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Systematic investigation into the influence of base and substituents on the coordination chemistry of Mn^{III} and Mn^{III/II} salicylate complexes

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A systematic investigation into the coordination chemistry of Mn^{III} salicylates is presented revealing the influence on the shape and dimensionality of the final products of base, the presence or absence of co-ligands and the substituents on the salicylates. We report the synthesis, structures, characterisation and magnetic properties of seven compounds, (NHEt₃) [Mn^{III}(3-MeOsal)₂(MeOH)(H₂O)] (1), [NaMn^{III}(3-MeO-sal)₂(MeOH)₂] (2), [NaMn^{III}(sal)₂(H₂O)(MeOH)] · (MeOH) (3), [KMn^{III}(sal)₂(H₂O)(MeOH)] · (MeOH) (4), [Mn^{III}Mn^{III}₂(3-MeOsal)₄(py)₆(H₂O)₂] · 4H₂O, (5), [Mn^{III}Mn^{III}₂(3-MeO-sal)₄(2,2'-bipy)(H₂O)₃(MeOH)₂] · 3MeOH (7). Magnetic studies show the presence of antiferromagnetic interactions between the paramagnetic centres in all cases.

Keywords: manganese(III); salicylic acid; coordination polymers; magnetic properties

1 Introduction

Recent years have witnessed a burgeoning interest in exploring the use of combinations of metal ions and organic ligands for the synthesis of coordination polymers of various dimensionalities such as 1D chains, 2D sheets and 3D frameworks, which are also known as metal-organic frameworks (MOFs) (1). This research is often driven by the possibility of creating new materials with various functions or even multiple functions and potential applications include gas storage (2), catalysis (3) and magnetism (4). In addition, coordination chemists have realised that specific coordination geometries of metal ions can be used to provide nodes which can then be linked by organic ligands acting as spacers (5) to give networks of specified topologies often corresponding to those found in mineral structures (6). More recently, polynuclear clusters have begun to be used as nodes in place of single metal ions (7), and more complicated organic ligands to act as linkers have been synthesised (8). Furthermore, the molecular building block (MBB) approach, in which a building block is created for the positional assembly of components, has emerged as a powerful strategy for the design and construction of solid-state materials (9).

It is well established that salicylic acid is a versatile ligand in polynuclear cluster chemistry (10), although in the field of coordination polymers the complexes of 3*d* transition metal elements and salicylic acid and substituted salicylic acids have received less attention than systems based on other aromatic carboxylic acids (11). Inspired by the MBB concept, we previously reported that substituted salicylates along with trivalent metal centres can lead to the formation of a monoanionic MBB-linker which, in conjunction with the details of the coordination sphere of the metal centre node, allows the dimensionality of the final product to be tuned (12). This monoanionic MBB consists of a trivalent metal centre ($M = Mn^{III}$ and Fe^{III}) which is octahedrally coordinated by two substituted salicylates or salicylate itself with one bidentate or two monodentate coligands to complete the coordination sphere. Two different MBBs, A and B, can form (Scheme 1) depending on whether the co-ligands X and Y occupy cis or trans positions. We note, of course, that both A and B themselves can occur in different isomeric forms. Of particular relevance to the work we report here. A can have two forms depending on whether the phenoxo (or carboxylato) oxygens from the two ligands in the equatorial square plane are mutually trans or cis to each other.

Thus we found, for example that in the series of 3D diamondoid networks formed using this MBB approach (12a), the Mn^{III}-MBB of type A (Scheme 1) has the *trans* axial positions occupied by nitrogen atoms of two pyridine ligands (X = Y = pyridine, Z = Me). When this is combined with Mn^{II}-'nodes', we found that if Mn^{II} is 4 or 5 coordinated, a 3D diamondoid net is constructed. On the other hand, when the Mn^{II} node adopts coordination

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Scheme 1. A schematic representation of the MBBs A and B built up from co-ligands X and Y and salicylate (with substituents Z) and a trivalent metal centre.

number 6, the arrangement of the ligands around Mn^{II} determine the structural motif such that a *cis* arrangement of two water molecule ligands results in a 3D diamondoid net, whereas a *trans* arrangement results in the construction of a 1D coordination polymer.

In this paper, we have focused our attention on the study of the influence of the base, the presence or absence of coligands and the influence of bulky substituents on the aromatic ring of the salicylate on the shape and dimensionality of the final products with reference to the seven compounds $(NHEt_3)[Mn^{III}(3-MeOsal)_2$ $(MeOH)(H_2O)]$ (1), $[NaMn^{III}(3-MeO-sal)_2(MeOH)_2]$ (2), $[NaMn^{III}(sal)_2(H_2O)(MeOH)] \cdot (MeOH)$ (3), $[KMn^{III}(sal)_2$ $(H_2O)(MeOH)] \cdot (MeOH)$ (4), $[Mn^{II}Mn_2^{III}(3-MeOsal)_4$ $(py)_6(H_2O)_2] \cdot 4H_2O$, (5), $[Mn^{II}Mn_2^{III}(3-MeO-sal)_4(py)_4$ $(H_2O)_4] \cdot 4MeOH$, (6) and $[Mn^{II}Mn_2^{III}(3-MeO-sal)_4(2,2'$ $bipy)(H_2O)_3(MeOH)_2] \cdot 3MeOH$ (7) which illustrate this.

2 Results and discussion

2.1 Synthesis

All compounds can be prepared by the reaction of the corresponding salicylate with a Mn^{II} salt on addition of either base (NaOH, KOH, Et_3N) or NBu_4MnO_4 in a methanolic solution at room temperature. Under such conditions, Mn^{II} is easily oxidised to Mn^{III} . All compounds are stable and retain their crystallinity on exposure to air.

2.2 Description of structures of compounds 1–7 2.2.1 (NHEt₃)[Mn^{III}(3-MeOsal)₂(MeOH)(H₂O)], 1

Compound 1 consists of an anionic mononuclear Mn^{III} complex with a triethylammonium counter cation (Figure 1). The equatorial plane of the metal centre is occupied by four phenoxo or carboxylate oxygen atoms (O1, O2, O5 and O6) belonging to two bidentate 3-MeO-sal^{2–} ligands (mode I, Scheme 2). The two phenoxo oxygens are *cis* to each other, as are the two carboxylate oxygens, so that the two salicylate ligands are related by idealised mirror symmetry. The axial positions X and Y are occupied by a methanol and a water molecule so that the Mn^{III} complex forms a MBB of type A (Scheme 1). The



Figure 1. Structure of $(NHEt_3)[Mn^{III}(3-MeOsal)_2(MeOH) (H_2O)]$, 1 (top) and packing diagrams viewed along the *b*-axis (centre) and *a*-axis (below). Hydrogen bonds are shown dotted.

four equatorial Mn—O bond lengths (1.885(2), 1.910(2), 1.883(2) and 1.921(2) Å) and the two axial bond lengths (2.245(2) and 2.265(2) Å) are typical for Mn^{III} with an elongated Jahn–Teller axis. There is a hydrogen bond between the N—H of the triethylammonium cation and the carboxylate oxygen O7. Further intermolecular hydrogen bonding, involving the aqua and methanol ligands together



Scheme 2. Coordination modes of the salicylates found in compounds 1-7 (mode I, 1, 5, 6, 7; mode II, 2; mode III, 5, 6, 7 and mode IV and mode IV 3, 4).

with $\pi - \pi$ stacking interactions (shortest C···C distance 3.413 Å), builds the complexes into 2D supramolecular sheets parallel to the [100] plane.

2.2.2 [MnNa(3-MeO-sal)₂(MeOH)₂], 2

The structure of compound **2** (Figure 2) consists of a 1D coordination polymer of Mn^{III} and Na^+ ions arranged alternately and bridged by the 3-MeO-sal²⁻ ligands. Mn1 is situated on a crystallographic inversion centre, thus forming the *trans* A type MBB, ligated by two bidentate

3-MeO-sal²⁻ ligands (through phenoxo and carboxylate oxygen atoms) and two methanol molecules in axial sites (X = Y = MeOH, Scheme 1). Mn1 shows the expected Jahn–Teller distortion, with equatorial bond lengths Mn1–O1 and Mn1–O2 being 1.8650(14) and 1.9279(13) Å, respectively, and that of Mn1–O5 being 2.2269(16) Å. Na1 lies on a crystallographic twofold axis and has a distorted octahedral environment being coordinated by phenoxo, carboxylato methoxy oxygen atoms from each of two adjacent MBBs. Mn1 and Na1 are thus bridged by μ -phenoxo (O1) and μ -carboxylato (O2)



Figure 2. Structure of the 1D polymer, [Mn^{III}Na(3-MeO-sal)₂(MeOH)₂], **2**. Organic H-atoms are omitted for clarity. Colour code (online): Mn^{III}, purple; Na, orange; C, black and O, red.

oxygen atoms (mode II, Scheme 2), with Mn—O—Na bond angles 104.58(6)° and 99.11(6)°, respectively, forming a 1D coordination polymer. The chain structure is reinforced by hydrogen bonds between the O—H groups of the methanol ligands and non-coordinated carboxylate oxygens from adjacent MBB. The distance between the Na and Mn ions is 3.3091(5) Å, whereas the distance between two Mn^{III} ions in the chain is 6.0658(6) Å. The inversion symmetry about Mn1 forces the Na···Mn···Na angles in the chain to be strictly 180°. However, the crystallographic twofold symmetry about Na1 allows the Mn···Na···Mn angle to be 132.85(4)°, resulting in the observed zigzag chain. Hydrogen-bonded chains of alternating 3*d* and sodium ions have been previously reported, for example with the 2,2′biphenol ligand (*13*).

2.2.3 $[NaMn^{III}(sal)_2(H_2O)(MeOH)] \cdot MeOH$, 3 and $[KMn^{III}(sal)_2(H_2O)(MeOH)] \cdot MeOH$, 4

Compounds 3 and 4 crystallise isomorphously in the triclinic space group P-1 with Z = 2; therefore, only the structure of 4 will be described here. The asymmetric unit contains two independent half-Mn^{III} cations (each on a crystallographic inversion centre) and one K⁺ cation (on a general site), two salicylates, one aqua ligand and one methanol ligand, and one lattice methanol. The two Mn^{III} centres Mn1 and Mn2 are each hexacoordinated in an octahedral environment. Each is chelated, through phenoxo and carboxylato oxygens, by two inversionrelated (sal)²⁻ ligands, forming centrosymmetric type A MBBs (Scheme 1), although the axial positions are occupied differently in the two cases. For Mn1, the axial positions are occupied by oxygen atoms O8 and O8' of two methanol ligands, whereas for Mn2 they are occupied by carboxylate oxygen O3 and its symmetry-equivalent, belonging to two Mn1-based MBBs. Mn1 is thus linked by syn-anti carboxylate bridges to Mn2 and Mn2', such as to form a 1D chain with alternating Mn1 and Mn2 centres, in which all Mn ··· Mn linkages are equivalent (Mn1··· Mn2 5.4954(12) Å) and the Mn centres are strictly co-linear; the chain is parallel to a + b. The K⁺ cation K1 is ligated by two oxygens from the Mn1 MBB (O1' and O2) and two from the Mn2 MBB (O4 and O5") (coordination modes V and IV, respectively, see Scheme 2) so reinforcing the structure of the chain. It is also ligated by O6 from an adjacent chain, and in this way the chains are linked into 2D sheets parallel to (001) through the K⁺ cations (Figure 3). The interchain Mn···Mn distances are all greater than 7.6 Å.

The structure of **3** is very similar to that of **4**, apart from the expected shorter Na–O bond lengths than the corresponding K—O distances in **4**; the replacement of K^+ by Na⁺ does not seem to have had a significant effect on the overall structure.

2.2.4 $[Mn^{II}Mn_2^{III}(3-MeOsal)_4(py)_6(H_2O)_2] \cdot 4H_2O, 5$

The mixed-valence trinuclear structure of 5 is shown in Figure 4. The central Mn^{II}, Mn(2), occupies an inversion centre. The two equivalent Mn^{III} centres, Mn(1) and Mn(1'), are each chelated (mode I, Scheme 2) in their equatorial planes by two 3-MeOsal²⁻ ligands, with two trans-related pyridine ligands in the Jahn-Teller axial sites, forming a type A MBB in which the salicylate ligands are cis-related. The non-chelating carboxylate oxygen O(3) from each of the Mn^{III} MBBs coordinates to Mn(2), forming syn-anti carboxylate bridges, with $Mn(1) \cdots Mn(2)$ being 5.134(5) Å; Mn(1), Mn(2) and Mn(1') are collinear as imposed by the crystallographic symmetry. The octahedral coordination environment of Mn(2) is completed by two pyridine and two aqua ligands. The Mn-ligand bond lengths are typical for the respective oxidation states. The four equatorial Mn(1)-O distances are in the range 1.874(2)-1.925(2) Å, whereas the two axial Mn(1)–N lengths are 2.348(3) and 2.358(3)Å; distances Mn(2)-O(3), Mn(2)-O(9) and Mn(2)-N(3) are 2.180(2), 2.200(2) and 2.262(3) Å, respectively. The trinuclear molecular structure is reinforced by hydrogen bonds involving the aqua ligands on Mn(2) and the four lattice waters per Mn₃ unit.

2.2.5 $[Mn_2^{II}Mn^{II}(3-MeO-sal)_4(py)_4(H_2O)_4] \cdot 2MeOH, 6$

The centrosymmetric structure of compound **6** (Figure 4(b)) is very similar to that of **5**, but with the difference that one of the two axial pyridine ligands on Mn(1) in **5** has been replaced by an aqua ligand in **6**. As in **5**, the *syn-anti* carboxylate bridges between the metal centres are reinforced by hydrogen bonding involving the aqua ligands on Mn(2) and the lattice methanol molecules. However, in contrast to **5**, the aqua ligand O(9) on Mn(1) now forms intermolecular hydrogen bonds. Each hydrogen on O(9) forms a bifurcated hydrogen bond to a phenoxo and a methoxy oxygen (either O(1) and O(4), or O(5) and O(8)) of a (3-MeO-sal)²⁻ ligand on an adjacent molecule (Figure 4(c)), such that each trinuclear unit is linked by hydrogen bonding to two other units, forming a staircase-like supramolecular 1D chain.

2.2.6 $[Mn_2^{III}Mn^{II}(3-MeO-sal)_4(2,2'-bipy)(H_2O)_3(MeOH)_2] \cdot 2MeOH, 7$

Compound 7 is also a trinuclear, mixed-valence manganese complex, but here the metal centres form a triangular array (Figure 5) in contrast to the linear arrangements in 5 and 6. The two Mn^{III} ions Mn(1) and Mn(2) both form type A MBBs and in both the respective salicylate ligands are oriented *cis* to each other within the equatorial plane. The two axial sites on Mn(1) are occupied by a methanol ligand and a water ligand. One of the axial sites on Mn(2) is



Figure 3. Structure of $[Mn^{III}K(sal)_2(OH_2)(MeOH)]$, 4: the 1D chain of Mn^{III} MBBs showing linkage to K⁺ cations (above) and the 2D sheet parallel to (001) (below). Organic H-atoms are omitted for clarity. Colour code (online): Mn^{III} , purple; K, plum; C, black and O, red.

occupied by an outer carboxylate oxygen O(3) from the MBB based on Mn(1) and the other by an aqua ligand. The outer carboxylates, O(7) and O(11), from each Mn^{III} MBB, coordinate to the Mn^{II} ion Mn(3) *cis* to each other. The distorted octahedral coordination sphere of Mn(3) is completed by coordination from the two nitrogens of the 2,2'-bipyridyl and the oxygens of two water molecules. The three metal centres are thus linked by three *syn, anti*-carboxylate bridges, forming an approximately isosceles triangle, in which the two Mn^{II} ···Mn^{III} distances, 4.6523(11) and 4.6874(11)Å, are significantly shorter than the Mn^{III} ···Mn^{III} separation of 5.2418(11)Å.

2.3 Magnetic properties

DC magnetic studies were carried out on polycrystalline samples of 3–7. The temperature dependence of the χT products in the 1.8–300 K temperature range at 1000 Oe is shown in Figure 6. Isomorphous compounds 3 and 4 show similar magnetic behaviour and the room temperature χT

products are 3.01 and 2.98 cm³ K/mol, respectively, consistent with the expected value of 3.0 cm³ K/mol for an isolated Mn^{III} ion (S = 2, g = 2). Upon lowering the temperature, the χT products gradually decrease to minima of 1.52 cm³ K/mol at 4.5 K and 1.56 cm³ K/mol at 3.5 K for 3 and 4, respectively, and then increase up to $2.0 \text{ cm}^3 \text{ K/mol}$ at 1.8 K for both compounds, indicating that antiferromagnetic interactions dominate between the Mn^{III} centres. The subsequent increase in χT below 5 K cannot be explained in terms of ferrimagnetic arrangements of spins since there are equal number of the two types of Mn^{III} centres within the structure. However, it could be associated with spin canting behaviour, although there is no evidence for the latter phenomenon from M versus H measurements, (Figure S1 of the Supplementary Information, available online). We thus assume that the upturn in the χT product at low temperature is due to slight canting of the spins within the layers in the crystal packing, but with the critical temperature being too low (below 1.8 K) for the canting to be observable in other measurements (Figures S2 and S3 of the Supplementary



Figure 4. Molecular structures of $[Mn^{II}Mn_2^{III}(3-MeO-sal)_4(py)_6(H_2O)_2] \cdot 4H_2O$ 5 (upper) and $[Mn_2^{III}Mn^{II}(3-MeO-sal)_4(py)_4(H_2O)_4] \cdot 2MeOH$ 6 (middle) with the intermolecular hydrogen bonding in 6 (lower). Colour code (online): Mn^{III} purple, Mn^{II} pink, C black, O red, N blue, H grey, hydrogen bonds are shown as dotted green lines, organic H-atoms are omitted for clarity.

Information, available online). This idea is supported by the structural data which show that the Jahn–Teller axes of Mn(1) and Mn(2) are not co-parallel, which is consistent with the presence of canting between their spins. Furthermore, the data indicate that no long-range ordering is promoted within the 2D layers, in contrast to related 3D networks published previously (*12a*). The *M* versus *H* measurements as a function of the field reveal a continuous increase in the magnetisation, which reaches a value of 2.7 and 3.1 $\mu_{\rm B}$ at 7 T for compounds **3** and **4**, respectively. The

lack of saturation in the *M* versus *H* plot suggests the presence of low-lying excited states that might be populated when a field is applied. At higher field when the magnetic interactions are overcome, a saturation of the magnetisation at around 3 μ_B should be observed, since all spins will be parallel as is indeed the case. The agreement between the experimental magnitude of the magnetisation and the expected value suggests that the magnetic interactions between the spins are weak.

Figure 5. Structure of the trinuclear cluster $[Mn_2^{III}Mn^{II}(3-MeO-sal)_4(2,2'-bipy)(H_2O)_3(MeOH)_2]$ in 7. Colour code (online): Mn^{III} purple; Mn^{II} pink; C black; O red; N blue and H grey.

Figure 6. Temperature dependence of the χT products for 3 and 4 (left) 5–7 (right) at 1000 Oe (with χ defined as the DC magnetic susceptibility equal to M/H and normalised per complex unit). The red solid lines correspond to the best fits, see the text for fitting parameters. Inset: the semi-log plots to magnify the low temperature regions.

Based on the structures, both compounds can be viewed as S = 2 Mn^{III} chains with the magnetic interaction, *J*, between the Mn^{III} sites mediated by *synanti* carboxylate bridges. Such a regular antiferromagnetic quantum S = 2 spin chain model can be modelled with the Hamiltonian (14):

$$H = -2J\sum_{i}S_{i}S_{i+1}.$$

The temperature dependence of the magnetic susceptibility above 7 K could be reproduced by the analytical expression deduced from the above equation. The fit of the data gives g = 1.99(1) and $J/k_B = -1.15(2)$ K for **3** and g = 2.00(1) and $J/k_B = -0.81(1)$ K for **4** (Table 1). The interaction parameter, J, is in good agreement with the weak antiferromagnetic interaction expected for such *synanti* carboxylate bridges (12a).

The data for compounds 5 and 6 show that they have similar magnetic behaviour as can be expected from the fact that both have the same trinuclear Mn^{III}-Mn^{III}-Mn^{III} metallic core. At 300 K, the χT products are 9.6 and 9.87 cm³ K/mol for 5 and 6, respectively, slightly lower than the expected value of 10.38 cm³ K/mol for one Mn^{II} (S = 5/2, g = 2) and two Mn^{III} (S = 2, g = 2) ions (Figure 6). On decreasing the temperature, the χT products decrease continuously reaching 1.75 and 1.70 cm³ K/mol, respectively, at 1.8 K, indicating that antiferromagnetic interactions dominate within the trinuclear complexes and compatible with S = 3/2 ground states. The magnetic behaviour of each compound follows the Curie-Weiss law over the full temperature range of 1.8-300 K (Figure S4 of the Supplementary Information, available online) with Curie constants, C, of 9.8 and 10.9 cm³ K/mol, comparable with the value of 10.375 cm³ K/mol expected for one Mn^{II} (S = 5/2, g = 2) and two Mn^{III} ions (S = 2, g = 2). The negative Weiss constants, θ , of -5.6 and -5.9 K, respectively, also indicate the presence of antiferromagnetic interactions between the spin carriers.

The *M* versus *H* measurements (Figures S5 and S6 of the Supplementary Information, available online) at 1.8 K both show a slow increase in the magnetisation with field, reaching values of 9.1 for **5** and 10.5 μ_B at 7 T for **6**. Full saturation of the magnetisation was not observed, probably as a result of the anisotropy of the high spin Mn^{III} ion and or the presence of low-lying excited states that might be populated when a field is applied. For fields high enough to overcome the antiferromagnetic interactions and align all the spins parallel, the saturation magnetisation should be 13 μ_B for g = 2. It is noteworthy that the *M* versus *H* curve of **6** is *S*-shaped, which is a further indication of the presence of antiferromagnetic interactions.

The temperature dependence of the magnetic susceptibility was modelled using a simple symmetrical trimer approach assuming that the $Mn^{II}-Mn^{III}$ interactions (J_1)

Table 1. Fitting parameters for compounds 3-7 obtained using the models discussed in the text.

Compounds	g	J_1/k_B in K for Mn ^{II} –Mn ^{III}	J_2/k_B in K for Mn ^{III} –Mn ^{III}
$[NaMn^{III}(sal)_2(H_2O)(MeOH)] \cdot MeOH (3)$	1.99(1)	_	- 1.15(2)
$[KMn^{III}(sal)_2(H_2O)(MeOH)] \cdot MeOH (4)$	2.00(1)	_	-0.81(1)
$[Mn^{II}Mn_{2}^{III}(3-MeOsal)_{4}(py)_{6}(H_{2}O)_{2}] \cdot 4H_{2}O(5)$	1.93(1)	-0.64(1)	_
$[Mn_2^{III}Mn^{II}(3-MeOsal)_4(py)_4(H_2O)_4] \cdot 4MeOH (6)$	2.00(1)	-0.57(1)	_
$[Mn_{2}^{III}Mn^{II}(3-MeOsal)_{4}(2,2'-bipy)(H_{2}O)_{3}(MeOH)_{2}] \cdot 3MeOH (7)$	1.98(1)	-0.63(1)	-0.50(3)

are identical by symmetry and with the Heisenberg spin Hamiltonian:

$$H = -2J_1(S_{1A}S_2 + S_{1B}S_2)$$

where J_1 is the exchange interactions in the trimer between adjacent Mn^{II} and Mn^{III} ions, $S_{1A} = S_{1B} = 2$ is for Mn^{III}, and $S_2 = 5/2$ is for Mn^{II}. The application of the van Vleck equation (15) to the Kambe vector coupling scheme (16)allows a determination of the low-field analytical expression of the magnetic susceptibility (17). The experimental data from 300 to 1.8 K can be reproduced very well using this model (Figure 6) with the best sets of parameters being $J_1/k_B = -0.64(1)$ K and g = 1.93(1) for **5** and $J_1/k_B = -0.57(1)$ K and g = 2.00(1) for **6**, respectively. This model gives an estimate for these values but does not take into account any contribution arising from zero-field splitting. The magnitude of these interactions through the syn-anti carboxylate bridge between Mn^{III} and Mn^{II} is comparable with those found for 3 and 4 and those in the literature (12a). It is noteworthy that for 6 below 5 K, the theoretical curve after fitting the data is a bit higher than the experimental values. We can ascribe this to the presence of additional intercomplex antiferromagnetic interactions facilitated by the hydrogen bonds found in the structures. Although changing the reaction solvent from pyridine for 5 to methanol for 6 does lead to some changes in structural details, the basic magnetic signature of the trinuclear core dominates the susceptibility data until relatively low temperatures allow for the influence of the changes in hydrogen bonding affecting the long-range interactions in the structure to be observed.

The room temperature magnetic susceptibility product of **7** at 1000 Oe is 10.0 cm³ K/mol (Figure 6) in agreement with the expected value (10.38 cm³ K/mol) for the presence of one Mn^{II} metal ion (S = 5/2, g = 2) and two Mn^{III} ions (S = 2, g = 2). On decreasing the temperature, the χT product continuously decreases to reach 1.7 cm³ K/mol at 1.8 K, indicating dominant antiferromagnetic interactions in the triangular complex, compatible with an S = 3/2 ground state. The *M* versus *H* measurements at 1.8 K reveal similar magnetic behaviour to compounds **5** and **6**. The magnetisation curve again shows a steadily continuous increase to reach a value of 9.6 $\mu_{\rm B}$ at 7 T (Figure S7 of the Supplementary Information, available online), suggesting the presence of low-lying excited states that might be populated when a field is applied. This observation again indicates that the antiferromagnetic interactions are weak in this complex.

The temperature dependence of the magnetic susceptibility was treated with the symmetrical trimer model and the $Mn^{II}-Mn^{III}$ interactions (J_1) were considered equivalent although this is not imposed by crystal symmetry. Nevertheless, this is a good approximation given that the *syn-anti* carboxylate bridges are very similar and the Heisenberg spin Hamiltonian can then be written as

$$H = -2J_1(S_{1A}S_2 + S_{1B}S_2) - 2J_2(S_{1A}S_{1B})$$

where J_1 and J_2 are the exchange interactions in the trimer between Mn^{II} and Mn^{III} ions and between two Mn^{III} ions, respectively. $S_{1A} = S_{1B} = 2$ is for Mn^{III} and $S_2 = 5/2$ is for Mn^{II} centres. The application of the van Vleck equation (15) to Kambe's vector coupling scheme (16) allows a determination of the low field analytical expression of the magnetic susceptibility given (17). This model reproduces the experimental data very well from 300 to 1.8 K (Figure 5) with the best set of parameters $J_1/k_B = -0.63(1)$ K, $J_2/k_B = -0.50(3)$ K and g = 1.98(1). The magnitude of these interactions through the *syn-anti* carboxylate bridges between Mn^{II} and Mn^{III} or between two Mn^{III} ions is comparable with those obtained for compounds **5** and **6** and published data (12a).

2.4 Discussion

Now, we can consider what we have found to be the guiding principle behind this coordination chemistry, or, to put it in another way, how we can understand how to use the happy chance of serendipity, or serendipitous self-assembly, to persuade chemical systems towards our targets. In fact, we can compare this interplay and interaction of organic and inorganic moieties with what occurs in biological systems in terms of ordering and fitting structures for specific purposes. We can also relate this to recent endeavours in the field of natural product synthesis by which it has been shown that metal centres can lead to regio-, stereo-, enantio-selectivity as well as increasing the 'atom efficiency' of chemical reactions (*18*). In particular, we have here a type of 'policeman' molecular entity (MBB) standing at a junction and directing how the chemical traffic should proceed. The nature of the policeman's signals places the reactants in ideal positions in order to create specified structures. The development of this principle will allow us to set goals in targeted syntheses so that the serendipitous self-assembly approach becomes more like the programmed approach of organic synthesis. Furthermore, this is an important point of relevance to Systems Chemistry, for if we are ever going to recreate the extremely complicated chemistry behind complex molecular machinery such as is found, for example in Photosystem II, then we need to develop coordination chemistry principles to a higher level and, indeed, the level in which the exquisite control over the oxidation, spin and lability states of metal ions which is exercised in the biological chemistry of organisms on our planet can be achieved.

Scheme 3 shows a representation of the 'policeman' important in the context of the results we present here. The relevant structure-directing features are the *trans* arrangement of the outer carbonyl oxygens, which define the geometry of the node, and the nature of the substituents Z on the phenyl ring. In the cases we have discussed here, Z is always at the third position, but we have discussed elsewhere about the influence on the resulting superstructure if we move Z to other positions on the phenyl ring (12a).

Here, we find that whenever a sodium source is used (NaN₃, NaOAc, Na₂CO₃, 3-MeO-salHNa or salHNa), we always obtain compound **2** as the most favoured product and this is also true for the reactions with the ligand 3-MeO-salHNa and **3** for reactions with ligand salH₂. Also, comparing compounds **5** and **6**, excess pyridine in the reaction solution results in all the axial positions of the metal centres in the MBB as well the 'nodes' being occupied. Furthermore, delaying the addition of the base to the reaction solution of **6** (see Section 5 for details) results in the isolation of the different MBB **5**. From a structural point of view, compound **1**, which is a mononuclear compound, can be isolated with excess of Et₃N, although changing the base to NaOH in **2** results in a heterometallic 1D coordination polymer. A comparison of the structures of

Scheme 3. A schematic representation of MBB.

compounds 2-4 shows that the bulky methoxy substituent on the phenyl ring of 2 'blocks' the dimensionality of the final product to give a molecular compound, whereas 3 and 4 are heterometallic 2D coordination polymers. A similar effect is observed in compounds 5 and 6, which are trinuclear, in contrast to what we found previously, in which the substituent was methyl rather than methoxy and a 3D diamondoid framework resulted. Thus, the bulky MeO substituent does not allow for the MBB to be extended into a 3D structure in this way (12a). The change in co-ligand also affects the structural motif of the final product. We have seen previously (12b) that using 2,2'-bipy as co-ligand leads to a type B MBB (Scheme 1, right), although in the case of compound 7 further coordination on the 'node' sterically favours the formation of a triangular structure formed.

3 Conclusion

A systematic investigation into the coordination chemistry of Mn^{III} salicylates has been made. It has been possible to judge the influence of base, the presence or absence of coligands and the nature of the substituents on the phenyl ring of the salicylate on the shape and dimensionality of the final products by considering the seven new compounds summarised in Table 2 as well as previous results on related systems revealing the usefulness of this MBB approach in directing product formation. In particular, comparing the results to those obtained by us previously (12a) in which similar trinuclear units can form the repeating units of the polymeric chain and networks, this study demonstrates that the bulkier methoxy group of 3-MeO-salH₂ prevents the bridging of the Mn^{III} centres to the Mn^{II} centres of another trinuclear unit. Instead, the coordination sphere of each Mn^{II} is completed by two pyridine molecules, leading to discrete structures rather than diamondoid networks. Although the modification of solvents and substituents on salicylate influences the final resulting structures, this does not affect the magnetic properties in any significant way. All complexes show antiferromagnetic interactions between the metal centres similar to those observed in the extended systems. However, as a result of the 3D nature of the networks we described previously, these showed remanent magnetisation consistent with ferrimagnetic long-range ordering (12a).

4 Experimental

4.1 Physical measurements

All chemicals and solvents were obtained from commercial sources and were used as received. The reactions were carried out under aerobic conditions. The elemental analyses (C, H and N) were carried out using an Elementar Vario EL analyser, FT-IR spectra were measured on a

		MBB				
Compounds	Z	X	Υ	'Node'	Dimensionality	Work
$ \begin{array}{c} 1\\ 2\\ 3\\ 3\\ 4\\ 4\\ 4\\ 4\\ 4\\ 5\\ 6\\ 6\\ 6\\ 6\\ 6\\ 6\\ 6\\ 6\\ 6\\ 6\\ 6\\ 6\\ 6\\$	3-OCH ₃ 3-OCH ₃ H H H H 3-OCH ₃ 3-OCH ₃ 3-OCH ₃ 3-OCH ₃ H H H H H H H H H H H H H H H H H H H	$\begin{array}{c} H_2O\\ CH_3OH\\ CH_3OH\\ O\left({\rm carboxylate} \right)\\ CH_3OH\\ Py\\ Py\\ Py\\ Py\\ Py\\ Py\\ Py\\ Py\\ Py\\ Py$	CH ₃ OH CH ₃ OH CH ₃ OH O (carboxylate) CH ₃ OH Py Py Py Py Py Py Py Py Py Py Py Py Py	$\begin{array}{c} \text{NHE} t_3 \\ \text{Na} \\ \text{Na} \\ \text{Na} (H_2 \text{O}) \\ \text{Na} (H_2 \text{O}) \\ \text{K} (H_2 \text{O}) \\ \text{K} (H_2 \text{O}) \\ \text{K} (H_2 \text{O}) \\ \text{K} (H_2 \text{O}) \\ \text{Mn}^{\text{II}} [trans-Py_2 (H_2 \text{O})_2] \\ \text{Mn}^{\text{II}} [tras-Py_2 (H_2 \text{O})_2] \\ \text{Mn}^{\text{II}} (H_2 \text{O})_2 (H_2 \text{O})_2 (H_3 \text{OH})] \\ \text{Mn}^{\text{II}} (H_2 \text{Me}-Py)_2 (H_2 \text{O})_2 (H_3 \text{OH})] \\ \text{Mn}^{\text{II}} (H_2 \text{Me}-Py)_2 (H_2 \text{O})_2 (H_3 \text{OH})] \\ \text{Mn}^{\text{II}} (H_2 \text{O})_2 (H_3 \text{OH})_2 \\ \text{Mn}^{\text{III}} (H_2 \text{O})_2 (H_3 \text{OH})_2 \\ \text{Mn}^{\text{III}} (H_2 \text{O})_2 (H_3 \text{OH})_2 \\ \text{Mn}^{\text{IIII}} (H_2 \text{O})_2 (H_3 \text{OH})_2 \\ \text{Mn}^{\text{IIIIII}} (H_2 \text{O})_2 (H_3 \text{OH})_2 \\ \text{Mn}^{IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII$	0D (monouclear) 1D 2D 2D 2D 2D 2D 2D 0D (trinuclear) 0D (trinuclear) 0D (trinuclear) 0D (trinuclear) 0D (mononuclear) 1D 0D (monouclear) 1D 3D diamondoid 3D diamondoid 3D diamondoid 1D	This work This work Ref. (11a) Ref. (12a) Ref. (12a) Ref. (12a) Ref. (12a) Ref. (12a) Ref. (12a)

Table 2. The MBB type A found for Mn^{III} in the literature (for Z, X and Y see Scheme 1).

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Perkin-Elmer Spectrum One spectrometer with samples prepared as KBr discs, and X-ray powder diffraction patterns for all compounds were measured at room temperature using a Stoe STADI-P diffractometer with Cu-K α radiation. Phase purity was confirmed by comparison of the powder diffraction pattern of bulk product with that simulated from the crystal structure. Magnetic susceptibility measurements were obtained using a Quantum Design SQUID MPMS-XL susceptometer. The magnetometer operates between 1.8 and 400 K for DC applied fields of -7 to +7 T. Measurements were carried out on polycrystalline samples of 18.6 mg (3), 17.8 mg (4), 26.96 mg (5), 9.6 mg (6) and 16.2 mg (7). AC susceptibility measurements were measured with an oscillating AC field of 3 Oe and AC frequencies ranging from 1 to 1500 Hz. The magnetic data were corrected for the sample holder and the diamagnetic contribution. The samples were first checked for the presence of ferromagnetic impurities by measuring the magnetisation as a function of the field at 100 K. For pure paramagnetic or diamagnetic systems, a perfect straight line is expected and is indeed observed for these compounds indicating the absence of any ferromagnetic impurities. Single-crystal X-ray crystallographic data were collected at 150 K on a Stoe IPDS II area detector diffractometer (1, 4 and 6), or at 100 K on a Bruker SMART Apex CCD diffractometer (2, 3, 5 and 7) using graphite-monochromated Mo-K α radiation (Table 3). Semi-empirical absorption corrections were applied using SADABS (19a) or XPREP in SHELXTL (19b). The structures were solved using direct methods, followed by full-matrix least-squares refinement against F^2 (all data) using SHELXTL (19b). Anisotropic refinement was used for all ordered non-H atoms; organic H atoms were placed in calculated positions, whereas coordinates of hydroxo or water H atoms were refined in most cases. CCDC 776386-776392 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.2 Synthesis

4.2.1 Compound 1

Mn(ClO₄)₂·6H₂O (0.180 g, 0.5 mmol) was added to a methanolic solution (20 ml) of 3-MeO-salH₂ (0.168 g, 1 mmol) and Et₃N (0.130 ml, 2 mmol) to give a yellow solution. After 1 h, a small amount of precipitate was observed and colour of the solution turned greyish black. The solution was stirred for 2 h. The solution was filtered and the filtrate was left to evaporate. Black diamond-shaped crystals were obtained the next day. Yield: 78%. Anal. calcd for C₂₃H₃₄MnNO₁₀ (found): C, 51.21 (51.19); H, 6.31 (6.34); N, 2.59 (2.56)%. IR (KBr disc, cm⁻¹): 3435 (b), 2935 (m), 1594 (s), 1546 (s), 1492 (s), 1320 (m), 1248 (s), 1150 (s), 1056 (m), 758 (m), 678 (m), 435 (w).

4.2.2 Compound 2

Mn(ClO₄)₂·6H₂O (0.036 g, 0.2 mmol) was added to a methanolic solution (15 ml) of 3-MeO-salH₂ (0.017 g, 0.1 mmol) and Et₃N (0.013 ml, 0.2 mmol) to give a light yellow solution. After a few minutes, NaN₃ (0.013 g, 0.2 mmol) dissolved in 5 ml H₂O was added slowly followed by stirring for 2 h. The resulting black solution was filtered and left to evaporate. After 2 days, small black crystals were obtained. The crystals were isolated by filtration, washed with methanol and dried in air. Yield: 32%. Anal. calcd for C₁₈H₂₀MnNaO₁₀ (found): C, 45.57 (45.48); H 4.22 (4.25)%. Selected IR data (KBr disc, cm⁻¹): 3498 (s), 2984 (m), 2932(m), 1596 (s), 1579 (s), 1545 (s), 1476 (s), 1325 (s), 1252 (m), 1208 (m), 1154 (m), 1069 (s), 856 (s), 809 (m), 755 (s), 698 (s), 465 (m), 420 (m).

4.2.3 Compound 3

Mn(OAc)₂ · 4H₂O (0.250 g, 1.0 mmol) was added to a methanolic solution (20 ml) of Na(SalH) (0.240 g, 1.5 mmol) to give a black solution. The solution was stirred for 2 h. The solution was filtered and the filtrate was left to evaporate slowly. Black crystals were obtained the next day. Yield: 78%. Anal. calcd for C₁₆H₁₈MnNaO₉ (found): C, 44.46 (44.12); H, 4.20 (4.31)%. IR (KBr disc, cm⁻¹): 3378 (b), 3062 (w), 2928 (w), 1604 (s), 1577 (s), 1534 (s),1460 (s), 1367 (s), 1345 (s), 1231 (s), 1145 (s), 1104 (w), 1040 (m), 897 (m), 842 (s), 754 (s), 694 (m), 656 (m) 592 (m).

4.2.4 Compound 4

Mn(OAc)₂ · 4H₂O (0.250 g, 1.0 mmol) was added to a methanolic solution (20 ml) of SalH₂ (0.210 g, 1.5 mmol) and KOH (0.168 g, 3.0 mmol) was added giving a black solution which was stirred for 2 h and then filtered and left to evaporate slowly. Black crystals were obtained the next day. Yield: 78%. Anal. calcd for C₁₆H₁₈KMnO₉ (found): C, 42.86 (42.77); H, 4.05 (3.98)%. IR (KBr disc, cm⁻¹): 3379 (b), 3062 (w), 2928 (w), 1603 (s), 1579 (s), 1535 (s),1461 (s), 1365 (s), 1344 (s), 1230 (s), 1142 (s), 1104 (w), 1040 (m), 897 (m), 843 (s), 755 (s), 694 (m), 656 (m) 592 (m).

4.2.5 Compound 5

3-MeO-salH₂ (1.01 g, 6.00 mmol) and Mn(OAc)₂·4H₂O (0.5 g, 2.0 mmol) were dissolved in pyridine (10 ml) to give a clear yellow solution. The solution was stirred while solid (NBu₄)(MnO₄) (0.15 g, 0.4 mmol) was added in small portions over approximately 10 min leading to a black liquor which was layered with an equal volume of petroleum ether. After 2 days, dark green crystals suitable for X-ray diffraction studies were deposited. The crystals were isolated by filtration, washed with ether and dried in

Table 3. Crystallographic	data and structure refi	inement for compound	s 1–7.				
	1	2	3	4	S	9	7
Formula FW (g mol ⁻¹)	$C_{23}H_{34}MnNO_{10}$ 539.45	$C_{18}H_{20}MnNaO_{10}$ 474.27	C ₁₆ H ₁₈ MnNaO ₉ 432.23	$\mathrm{C_{16}H_{18}KMnO_9}$ 448.34	C ₆₂ H ₆₆ Mn ₃ N ₆ O ₂₂ 1412.03	$C_{54}H_{60}Mn_3N_4O_{22}$ 1281.88	C ₄₆ H ₅₄ Mn ₃ N ₂ O ₂₃ 1167.73
Crystal dimensions (mm)	$0.33 \times 0.24 \times 0.05$	$0.32 \times 0.14 \times 0.06$	$0.24 \times 0.18 \times 0.08$	$0.26 \times 0.22 \times 0.03$	$0.29 \times 0.21 \times 0.031$	$0.21 \times 0.17 \times 0.04$	$0.23 \times 0.09 \times 0.03$
Colour	Black	Black	Black	Black	Greenish-black	Greenish-black	Black
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	C2/c	P-1	P-1	$P2_1/n$	P-1	P-1
$T(\mathbf{K})$	150(2)	100(2)	100(2)	150(2)	100(2)	150(2)	150(2)
<i>a</i> (Å)	13.0949(10)	22.064(2)	7.7573(4)	8.0301(14)	12.8326(6)	9.6054(14)	13.0629(10)
b (Å)	8.7941(7)	8.5408(8)	10.5460(6)	10.6788(19)	16.9338(8)	11.4207(17)	13.7564(10)
c (Å)	22.1208(19)	12.1315(11)	12.6971(7)	12.772(2)	14.7252(7)	14.352(2)	15.8000(12)
α (°)	90	90	102.952(1)	104.102(14)	90	112.841(11)	85.897(1)
β (°)	100.630(7)	122.805(2)	104.532(1)	103.994(14)	99.885(1)	103.739(12)	69.393(1)
λ (°)	90	90	111.017(1)	109.668(14)	90	91.718(12)	67.905(1)
$V(\text{\AA}^3)$	2503.7(4)	1921.5(3)	880.07(8)	935.3(3)	3152.4(3)	1396.3(4)	2456.3(3)
Z	4	4	2	2	2	1	2
$ ho_{ m calcd}~({ m gcm^{-3}})$	1.431	1.639	1.631	1.592	1.488	1.525	1.579
μ (Mo-K α) (mm ⁻¹)	0.583	0.766	0.824	0.975	0.675	0.753	0.848
$F(0 \ 0 \ 0)$	1136	976	444	460	1462	663	1206
Data measured	17321	4727	5140	6213	15699	10088	12885
Unique data	4822	2162	3758	3835	7047	5825	9933
$R_{ m int}$	0.0605	0.0312	0.0122	0.0413	0.0271	0.0547	0.0549
Data with $I > 2\sigma(I)$	3471	1706	3498	3122	6442	4025	5554
Parameters/restraints	328/4	143/0	266/5	259/0	441/6	390/5	6/069
wR_2 (all data)	0.1486	0.0804	0.0879	0.1197	0.1427	0.1537	0.1428
S on F^2 (all data)	0.996	1.001	1.077	1.001	1.154	0.992	0.958
R_1 (data with $I > 2\sigma$ (I)]	0.0599	0.0368	0.0338	0.0476	0.0628	0.0592	0.0574
Largest difference neak/hole (e $Å^{-3}$)	+0.61/-0.91	+0.51/-0.37	+0.45/-0.44	+0.34/-0.95	+1.13/-1.00	+0.70/-0.89	+1.25/-0.50
CCDC number	776386	776387	776388	776389	776390	776391	776392

-÷ nt fo ĥ Ę ud stru data hi. otallo £ 3 Table

air. Yield: 72%. Anal. calcd for $C_{62}H_{62}Mn_3N_6O_{22}$ (found): C, 52.82 (52.84); H, 5.91 (5.97); N, 4.44 (4.40)%. Selected IR data (KBr disc, cm⁻¹): 3505 (s), 3461 (b), 2986 (m), 2934 (m), 1594 (s), 1578 (s), 1549 (s), 1474 (s), 1443 (s), 1372 (m), 1348 (m), 1327 (s), 1249 (m), 1206 (m), 1152 (m), 1066 (s), 853 (s), 809 (m), 760 (s), 699 (s), 674 (m), 470 (m), 417 (m).

4.2.6 Compound 6

MnCl₂ · 4H₂O (0.079 g, 0.4 mmol) was added to a methanolic solution (20 ml) of 3-MeO-salH₂ (0.101 g, 0.6 mmol) and pyridine (0.202 ml, 1.6 mmol) to give a light yellow solution. The solution was left stirring overnight and then Et₃N (0.100 ml, 0.7 mmol) was added slowly. Within a few minutes, the solution turned blacks. The following day black needle-shaped crystals were obtained. The crystals were collected by filtration, washed with cold methanol and air dried. Yield: 64%. Anal. calcd for C₅₄H₆₀Mn₃N₄O₂₂ (found): C, 49.71 (50.54); H, 4.62 (4.68); N, 4.31 (4.36)%. Selected IR data (KBr disc, cm⁻¹): 3448 (s), 3465 (b), 2985 (m), 2932 (m), 1592 (s), 1575 (s), 1542 (s), 1469 (s), 1444 (s), 1366 (m), 1342 (m), 1324 (s), 1237 (m), 1145 (m), 1062 (s), 849 (s), 798 (m), 754 (s), 694 (s), 670 (m), 465 (m), 419 (m).

4.2.7 Compound 7

Mn(OAc)₂·4H₂O (0.368 g, 1.5 mmol) was added to a methanolic solution (20 ml) of 3-MeO-salH₂ (0.168 g, 1 mmol). After 5 min, 2,2'-bipy (0.039 g, 5 mmol) was added giving a yellow solution and then Et₃N (0.100 ml, 0.7 mmol) was added. The resulting black solution was left to stand and after a few days black crystals suitable for X-ray analysis were obtained. The crystals were collected by filtration, washed with cold methanol and air dried. The crystals lost crystallinity when left in air without the mother liquor for more than 1 week. Yield: 48%. Anal. calcd for C₄₆H₅₄Mn₃N₂O₂₃ (found): C, 47.23 (47.26); H, 4.61 (4.62); N, 2.39 (2.40)%. Selected IR data (KBr disc, cm⁻¹): 3400 (b), 2925 (m), 1587 (s), 1551 (s), 1480 (s), 1442 (s), 1363 (m), 1335 (m), 1244 (m), 1065 (m), 857 (m), 750 (m), 430 (w).

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