supplementary data

Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre with deposition No. CCDC 630845. Copy of the information can be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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