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Synthesis, structure and magnetic properties of the first two-dimensional infinite sheet-like mixed-valence manganese(II,III) complex with bridging salicylate and pyridine-2-carboxylate ligands †

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A two-dimensional infinite sheet-like mixed-valence manganese(II,III) complex $[\{Na_2Mn_4(sal)_4(pyca)_4(MeOH)_2\}_n]\cdot 2nH_2O$ (H_2sal = salicyclic acid and Hpyca = pyridine-2-carboxylic acid) has been prepared and characterized by X-ray crystallography and magnetic measurements. The structure consists of a $[Mn_4(sal)_4(pyca)_4(MeOH)_2]_n^{2n-}$ anion, $2nNa^+$ cations and $2n$ non-coordinated H_2O. In every $[Mn_4(sal)_4(pyca)_4(MeOH)_2]^{2-}$ unit there are two six-co-ordinate Mn^{III} [Mn(1) and Mn(2)] located at symmetry centres, and two six-co-ordinate Mn^{II} [Mn(3) and Mn(3′)]. Atoms Mn(1) and Mn(3) [or Mn(2) and Mn(3)] are connected by a salicylate (pyridine carboxylate) carboxylate in a *syn-anti* configuration, while Mn(3) and Mn(3′) are bridged by two oxygen atoms of two pyridine carboxylates. The Na^+ cation is six-co-ordinated, having contacts with six oxygens of carboxylate groups of Mn(1), Mn(2) and Mn(3) polyhedral units. The magnetic behaviour of the complex in the temperature range 1.4–300 K has been interpreted in terms of a dimer unit $[Mn^{II}_2(pyca)_2]$ and two manganese(III) polyhedral units assuming the Mn^{III} to obey a Curie–Weiss law, and the values obtained for J, g and θ were -0.98 cm^{-1}, 2.00 and -5.66 K (-3.93 cm^{-1}), respectively.

The chemistry of manganese in various oxidation states and various nuclearities with primarily carboxylate ligation is currently receiving much attention[1] for a variety of reasons, including Mn-containing biological systems[2] and the desire to prepare molecular species with high-spin ground states.[3] A number of mixed-valence manganese multinuclear complexes[4–7] as well as one-dimensional chain complex polymers of Mn^{II} or Mn^{III} [8–12] have been structurally and magnetically characterized, but no two-dimensional sheet-like or three-dimensional network mixed-valence manganese(II,III) complex has been reported till now. In this paper we present the preparation, crystal structure and magnetic behaviour of the first two-dimensional infinite sheet-like mixed-valence manganese(II,III) complex $[\{Na_2Mn_4(sal)_4(pyca)_4(MeOH)_2\}_n]\cdot 2nH_2O$ (H_2sal = salicylic acid, Hpyca = pyridine-2-carboxylic acid).

Experimental

Preparation

All reagents were reagent grade; $[NBu_4][MnO_4]$ was prepared as described previously.[13] All manipulations were performed under aerobic conditions; appropriate care should be taken in the use of $[NBu_4][MnO_4]$. The compound $[\{Na_2Mn_4(sal)_4(pyca)_4(MeOH)_2\}_n]\cdot 2nH_2O$ **1** was prepared as follows. Sodium salicylate (3.50 mmol), pyridine-2-carboxylic acid (3.50 mmol) and $Mn(O_2CMe)_2\cdot 4H_2O$ (2.50 mmol) were dissolved in methanol (45 cm^3) to give a clear yellow-green solution. The solution was stirred while solid $[NBu_4][MnO_4]$ (0.80 mmol) was added in small portions over approximately 20 min leading to a black liquor. After stirring for 30 min the solution was filtered to remove a little brown material and the filtrate layered with hexane. A month later dark green crystals suitable for X-ray diffraction studies were obtained, yield *ca.* 64% (based on available Mn) (Found: C, 46.10; H, 3.25; Mn, 16.00; N, 3.85. Calc. for $C_{54}H_{44}Mn_4N_4Na_2O_{24}$: C, 46.35; H, 3.15; Mn, 15.70; N, 4.00%).

Physical measurements

Magnetic measurements on powder samples were carried out with a CF-1 type extracting sample magnetometer in the temperature range 1.4–300 K. A correction for the diamagnetism of the complex was estimated from Pascal's constants to be -640.01×10^{-6} cm^3 mol^{-1} (per 4Mn) and the temperature-independent paramagnetism as 50×10^{-6} cm^3 mol^{-1} per Mn^{III}.[14]

Crystallography

Cell parameters and reflection intensities were measured at 293(2) K on an Rigaku AFC6 four-circle diffractometer. The unit-cell parameters were determined on the basis of reflections having 2θ 21.52–25.36. Intensity measurements employed graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) and the ω–2θ scan mode in the range $3 < 2\theta < 50°$. Lorentz-polarization corrections were made but not absorption corrections. The structure solution by direct methods (MULTAN)[15] revealed the metal atom coordinates and subsequent Fourier-difference methods yielded the positions of all remaining non-H atoms and most of the hydrogen atoms. All non-H atoms were refined anisotropically, while the hydrogen atoms, located from the Fourier-difference map, were allowed to ride on the related carbon atoms with fixed isotropic thermal parameters. Refinement on F^2 converged at R = 0.0606 and R' = 0.1600 for 3197 observed reflections with $F_o > 4\sigma(F_o)$ of 4138 independent ones; $w = 1/[\sigma^2(F_o^2) + (0.1397P)^2 + 0.63P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$. Scattering factors were taken from ref. 16. A summary of the crystal data is given in Table 1.

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† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

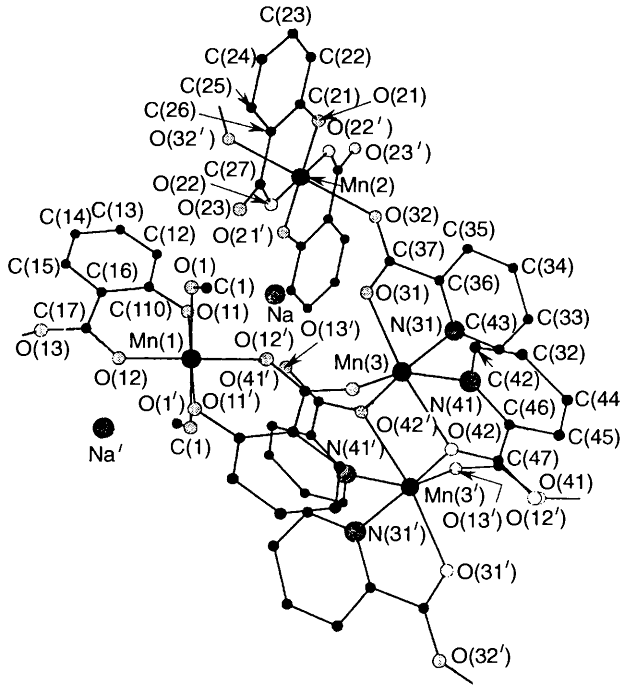


Fig. 1 Perspective view of the unit $Na_2[Mn_4(sal)_4(pyca)_4(MeOH)_2]\cdot 2H_2O$ of the complex (the two water molecules of crystallization and all hydrogen atoms are omitted for clarity)

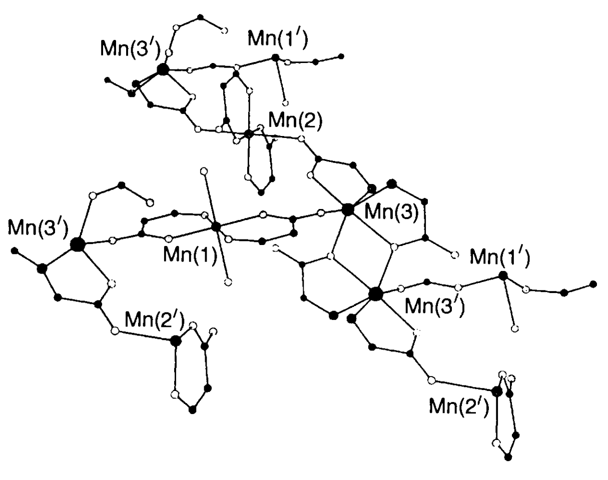


Fig. 2 Perspective view of part of $[Mn_4(sal)_4(pyca)_4(MeOH)_2]_n{}^{2n-}$ (all hydrogen atoms and some carbon atoms of benzene rings are omitted for clarity)

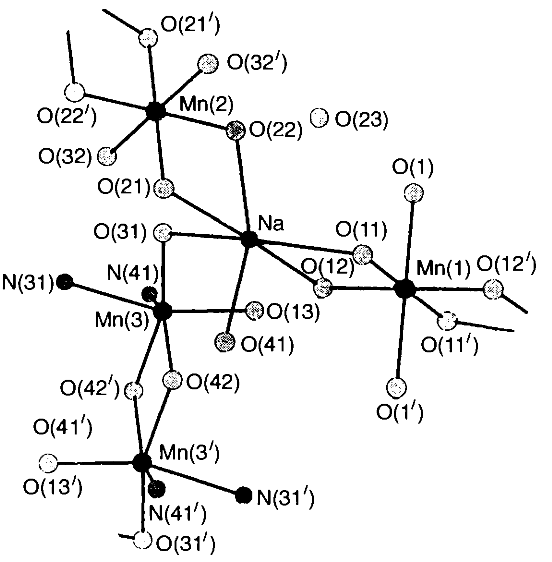


Fig. 3 View of part of $[\{Na_2Mn_4(sal)_4(pyca)_4(MeOH)_2\}_n]$ showing the co-ordination environment of Na^+ (only metal atoms and co-ordinated O, N atoms for clarity)

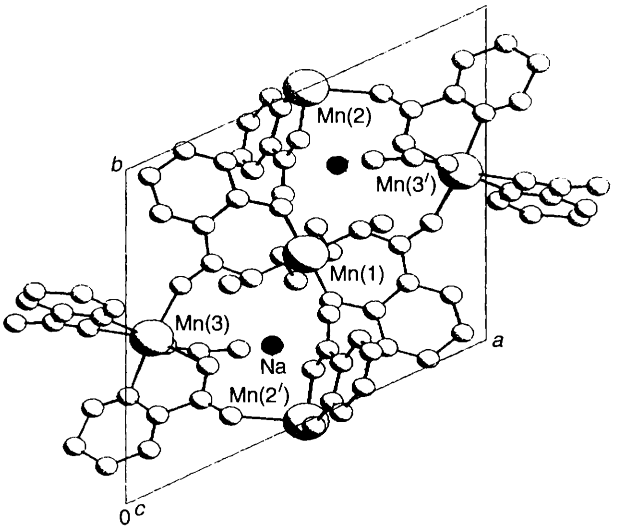


Fig. 4 View of the crystal packing down the *c* axis in a unit cell

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/68.

Results and Discussion

Crystal structure

Views of the structure are depicted in Figs. 1–4. The structure of the complex consists of a two-dimensional sheet-like $[Mn_4(sal)_4(pyca)_4(MeOH)_2]_n{}^{2n-}$ anion, $2n$Na$^+$ cations and $2n$ H_2O. In every $[Mn_4(sal)_4(pyca)_4(MeOH)_2]^{2-}$ unit of the anion there are two six-co-ordinate manganese(III) ions [Mn(1) and Mn(2)] located on the symmetry centre and two six-co-ordinate manganese(II) ions [Mn(3), Mn(3′)]. Atoms Mn(1) and Mn(3) are connected by a salicylate carboxylate in *syn-anti* configuration, while Mn(2) and Mn(3) are bridged by pyridine-2-carboxylate in *syn-anti* configuration; Mn(3) and Mn(3′) are bridged by two oxygen atoms of two carboxylates. So the crystal structure is a mixed-valence manganese(II,III) two-dimensional network with bridging carboxylate groups from salicylates and pyridine carboxylates (as shown in Figs. 2 and 4).

The Mn(1) octahedron. As illustrated in Fig. 1, Mn(1) is six-co-ordinate by two bidentate salicylate ligands which form an equatorial plane [O(11), O(12), O(11′), O(12′)] and two MeOH molecules [O(1), O(1′)] occupying the apical positions. The in-plane carboxylate and phenolate oxygens [O(12), O(11)] are at relatively short distances of 1.926(3) and 1.864(3) Å, respectively. In contrast, the co-ordinated methanol oxygens are at the longer distance of 2.233(3) Å. Such marked axial elongations are typical for high-spin d^4 systems. The Mn(1)–O bond lengths are similar to corresponding values in manganese(III) complexes,[11,12] so Mn(1) is assigned as Mn^{III}. The angles at Mn(1) subtended by *cis* and *trans* ligand atoms are reasonably close to theoretical values for an octahedron (90 and 180°, respectively, as shown in Table 2). The salicylate is planar. There is hydrogen bonding between the co-ordinated MeOH and salicylate carboxylate through O(1)–H(1) ··· O(11). The O(1) ··· O(11) distance is 2.847 Å.

Table 1 Crystal data for complex **1**

Formula	$C_{54}H_{44}Mn_4N_4Na_2O_{24}$
M	1398.68
Crystal symmetry	Triclinic
Space group	$P\bar{1}$
a/Å	12.350(3)
b/Å	13.681(3)
c/Å	11.450(3)
α/°	62.80(1)
β/°	83.90(1)
γ/°	61.66(1)
U/Å^3	1499.2(6)
Z	1
D_c/g cm^{-3}	1.549
μ(Mo-Kα)/mm^{-1}	0.922
Crystal size/mm	0.5 × 0.5 × 0.6
No. independent reflections	4138
No. observed reflections [$F_o > 4\sigma(F_o)$]	3197
Goodness of fit	1.061
R^a	0.0606
R'^b	0.1600
Largest difference peak and hole/e Å^{-3}	0.90, −0.38

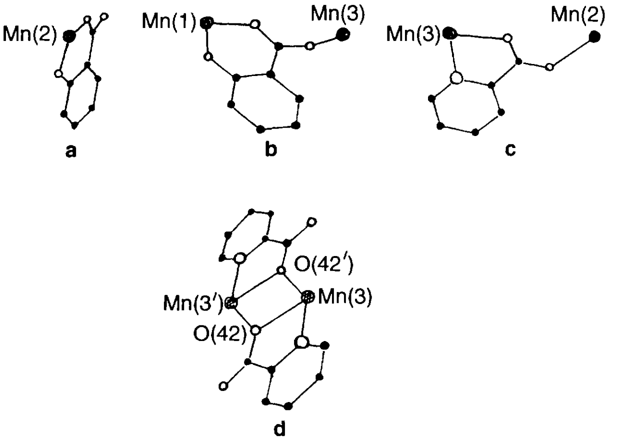
[a] $\Sigma|F_o - F_c|/\Sigma|F_o|$. [b] $\Sigma w(F_o - F_c)^2/\Sigma wF_o^2$.

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

Mn(1)–O(1)	2.233(3)	Mn(1)–O(11)	1.864(3)
Mn(1)–O(12)	1.926(3)	Mn(2)–O(21)	1.882(3)
Mn(2)–O(22)	1.915(3)	Mn(2)–O(32)	2.235(2)
Mn(3)–O(13′)	2.105(3)	Mn(3)–O(31)	2.149(2)
Mn(3)–O(42)	2.133(3)	Mn(3)–O(42′)	2.219(2)
Mn(3)–N(31)	2.295(3)	Mn(3)–N(41)	2.275(3)
Na–O(11)	2.450(3)	Na–O(12)	2.504(3)
Na–O(21)	2.750(9)	Na–O(22)	2.407(3)
Na–O(31)	2.384(3)	Na–O(41)	2.368(3)
Mn(1) ··· Mn(3)	5.593(2)	Mn(2) ··· Mn(3)	5.793(2)
Mn(1) ··· Mn(2)	6.616(2)	Mn(3) ··· Mn(3′)	3.469(2)
Mn(1) ··· Na	3.480(2)	Mn(2) ··· Na	3.511(2)
Mn(3) ··· Na	3.691(2)		
O(11)–Mn(1)–O(12′)	93.1(1)	O(11)–Mn(1)–O(12)	86.8(1)
O(11′)–Mn(1)–O(12)	93.1(1)	O(11)–Mn(1)–O(1′)	92.4(1)
O(12)–Mn(1)–O(1′)	90.4(1)	O(11)–Mn(1)–O(1)	87.6(1)
O(12)–Mn(1)–O(1)	89.6(1)	O(21)–Mn(2)–O(22′)	86.7(1)
O(21)–Mn(2)–O(22)	93.3(1)	O(21)–Mn(2)–O(32′)	88.2(1)
O(22)–Mn(2)–O(32′)	88.4(1)	O(21)–Mn(2)–O(32)	91.8(1)
O(22)–Mn(2)–O(32)	91.6(1)	O(13)–Mn(3)–O(42)	95.7(1)
O(13)–Mn(3)–O(31)	94.0(1)	O(42)–Mn(3)–O(31)	101.1(1)
O(13)–Mn(3)–O(42′)	104.1(1)	O(42)–Mn(3)–O(42′)	74.3(1)
O(31)–Mn(3)–O(42′)	161.6(1)	O(13)–Mn(3)–N(41)	84.9(1)
O(42)–Mn(3)–N(41)	144.5(1)	O(31)–Mn(3)–N(41)	114.3(1)
O(42′)–Mn(3)–N(41)	71.2(1)	O(13)–Mn(3)–N(31)	161.8(1)
O(42)–Mn(3)–N(31)	99.7(1)	O(31)–Mn(3)–N(31)	73.7(1)
O(42′)–Mn(3)–N(31)	89.3(1)	N(41)–Mn(3)–N(31)	87.9(1)

The Mn(2) octahedron. As can be seen in Fig. 1, Mn(2) is also six-co-ordinated with four of its sites occupied by bidentate salicylate oxygen atoms [O(21), O(22), O(21′), O(22′)], which are in a good equatorial plane. However the apical atoms are carboxylate oxygens [O(32), O(32′)] from two pyridine carboxylates bridging Mn(3) and Mn(3′). The Mn(2) is also assigned as Mn^{III} because the Mn(2)–O bond lengths [1.882(3) and 1.915(3) in plane and 2.235(2) Å apical] correspond to those of Mn(1).

The Mn(3) octahedron. The Mn(3) possesses an N_2O_4 octahedral environment by virtue of two bidentate pyridine carboxylates [N(31), O(31), N(41), O(42)] and two bridging carboxylate oxygen atoms [O(13′), O(42′)] from a salicylate carboxylate of Mn(1) and a pyridine carboxylate of Mn(3′), respectively. The best mean equatorial plane is comprised of O(31), O(42), O(42′) and N(41), and the deviation of Mn(3) from this plane is 0.1402 Å. The Mn(3)–O distances (average 2.152 Å) are significantly longer than those of Mn(1)–O and Mn(2)–O, but are similar to those in the literature for a manganese(II) complex [12] (average 2.192 Å). The Mn(3)–N bond lengths (average 2.285 Å) are consistent with Mn^{II}–N distances (average 2.280 Å).[12] So Mn(3) is assigned as Mn^{II}. The bond angles of the Mn(3) octahedron deviate from theoretical values (90 and 180° respectively, as shown in Table 2), due to the restriction by the five-membered chelate rings of the bidentate pyridine carboxylate and Mn_2O_2 [Mn(3), Mn(3′), O(42), O(42′)] four-membered ring in the bridging region which is a good planar rhombus with Mn(3)–O(42)–Mn(3′) 105.67° and O(42)–Mn(3)–O(42′) 74.33°.



In the present structure there are two kinds of binding mode for salicylate or pyridine-2-carboxylate ligands. To our knowledge, the bridging mode (**d**) of pyridine-2-carboxylate is rare.

Sodium octahedron. Charge balance is achieved by the incorporation of two Na^+ cations associated with each $[Mn_4(sal)_4(pyca)_4(MeOH)_2]^{2-}$ anion. Both are six-co-ordinated, having contacts with six oxygens [O(11), O(12), O(21), O(22), O(31), O(41)] from the carboxylate groups of the Mn(1), Mn(2) and Mn(3) octahedral units, respectively, as shown in Fig. 3. The average Na–O distance (2.477 Å) is very close to the value predicted by Shannon [17] (Na^+–O 2.40 Å) and similar to that of $Na_2[Mn(sal)_2(MeOH)_2][Mn(sal)_2]$ (Na^+–O 2.453 Å).[11] The average Mn ··· Na separation is 3.560 Å [Mn(1) ··· Na 3.480, Mn(2) ··· Na 3.511, Mn(3) ··· Na 3.691 Å] and much shorter than the Mn ··· Mn separations [Mn(1) ··· Mn(3) 5.593, Mn(2) ··· Mn(3) 5.793, Mn(1) ··· Mn(2) 6.616 Å]. The sodium and Mn(1) [or Mn(2)] octahedra share edges, while the octahedra of Mn(3) and Na share apices.

Magnetic properties

The temperature dependence of the magnetic susceptibility per $[Na_2Mn_4(sal)_4(pyca)_4(MeOH)_2]\cdot 2H_2O$ ($2Mn^{II}$, $2Mn^{III}$) unit of the complex in the form of χ_m *versus* T is shown in Fig. 5. The effective magnetic moment per 4Mn at 300 K is 10.65 μ_B which is in accord with the spin-only moment (10.86 μ_B) in the absence of any exchange interaction. Upon cooling, the magnetic moment remains unchanged down to about 140 K, then decreases from 10.58 μ_B at 130 K to 10.08 μ_B at 28 K, and to 3.76 μ_B at 1.49 K (Fig. 6).

The magnetic behaviour of the two-dimensional infinite sheet-like mixed-valence manganese(II,III) complex is quite complicated owing to exchange interactions, low-symmetry ligand field, g-tensor anisotropy and the d^4 ion Jahn–Teller effect, and no theoretical model is available. Accordingly, we simplified the magnetic system to the exchange interaction in a dinuclear Mn^{II}_2 unit bridged by two oxygen atoms of pyridine carboxylates $[Mn^{II}_2(pyca)_2]$ and two manganese(III) polyhedral units as point magnets.

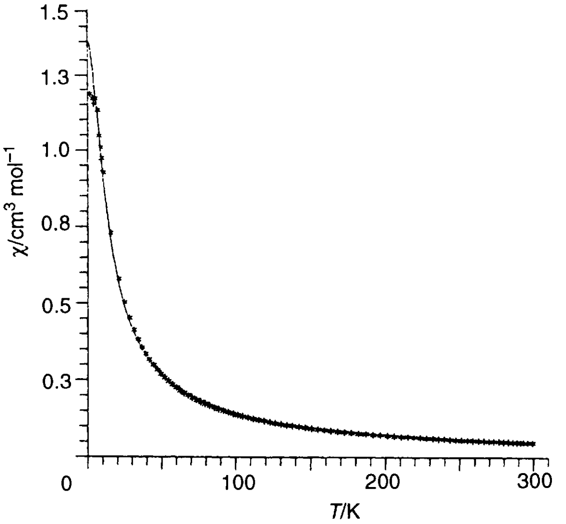


Fig. 5 Experimental (*) and calculated (–) temperature-dependent magnetic susceptibility per $[Na_2Mn_4(sal)_4(pyca)_4(MeOH)_2]\cdot2H_2O$

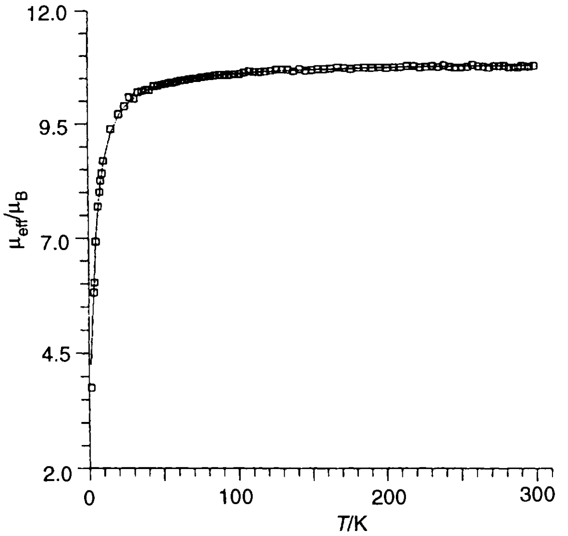


Fig. 6 Experimental (□) and calculated (–) temperature-dependence of μ_{eff} per $[Na_2Mn_4(sal)_4(pyca)_4(MeOH)_2]\cdot2H_2O$

The magnetic susceptibility can then be described by equation (1), where χ_1, χ_2 are the magnetic susceptibilities for

$$\chi_m = \chi_1 + 2\chi_2 \qquad (1)$$

the dinuclear manganese(II) unit and for Mn^{III}, respectively. For the dinuclear unit the exchange Hamiltonian is $H = -JS_1S_2$ where $S_1 = S_2 = \frac{5}{2}$, and the magnetic susceptibility expression[18] is (2) where N, g, β, x are the Avogadro

$$\chi_1 = (2Ng^2\beta^2/kT)\,[(e^x + 5e^{3x} + 14e^{6x} + 30e^{10x} + 55e^{15x})/(1 + 3e^x + 5e^{3x} + 7e^{6x} + 9e^{10x} + 11e^{15x})] \qquad (2)$$

number, g factor, Bohr magneton and J/kT, respectively, and J is the exchange coupling constant in the dinuclear unit. Assuming that the manganese(III) unit obeys the Curie–Weiss law, with Weiss constant θ as a weak exchange term and zero-field splitting of Mn^{III}, its magnetic susceptibility can be written as in equation (3).

$$\chi_2 = 2Ng^2\beta^2/[K(T - 0)] \qquad (3)$$

Using equation (1), a least-squares fit to the magnetic susceptibility data gave the parameters: $J = -0.98$ cm ^{1}, $g = 2.00$, $\theta = -5.66$ K (-3.93 cm^{-1}) and $R = 4.82 \times 10^{-4}$ $[=\Sigma(\chi_{calc} - \chi_{obs})^2/\Sigma(\chi_{obs})^2]$. The magnetic susceptibility (effective magnetic moment) calculated by using these parameters is shown as the solid line in Fig. 5 (Fig. 6). Considering that the exchange interaction through the salicylate carboxylate group, which links two Mn (Mn^{II} and Mn^{III} or two Mn^{III}) in *syn-anti* configuration is very weak (-0.2 cm ^{1}),[11,12] the Weiss constant θ is mainly attributable to zero-field splitting (D) of the manganese(III) ions and in agreement with literature values (-1 to -9 cm^{-1}) for most high-spin manganese(III) complexes.[11,12,19]

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