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Hydrothermal synthesis and magnetic properties of novel Mn(II) and Zn(II) materials with thiolato-carboxylate donor ligand frameworks*

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Received 11th February 2004, Accepted 13th April 2004 First published as an Advance Article on the web 6th May 2004

The hydrothermal reaction of thiosalicylic acid, $(C_6H_4(CO_2H)(SH)-1,2)$ with manganese(III) acetate leads to formation of the coordination solid $[Mn_5((C_6H_4(CO_2)(S)-1,2)_2)_4(\mu_3-OH)_2]$ (1) via a redox reaction, where resulting manganese(II) centres are coordinated by oxygen donor atoms and S-S disulfide bridge formation is simultaneously observed. Reaction of the same ligand under similar conditions with zinc(II) chloride yields the layered coordination solid $[Zn(C_6H_4(CO_2)(S)-1,2)]$ (2). Hydrothermal treatment of manganese(III) acetate with 2-mercaptonicotinic acid, $(NC_5H_3(SH)(CO_2H)-2,3)$ was found to produce the 1-dimensional chain structure $[Mn_2((NC_5H_3(S)(CO_2)-2,3)_2)_2(OH_2)_4] \cdot 4H_2O(3)$ which also exhibits disulfide bridge formation and oxygen-only metal interactions. Compound $\mathbf{3}$ has been studied by thermogravimetric analysis and indicates sequential loss of lattice and coordinated water, prior to more comprehensive ligand fragmentation at elevated temperatures. The magnetic behaviour of 1 and 3 has been investigated and both exhibit antiferromagnetic interactions. The magnetic behaviour of 1 has been modelled as two corner-sharing isosceles triangles whilst 3 has been modelled as a 1-dimensional chain.

Introduction

In contrast to the great deal of work on solvothermal synthesis with carboxylate ligands,1 there have been few reports of studies on mixed thiolato-carboxylate ligands. The majority of the small number of studies with such ligands under conventional conditions are based on thiosalicylic acid and its pyridine-based analogue, 2-mercaptonicotinic acid.2-4 A smaller number of complexes have also been prepared with the disulfide derivatives of these ligands (Scheme 1). These ligands are ideal building blocks for the formation of coordination solids since the organothiolato carboxylates in particular offer the possibility of variable coordination and chelation modes towards metal ions; some more common examples of these modes are shown in Scheme 2 for the dianion of mercaptonicotinic acid. These ligands are capable of coordinating in three ways; a) via sulfur only (I, II), most commonly formed with soft metals including Ag(I), Au(I) and Sn(II);² b) via thiolate and another donor (III, IV), with other metals such as Cu(II), Fe(II), Mn(II), Mo(II), Ni(II), Os(II) and Re(III);3 c) via carboxylate only, e.g. Cu(II) and Mn(II) (V, VI).4



Scheme 1 (a) Thiosalicylic acid (left) and corresponding disulfide 2,2'dithiobisbenzoic acid (right); (b) 2-mercaptonicotinic acid (left) and 2,2'dithiobisnicotinic acid (right).

†Electronic supplementary information (ESI) available: Kambe's method for an isolated bowtie; isosceles bowtie energies. See http://www.rsc.org/ suppdata/dt/b4/b401887g/



Scheme 2 Typical coordination modes for 2-mercaptonicotinic acid.

The incorporation of thiolate-S as a single atom bridge between adjacent 3d-transition metal sites in an inorganic polymer is highly desirable in terms of magnetic behaviour. This is because the orbital energies are better matched for S than for the much more common oxygen-bridged species, hence there will be greater delocalisation of spin density towards the bridging atom.5 This is beneficial since strong superexchange interactions within chains (versus weaker dipolar interactions between individual chains) are more likely to produce good model compounds for the study of low-dimensional magnetic behaviour. With this in mind, we have studied the reactions of some 3d-metals with the anions of thiosalicylic acid and 2-mercaptonicotinic acid under hydrothermal conditions.⁶ Here we describe the reactivity of Mn(II)/(III) and Zn(II) with these ligands which results in the formation of new coordination polymers. For Zn this leads to isolation of an O,S coordinated network whereas for Mn we observe unprecedented in situ reduction of thiolate ligands yielding complexes containing the corresponding disulfide.

Results and discussion

Compounds with thiosalicylic acid

Reaction of manganese(II) chloride and thiosalicylic acid deprotonated with KOH in a 1:1:2 molar ratio in superheated water yielded a few colourless small square plates of [Mn₅((C₆H₄(CO₂)(S)- $(1,2)_2)_4(\mu_3-OH)_2$ (1). This was subsequently prepared in good yield without added base using the corresponding metal(III) acetate and

10.1039/b401887

DOI: 1

ligand (5:8 molar ratio); reproducibility was also greatly improved. This unusual coordination complex consists of a framework which is generated by many 1,1- and 1,3-carboxylate bridges, as well as μ_3 -hydroxide ligands. The structure of the air- and moisture-stable crystalline phase was initially identified by X-ray analysis and has been confirmed by elemental analysis and spectral data.

The formation of 1 is dependent on the *in situ* oxidation of the ligand to form disulfide S-S bridges. It is suggested that the thiosalicylic acid becomes doubly-deprotonated via free AcO-, in order to generate the $(C_6H_4(CO_2)(S)-1,2)^{2-}$ species. Then by redox reaction, two equivalents of manganese(III) are reduced to give manganese(II) while a pair of thiolate-S atoms become oxidised, thus forming the disulfide moiety 2,2'-dithiobisbenzoate, $(C_6H_4(CO_2)(S)-1,2)_2^{2-1}$ The idealised stoichiometry for the formation of 1 (Scheme 3) requires equimolar amounts of Mn(III) acetate and ligand along with excess H₂O to provide hydroxide ions. Our most effective synthetic procedure, which was based on a 5:8 molar ratio, is most likely dependent on the presence of three excess equivalents of ligand which moderate the overall reaction pH. The observed preference of manganese(II) to coordinate with oxygen donor sites rather than with the softer thiolato donor atom is evidence for the relative hardness of manganese(II) as a lewis acid. The oxidation is not purely the result of the presence of Mn(III) in the reaction, since the same product is observed in slightly lower yield when Mn(II) is employed as the starting material. Furthermore, no oxidation to disulfides is observed in reactions involving thiophilic metals such as Co(II)⁷ and Zn(II) (see compound 2 below) suggesting that thiolate is more susceptible to oxidation when uncoordinated to a transition metal. The behaviour observed here is accentuated for reactions involving this particular ligand given the ortho-arrangement of ring substituents, which might otherwise be expected to favour metal chelation between carboxylate oxygen and thiolate anion, thus forming a puckered six-membered ring which we have observed for other 3d-metals and this ligand system including 2 herein. It was not possible to synthesise 1 directly by using the disulfide ligand as starting material. Various attempts over the temperature range 140-220 °C using both Mn(II) and Mn(III) and multiple stoichiometries all resulted in the formation of yellow solutions with no solid product.

 $8 \operatorname{Mn}(\operatorname{OAc})_3 + 2 \operatorname{H}_2\operatorname{O} + 8 (\operatorname{C}_6\operatorname{H}_4(\operatorname{CO}_2\operatorname{H})(\operatorname{SH})-1,2) \rightarrow$ [Mn₅(C₆H₄(CO₂)(S)-1,2)₈(µ₃-OH)₂] + 3 Mn(OAc)₂ + 18 HOAc **Scheme 3** Idealised equation for the formation of **1**.

The X-ray crystal structure of **1** was determined at -93 °C. It crystallises in the triclinic space group $P\overline{1}$ with Z = 1 as the formula unit contains an inversion centre *i.e.* is comprised of two asymmetric units. There are three manganese(II) environments in the asymmetric unit, as shown in Fig. 1. Mn1 lies on an inversion centre whereas Mn2 and Mn3 are located on general positions. Selected bond lengths and angles are given in Table 1.

The octahedral coordination environment around Mn1 has distortions from perfect geometry in the range 84.66(8)-98.59(8)° while Mn2 is a more distorted pseudo-octahedron with bond angles in the range 77.53(8) to 97.07(8)°. In contrast, Mn3 is tetrahedrally coordinated to four oxygen atoms with significant distortion, where the bond angle for the O4A-Mn3-O9 moiety is only 84.93(8)°. All three metal environments are linked via the μ_3 -hydroxide ligand (O9). Mn1 and Mn2 are also bridged by a syn, syn-carboxylate interaction where the (-O1-C7-O2-) moiety is approximately perpendicular to the Mn₃ plane. Mn1 is also linked to Mn3 by a μ_2 -oxygen atom from a carboxylate. A polyhedral view of the formula unit of 1 is shown in Fig. 2. The octahedral Mn1 and Mn2 centres form an undulating vertex-sharing chain while tetrahedral Mn3 environments are edge-sharing with the Mn1 polyhedra, and vertex-sharing with the Mn3 polyhedra. The result of this extensive bridging is the formation of four-membered metal-oxygen rings and a bowtie chain topology of manganese(II) centres (Fig. 3). The average dihedral angle between aromatic groups due to disulfide bridging is 87.0(2)° hence adjacent rings are close to perpendicular.

Table 1 Selected bond distances (A) and angles (°) for compound 1				
Mn1–O1	2.151(2)	Mn2–O9 2.130(2)		
Mn1–O4	2.242(2)	Mn3–O4A 2.141(2		
Mn1-O9	2.103(2)	Mn3–O5A 2.032(2)		
Mn2–O2	2.100(2)	Mn3–O8 2.058(2)		
Mn2–O3	2.187(2)	Mn3–O9 2.059(2)		
Mn2-O6	2.3179(19)	S1–S3A 2.0420(11		
Mn2-O6A	2.315(2)	S2–S4A 2.0463(11		
Mn2–OA	2.124(2)		, í	
O1-Mn1-O4	84.66(8)	O6-Mn2-O6A	80.24(7)	
O1-Mn1-O9	95.91(8)	O6-Mn2-O7A	90.47(8)	
O4-Mn1-O9	98.59(8)	O6–Mn2–O9 77.53		
Mn1-O9-Mn2	113.21(9)	O6A-Mn2-O7A	87.75(8)	
Mn1-O4-Mn3A	93.33(8)	O6A-Mn2-O9	83.63(8)	
Mn1-O9-Mn3	100.04(9)	O7A-Mn2-O9	166.24(8)	
O2-Mn2-O3	94.87(8)	Mn2-O6-Mn2A	99.76(7)	
O2-Mn2-O6	169.86(8)	Mn2-O9-Mn3	122.41(11)	
O2-Mn2-O6A	91.44(8)	O4A-Mn3-O5A	114.68(9)	
O2-Mn2-O7A	95.02(8)	O4A-Mn3-O8	110.63(9)	
O2-Mn2-O9	95.90(8)	O4A-Mn3-O9	84.93(8)	
O3-Mn2-O6	92.90(7)	O5A-Mn3-O8	118.66(10)	
O3-Mn2-O6A	171.69(7)	O5A-Mn3-O9	105.75(9)	
O3-Mn2-O7A	97.07(8)	O8–Mn3–O9 117.50(9)		
O3-Mn2-O9	90.33(8)		. /	



Fig. 1 ORTEP representation of the asymmetric unit of 1 and associated symmetry equivalent atoms drawn at the 50% probability level. Hydrogen atoms omitted for clarity.



Fig. 2 Polyhedral representation of a single Mn_5 unit in 1. Octahedra containing Mn1 and Mn2 are drawn in pink, whilst Mn3-centred tetrahedra are shown in blue. Oxygen atoms drawn in red, sulfur atoms are yellow.



Fig. 3 Bowtie chain topology of adjacent manganese(II) centres in 1.

Consideration of the extended structure of **1** reveals that chains run parallel to the crystallographic *a*-axis and neighbouring chains of metal atoms are well isolated from one another, chiefly due to the



Fig. 4 Polyhedral representation showing the packing of chains of manganese(II) bowties (left) running along the crystallographic *a*-aixs as viewed normal to [0 7 1], separated by disulfide bridging interactions and (right) solvent-accessible void formed between parallel chains in **1**, as viewed in the *bc*-plane.

formation of disulfide bridges between adjacent ligands (Fig. 4 left). A view of the solid with the manganese chains normal to the page (Fig. 4 right) shows the presence of small gaps within the aromatic regions of the structure. According to calculations made using the VOID utility in PLATON,8 there is no solvent-accessible space within the structure. However the disulfide ligands are severely buckled and cavities could be formed by reducing the degree of buckling, thereby expanding the interchain distance. We attempted to extend the channels by incorporation of aromatic molecules that would interact strongly with the aromatic rings in the ligands. Finely-ground crystalline samples of 1 were therefore treated with toluene and pyridine under solvothermal conditions at 200 °C over 18 h periods. However, upon examination of the resultant crystals by infra-red spectroscopy and X-ray determination of the unit cell parameters, no change was observed in the solid in either case. This finding is supported by the collection of highly accurate microanalysis data for 1, calculated on the assumption that no solvent of crystallisation is present.

The infra-red spectrum shows a sharp peak at *ca.* 3588 cm⁻¹ due to the hydroxide O–H stretch. There is a complex series of peaks in the region 1650-1560 cm⁻¹ due to the stretching modes for coordinated thiosalicylate carbonyl or carboxylate C=O groups.

Investigation into the reactivity of thiosalicylic acid under similar conditions with other 3d-transition metals produced the zinc-containing coordination solid $[Zn(C_6H_4(CO_2)(S)-1,2)]$ (2) where Zn–S bonding is observed and whose extended structural arrangement is in many respects similar to the Co(II)-containing solid which we reported previously.⁷ The synthesis of 2 was most successful using a 1:1:2 (stoichiometric) ratio of ZnCl₂: thiosalicylic acid: KOH which afforded large (>1 mm²) colourless crystalline square plates, present amongst a bulk phase of homogenous white powder. Slow-cooling of the hydrothermal mixture was preferable in all cases but crystalline samples were also formed in lower yield using one equivalent of excess KOH.

The sheet-like structure of 2 was determined by X-ray crystallography. The asymmetric unit consists of one formula unit with a single metal environment which inhabits the C2/c monoclinic space group (Z = 8), shown in Fig. 5; selected bond lengths and angles are given in Table 2. The pseudo-trigonal bipyramidal coordination enviroment around Zn1 shows significant distortion since there is chelation of the carboxylate with a bite angle of 57.01(11)°. The bonding distance of Zn1A–O2 (1.997(3) Å) is significantly shorter than for Zn1A-O1 (2.481(3) Å) and compares more favourably with literature values for Zn-O bonding distances,9 which suggests that the coordination about the zinc(II) centre is intermediate between tetrahedral and trigonal bipyramidal where Zn1A-O1 is the longer-range contact. We have performed Bond Valence Sum (BVS) calculations¹⁰ on the coordination environment around Zn1 using tabulated values9 which suggests that individual valencies are 0.521 (Zn1-S1), 0.519 (Zn1-S1A), 0.454 (Zn1-O1A), 0.122 (Zn1–O1B) and 0.453 (Zn1–O2A). This means that when formally trigonal bipyramidal, Zn1 has a total BVS of 2.069; in the tetrahedral case however (where the Zn1–O1A bond is disregarded), the value was found to be 1.947. The average of these two extreme cases gives an agreeable BVS for Zn1 of 2.008. These results are somewhat inconclusive as they differ from the ideal value of 2 by approximately equal amounts, but do suggest that the Zn1–O1A bond is very weak. It is also interesting that the Zn1A–O1–Zn1B bond angle (149.58(15)°) is considerably expanded from the expected 120°. Atom O1 also bridges to an equivalent zinc atom (Zn1B) forming part of a puckered 6-membered ring moiety including the S1 site which itself bridges adjacent metal atoms where the angle Zn1–S1–Zn1B is found to be 100.78(4)°. The Zn1–S1 bond distance is 2.3314(13) Å which compares to 2.2996(7) Å in the similar cobalt(11) compound.⁷



Fig. 5 ORTEP view of the asymmetric unit and complete coordination environments of unique atoms in **2**. Thermal ellipsoids drawn at the 50% probability level.

The extended structure of **2** is based on zinc thiolate zigzag chains (Fig. 6) in which the organic groups alternate from side-to-side of the chain so that there is no π -stacking. The chains are formed into sheets (Fig. 7) by the coordination of the carboxylate to zinc(II) ions in neighbouring chains. The aromatic rings are arranged in such a way as to keep those in adjacent chains well separated from one another. Each 2-dimensional sheet takes the form of a quadratic layer of 8-membered rings in the *bc*-plane, where each ring is formed of the repeat unit (–Zn1–O1–Zn1–S1–). Chains of metal centres run parallel to the crystallographic *c*-axis. Each individual sheet is well isolated from the next by a double aromatic layer (Fig. 8).

Table 2Selected bond lengths (Å) and angles (°) for 2						
Zn1–S1	2.3314(13)	Zn1–O1A	2.481(3)			
Zn1–S1A	2.3328(13)	Zn1–O2A	1.997(3)			
Zn1–O1B	1.996(3)	S1–C2	1.792(4)			
S1–Zn1–S1A	104.76(4)	01B–Zn1–O1A	$125.14(4) \\ 57.01(11) \\ 100.78(4) \\ 149.58(15)$			
S1–Zn1–O1B	111.72(9)	01A–Zn1–O2A				
S1–Zn1–O1A	121.39(8)	Zn1–S1–Zn1B				
S1–Zn1–O2A	109.23(10)	Zn1A–O1–Zn1B				
S1A–Zn1–O1B S1A–Zn1–O1A S1A–Zn1–O2A	92.05(9) 87.33(8) 139.92(10)	Zn1–S1–C2 Zn1B–S1–C2	101.03(14) 97.69(15)			



Fig. 6 Extended structure of compound 2. Zinc(II) centres are shown in green.



Fig. 8 Polyhedral representation showing degree of separation of individual sheets of Zn(II) trigonal bipyramids in 2.

2-Mercaptonicotinic acid complex

In light of the structure of **1**, we decided to investigate whether Mn(II) might be encouraged to coordinate to a sulfur donor site if other chelation modes were made available. This led us to attempt the hydrothermal reaction of Mn(II) with 2-mercaptonicotinic acid which, in addition to the 5-membered chelation mode provided by thiosalicylic acid, provides the possibility for formation of a 4-membered chelate of the form (–NCS–M–) (Scheme 2, III).

Upon reaction of $MnCl_2$ and 2-mercaptonicotinic acid deprotonated with KOH in a 1:2:4 (stoichiometric) ratio in superheated water, we were successful in isolating large yellow rod-shaped crystals in reasonable yield. The identity of a single crystal was determined by X-ray structural analysis as $[Mn_2((NC_5H_3(S)(CO_2)-2,3)_2)_2(OH_2)_4]$ ·4 H₂O (**3**). The behaviour of Mn(II) with the 2-mercaptonicotinate dianion is similar to that seen for **1**, since once again, disulfide bridge formation is favoured over Mn–S bond formation. Also as for the formation of **1**, compound **3** could not be synthesised directly from the disulfide, 2,2'-dithiobisnicotinic acid.

The polymer **3** crystallises in the triclinic space group $P\overline{1}$ with Z = 2. There are two crystallograpically distinct Mn(II) ions in the asymmetric unit (Fig. 9, with associated bond lengths and angles in Table 3), both of which conform closely to perfect octahedral geometry, the more distorted ion, Mn2, having bond angles within the extremes 84.77(10) and 97.51(10)°. Both manganese ions have trans-H2O ligands while all equatorial coordination sites are occupied by oxygen atoms of different carboxylate moieties which all form 1,3 bridges to adjacent metals. All carboxylate oxygen atoms are coordinated in this way, where all of the carboxylates bridge in a syn, anti-mode. The anti-Mn(II) is close to the plane of the carboxylate whilst the bond to the syn-Mn(II) is approximately normal to the plane, giving rise to a staggered conformation along the chain (Fig. 10). This is accentuated by dihedral angles in the adjoining disulfide bridges (Fig. 11) of 91.32(13) and 91.78(13)° for (C1-S1-S2-C7) and (C13-S3-S4-C19) respectively. There are four molecules of H₂O of crystallisation present in the asymmetric unit, which are located in small gaps in the structure formed by its buckled conformation. All hydrogen atoms belonging to these H2O molecules were located in the electron difference map and found to be disordered over three sites as shown, each having an occupancy of 2/3. In each case, one proton is found to point directly at its neighbouring pyridine-N. It is noteworthy that all nitrogen atoms are uncoordinated and the comparatively weak inter-molecular interaction with H₂O is observed in preference to coordination to an Mn(II) ion.



Fig. 9 ORTEP view of the asymmetric unit and completed coordination environments of **3**, drawn with 50% probability ellipsoids. Hydrogen atoms belonging to lattice H_2O molecules are shown as equally disordered over three sites.



Fig. 10 A single chain of 8-membered rings formed by *syn,anti*-bridges.



Fig. 11 Polyhedral view of **3** parallel to the *ac*-plane showing how the orientation of octahedra varies in adjacent chains.

The supramolecular structure of 3 is comprised of isolated chains of *syn,anti*-carboxylate bridged Mn(II) ions forming 8-membered

Table 3 Selec	ted bond distances (Å)) and angles (°) for co	ompound 3
Mn1–O1	2.114(2)	Mn2–O4A	2.112(2)
Mn1–O2A	2.206(2)	Mn2–O5	2.227(2)
Mn1–O7A	2.118(2)	Mn2–O6A	2.132(2)
Mn1–O8A	2.204(2)	Mn2011	2.295(2)
Mn1–O9	2.212(3)	Mn2012	2.142(2)
Mn1-O10	2.220(2)	S1-S2	2.0409(10)
Mn2–O3	2.183(2)	S3-S4	2.0451(10)
O1-Mn1-O2A	90.48(8)	O3-Mn2-O4A	91.48(8)
O1-Mn1-O7A	179.08(8)	O3-Mn2-O5	177.47(8)
O1-Mn1-O8A	88.97(8)	O3-Mn2-O6A	87.90(8)
O1-Mn1-O9	86.99(9)	O3-Mn2-O11	91.19(9)
O1-Mn1-O10	92.99(9)	O3-Mn2-O12	94.06(10)
O2A-Mn1-O7.	A 89.32(8)	O4A-Mn2-O5	90.38(8)
O2A-Mn1-O8	A 179.14(7)	O4A-Mn2-O6A	173.67(7)
O2A-Mn1-O9	88.91(10)	O4A-Mn2-O11	84.77(9)
O2A-Mn1-O1	0 90.78(12)	O4A-Mn2-O12	97.50(9)
O7A-Mn1-O8	A 91.24(8)	O5-Mn2-O6A	90.07(8)
O7A-Mn1-O9	93.91(9)	O5-Mn2-O11	87.28(9)
O7A-Mn1-O1	0 86.11(9)	O5-Mn2-O12	87.38(10)
O8A-Mn1-O9	90.39(10)	O6A-Mn2-O11	88.91(9)
O8A-Mn1-O1	0 89.91(12)	O6A-Mn2-O12	88.87(9)
O9-Mn1-O10	179.69(15)	O11-Mn2-O12	174.22(11)

rings consisting of the repeat unit (-Mn-O-C-O-). Chains run along the crystallographic *a*-axis with the disulfide bridges in between, thus forming stepped 2-dimensional sheets (Fig. 12). Each alternating chain is comprised of exclusively Mn1 or Mn2 centres, with adjacent chains canted against the next with coordinated H₂O molecules pointing above and below the sheets. There is no evidence of ring-stacking π - π interactions since alternate layers are offset against the next.



Fig. 12 Packing diagram of 3 showing stepped 2-dimensional sheets running bottom left to top right.

Thermogravimetric analysis of compound 3

The graph of mass versus temperature (Fig. 13) shows discrete stepwise loss of increasingly less labile components in 3. The first mass loss to be observed occurs over the approximate temperature range 50-130 °C (i), conforming closely to the mass loss calculated for 4 equivalents of H₂O, presumably from the crystal lattice. The low temperature at which H₂O loss begins suggests that there may be a degree of dynamic exchange of lattice H2O between the crystal and the atmosphere at room temperature. Phase (ii) conforms accurately to the loss of 4 equivalents of coordinated H₂O between 130-200 °C. The fully dehydrated sample is then stable towards further thermal degradation until temperatures in excess of 300 °C, with no further weight loss noted over the range 200-305 °C. Above this range, decarboxylation of the ligand framework occurs with the loss of 4 equivalents of CO₂ per formula unit at approx. 400 °C (iii). Loss of sulfur from the ligand framework occurs over temperatures of 405-490 °C (iv). We have observed decarboxylations of similar ligands at significantly lower temperatures¹¹ than that observed here for 3 whilst the sulfur atoms are embedded within the ligand in this case; hence decarboxylation is to be expected before the loss of any sulfur.



Magnetic behaviour of the manganese compounds 1 and 3

The magnetic behaviour of 1 follows Curie–Weiss behaviour down to *ca*. 50 K with a Curie constant of 24.0(3) cm³ mol⁻¹ K⁻¹ which is close to the predicted value of 21.9 cm³ mol⁻¹ K⁻¹ for $5 \times S = 5/2$. As there should be negligible orbital contribution to the magnetic moment for a material containing only Mn(II), we may assume that the Weiss constant, $\theta = -93(2)$ K, arises solely from moderately strong antiferromagnetic coupling. At the simplest level we can apply the results of Weiss's mean field theory¹² (MFT) to the measured Weiss constant θ (eqn. 1) in order to estimate *J*. If we define the Heisenberg–Dirac–Van Vleck Hamiltonian as:

$$\check{\mathbf{H}} = -2\sum_{ij} J_{ij} \check{\mathbf{S}}_i \cdot \check{\mathbf{S}}_j \tag{1}$$

the appropriate form of MFT gives:

$$\theta = \frac{2S(S+1)zJ}{3k_{\rm B}} \tag{2}$$

This yields a coupling constant J = -5.33 K (for z = 3). This is certainly a very crude approach as it neglects the structural anisotropy of the exchange lattice and averages the number of nearest neighbour spins, however it provides us with a magnitude for the coupling.

Structural considerations allow us to find more likely models to account for the observed magnetism, as the shortest superexchange pathways mediate the strongest spin-spin interactions. In the structure of 1 there are three possible superexchange pathways: three-atom carboxylate bridges, one-atom carboxylate bridges and one-atom hydroxide bridges. The hydroxide bridges form bowtie shaped clusters centred on Mn1, these are linked into a chain by two single atom carboxylate bridges between Mn2 and O6 (as shown in Fig. 3). The addition of the three atom carboxylate bridges produces a more complex chain topology. The individual chains are separated by the disulfide ligand with interchain distances equal to the b- and c-axis lengths (approimately 12.1 Å and 13.7 Å respectively). There are two approaches which can be employed to investigate the problem of this exchange-coupled chain. Both assume that coupling within the bowtie motif is relatively strong. The first approach assumes the coupling within these Mn₅ subunits is very strong such that they behave as an individual net spin joined to form a regular chain. This is unlikely since a) the Weiss constant is consistent with a set of weakly-interacting spins, and b) there is no broad maximum in χ which is expected for an antiferromagnetically-coupled linear chain. An alternative approach is to assume that interactions within the bowtie are stronger than those between the subunits. In this case, the behaviour can be modelled as a cluster of two vertex-sharing triangles. The most realistic model for this would be to use two scalene triangles, however Kahn has demonstrated⁵ that this approach cannot lead to three unequivocal values for the exchange couplings. We therefore have to make a simplifying approximation that the triangles are isosceles (Fig. 14).

The Hamiltonian for a single bowtie is:

$$\check{\mathbf{H}} = -2J(\check{\mathbf{S}}_1 \cdot \check{\mathbf{S}}_2 + \check{\mathbf{S}}_1 \cdot \check{\mathbf{S}}_3 + \check{\mathbf{S}}_1 \cdot \check{\mathbf{S}}_4 + \check{\mathbf{S}}_1 \cdot \check{\mathbf{S}}_5)
-2J'(\check{\mathbf{S}}_2 \cdot \check{\mathbf{S}}_3 + \check{\mathbf{S}}_4 \cdot \check{\mathbf{S}}_5)$$
(3)



Fig. 14 Single bowtie unit in 1 labelled to show the notation used in the spin Hamiltonian.

Application of Kambé's vector coupling method¹³ allows the corresponding eigenvalues to be determined. The following spin operators shown in eqn. 4 were defined:

$$\begin{split} \tilde{\mathbf{S}}_{A} &= \tilde{\mathbf{S}}_{2} + \tilde{\mathbf{S}}_{3} \\ \tilde{\mathbf{S}}_{B} &= \tilde{\mathbf{S}}_{4} + \tilde{\mathbf{S}}_{5} \\ \tilde{\mathbf{S}}_{C} &= \tilde{\mathbf{S}}_{A} + \tilde{\mathbf{S}}_{B} \\ \tilde{\mathbf{S}}_{T} &= \tilde{\mathbf{S}}_{C} + \tilde{\mathbf{S}}_{1} \end{split}$$
(4)

The energy of each spin state is then a function of S_A , S_B , S_C , S_T and S (eqn. 5).

$$E = -J[S_{\rm T}(S_{\rm T}+1) - S_{\rm C}(S_{\rm C}+1) - S(S+1)] -J'[S_{\rm A}(S_{\rm A}+1) + S_{\rm B}(S_{\rm B}+1) - 4S(S+1)]$$
(5)

For five Mn(II) ions with S = 5/2, 780 spin states are possible with total spins ranging from $S_{\rm T} = 1/2$ to $S_{\rm T} = 25/2$. Substitution into the Van Vleck equation produces an expression for the susceptibility (see electronic supplementary information[†]). Initial attempts to model the susceptibility were performed with J = J'. This proved unsuccessful. Whilst it provided a reasonable curve fit to the high temperature data (J = -5.25 K), it deviated substantially at lower temperatures (dotted line in Fig. 15) and was unable to reproduce the inflexion point and abrupt rise in χ below *ca*. 25 K. However, the inequivalent nature of the angles at the μ_3 -hydroxide bridge indicated a more asymmetric (isosceles) model might be appropriate. This then provides an excellent fit to the data down to 10 K (J = -2.5 K, J' = -6.8 K), reproducing closely the inflexion point and rapid rise in χ upon cooling. The model was further refined by inclusion of a mean field term to model the inter-cluster interactions at low temperatures, represented as a solid line in Fig. 15. This gives $\theta = -2.1$ K which corresponds (using MFT) to $J_{\text{inter}} = -0.4$ K. This model further predicts a broad maximum at temperatures below our data corresponding to short range antiferromagnetic ordering within the chains. Both J and J'fall within the range previously observed for Mn(II) ions joined by a single atom oxygen bridge,¹⁴ whilst J_{inter} is rather low. To explain the general form of the observed susceptibility the distribution of spin state energies for the equilateral and isosceles bowtie needs to be considered. As the temperature is lowered, the depopulation of the high-energy states occurs at different rates for the two different spin state topologies. In the case of the equilateral bowtie the depopulation will be uniform, this can be seen by the regular spacing of the energy levels (Fig. 16). On the other hand, the isosceles bowtie does not have such an even energy level distribution but has a concentration of states at relatively low energy. By consideration of the eigenvalues we have been able to derive the ground state spin arrangement for both the equilateral and isosceles clusters (Fig. 17). In the symmetric bowtie, the lowest lying spin state has the eigenfunction $|S_A, S_B$, $S_{\rm C}$, $S_{\rm T}$ > corresponding to |2,2,4,3/2> with $S_{\rm T}$ = 3/2, whereas for the isosceles bowtie the spin ground state is $S_{\rm T} = 1/2$ corresponding to the eigenfunction |1,1,2,1/2>. The ground states for both the equilateral and isosceles clusters are frustrated, as would be expected for a system containing triangular plaquettes. In both cases the spins on Mn2, Mn3, Mn4 and Mn5 oppose (to some degree) that on Mn1 as the interaction between Mn1 and the other four ions is predominantly antiferromagnetic.



Fig. 15 Plot of χ_p versus *T* for 1. The dashed line represents the fit obtained with the equilateral triangle model, the solid line shows the fit obtained with the final model.



Fig. 16 Energy level diagram for a symmetrical bowtie of Mn(II) ions (top) and corresponding diagram for an asymmetrical bowtie (bottom).



Fig. 17 Symmetric (a) and asymmetric (b) spin ground states in 1. Fractions relate to the projection of each S = 5/2 spin parallel to the applied field.

Compound **3** exhibits Curie–Weiss behaviour down to 25 K with C = 5.03(5) cm³ mol⁻¹ K⁻¹ (compared to 4.4 cm³ mol⁻¹ K⁻¹ for a single S = 5/2 ion) and $\theta = -21(1)$ K. Again, we can use mean field theory to give an order of magnitude approximation to the coupling constant giving J = -1.75 K. This relatively small coupling is expected as the strongest exchange interactions in compound **3** are due to *syn,anti*-carboxylate bridges (Fig. 10), which are expected to mediate weak antiferromagnetic coupling.¹⁵

There are two crystallographically distinct manganese environments, Mn1 and Mn2. Each chain contains only one type of manganese and the chains alternate within the sheets formed by linking through the disulfide ligand. The shortest separation of the chains is large (10.73 Å, equal to the distance from 0, 1/2, 0 to 0, 0, 1/2) and to first approximation the *inter*-chain coupling should be negligible. Whilst there is no analytical solution for the Hamiltonian describing a 1-D chain of interacting spins, the numerical approximations of Fisher¹⁶ and Weng¹⁷ have been shown to give satisfactory results. The Fisher equation (6) is derived from considering a system of classical spins.

$$\chi_{\rm P} = \frac{Ng^2 \mu_{\rm B}^2 S(S+1)}{3k_{\rm B}T} \left(\frac{1+u}{1-u}\right)$$

where
$$u = \coth\left[\frac{2JS(S+1)}{k_{\rm B}T}\right] - k_{\rm B}T \left[2JS(S+1)\right]^{-1}$$
(6)

whereas the Weng method (eqn. 7) uses numerical approximations with a chain of quantum spins.

$$\chi_{\rm p} = \frac{Ng^2\mu_{\rm B}^2}{k_{\rm B}T} \left(\frac{2.9167 + 208.04(|J|/k_{\rm B}T)^2}{1 + 15.543(|J|/k_{\rm B}T) + 2707.2(|J|/k_{\rm B}T)^3} \right)$$
(7)

Both equations give good fits to the observed susceptibility. Fig. 18 shows the best fit which is the Fisher equation with g allowed to refine whilst Fig. 19 shows the deviations found for the other three models.



Fig. 18 Graph of χ_p versus *T* for **3**. Measured data are represented by open circles, the best fit to the data (Fisher with g = 2.058) is shown by a solid line.



Fig. 19 Deviations from the measured data for the 4 fits; red dashes Fisher with g = 2, blue solid Fisher with g = 2.058, green dot-dash Weng with g = 2, magenta dots Weng with g = 2.048.

The large spin (S = 5/2) and small spin anisotropy due to negligible spin orbit coupling result in manganese(II) chains being well suited to use of the Fisher equation. The value of *J* obtained (J = -0.99 K) gives a good fit, though the exact position of the maximum is not exactly replicated. Allowing *g* to refine gives a much better fit (g = 2.058), though this is difficult to justify for an ion with small zero field splitting. The difficulty in modelling

the susceptibility may be due to the uncertainty in the mass of the sample. The TGA shows that water is being lost from the interlayer space close to room temperature so the sample may not contain exactly 4 equivalents of water per formula unit. This would produce a scaling error equivalent to an increase from 2.00 in the value of g. The Weng equation gave similar results (J = -1.25 K), with the position of the maximum again not exactly modelled.

For both the Fisher and Weng equations we obtain values of the magnetic coupling consistent with what we have observed before for well-isolated Mn(II) chains with *syn,anti*-carboxylate bridges.¹⁸ For both models we have assumed that the crystallographically distinct chains have identical exchange interactions. Use of a "double" Fisher or Weng equation, which is effectively a sum of two such equations, may be defensible if the two chains were very different, in this case it will produce an over-parameterised model with strongly correlated refinement of J_1 and J_2 .

Experimental

Reagents

 $Mn(OAc)_3 \cdot 2H_2O$ and $MnCl_2$ were purchased from Lancaster. Thiosalicylic acid, $(C_6H_4(CO_2H)(SH)-1,2)$ and 2-mercaptonicotinic acid, $(NC_5H_3(SH)(CO_2H)-2,3)$ were purchased from Avocado. The disulfide ligands 2,2'-dithiobisbenzoic acid, $(C_6H_4(CO_2H)(S)-1,2)_2$,¹⁹ and 2,2'-dithiobisnicotinic acid, $(NC_5H_3(S)(CO_2H)-2,3)_2$,²⁰ were prepared by literature methods and each was recrystallised from the minimum volume of absolute ethanol prior to use.

General procedure

All reaction mixtures were prepared to give a total volume of 10 cm³ and heated in 23 cm³ capacity Teflon-lined Parr autoclaves. For reactions involving 2-mercaptonicotinic acid, solids were weighed in a nitrogen-filled glove box and all solvents were degassed beforehand using standard methods. Infrared spectra of solid-phase products in KBr matrix disks were measured in the range 4000–400 cm⁻¹ with a Perkin-Elmer RXI FT-IR spectrophotometer. C, H, N micro-analyses were performed by the in-house service.

Synthesis

[Mn₅((C₆H₄(CO₂)(S)-1,2)₂)₄(μ_3 -OH)₂] (1). To a stirred suspension of thiosalicylic acid (155 mg, 1.01 mmol) in H₂O (6.0 cm³) was added Mn(OAc)₃·2H₂O (168 mg, 0.627 mmol) in H₂O (4.0 cm³) and the combined mixture was heated for 18 h at 200 °C, then cooled over a further 6 h to room temp. Large colourless square plate-like crystals of **1** were isolated from the resulting pale yellow solution and residual brown solid by decanting with several portions of H₂O and then filtered *in vacuo* (yield 135 mg, 70%). Anal. Found: C, 44.12; H 2.27. C₅₆H₃₄Mn₅O₁₈S₈ requires: C, 44.08; H, 2.25%. ν_{max} (KBr/cm⁻¹): 3588 m, 3057 w, 1654 w, 1648 w, 1602 s, 1590 s, 1567 s, 1457 m, 1437 m, 1407 s, 1394 s, 1364 s, 1279 s, 1157 m, 1054 w, 1038 m, 863 w, 841 w, 816 w, 786 w, 754 m, 742 m, 702 m, 654 m, 571 w.

 $[Zn(C_6H_4(CO_2)(S)-1,2)]$ (2). To a rapidly stirred solution of thiosalicylic acid (156 mg, 1.01 mmol) and KOH (2.00 mmol) in H₂O (4.0 cm³) was added a solution of ZnCl₂ (136 mg, 0.99 mmol) in H₂O (4.0 cm³) to give a viscous white mixture which was heated at 210 °C for 18 h and cooled at a rate of 0.1 °C min⁻¹ to below 80 °C and then more rapidly to room temp. The resulting solids were decanted with several portions of H₂O to remove the lightest residues and then filtered and dried in air. Large colourless 2-dimensional sheet-like crystals of 2 were isolated from the remaining non-crystalline solids manually under a light microscope and washed in hexane (yield 48 mg, 22%). Anal. Found: C, 34.90; H, 1.73. C₇H₄O₂SZn requires: C 38.64; H, 1.85%. More accurate values for C could not be obtained since white powder present on the surface of large crystals of 2 could not be fully removed prior to analysis. v_{max} (KBr/cm⁻¹): 3448 br w, 3052 w, 2924 w, 2849 w, 1654 w, 1590 m, 1568 s, 1527 s, 1500 w, 1466 w, 1436 m, 1419 m, 1272 w, 1259 w, 1156 w, 1118 w, 1056 w, 1040 w, 886 m, 807 w, 738 m, 696 w, 670 w, 651 w, 575 w.

Table 4 Crystallographic structure details and structural refinement for complexes 1–3

		1	2	3
	Chemical formula	C ₅₆ H ₃₄ Mn ₅ O ₁₈ S ₈	C ₇ H ₄ O ₂ SZn	$C_{24}H_{28}Mn_2N_4O_{16}S_4$
	Crystal habit	Colourless square plate	Colourless thin sheet	Pale yellow rod
	Crystal dimensions/mm	$0.23 \times 0.18 \times 0.05^{-1}$	$0.23 \times 0.10 \times 0.03$	$0.35 \times 0.21 \times 0.12$
	Crystal system	Triclinic	Monoclinic	Triclinic
	Space group	PĪ	C2/c	PĪ
	a/Å	8.9619(2)	27.0809(7)	9.2801(2)
	b/Å	12.0924(3)	7.5696(4)	10.5377(2)
	c/Å	13.6786(4)	7.1040(4)	16.8864(4)
	a/°	82.3830(10)	90	95.1726(11)
	β/°	86.7680(12)	93.11(3)	97.8935(11)
	γ/°	78.8418(8)	90	102.7070(9)
	$V/Å^3$	1440.79(6)	1454.11(12)	1583.20(6)
	Ζ	1	8	2
	$D_c/\mathrm{g~cm^{-3}}$	1.759	1.987	1.818
	M^{-}	1526.01	217.53	866.62
	<i>F</i> (000)	767	864	884
	<i>T</i> /°C	-93	-93	-93
	$2 heta_{ m max}/^{\circ}$	55.84	55.88	52.14
	μ (Mo-K α)/mm ⁻¹	1.430	3.598	1.145
	Transmission	0.908-0.750	0.906-0.751	0.988-0.903
	No. of reflections measured	14738	7196	16800
	No. of unique reflections	6820	1735	6212
	$R_{\rm int}$	0.0505	0.0601	0.0426
	$R^a(F > 4\sigma(F))$	0.0428	0.0456	0.0420
	$wR^b(F^2, \text{ all data})$	0.0927	0.1033	0.1102
	No. of reflections used	6820	1735	6122
	No. of parameters	462	116	561
	No. of restraints	0	0	6
	S ^c	1.035	1.199	1.052
	Max. $\Delta \rho / e \text{ Å}^{-3}$	0.666	0.873	-0.411

 ${}^{a}R(F) = \sum ||F_o| - |F_c|| / \sum |F_o| - bwR(F^2) = \left[\sum \{w(F_o^2)^2\}\right]^{0.5}; w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP, \text{ where } P = [F_o^2 + 2F_c^2]/3 \text{ and } a \text{ and } b \text{ are constants adjusted by the program.}$ ${}^{c}S = \left[\sum \{w(F_o^2 - F_c^2)^2\}/(n-p)\right]^{0.5}, \text{ where } n \text{ is the number of data and } p \text{ the number of parameters.}$

[Mn₂(NC₅H₃(S)(CO₂)-2,3)₂)₂(OH₂)₄]·4H₂O (3). 2-Mercaptonicotinic acid (155 mg, 1.01 mmol) and Mn(OAc)₃·2H₂O (134 mg, 1.00 mmol) were combined and dissolved into H₂O (10.0 cm³) and stirred for ~5 min. The brown suspension was heated for 15 h at 200 °C and cooled to room temp. over 6 h which afforded air-stable pale yellow rod-like clusters of **3** in high purity which were washed with H₂O and filtered (yield 92 mg, 42%). Anal. Found: C, 33.22; H, 3.12; N, 6.22. C₂₄H₂₈Mn₂N₄O₁₆S₄ requires: C, 33.26; H, 3.26; N, 6.46%. v_{max} (KBr/cm⁻¹): 3589 m, 3547 m, 3179 br m, 1587 s, 1570 s, 1552 s, 1445 m, 1400 s, 1383 s, 1248 w, 1166 m, 1121 w, 1074 m, 967 w, 841 m, 781 m, 723 m, 658 w.

X-Ray crystallography

Crystals were mounted on thin glass fibres using perfluoropolyether oil which was frozen in situ by the cold nitrogen gas Cryostream flow. Data were collected using an Enraf Nonius Kappa CCD diffractometer using monochromated Mo K α radiation (λ = 0.71073 Å). Absorption corrections were made based on ψ - and ω -scans (SORTAV).²¹ Structures were solved using direct methods and refined on F² using SHELXTL-97 software.²² All non-hydrogen atoms were refined anisotropically. For structure 3, attempts were made to solve the structure in the higher symmetry C2/c monoclinic space group, which proved unsuccessful. Whilst the positions of the metal ions and ligands seem to be related by these symmetry elements the positions of the non-coordinated water molecules lead to the lowering in symmetry of the space group. Furthermore, analysis of the atomic positions using the NEWSYM utility in PLATON⁸ suggested that no further symmetry elements are present. For structures 1-3 all hydrogen atoms were located in difference maps and allowed to refine freely on their parent atoms. For 3, hydrogen atoms belonging to non-coordinated water molecules were found to be equally disordered over three sites, hence they were refined using fixed partial occupancies (assigned as 2/3). In order to improve the overall stability of refinement for 3, all hydrogen atoms (both full and part occupancy) belonging to coordinated H₂O and H₂O of crystallisation were assigned fixed common U values. See Table 4 for further crystallographic information.

CCDC reference numbers 231140, 231141 and 231142. See http://www.rsc.org/suppdata/dt/b4/b401887g/ for crystallographic data in CIF or other electronic format.

Thermogravimetric analysis

Thermogravimetric data for a 2.15930 mg sample of **3** were collected with a Polymer Laboratories TGA-1500 apparatus over the temperature range 20-1000 °C.

SQUID magnetometry

All data were measured on homogenised crystalline samples using a Quantum Design MPMS-5 magnetometer over the temperature range 5–300 K with an external applied field in the range 0–50 000 G. The data were corrected for diamagnetism using Pascal's constants.⁵

Acknowledgements

We thank Ms. M. Nilwala S. Kottegoda for the collection of thermogravimetric data for **3**, Dr. John E. Davies for assistance with crystallographic determinations and EPSRC (S.M.H, R.A.M.) for financial support.

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