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Synthesis and characterisation of polymeric manganese and zinc 5-hydroxyisophthalates

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Abstract

The crystallisation of 5-hydroxyisophthalic acid with divalent Mn or with Mn or Zn and either 2,2-bipyridine (2,2-bipy) or pyridine-2-(1*H*-pyrazol-3-yl) gave solids of composition $[Mn(C_8H_4O_5)(H_2O)_3]\cdot 2H_2O$ (1), $[Mn(C_8H_4O_5)(2,2'-bipy)]\cdot H_2O$ (2), $[Mn_2(C_8H_4O_5)_2(C_8H_7N_3)_2]\cdot H_2O$ (3) and $[Zn(C_8H_4O_5)(2,2'-bipy)]$ (4). Each compound has 1D co-ordinative chains that are connected by hydrogen bonds. Compounds 2–4 contain $M_2C_2O_4$ rings with pseudo-chair geometries. The Mn atoms in 2 are coupled antiferromagnetically. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Encouraged by our successful synthesis of co-ordination polymers using metal acetates, benzene-1,3,5-tricarboxylic acid (H₃BTC) and 2,2'-bipyridine (2,2-bipy) [1], we chose to investigate the effect of replacing H₃BTC with 5-hydroxyisophthalic acid. This was selected because like H₃BTC it has two carboxylic acids arranged *meta*, but at a position *meta* to both carboxyl groups is a phenol hydroxyl group. The phenol hydroxyl was intended as a mimic for the third carboxyl group which remains protonated in our recently reported layered polymers [1]. Manganese(II) metal-ions were of interest because high spin manganese(II) ions possess five unpaired electrons which can couple ferromagnetically [1].

2. Experimental

All organic chemicals were purchased from Lancaster while metal salts were purchased from Aldrich or BDH. Hydrothermal, infra-red and TGA experiments were performed using previously described equipments [1].

2.1. $[Mn(C_8H_4O_5)(H_2O_3)] \cdot 2H_2O$ (1)

5-Hydroxyisophthalic acid (2.81 g, 15.6 mmol), manganese(II) acetate tetrahydrate (3.8 g, 15.5 mmol) and water (100 ml) were heated under reflux for 5 min before being allowed to cool. After cooling to room temperature (r.t.) the mixture was filtered. The volume was reduced in vacuo until a white solid formed to which water (10 ml) was added. After allowing the mixture to stand overnight a solid was collected by filtration, washed with water and air-dried to give 1 as a white microcrystaline solid (4.2 g, 83%). Anal. Found: C, 29.2; H, 4.2; N, < 0.3. Calc. for [Mn(C₈H₄O₅)-(H₂O)₃]·2H₂O: C, 29.6; H, 4.3; N, 0.0%. IR (KBr, cm⁻¹): 3546br, 3460br, 3411br, 3250br, 1663w, 1654w, 1636m, 1619m, 1559s, 1543s, 1507m, 1500m, 1458m, 1397s, 1368sh, 1308m, 1280m, 1233w, 1134w, 1107w, 1002w, 983m, 941w, 914w, 891w, 817m, 780s, 739s.

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TGA: an endothermic mass loss of 26.7% occurs between r.t. and 110°C (for total dehydration a mass loss of 27.7% is required).

2.2. $[Mn(C_8H_4O_5)(2,2'-bipy)] \cdot H_2O$ (2)

5-Hydroxyisophthalic acid (101 mg, 0.56 mmol), manganese(II) acetate tetrahydrate (137 mg, 0.56 mmol), 2,2'-bipyridyl (87 mg, 0.56 mmol) and water (10 ml) were placed in a 23 ml Parr bomb. After sealing the bomb was heated at 100°C h⁻¹ to 220°C. After 2 h the bomb was cooled at 5°C h⁻¹ to 180°C. After a further 6 h the bomb was cooled at $5^{\circ}Ch^{-1}$ to r.t. The yellow crystalline product (147 mg, 65%) was collected by filtration, washed with water and air-dried. When the experiment was repeated with slower cooling from 180°C $(2^{\circ}C h^{-1})$ darker particles were produced in addition to 2. Anal. Found: C, 52.6; H, 3.2; N, 6.7. Calc. for $[Mn(C_8H_4O_5)(C_{10}H_8N_2)(H_2O)]$: C, 52.8; H, 3.5; N, 6.8%. IR (KBr, cm⁻¹): 3402brs, 1664m, 1655m, 1619m, 1604s, 1595w, 1577s, 1541vs, 1488m, 1473m, 1439s, 1415w, 1385vs, 1313m, 1298w, 1273m, 1247w, 1215m, 1152w, 1119w, 1103m, 1093sh, 1062w, 1044w, 1018m, 1009w, 1000w, 977m, 946w, 936w, 906w, 890w, 846w, 801m, 786m, 765m, 736sh, 725m, 685w, 650m, 627w, 564w, 490w, 470w, 455w, TGA: between 80 and 190°C a mass loss of 4.5% occurred (for the conversion of the monohydrate to an anhydrous solid a mass loss of 4.4% is required). Above 330°C decomposition occurred.

2.3. $[Mn_2(C_8H_4O_8)_2(C_8H_7N_3)_2] \cdot H_2O$ (3)

5-Hydroxyisophthalic acid (102 mg, 0.57 mmol), manganese(II) acetate tetrahydrate (138 mg, 0.56 mmol), pyridine-2-(1*H*-pyrazol-3-yl) (149 mg, 1.026 mmol) and water (20 ml) were placed in a 45 ml bomb. The resulting mixture was heated at 100°C h⁻¹ to 240°C. After 2 h the bomb was cooled to 180°C at 5°C h⁻¹ and after 6 h the bomb was cooled at 2°C h⁻¹ to r.t. before being opened. The colourless solid (161 mg, 74%) was harvested but was not phase pure. IR (KBr, cm⁻¹): 1615m, 1577m, 1561m, 1541s, 1516w, 1489w, 1433m, 1411sh, 1386s, 1361m, 1300m, 1272m, 1218w, 1105w, 1089w, 1059w, 1018w, 1002w, 978w, bipyridyl (89 mg, 0.57 mmol) and water (10 ml) were placed in a 23 ml Parr bomb. After sealing this bomb was heated at 100°C h⁻¹ to 220°C. After 2 h the bomb was cooled at 5°C h⁻¹ to 180°C. After a further 6 h the bomb was cooled at 2°C h⁻¹ to r.t. The colourless crystals (170 mg, 75%) were collected by filtration, washed with water and dried in air. *Anal.* Found: C, 53.3; H, 2.8; N, 6.7. Calc. for [Zn(C₈H₄O₅)(C₁₀H₈N₂)]: C, 53.8; H, 3.0; N, 7.0%. IR (KBr, cm⁻¹): 3440brs, 3240br, 1626s, 1609s, 1574vs, 1547sh, 1493m, 1475m, 1442s, 1425s, 1384s, 1318w, 1288w, 1276w, 1250w, 1224w, 1211w, 1174w, 1159w, 1126w, 1103w, 1078w, 1057w, 1020m, 1004w, 976m, 933w, 913w, 889m, 787m, 768m, 734m, 718m, 651w, 628w, 467m, 417m. TGA: above 190°C a mass loss due to general decomposition occurred.

2.5. X-ray crystallographic studies

2.5.1. Structure determinations

Data for 1 and 4 were collected on a Bruker SMART 1000 CCD diffractometer at 295 K, with data collection using SMART [2] and data reduction using SAINT [2]. Absorption correction was applied using SADABS [2]. Data for 2 and 3 were collected on an Enraf–Nonius Kappa-CCD diffractometer at 150 K with data collection and reduction using DENZO [3] and COLLECT [4]. Absorption correction was applied using SORTAV [5]. All structures were solved by direct methods using SHELXS-97 [6] and refined by least-squares methods using SHELXL-97 [6]. In all cases, refinement proceeded smoothly to the values given and all non-water H-atoms were placed geometrically. For structures 1–3, H atoms on water molecules were identified from the difference Fourier map.

2.6. Magnetic measurements

Variable-temperature susceptibility measurements were carried out in the temperature range of 2–300 K at a magnetic field of 0.1 T for a polycrystalline sample with a SQUID magnetometer (Quantum Design MPMS-XL-5). The susceptibility data were corrected from the diamagnetic contributions as deduced by using Pascal's constant tables and were fitted with the van Vleck equation for a S = 5/2 dimer with a monomeric paramagnetic impurity (c):

$$\chi_{\rm m} = (1-c) \frac{N_{\rm A}g^2\beta^2}{k_{\rm B}T} \frac{2e^{2x} + 10e^{6x} + 28e^{12x} + 60e^{20x} + 110e^{30x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x}} + c \frac{35g^2}{32}$$

968w, 930w, 890w, 814w, 801m, 784m, 766m, 725m, 640w, 617w.

2.4. $[Zn(C_8H_4O_5)(2,2'-bipy)]$ (4)

5-Hydroxyisophthalic acid (103 mg, 0.57 mmol), zinc(II) acetate dihydrate (124 mg, 0.565 mmol), 2,2'-

where $x = J/k_{\rm B}T$.

With the molecular field approach the expression for the susceptibility becomes:

$$\chi'_{\rm m} = \frac{\chi_{\rm m}}{1 - \frac{2zJ'\chi_{\rm m}}{N_{\rm A}g^2\beta^2}}$$



Fig. 1. Top: drawing of the manganese co-ordination environment in 1. Middle: drawing of a 1D co-ordinative chain. Bottom: drawing showing hydrogen bonds between adjacent layers.

The theoretical curve of the magnetisation has been calculated by using the computation program MAG-PACK [7].

3. Results and discussion

3.1. $[Mn(C_8H_4O_5)(H_2O)_3] \cdot 2H_2O$ (1)

5-Hydroxyisophthalic acid was chosen as a co-ordination polymer precursor because it has tridentate functionality like benzene-1,3,5-tricarboxylic acid, except that one of the carboxylic acid groups has been replaced with a hydroxyl group. No crystal structures of 5-hydroxyisophthalates were found in the Cambridge Structural Database [8] although an infinite array has been reported which contains 5-hydroxyisophthalic acid as a building block [9]. After alkylation of the phenol group the diacid has been used as a building block in polymers [10]. An initial attempt at the hydrothermal manganese(II)-5-hydroxyisophthalate synthesis of vielded a colourless solution. Slow evaporation gave crystals of the hydrated polymeric carboxylate 1 (Fig.

Table 1 Selected bond lengths (Å) and angles (°) for 1

Mn(1)–O(7)	2.120(2)	O(7)–Mn(1)–O(8)	177.95(10)
Mn(1)–O(8)	2.166(2)	O(7)–Mn(1)–O(6)	89.33(11)
Mn(1)–O(6)	2.178(2)	O(8)-Mn(1)-O(6)	90.28(10)
Mn(1)-O(4) # 1	2.2550(19)	O(6)-Mn(1)-O(2)	82.96(8)
Mn(1)–O(2)	2.2767(18)	O(2)-Mn(1)-O(1)	55.66(6)
Mn(1) - O(1)	2.4059(19)	O(4) # 1-Mn(1)-O(1)	83.21(6)
$Mn(1)-O(5) \neq 1$	2.4477(18)	O(4) # 1-Mn(1)-O(5) # 1	55.38(6)
		O(6)-Mn(1)-O(5) # 1	83.12(8)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2, y+1/2, -z; #2 -x+1/2, y-1/2, -z.

Table 2 Hydrogen bonds (Å and °) for 1

D–H…A	d(D-H)	$d(H \cdots A)$	$d(D \cdot \cdot \cdot A)$	∠(DHA)
$O(3)-H(3A)\cdots O(10) \neq 3$	0.82	1.80	2.610(3)	170.7
O(6)–HW6A…O(3) # 4	0.93(4)	1.83(4)	2.749(3)	170(4)
O(6)–HW6B…O(2) # 3	0.70(3)	2.15(3)	2.827(4)	162(3)
O(7)–HW7A…O(4) # 5	0.78(4)	2.05(4)	2.818(3)	167(4)
O(7)−HW7B…O(9) # 3	0.89(4)	1.83(4)	2.712(4)	175(3)
O(8)–HW8A…O(1) # 6	0.96	1.87	2.756(3)	152.9
O(8)−HW8B…O(9) # 7	0.85	2.28	3.115(4)	168.3
O(9)-HW9A…O(2)	0.96	2.12	2.868(3)	133.6
O(9)−HW9B…O(3) # 8	0.96	2.41	3.038(4)	123.1
O(10)−HW1A…O(5) # 9	0.78(5)	2.09(5)	2.853(4)	165(5)
O(10)–HW1B…O(5) # 1	0.71(5)	2.16(5)	2.864(4)	169(6)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2, y+1/2, -z; #2 -x+1/2, y-1/2, -z; #3 -x+1, -y+1, -z+1; #4 -x+1/2, y+1/2, -z+1; #5 x+1/2, -y+1/2, z; #6 -x, -y+1, -z; #7 -x, -y+1, -z+1; #8 x-1/2, -y+1/2, z; and #9 -x+1, -y+1, -z.

Table 3 Selected bond lengths (Å) and angles (°) for 2

Mn1–O3 # 1	2.1175(15)	O3 # 3-Mn1-O4 # 2	94.67(6)
Mn1–O4 # 2	2.1524(15)	N1-Mn1-N2	72.31(7)
Mn1–N1	2.2362(18)	O1-Mn1-O2	58.00(5)
Mn1–N2	2.2507(18)		
Mn1–O2	2.2512(14)		
Mn1–O1	2.2868(14)		
Mn1 # 1–O3	2.1175(15)		
Mn1 # 3–O4	2.1524(15)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z, #2 x+1/2, -y, z+1/2, #3 x-1/2, -y, z-1/2.

Table 4							
Hydrogen	bonds	(Å	and	°)	for	2	

<i>d</i> (D–H)	<i>d</i> (H···A)	$d(\mathbf{D}\cdots\mathbf{A})$	∠(DHA)
0.840	1.830	2.649	164.45
0.827	2.120	2.863	149.37
0.821	2.025	2.795	156.05
	d(D-H) 0.840 0.827 0.821	d(D-H) d(H···A) 0.840 1.830 0.827 2.120 0.821 2.025	d(D-H) d(H···A) d(D···A) 0.840 1.830 2.649 0.827 2.120 2.863 0.821 2.025 2.795

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z; #2 x+1/2, -y, z+1/2; #3 x-1/2, -y, z-1/2; #4 -x -1/2, y, -z-1/2; and #5 -x, -y, -z.

1). The manganese has a distorted pentagonal bipyramidal co-ordination geometry. In equatorial sites are four-carboxylate oxygens from chelating carboxylate ligands and one-water oxygen O6. In the axial sites are two-water oxygens O7 and O8. Two non-co-ordinated waters are present which hydrogen bond to carboxylate groups, the phenol group and other waters. The solid contains 1D co-ordinative chains of manganese atoms bridged by the carboxylate ligands. These chains are interlinked by means of a network of hydrogen bonds. The hydrogen bond network links each chain to other parallel chains which are approximately 3.8 Å above and below and to chains which are alongside (Tables 1-9).

One-water HW6B hydrogen bonds to a carboxylate oxygen O2 forming a Mn₂O₄H₂ ring which interlinks the chains. While the phenol hydrogen H3A hydrogen bonds to a water oxygen O10, one of the water hydrogens HW1B then hydrogen bonds to O5 forming a bridge between the chains. Carboxylate oxygen O4 hydrogen bonds to HW7A while HW7B binds to a water oxygen O9. Also binding to O9 is another water hydrogen HW8B while the other hydrogen in this water HW8A binds to O1 forming a hydrogen bond bridge between O1 and O4 within a chain. A water molecule oxygen O9 hydrogen bonds to the axial waters O7 and O8 which are co-ordinating to the manganese. Hydrogens within axial waters hydrogen bond to carboxylate oxygens forming two further bridges between the stacked chains. These hydrogen bonds exist between carboxylate oxygens O1 and O4 and water hydrogens

HW8A and HW7A, respectively. The water hydrogens attached to O10 hydrogen bond to carboxylate oxygens O5 in different layers. The water hydrogens attached to

Table 5 Selected bond lengths (Å) and angles (°) for 3

	0.100(0)		00.0(1)
Mn1-O2 # 1	2.128(3)	O2 # I-MnI-OI	93.8(1)
Mn1–O1	2.134(3)	O2 # 1-Mn1-O3 # 2	89.5(1)
Mn1–O3 # 2	2.234(3)	O1–Mn1–O3 # 2	96.4(1)
Mn1–N2	2.239(3)	O2 # 1-Mn1-N2	124.1(1)
Mn1–N1	2.247(4)	O1-Mn1-N2	96.2(1)
Mn1−O4 # 2	2.328(3)	O3 # 2-Mn1-N2	143.0(1)
		O2 # 1-Mn1-N1	83.5(1)
		O1–Mn1–N1	164.2(1)
		O3 # 2-Mn1-N1	99.2(1)
		N2-Mn1-N1	72.9(1)
		O2 # 1-Mn1-O4 # 2	145.2(1)
		O1–Mn1–O4 # 2	100.1(1)
		O3 # 2-Mn1-O4 # 2	57.5(1)
		N2-Mn1-O4 # 2	86.1(1)
		N1-Mn1-O4 $\#$ 2	90.7(1)

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2, y, -z+1/2; #2 x-1/2, -y, z-1/2; and #3 x+1/2, -y, z+1/2.

Table 6 Hydrogen bonds (Å and °) for **3**

D–H···A	<i>d</i> (D–H)	$d(H \cdots A)$	d(D - A)	∠(DHA)
$\overline{N(3)-H(3A)\cdots O(4) \# 4}$	0.88	2.05	2.875(5)	155.0
O(5)–H(5)···O(6) # 5	0.84	1.81	2.640(4)	169.9
O(6)-H(6WA)O(1)	0.78(5)	2.06(5)	2.781(4)	154(5)
O(6)-H(6WB)O(3)	0.93(8)	2.02(8)	2.859(4)	149(6)
#2				

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2, y, -z+1/2; #2 x-1/2, -y, z-1/2; #3 x+1/2, -y, z+1/2; #4 -x+1, -y, -z+1; and #5 -x+1/2, y, -z+1/2.

Table 7 Selected bond lengths (Å) and angles (°) for **4**

Zn1-O2 # 1 Zn1-O5 # 2 Zn1-O1 Zn1-N2 Zn1-N1	1.985(1) 1.985(1) 2.054(1) 2.156(1) 2.163(2)	O2 # 1–Zn1–O5 # 2 O2 # 1–Zn1–O1 O5 # 2–Zn1–O1 O2 # 1–Zn1–N2 O5 # 2–Zn1–N2 O1–Zn1–N2 O2 # 1–Zn1–N1	118.3(1) 103.96(6) 88.5(1) 98.2(1) 143.4(1) 85.2(1) 101.3(1)	
		O2 # 1–Zn1–N1 O5 # 2–Zn1–N1	101.3(1) 93.7(1)	

Symmetry transformations used to generate equivalent atoms: #1 -x, -y, -z; #2 -x+1, -y, -z.

Table 8 Hydrogen bonds (Å and °) for **4**

D–H···A	d(D-H)	d(H…A)	$d(D \cdots A)$	∠(DHA)
O3–H3a…O4	0.820	1.910	2.724	171.44

Symmetry transformations used to generate equivalent atoms: #1 -x, -y, -z; #2 -x+1, -y, -z; and #3 -x+2, -y-1, -z.

O6 are hydrogen bonded to the phenol oxygen and a carboxylate oxygen O2 forming a link between the layers.

3.2. $[Mn(C_8H_4O_5)(2,2'-bipy)] \cdot H_2O$ (2)

The hydrothermal reaction of 5-hydroxyisophthalic acid with manganese acetate and 2,2'-bipyridyl gave 2 as a bright vellow crystalline solid. In the structure of 2 manganese cations and carboxylate ligands form 1D chains which are linked by a hydrogen bonding network consisting of the phenol proton, the water molecule and carboxylate oxygens into sheets (Fig. 2). Between the mats of carboxylates are layers of parallel bipy ligands. The closest approach between two bipy ligands is 3.379 Å (C9–C9 distance). The manganese atoms are in pairs in a Mn₂C₂O₄ ring and the intermanganese distance is 4.058 Å. The next-nearest neighbouring manganese atom is 6.223 Å away. The substitution of the carboxylic acid group in H₃BTC for a hydroxyl group has resulted in a considerable change in the crystal structure. The different hydrogen bonding properties of the two groups are likely to have a greater influence on the structure.

The manganese atoms are in a grossly distorted octahedral environment. One carboxylate group O1–C8–O2 and a 2,2'-bipy are chelating the manganese while two other carboxylates are bridging between manganese atoms forming an eight-membered boat shaped ring. The torsion angle Mn1–O4 # 2–O3 # 2–Mn1 #4 is -40.4° . The nitrogen atoms of the bipy are cis to O1 while only one nitrogen is cis to O2. The O1-Mn1-O2 and N1-Mn1-N2 angles are much smaller than the 90° expected for a perfect octahedral complex. While the O4 # 2–Mn1–O3 # 3 angle is significantly different from 90° it is closer to the ideal octahedral angle. Three hydrogen bonds help hold the layers of manganese carboxylates together. The phenol proton H5 hydrogen bonds to the water molecule O1W which then hydrogen bonds to oxygens O4 and O2 in carboxylate groups in different molecules. The aromatic rings of the bipy ligands are approximately 3.6 Å from each other and appear to be π stacked.

A large number of $Mn_2C_2O_4$ rings containing six co-ordinate manganese linked together by bridging carboxylate ligands are present in the crystallographic literature. Many rings contain additional bridging ligands such as oxide [11–13], water [14,15] or more complex ligands [11]. However, some examples do exist of $Mn_2C_2O_4$ rings which are not supported by additional bridging ligands. These include mixed Mn(II)-Mn(III) carboxylates [16] and Mn(II) carboxylates [17–22]. Table 9

Summary	of	key	crystal	llographic	data	for	compounds	1-	-4
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Compound	1	2	3	4
Empirical formula	C ₈ H ₁₄ MnO ₁₀	C ₁₈ H ₁₄ MnN ₂ O ₆	C ₁₆ H ₁₃ MnN ₃ O ₆	C ₁₈ H ₁₂ ZnN ₂ O ₅
Formula weight	325.13	409.25	398.23	401.67
Temperature (K)	302(2)	150(2)	150(2)	301(2)
Crystal system	P2(1)/a	P2/n	P2/n	$P\overline{1}$
Space group	monoclinic	monoclinic	monoclinic	triclinic
Unit cell dimensions				
a (Å)	7.5211(7)	8.5040(2)	8.2886(3)	8.5027(4)
b (Å)	18.4930(18)	11.0319(4)	10.9165(4)	10.1489(5)
c (Å)	9.5673(9)	18.4365(5)	17.9845(6)	10.7619(5)
α (°)				85.3720(10)
β (°)	108.00(1)	102.81(2)	100.38(2)	67.254(1)
γ (°)				69.267(1)
$V(Å^3)$	1265.6(2)	1686.6(1)	1600.6(1)	799.3(1)
Ζ	4	4	4	2
D_{calc} (Mg m ⁻³)	1.706	1.612	1.653	1.669
Absorption coefficient (mm ⁻¹)	1.089	0.823	0.866	1.570
Absorption correction	semi-empirical	empirical	empirical	semi-empirical
Crystal size (mm)	$0.3 \times 0.1 \times 0.05$	$0.25 \times 0.25 \times 0.10$	$0.1\times0.1\times0.1$	$0.37 \times 0.20 \times 0.20$
Reflections collected/ R_{int}	8062/0.0564	8181/0.0437	12 932/0.0565	7726/0.0164
Completeness to max 2θ	81.9%	98.4%	79.6%	90.2%
Data/restraints/parameters	3984/0/207	3416/0/252	4141/0/244	4612/0/236
Goodness-of-fit on F^2	0.881	1.040	1.044	1.098
Final R indices $R_1/\omega R_2$ $[F^2 > 2\sigma(F^2)]$	0.0452/0.0911	0.0387/0.0833	0.0636/0.1392	0.0319/0.0860
R indices (all data)	0.0937/0.1090	0.0591/0.0903	0.1070/0.1550	0.0391/0.0886
Largest difference peak and hole (e $Å^{-3}$)	0.374 and -0.547	0.323 and -0.387	0.945 and -0.928	0.461 and -0.424



Fig. 2. Left: drawing of the Mn co-ordination environment in 2. Right: drawing showing the hydrogen bonding between sheets.

3.3. $[Mn_2(C_8H_4O_8)_2(C_8H_7N_3)_2] \cdot H_2O$ (3)

The Mn(II) has a distorted octahedral co-ordination environment which contains four oxygen and two nitrogen atoms (Fig. 3). Two oxygens from a chelating carboxylate and one oxygen from a bridging carboxylate are *cis* to the pyridine nitrogen. The site *trans* to the pyridine nitrogen is occupied by an oxygen from a bridging carboxylate. Like the solids formed from zinc and manganese acetates, hydroxyisophalic acid and 2,2'-bipy, eight-membered $M_2C_2O_4$ rings are present. The structure consists of layers of metal atoms and carboxylate ligands which are separated by layers of the nitrogen heterocycles. The structure is similar to that of **2** which is not surprising in view of the similarity of 2,2'-bipyridyl and pyridine-2-(1*H*-pyrazol-3-yl).

3.4. $[Zn(C_8H_4O_5)(2,2'-bipy)]$ (4)

By heating zinc acetate, 5-hydroxyisophthalic acid and 2,2-bipy under hydrothermal conditions **4** was obtained as a colourless solid (Fig. 4). The zinc has a distorted square-pyramidal geometry. The 2,2-bipy nitrogens and two carboxylate oxygens are equatorial while a third carboxylate oxygen is in the axial site. In common with structure **2** the metal atoms are in eightmembered $M_2C_2O_4$ rings. The relative arrangement of the eight-membered rings to the carboxylate layers is different to that observed for **2**. An interlayer hydrogen bond between the phenolic hydrogen H3A and a carboxylate oxygen O4 exists. A number of zinc carboxylates containing five co-ordinate zinc atoms in $Zn_2C_2O_4$ rings are known [23–29]. However, only two [23,29] of



Fig. 3. Top: drawing of the Mn co-ordination environment in 3. Bottom: drawing showing the sheets.



Fig. 4. Top: drawing showing the Zn co-ordination environment in 4. Bottom: drawing showing the different orientation of the sheets.

these $Zn_2C_2O_4$ rings lacked bridging ligands which provide additional links between the zincs.

4. Magnetic properties

The magnetic properties of compound [Mn(C₈H₄O₅)-(2,2'-bipy)(H₂O)] (2) are depicted in Fig. 5 with a plot of the product of $\chi_m T$ (proportional to the square of the magnetic moment) versus temperature. At room temperature the $\chi_m T$ value is 8.52 emu K mol⁻¹ per manganese dimer, which is very close to the value expected for two magnetically isolated manganese(II) centres with a spin sextuplet (S = 5/2). $\chi_m T$ reveals a continuous decrease upon cooling, reaching a value of 1.78 emu K mol⁻¹ at 2 K. Such a behaviour is characteristic of antiferromagnetic coupling between two spin sextuplets of the manganese(II) ions. This behaviour is better observed in the χ_m versus temperature plot (Fig. 6) where a maximum in the susceptibility can be observed at very low temperatures (2.8 K). Accordingly, the susceptibility data were analysed with the van Vleck equation for a dimer of high spin octahedral manganese(II) ions (S = 5/2) with the isotropic Heisenberg hamiltonian $H_{ex} = -2JS_AS_B$, where J is the magnetic coupling parameter (see Section 2). A fitting of the data to this model leads to g = 1.99, J = -0.37 cm⁻¹ and a monomeric Mn(II) paramagnetic impurity of 1.5%. The agreement is excellent in the whole temperature range (solid lines in Figs. 5 and 6). This result indicates that although the structure of compound 2 consists of chains of manganese dimers, the exchange interaction is restricted to the Mn(II)-Mn(II) pairs which are magnetically coupled through two -OCO- bridges. In this case the spin coupling through the 5-hydroxyisophthalate anion is negligible. This antiferromagnetic coupling between the manganese(II) ions connected only through two -OCO- bridges has already been observed in other similar Mn(II) dimers and chains, where J values ranging from -0.33 to -1.76 cm⁻¹ have been determined [30-35]. The good magnetic isolation produced by the 5-hydroxyisophthalate anion resembles that observed in the related benzene-1,3,5-tricarboxylate [1], isophthalate [35] and terephthalate anions [32,36] In fact, the introduction of a molecular mean field [35] in the fitting procedure, accounting for interdimer interactions (via the 5-hydroxyisophthalate anion) or interchain interactions (via the hydrogen bonding network), does not improve the agreement with the experiment and the values of the parameters remain unaffected. For example, this model leads to g = 1.99, J = -0.37 cm⁻¹, zJ' = -0.005 cm⁻¹ and a paramagnetic impurity of 1.3%. The obtained molecular field parameter, zJ', is very small (-0.005 cm⁻¹) compared to those reported for the isophthalate (-0.03 cm⁻¹) [30] and terephthalate bridges (-0.04 and -0.065 cm⁻¹) [32,36].

The isothermal magnetisation data at 2 K (Fig. 7) also indicate that there is no significant interdimer interactions even at very low temperatures. Thus, the magnetisation data can be very well reproduced with



Fig. 5. Plot of the product of the susceptibility times the temperature per Mn dimer vs. temperature for compound $\mathbf{2}$. The solid line is the best-fit to a model of antiferromagnetic coupled Mn(II) dimer (see text). Inset: the low temperature region.



Fig. 6. Plot of the susceptibility per Mn dimer vs. temperature for compound 2. The solid line is the best-fit to a model of antiferromagnetic coupled Mn(II) dimer (see text). Inset: the low temperature region showing the maximum in the susceptibility data.



Fig. 7. Plot of the isothermal magnetisation at 2 K for compound 2. Solid line represents the theoretical behavior for a Mn(II) dimer with the same parameters as those obtained from the susceptibility data.

the same parameters as those deduced from the susceptibility versus temperature data without introducing any molecular field term (solid line in Fig. 7). Magnetic data for compound **3** was not obtained because this solid was not prepared phase pure. However, because it has a similar structure to **2** it is likely that similar magnetic properties would be observed.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 156783–156786 for compounds 1–3, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

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