Synthesis, crystal structures and magnetic properties of 1D polymeric $[Mn^{III}(salen)N_3]$ and $[Mn^{III}(salen)Ag(CN)_2]$ complexes

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The syntheses, crystal structures and variable temperature (5–300 K) magnetic susceptibility measurements of two salen complexes of manganese(III) [where H_2salen = *N*,*N*′-bis(salicylidene)-1,2-diaminoethane] having azido and dicyano argentate(I) as bridging ligands are reported. Both complexes belong to one-dimensional systems in which the azido functions as μ-(1,3) and $Ag(CN)_2^-$ as ···NC– Ag–CN··· bridging ligands. The azido-bridged compound is antiferromagnetic with an intrachain interaction constant $J = -4.52(4)\ cm^{-1}$ (Weng model) or $J = -5.19(8)\ cm^{-1}$ (Fisher model), and it is a candidate to observe the Haldane gap in a $S = 2$ system. The silver cyanide bridged complex shows single ion behaviour of the Mn(III) ion, perhaps in combination with a very weak antiferromagnetic interaction.

The azide ion, N_3^-, can coordinate to metal ions by different bridging modes[1–3] *viz.*, μ-(1,3), μμ-(1,1) along with a rarely occurring one, μ-(1,1,1). The cis and trans arrangement of the bridged azide is also noteworthy. The polymeric chains of Mn(III) often exhibit interesting magnetic properties and could be used as precursors of molecular-based magnets. The role of manganese-containing enzymes is well-known in biology, and these Mn compounds could in some way mimic the active site of these metalloenzymes. A literature survey reveals that only a few structurally characterised complexes of Mn(III) having N_3^- bridges have been reported. In 1998 two studies[4,5] appeared almost concurrently on the synthesis, crystal structure and magnetic properties of a one-dimensional azide-bridged manganese(III) complex, $[Mn(salpn)N_3]$ [H_2salpn = *N*,*N*′-bis(salicylidene)-1,3-diaminopropane]. The Mn(III) Schiff base complex $[Mn(salen)N_3]$ [H_2salen = *N*,*N*′-bis(salicylidene)-1,2-diaminoethane] has also been reported but was not characterised by X-ray crystallography[6] due to a failure to obtain suitable crystals for X-ray diffraction. However, based on the spectral and magnetic studies, it was suggested to have a linear chain structure identical to that in $[Mn(acac)_2N_3]$[7] (H_2acac = acetylacetone). Here, N_3^- functions as a μ-(1,3) bridge leading to a polymeric chain.

Like azide, one of the most widely used and versatile antiferromagnetic and ferromagnetic couplers is the cyanide ligand. Cyanometallates have frequently been employed for the design of various 1-D, 2-D or 3-D network architectures and their magnetic properties have been studied in an effort to prepare molecular-based magnetic materials. The most common cyanometallates for this purpose are $M(CN)_6^{n-}$ ($n = 2$ or 3; M = Fe, Co, Cr, V, Mn)[8] and $[M(CN)_4]^{2-}$ (M = Ni, Pt, Cd, Zn, Cu).[9] Linear metallocyanates may be employed to design various types of polymeric materials.Being interested in constructing heterobimetallic polymeric materials, we have employed $Ag(CN)_2^-$ as a building block. In addition to serving as a cyanide bridge, it can also participate in $Ag^I \cdots Ag^I$ interactions leading to polymeric structures. There are several reports in which $Ag(CN)_2^-$ has been used to construct heterobimetallic polymeric materials of various topologies with different transition metals,[10] but to our knowledge there is no report on any synthesis of Mn^{III}–Ag^I heterobimetallic polymers. In this paper we wish to report the synthesis, single crystal X-ray structures and variable temperature magnetic properties of $[Mn(salen)N_3]$ and $[Mn(salen)Ag(CN)_2]$.

Experimental

Materials and methods

High purity ethylenediamine, salicylaldehyde and sodium azide were purchased from Aldrich and used as received. All other reagents were of analytical grade. Elemental analysis (C, H, N) was carried out using a Perkin–Elmer 240 elemental analyser. Infrared spectra (400–4000 cm^{-1}) were recorded from KBr pellets on a Nicolet Magna IR 750 series II FTIR spectrophotometer. Magnetic measurements were carried out with a MPMS SQUID magnetometer under 10 and 5 kOe magnetic fields for **1** and **2**, respectively. Diamagnetic corrections were made using Pascal's constants.

Synthesis

Caution! Since the azide complexes of metal ions are potentially explosive, only small amounts of the materials should be handled with care.

$[Mn^{III}$ (salen)($\mu_{1,3}$-N_3)] (1). This compound was conveniently synthesised by reaction of $[Mn^{III}(salen)OAc]\cdot H_2O$[11] and sodium azide from a methanol–water mixture. Sodium azide (0.065 g, 1 mmol) was dissolved in 40 cm^3 of water in a 100 cm^3 beaker. To this solution was slowly added 40 cm^3 of a methanolic solution of $[Mn^{III}(salen)OAc]\cdot H_2O$ (0.4 g, 1 mmol).

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Upon standing at room temperature for 2 h, brown-black crystals separated out. These were filtered, washed first with the mother liquor, followed by diethyl ether (30 cm^3), and dried *in vacuo* over calcium chloride. Yield 80%. Anal. calcd for $C_{16}H_{14}N_5O_2Mn$: C, 52.89; H, 3.86; N, 19.28; found: C, 52.65; H, 3.92; N, 19.20.

[Mn^{III}(salen)Ag(CN)$_2$] (2). To an aqueous solution (20 cm^3) of potassium dicyanoargentate(I), [KAg(CN)$_2$] (0.2 g, 1 mmol), was slowly added a methanolic solution (40 cm^3) of [Mn(salen)OAc]·H$_2$O (0.4 g, 1 mmol) in a 100 cm^3 beaker. Upon standing for 3 days at room temperature, black crystals separated out. These were filtered, washed successively with mother liquor and diethyl ether, and dried *in vacuo*. Yield 80%. Anal. calcd for $C_{18}H_{14}N_4O_2MnAg$: C, 44.90; H, 2.91; N, 11.64; found: C, 44.82; H, 3.02; N, 11.69.

Crystal data collection and refinement

Suitable single crystals of the complexes **1** and **2** were mounted on an Enraf–Nonious CAD4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71070$ Å) at 293 K. Information regarding the crystallographic data collection and refinement of the structures is complied in Table 1. Unit cell parameters and orientation matrixes were determined by a least-squares fit. Intensity data were corrected for Lorentz polarisation but not for absorption. All calculations for data reduction, structure solution and refinement were done by standard procedures (SHELXS97),[12] (SHELXL97).[13] For **2**, our programme for data reduction merges reflections if the absorption correction is not made. These data are input in SHELX, which cannot calculate a value for R_{int} in this case. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques on F^2. All the hydrogen atoms were located in Fourier-difference maps and refined isotropically. The final crystal structures were drawn using the ORTEP programme.[14]

CCDC reference numbers 188032–188033. See http://www.rsc.org/suppdata/nj/b2/b200384h/ for crystallographic files in CIF or other electronic format.

Results and discussion

The IR spectrum of **1** shows a very strong band at around 2027 cm^{-1}, assigned to the asymmetric stretching vibrations of the bridged azido. The corresponding vibration of the C–N bond of the salen ligand is at 1626 cm^{-1}. For **2** the asymmetric stretching vibration for C≡N is observed at 2140 cm^{-1}, which is close to that reported for several other metal cyanide bridges.[10]

Table 1 Data collection and structure refinement for complexes **1** and **2**

Empirical formula	$C_{16}H_{14}N_5O_2Mn$ (**1**)	$C_{18}H_{14}N_4O_2AgMn$ (**2**)
Formula weight	363.26	481.14
Crystal system	Orthorhombic	Monoclinic
Space group	$Pca2_1$ (no. 29)	$P2_1/c$ (no. 14)
a/Å	10.9390(3)	8.148(5)
b/Å	12.9470(2)	6.509(5)
c/Å	11.1140(4)	33.158(5)
β/°	90	96.346(5)
U/Å^3	1574.05(8)	1747.8(17)
Z	4	4
μ(Mo-Kα) /mm^{-1}	0.858	1.863
T/K	293	293
Total data	20 584	2802
Unique data	3601	2802
R_{int}	0.043	
Data [$I > 2\sigma(I)$]	3193	2292
R [$I > 2\sigma(I)$]	0.0295	0.0348
wR^a [$I > 2\sigma(I)$]	0.0727	0.0888

[a] $w = 1/[\sigma^2(F_o^2) + (0.0403\ P)^2 + 0.1134\ P]$ where $P = (F_o^2 + 2\ F_c^2)/3$ for **1**; $w = 1/[\sigma^2(F_o^2) + (0.0336\ P)^2 + 2.15\ P]$ where $P = (F_o^2 + 2\ F_c^2)/3$ for **2**.

Description of the structures of complexes 1 and 2

Complex **1** features an azido-bridged Mn(III) chain as shown in Fig. 1. The Mn(III) ion assumes a slightly distorted octahedral geometry in which the metal ion binds to one salen in the equatorial mode and two azide ions in axial positions. Each azide functions as a trans-μ-(1,3) bridge, resulting in a one-dimensional polymer. Based on the classification by Escuer *et al.*,[15] it can be categorised as a type I azido chain. In the equatorial plane the Mn–O(1), Mn–O(2), Mn–N(1) and Mn–N(2) bond lengths are 1.875(15), 1.888(16), 1.989(17) and 1.978(18) Å, respectively, which are comparable to those observed in other Mn(III) salen complexes. The O(1) and N(2) atoms are 0.041 and 0.043 Å above the mean plane whereas the O(2) and N(1) are 0.041 and 0.043 Å below the mean plane. The central Mn(III) ion itself is, however, 0.019 Å above the mean equatorial plane. The coordination of the azide bridge is nearly symmetrical: Mn(1)–N(11)–N(12) = 118.42(16)° and Mn(1a)–N(13)–N(12) = 114.64(16)°. Owing to Jahn–Teller distortion, the axial Mn–N(11) and Mn–N(13) distances of 2.280 and 2.334 Å, respectively, are considerably longer. The intrachain Mn···Mn distance is 5.56 Å. However, the interchain Mn···Mn separation is considerably larger at 9.99 Å. Selected bond distances and angles are listed in Table 2.

The coordination environment of the Mn(III) ion in complex **2** with atom numbering scheme is shown in Fig. 2. The coordination environment of each manganese atom is best described by a distorted octahedral geometry. Two nitrogen atoms and two oxygen atoms of the Schiff base ligand [having Mn–O(1), Mn–O(2), Mn–N(1) and Mn–N(2) distances of 1.886(3), 1.874(3), 1.985(4), 1.990(4) Å, respectively] define the equatorial plane around the Mn atom. The axial sites are occupied by two nitrogen atoms of the bridging [N–C–Ag–C–N] moiety and show bond distances Mn–N(98) = 2.321(4) and Mn–N(99) = 2.286(4) Å, respectively. The central Mn(III) ion is slightly above the equatorial plane (0.006 Å). The O(1) and N(2) atoms are 0.037 and 0.039 Å above the mean plane whereas the O(2) and N(1) atoms are 0.037 and 0.039 Å,

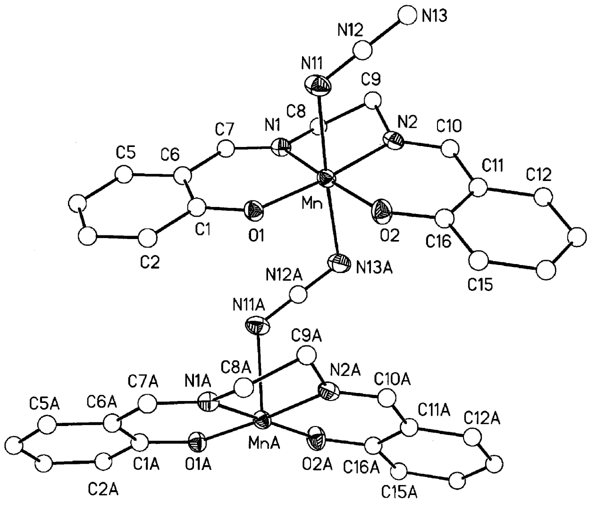

Fig. 1 ORTEP view of **1**, showing the atom labeling scheme. Hydrogen atoms are omitted for clarity and thermal ellipsoids are represented at the 30% probability level.

Table 2 Selected bond distances (Å) and angles (°) for complexes **1** and **2**[a]

Complex **1**			
Mn–O(1)	1.8754(15)	Mn–O(2)	1.8878(16)
Mn–N(1)	1.9885(17)	Mn–N(2)	1.9780(18)
Mn–N(11)	2.280(2)	Mn–N(13a)	2.334(2)
O(1)–Mn–O(2)	94.32(7)	O(1)–Mn–N(1)	91.73(7)
O(1)–Mn–N(2)	173.73(7)	O(1)–Mn–N(11)	91.77(7)
O(1)–Mn–N(13a)	91.50(7)	O(2)–Mn–N(1)	172.99(7)
O(2)–Mn–N(2)	91.85(7)	O(2)–Mn–N(11)	89.99(7)
O(2)–Mn–N(13a)	89.80(7)	N(1)–Mn–N(2)	82.20(7)
N(1)–Mn–N(11)	93.38(7)	N(1)–Mn–N(13a)	86.49(7)
N(2)–Mn–N(11)	87.06(7)	N(2)–Mn–N(13a)	89.68(7)
N(11)–Mn–N(13a)	176.73(8)		
Complex **2**			
Ag–C(99)	2.067(5)	Ag–C(98b)	2.070(5)
Mn–O(1)	1.886(3)	Mn–O(2)	1.874(3)
Mn–N(1)	1.985(4)	Mn–N(2)	1.990(4)
Mn–N(98)	2.321(4)	Mn–N(99)	2.286(4)
C(98b)–Ag–C(99)	155.00(17)	O(1)–Mn–O(2)	94.14(12)
O(1)–Mn–N(1)	91.59(13)	O(1)–Mn–N(2)	174.01(13)
O(1)–Mn–N(98)	95.18(12)	O(1)–Mn–N(99)	94.28(12)
O(2)–Mn–N(1)	173.73(14)	O(2)–Mn–N(2)	91.58(13)
O(2)–Mn–N(98)	93.80(14)	O(2)–Mn–N(99)	94.86(14)
N(1)–Mn–N(2)	82.77(14)	N(1)–Mn–N(98)	83.14(13)
N(1)–Mn–N(99)	87.23(13)	N(2)–Mn–N(98)	86.19(13)
N(2)–Mn–N(99)	83.45(13)	N(98)–Mn–N(99)	166.66(13)

[a] Symmetry codes: (a) $\frac{1}{2}-x, y, \frac{1}{2}+z$ for **1**; (b) $1+x, -1+y, z$ for **2**.

respectively, below the plane. The bridging Mn–N(98)–N(98) and Mn–N(99)–N(99) angles are 170.4(3)° and 144.4(3)°, respectively. The [N–C–Ag–C–N] moiety is almost linear and forms endless chains involving the Mn^{III}(salen) moiety. They are parallel with diagonal directions *a*, *b* and the distance Ag···Ag is about 6.5 Å. No direct Ag···Ag interaction can be conceived. Main bond distances and angles are listed in Table 2.

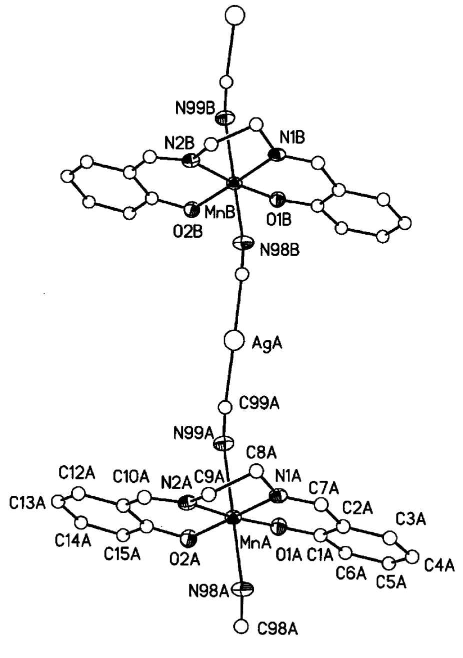

Fig. 2 ORTEP view of **2**, showing the atom labeling. Hydrogen atoms are omitted for clarity and thermal ellipsoids are represented at the 30% probability level.

Magnetic properties

The thermal variation of the molar susceptibility χ_M shows a broad maximum around *ca.* 43 K for **1**, which is indicative of antiferromagnetic coupling within a chain-type structure (Fig. 3). Using the expression for an antiferromagnetic one-dimensional $S = 2$ chain given by Weng and modified by Hiller,[16] a reasonably good fit is possible from room temperature down to 5 K. The J values were obtained by minimising the function $R = \sum(\chi_M^{calc} - \chi_M^{obs})^2/\sum(\chi_M^{obs})^2$. The best-fit parameters are: $J = -4.52(4)$ cm^{-1}, $g = 2.006(8)$ and $R = 4.5 \times 10^{-4}$

Except at very low temperatures where some anisotropy may be significant, manganese(III) is expected to be Heisenberg-like in its magnetic properties[6] We, therefore, also made an attempt to explain the magnetism in terms of the Heisenberg 1D chain using the Fisher[17] expression:

$$\chi = \frac{N\beta^2 g^2}{3kT} S(S+1) \quad \left[\frac{1+U}{1-U}\right]$$

$$U = \coth\frac{-2JS(S+1)}{kT} - \frac{-2JS(S+1)}{kT}$$

Fitting of the observed data gave best-fit parameters as: $J = -5.19(8)$ cm^{-1}, $g = 2.05(1)$, and $R = 9.4 \times 10^{-4}$.

Owing to the small axial overlap, the manganese(III) azide-bridged linear chain having long axial bonds has only one dominant exchange pathway, and it results in a weak antiferromagnetic interaction. The only magnetic orbital that can make significant contribution to the coupling is the one derived from the Mn(III) d_{z^2} orbital. The axial ligands will provide mainly a σ-type superexchange pathway. A superexchange mechanism involving the π orbitals of the bridging group may well be conceived. The intrachain Mn···Mn distance (5.56 Å) in **1** is comparable to that observed (5.63 Å) in [Mn(acac)$_2$N$_3$][18]. The magnitudes of the exchange interaction in these two complexes are also close. The J values obtained for **1** are comparable to those reported[4,5] for [Mn(salpn)N$_3$]. The two values ($J = -5.19$ and -4.52 cm^{-1}) obtained by us using two different models are virtually identical to those reported by Kennedy and Murray[6] ($J = -5.42$ and -4.45 cm^{-1}) through powder susceptibility and magnetisation measurements.

It may be pointed out that a sharp increase in susceptibility at temperatures below 15 K was observed in [Mn(salpn)N$_3$].[4,5] No such behaviour is observed in the title [Mn(salen)N$_3$] compound, ruling out long-range order or impurity. To the best of our knowledge, just one experimental example of a Haldane gap system with $S = 2$ has been documented, in 1996,[19] although several numerical studies have been performed since Haldane's conjecture in 1983.[20] All theoretical work predicts

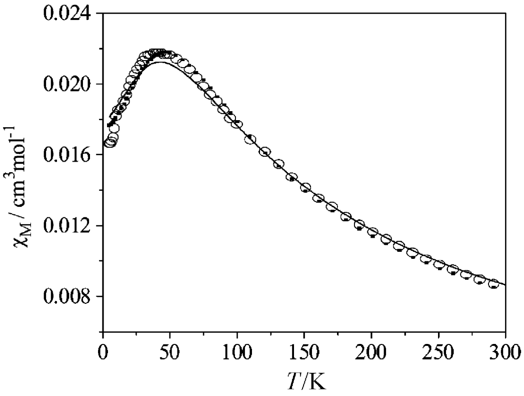

Fig. 3 Variable-temperature magnetic susceptibility data for **1**. Experimental points are represented by (○). (—) data fitted by Fisher model. (■) data fitted by Weng model.

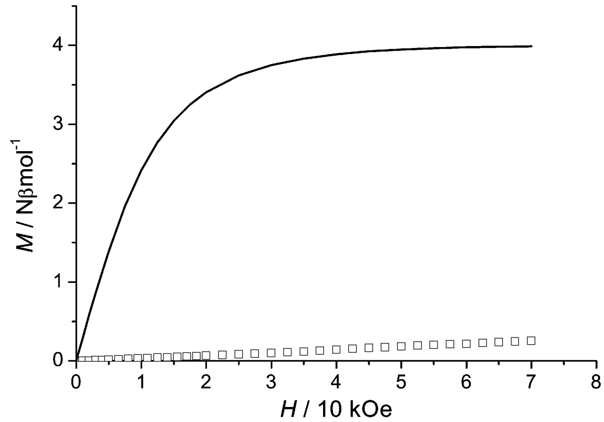

Fig. 4 Field dependence of magnetisation of **1** at 1.83 K; the line is calculated using the Brillion function for an isolated Mn(III) ion.

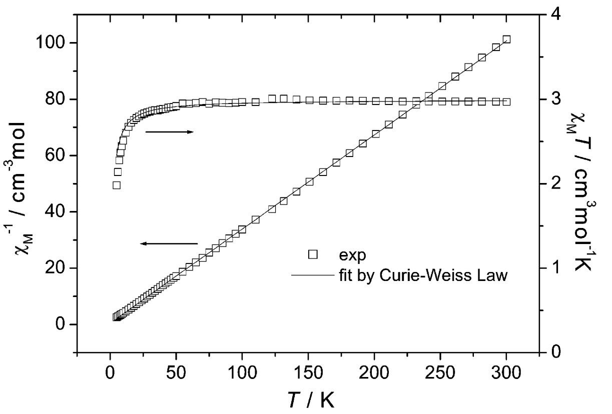

Fig. 5 Variable-temperature magnetic susceptibility data for **2**. Experimental points are represented by (□). (—) data fitted by the Curie–Weiss Law.

that the gap between the singlet ground state and the first excited triplet state E_g for an $S = 2$ chain is correlated with the intrachain antiferromagnetic interaction J as $E_g = (0.05\text{–}0.09)J$. The J for the title $S = 2$ chain, a candidate for observing a Haldane gap, is *ca.* 7 K; therefore, E_g may be estimated at *ca.* 0.5 K. The field dependence of the magnetisation at 1.83 K (Fig. 4) shows a very low value, even at 70 kOe, compared with the calculated value using a Brillion function for an isolated Mn(III) ion with $S = 2$, $g = 2.0$, also suggesting a singlet ground state; however, the critical field (H_c) to a gapless state was not observed up to 70 kOe. Apparently, more experimental evidence is needed, especially low-temperature and high-field investigations.

Complex **2**, on the other hand, shows single ion behaviour mainly, perhaps combined with a very weak antiferromagnetic coupling between Mn(III) ions (Fig. 5). The magnetic susceptibility obeys the Curie–Weiss law [$\chi_M = C/(T-\theta)$] with $C = 2.994(3)$ cm^3 mol^{-1} K and $\theta = -1.4(1)$ K. The Curie constant C corresponds to one Mn(III) ion with $S = 2$ and $g = 1.998$. The slight decrease of $\chi_M T$ below 30 K and the negative Weiss constant θ suggest a very weak, if it exists at all, antiferromagnetic interaction between Mn(III) ions.

The stronger coupling observed for **1** than in **2** may arise from a more symmetrical orbital system in the azide bridge in comparison to the silver cyanide group. It is quite likely that the Ag(I) ion inhibits the magnetic interaction between the manganese(III) centres in **2**, leading to a very weak antiferromagnetic interaction. The long Mn···Mn distance (10.43 Å) in **2** would also be quite unfavorable for a more direct pathway.

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