



ACADEMIC
PRESS

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Solid State Chemistry 172 (2003) 212–218

JOURNAL OF
SOLID STATE
CHEMISTRY

<http://elsevier.com/locate/jssc>

Synthesis and structure of three manganese oxalates: $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $[\text{C}_4\text{H}_8(\text{NH}_2)_2][\text{Mn}_2(\text{C}_2\text{O}_4)_3]$ and $\text{Mn}_2(\text{C}_2\text{O}_4)(\text{OH})_2$

Zoe A.D. Lethbridge, Aileen F. Congreve, Emma Esslemont, Alexandra M.Z. Slawin, and Philip Lightfoot*

School of Chemistry, University of St. Andrews, Purdie Building, North Haugh, St. Andrews, Fife KY16 9ST, UK

Received 5 September 2002; received in revised form 6 December 2002; accepted 14 December 2002

Abstract

Three manganese oxalates have been hydrothermally synthesized, and their structures determined by single-crystal X-ray diffraction. $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (**I**) is orthorhombic, $P2_12_12_1$, $a = 6.262(4) \text{ \AA}$, $b = 13.585(5) \text{ \AA}$, $c = 6.091(4) \text{ \AA}$, $V = 518.2(4) \text{ \AA}^3$, $Z = 4$, final R , $R_w = 0.0832$, 0.1017 for 561 observed data ($I > 3\sigma(I)$). The one-dimensional structure consists of chains of oxalate-bridged manganese centers. $[\text{C}_4\text{H}_8(\text{NH}_2)_2][\text{Mn}_2(\text{C}_2\text{O}_4)_3]$ (**II**) is triclinic, $P\bar{1}$, $a = 5.9305(5) \text{ \AA}$, $b = 7.7763(7) \text{ \AA}$, $c = 8.1707(7) \text{ \AA}$, $\alpha = 81.489(2)^\circ$, $\beta = 81.045(2)^\circ$, $\gamma = 86.076(2)^\circ$, $V = 367.72(5) \text{ \AA}^3$, $Z = 1$, final R , $R_w = 0.0467$, 0.0596 for 1773 observed data ($I > 3\sigma(I)$). The three-dimensional framework is constructed from seven coordinate manganese and oxalate anions. The material contains extra-framework diprotonated piperazine cations. $\text{Mn}_2(\text{C}_2\text{O}_4)(\text{OH})_2$ (**III**) is monoclinic, $P2_1/c$, $a = 5.926(1) \text{ \AA}$, $b = 5.695(1) \text{ \AA}$, $c = 7.494(2) \text{ \AA}$, $\beta = 91.10(3)^\circ$, $V = 252.88(9) \text{ \AA}^3$, $Z = 1$, final R_1 , $wR2 = 0.0710$, 0.1378 for 268 observed data ($I > 2\sigma(I)$). The structure is also three dimensional, with layers of MnO_6 octahedra pillared by oxalate anions. The hydroxide group is found bonded to three manganese centers resulting in a four coordinate oxygen.

© 2003 Elsevier Science (USA). All rights reserved.

Keywords: Manganese; Oxalate; Framework; Amine templated; Hydrothermal synthesis

1. Introduction

Hydrothermal synthesis has proved invaluable as a method of producing new framework materials. A wide variety of elements have now been incorporated into such structures in order to create new topologies and properties [1]. With the use of organic ligands, transition metals and active guest species, useful electronic, magnetic or optical properties may be conferred on the material. Our recent research has aimed to synthesize transition metal frameworks containing two different anions, specifically phosphate and oxalate. We have been successful in synthesizing aluminum [2], iron [3] and several manganese [4,5] containing materials. This has involved the use of a number of different amines as structure directing agents. In the course of this work a number of other materials have been synthesized, three of which are reported here. The cell parameters of $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (**I**) have been reported

previously [6], but here we describe the structure for the first time. The amine-containing manganese oxalate $[\text{C}_4\text{H}_8(\text{NH}_2)_2][\text{Mn}_2(\text{C}_2\text{O}_4)_3]$ (**II**) was found as a minor phase in the preparation of the manganese phosphate oxalate $[\text{C}_4\text{H}_8(\text{NH}_2)_2][\text{Mn}_4(\text{HPO}_4)_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_2]$ [5]. Attempts to synthesize a pure sample of **II** were unsuccessful, however they did result in a new manganese oxalate hydroxide, $\text{Mn}_2(\text{C}_2\text{O}_4)(\text{OH})_2$ (**III**).

2. Experimental

$\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (**I**) was prepared by hydrothermal reaction of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{H}_3\text{PO}_4(\text{aq})$ (85%), oxalic acid, dipropylamine and H_2O in approximate molar ratio 2:1:1:1:555. The mixture, pH 1, was heated in a polypropylene bottle at 102°C for 69 h. After cooling, the mixture was filtered and washed with distilled water and dried in air to give a white solid consisting predominantly (>50% as judged by powder X-ray diffraction) of another manganese oxalate dihydrate,

*Corresponding author. Fax: +44-133-446-3808.

E-mail address: pl@st-andrews.ac.uk (P. Lightfoot).

JCDPS 25–544, and needles of I (JCPDS 32–647). These are denoted α - $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (25–544) and γ - $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (I, 32–647) by Huizing et al., who reported the synthesis and unit-cell parameters from powder X-ray diffraction in 1977 [6]. Single-crystal diffraction on a needle of I was carried out on a Rigaku AFC7S automated four-circle diffractometer with $\text{MoK}\alpha$ radiation. Structure solution and refinement were carried out using the SIR 92 [7] and TEXSAN [8] suites. Crystallographic details are given in Table 1.

$[\text{C}_4\text{H}_8(\text{NH}_2)_2][\text{Mn}_2(\text{C}_2\text{O}_4)_3]$ (II) was prepared as a minor phase (<5%, not detectable by powder X-ray diffraction) in the synthesis of $[\text{C}_4\text{H}_8(\text{NH}_2)_2][\text{Mn}_4(\text{HPO}_4)_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})](\text{H}_2\text{O})_2$ previously reported by us [5]. $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, piperazine and H_2O were mixed in a 1:1:1:400 ratio giving a mixture with a pH of 6, and heated in a PTFE-lined stainless-steel autoclave at 120°C for 48 h. After cooling, the mixture (pH 5.5) was filtered, washed with distilled water and dried in air to give $[\text{C}_4\text{H}_8(\text{NH}_2)_2][\text{Mn}_4(\text{HPO}_4)_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})](\text{H}_2\text{O})_2$ and a small amount of II. Single-crystal diffraction on II was carried out at station 9.8, SRS, Daresbury. Structure solution and refinement were carried out using the SIR 92 and TEXSAN suites. Crystallographic details are given in Table 1.

$\text{Mn}_2(\text{C}_2\text{O}_4)(\text{OH})_2$ (III) was prepared, along with II, from the hydrothermal reaction of $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, piperazine and H_2O in an approximate ratio of 2:0.8:800/2.5:1:1000. The mixture was heated in a PTFE-lined stainless-steel autoclave at 160°C for 48 h. After cooling, the mixture was filtered and washed with

distilled water, then dried in air. The same products were also obtained using the above reagents in ratios of 2:1.7:800/1.2:1:470 and 3:1.7:800/1.8:1:470, the former consisting of mainly III (>70%), the latter mainly II (>70%). Neither II nor III was obtained as a pure sample. Single-crystal diffraction of III was carried out on a Bruker SMART diffractometer with CCD detector and $\text{MoK}\alpha$ radiation. Structure solution and refinement were carried out using SHELXS [9] and SHELXL [10], respectively. For all three structures, hydrogen atom coordinates were refined freely, with isotropic displacement parameters constrained as riding atoms. Crystallographic details are given in Table 1.

3. Results and discussion

$\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (I) is a one-dimensional structure, with chains of oxalate-bridged manganese centers running along the *c* direction. Atomic coordinates are given in Table 2. Fig. 1 shows the atom labelling scheme and thermal ellipsoids. Manganese is confirmed as 2+ by bond valence sums (sum 2.06) [11], and exists in distorted octahedral coordination, with the smallest angle (74.0(2)°) found where bidentate oxalate coordination occurs (see Table 3 for selected bond lengths and angles). Mn(1) is axially connected to two water molecules, O(5) and O(6). The four remaining manganese coordination sites are occupied by oxalate oxygen atoms. O(1) is three coordinate, bonded to C(1) and two Mn(1) atoms. The terminal oxygen O(3) is connected

Table 1
Details of structure solution and refinement

	I	II	III
Formula	$\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	$[\text{C}_4\text{H}_8(\text{NH}_2)_2][\text{Mn}_2(\text{C}_2\text{O}_4)_3]$	$\text{Mn}_2(\text{C}_2\text{O}_4)(\text{OH})_2$
Formula weight	178.99	462.09	463.83
Crystal size (mm)	0.35, 0.10, 0.05	0.025, 0.025, 0.015	0.15, 0.10, 0.03
ρ_{calc} (g cm^{-3})	2.294	2.087	3.046
Crystal color	Colorless	Colorless	Colorless
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$
<i>a</i> (Å)	6.262(4)	5.9305(5)	5.926(1)
<i>b</i> (Å)	13.585(5)	7.7763(7)	5.695(1)
<i>c</i> (Å)	6.091(4)	8.1707(7)	7.494(2)
α (°)	90	81.489(2)	90
β (°)	90	81.045(2)	91.10(3)
γ (°)	90	86.076(2)	90
Volume (Å ³)	518.2(4)	367.72(5)	252.88(9)
Z	4	1	1
Wavelength (Å)	0.7107	0.6900	0.71073
μ (cm^{-1})	2.501	1.792	4.950
Total reflections (2 θ max)	576 (50°)	1992 (50°)	360 (46.5°)
Observed reflections ($I > 3\sigma(I)$ I, II; $I > 2\sigma(I)$ III)	561	1773	268
No. of variables	95	136	50
Abs. correction	Psi-scan	None	None
Max/min difference peak ($\text{e}\text{\AA}^{-3}$)	0.69, -1.04	0.60, -0.69	0.804, -0.973
R, R_w I, II; R_1, wR_2 (all data) III	0.0832, 0.1017	0.0467, 0.0596	0.0710, 0.1378 0.104, 0.151

Table 2
Atomic coordinates and equivalent isotropic temperature factors for $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (I)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq)
Mn(1)	0.1894(2)	0.42079(9)	0.0720(2)	1.49(3)
O(1)	0.201(1)	0.4408(4)	0.442(1)	1.8(1)
O(2)	0.099(1)	0.2810(4)	0.2103(9)	2.0(1)
O(3)	0.112(1)	0.1887(4)	0.5113(9)	1.9(1)
O(4)	0.146(1)	0.3553(4)	0.752(1)	2.4(2)
O(5)	0.526(1)	0.3677(5)	0.073(1)	1.9(1)
O(6)	−0.121(1)	0.4907(5)	0.078(2)	2.9(2)
C(1)	0.158(1)	0.3613(6)	0.549(1)	1.5(2)
C(2)	0.119(1)	0.2680(6)	0.412(1)	1.3(2)

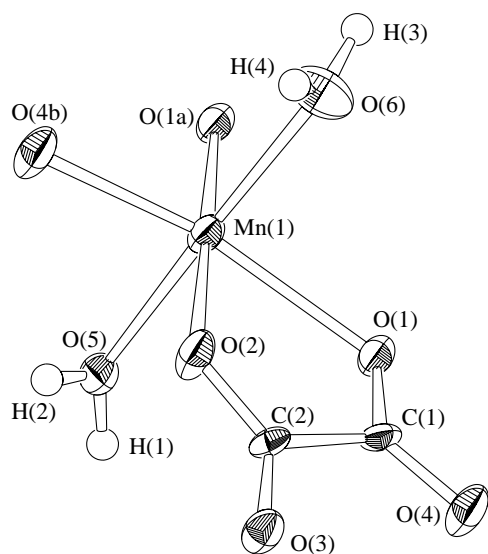


Fig. 1. Building unit of $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (I) showing the atom labelling scheme, with thermal ellipsoids at 50%. Symmetry labels: (a) $1/2-x, 1-y, -1/2+z$; (b) $x, y, -1+z$.

Table 3
Selected bond lengths (Å) and angles (°) for $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (I)

Mn(1)	O(1)	2.273(6)	C(1)	O(1)	1.289(9)		
Mn(1)	O(1)	2.153(6)	C(2)	O(2)	1.25(1)		
Mn(1)	O(2)	2.153(6)	C(2)	O(3)	1.236(9)		
Mn(1)	O(4)	2.159(6)	C(1)	O(4)	1.24(1)		
Mn(1)	O(5)	2.225(7)	C(1)	C(2)	1.54(1)		
Mn(1)	O(6)	2.163(7)					
O(1)	Mn(1)	O(1)	104.5(2)	O(1)	Mn(1)	O(6)	84.8(3)
O(1)	Mn(1)	O(2)	74.0(2)	O(2)	Mn(1)	O(4)	87.5(2)
O(1)	Mn(1)	O(4)	161.5(2)	O(2)	Mn(1)	O(5)	87.8(3)
O(1)	Mn(1)	O(5)	90.4(3)	O(2)	Mn(1)	O(6)	98.3(3)
O(1)	Mn(1)	O(6)	87.6(3)	O(4)	Mn(1)	O(5)	89.4(3)
O(1)	Mn(1)	O(2)	176.4(3)	O(4)	Mn(1)	O(6)	94.7(3)
O(1)	Mn(1)	O(4)	94.0(2)	O(5)	Mn(1)	O(6)	172.8(3)
O(1)	Mn(1)	O(5)	88.9(2)				

only to C(2), although this bond is not significantly shorter than those of O(2) and O(4) (see Table 3). All oxalate anions are equivalent and display bi- and

bismonodentate coordination to manganese. Coordination modes of oxalate were discussed recently by Hernández-Molina et al. [12], who report this coordination mode as being seen previously only with copper. Through the three coordinate O(1), manganese octahedral share corners to form chains along the *c*-axis (Fig. 2). These chains pack together in two orientations in a herringbone pattern, illustrated in Fig. 3. O(3) and the coordinated water molecules of neighboring chains are found close together as a result of this packing, introducing hydrogen bonds between the chains. α - $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (JCPDS 25–544) also consists of one-dimensional chains, with each manganese coordinated to two bisbidentate oxalate and two water molecules [13].

$[\text{C}_4\text{H}_8(\text{NH}_2)_2][\text{Mn}_2(\text{C}_2\text{O}_4)_3]$ (II) is a three-dimensional manganese oxalate framework which contains diprotonated piperazine cations. The building unit is shown in Fig. 4, atomic coordinates in Table 4 and selected bond

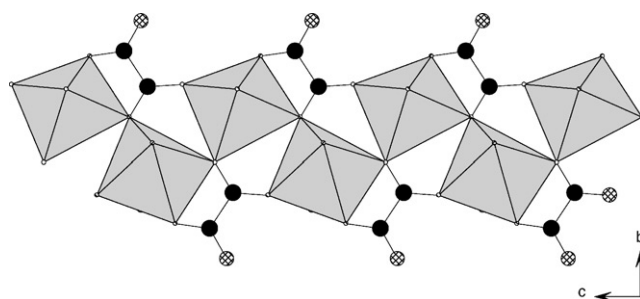


Fig. 2. Chains of oxalate-bridged manganese centers in $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (I). MnO_6 polyhedra, gray; C, black, O, hatched.

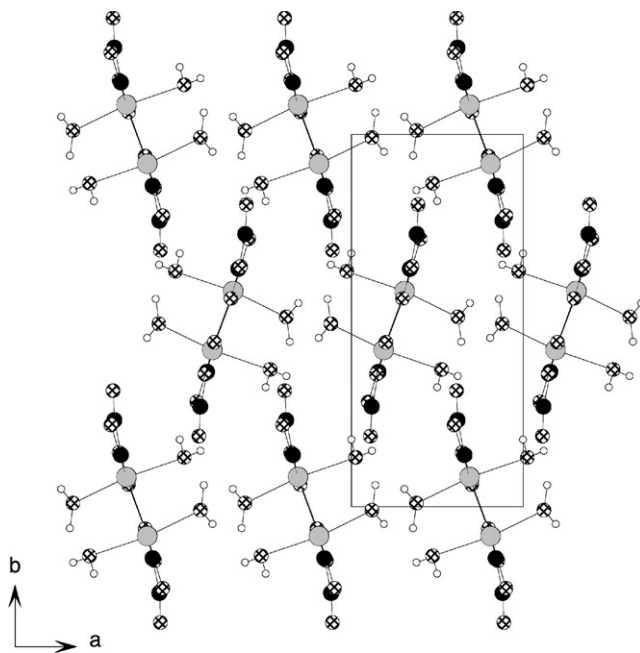


Fig. 3. Packing of chains in $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (I). Mn, gray; C, black; O, hatched; H, small white spheres.

lengths and angles are given in Table 5. The manganese atom is seven coordinate in this structure, with oxygen bond lengths ranging from 2.216(2) to 2.347(3) Å. Bond valence sums confirm the manganese as 2+, with a value of 2.03. The basic structural unit is a dimer constructed from two MnO₇ polyhedra sharing an edge, as shown in Fig. 5. The oxygen atom through which the manganese polyhedra share an edge (O(3)) is three coordinate, bonded to an oxalate carbon and the two manganese atoms. O(3) has a bond valence sum of 1.99 as would be expected, i.e. this value has not been affected by the three-fold coordination. The O–Mn–O

angles vary between 71.97(8)° (O(3)–Mn(1)–O(4)) and 164.9(1)° (O(1)–Mn(1)–O(6)), the smallest angles being due to bidentate oxalate coordination.

Each manganese atom is connected to two oxalate anions that have bisbidentate coordination (containing C(1) and C(3)). The third oxalate anion is connected to

Table 4
Atomic coordinates and equivalent isotropic temperature factors for [C₄H₈(NH₂)₂][Mn₂(C₂O₄)₃] (II)

Atom	x	y	z	B(eq)
Mn(1)	0.44784(8)	0.36712(6)	0.85331(6)	0.776(9)
O(1)	0.5218(5)	0.6054(3)	0.6703(3)	1.32(4)
O(2)	0.5513(4)	0.7109(3)	0.3981(3)	1.06(4)
O(3)	0.2754(4)	0.5382(3)	1.0335(3)	0.95(4)
O(4)	−0.0639(4)	0.5882(3)	1.1875(3)	1.26(4)
O(5)	0.6838(4)	0.1249(3)	0.8494(3)	1.35(4)
O(6)	0.7219(5)	−0.1543(3)	0.9616(3)	1.57(5)
N(1)	0.0550(6)	0.1139(4)	0.6095(4)	1.48(5)
C(1)	0.5214(5)	0.5908(4)	0.5221(4)	0.92(5)
C(2)	0.0579(5)	0.5381(4)	1.0654(4)	0.84(5)
C(3)	0.3819(5)	0.0099(4)	1.0541(4)	1.01(5)
C(4)	0.1514(6)	−0.0689(5)	0.6197(5)	1.70(7)
C(5)	−0.0096(6)	−0.1832(5)	0.5639(5)	1.62(6)

Table 5
Selected bond lengths (Å) and angles (°) for [C₄H₈(NH₂)₂][Mn₂(C₂O₄)₃] (II)

Mn(1)	O(1)	2.224(2)	O(4)	C(2)	1.233(4)		
Mn(1)	O(2)	2.225(2)	O(5)	C(3)	1.260(4)		
Mn(1)	O(3)	2.216(2)	O(6)	C(3)	1.243(4)		
Mn(1)	O(3)	2.220(2)	N(1)	C(4)	1.492(5)		
Mn(1)	O(4)	2.347(3)	N(1)	C(5)	1.497(5)		
Mn(1)	O(5)	2.269(3)	C(1)	C(1)	1.554(6)		
Mn(1)	O(6)	2.248(3)	C(2)	C(2)	1.561(6)		
O(1)	C(1)	1.233(4)	C(3)	C(3)	1.547(6)		
O(2)	C(1)	1.272(4)	C(4)	C(5)	1.511(5)		
O(3)	C(2)	1.276(4)					
O(1)	Mn(1)	O(2)	74.03(8)	O(3)	Mn(1)	O(3)	74.28(9)
O(1)	Mn(1)	O(3)	87.99(9)	O(3)	Mn(1)	O(4)	71.97(8)
O(1)	Mn(1)	O(3)	81.82(9)	O(3)	Mn(1)	O(5)	139.36(9)
O(1)	Mn(1)	O(4)	87.76(9)	O(3)	Mn(1)	O(6)	83.73(9)
O(1)	Mn(1)	O(5)	121.36(9)	O(3)	Mn(1)	O(4)	144.94(9)
O(1)	Mn(1)	O(6)	164.9(1)	O(3)	Mn(1)	O(5)	82.33(9)
O(2)	Mn(1)	O(3)	144.28(8)	O(3)	Mn(1)	O(6)	107.84(9)
O(2)	Mn(1)	O(3)	130.92(9)	O(4)	Mn(1)	O(5)	130.71(9)
O(2)	Mn(1)	O(4)	76.63(9)	O(4)	Mn(1)	O(6)	77.71(9)
O(2)	Mn(1)	O(5)	75.27(9)	O(5)	Mn(1)	O(6)	72.29(9)
O(2)	Mn(1)	O(6)	105.96(9)				

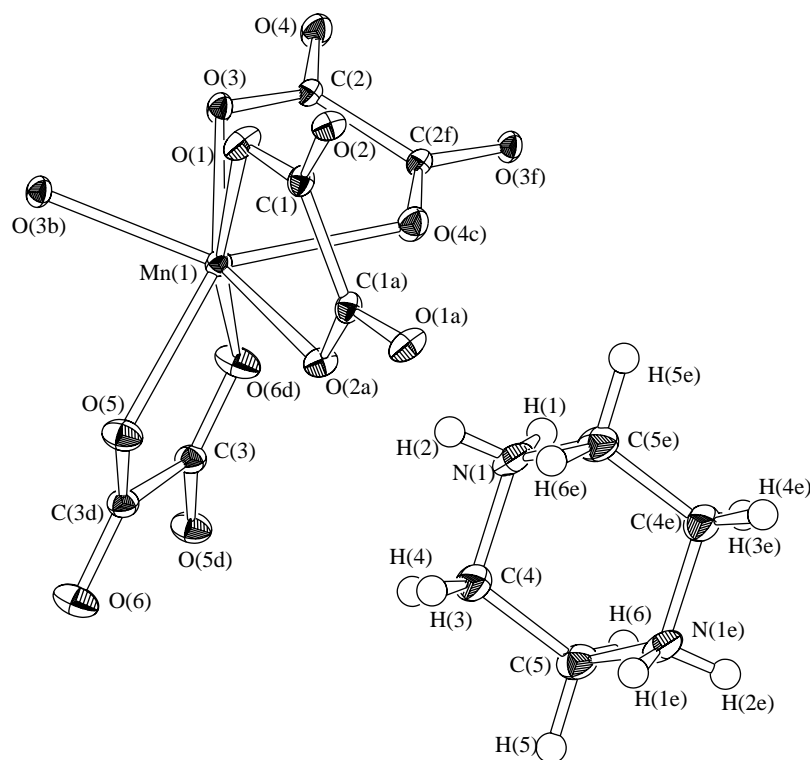


Fig. 4. Building unit of [C₄H₈(NH₂)₂][Mn₂(C₂O₄)₃] (II) showing the atom labelling scheme, with thermal ellipsoids at 50%. Symmetry labels: (a) 1−x, 1−y, 1−z; (b) 1−x, 1−y, 2−z; (c) −x, 1−y, 1+z; (d) 1−x, −y, 2−z; (e) −x, −y, 1−z; (f) −x, 1−y, 2−z.

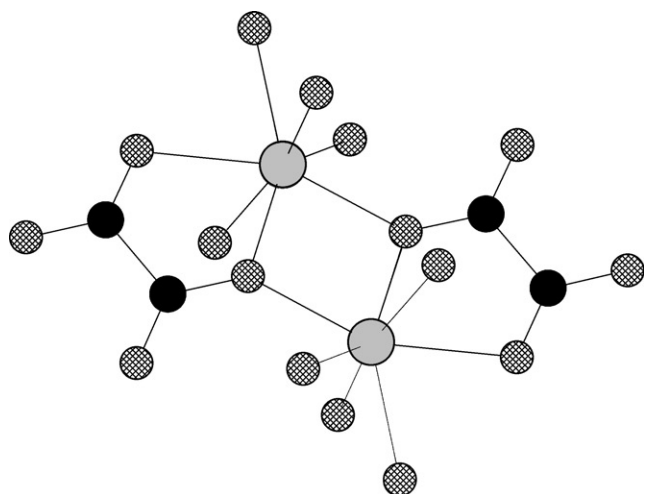


Fig. 5. Edge-sharing Mn_2O_{12} dimer with oxalate coordination in $[\text{C}_4\text{H}_8(\text{NH}_2)_2][\text{Mn}_2(\text{C}_2\text{O}_4)_3]$ (**II**), shading as before.

four manganese atoms, two through bidentate coordination (via O(4) and O(3)), and two through monodentate coordination (O(3)). This coordination mode has been previously seen in materials containing iron, cobalt, nickel, zinc and cadmium, but not manganese [12].

The manganese dimers are interconnected by oxalates in all three directions, leading to a three-dimensional structure, shown in Fig. 6. Channels exist in all three directions, forming cavities at their intersections where piperazine cations are found.

$\text{Mn}_2(\text{C}_2\text{O}_4)(\text{OH})_2$ (**III**) is a three-dimensional structure, consisting of manganese–oxygen layers which are bridged by oxalate anions. Atomic coordinates are given in Table 6, the building unit is illustrated in Fig. 7 and selected bond lengths and angles are given in Table 7.

Manganese is found in distorted octahedral coordination, with a bond valence sum of 1.97. Each manganese is coordinated to two oxalate groups and three hydroxide groups, with shorter bonds found between Mn(1) and these hydroxide oxygens (O(3)) than the oxalate oxygens (O(1) and O(2)). This was also observed in the iron analogue of **III**, which has been reported by Molinier et al. [14]. The oxalate anions show bismono- and bisbidentate coordination as also observed in **II**. MnO_6 octahedra form *cis*-edge-sharing chains along the *b*-axis via O(1) (oxalate) and O(3) (hydroxide). The chains are linked to each other by corner sharing through O(3), to form layers in the *bc* plane (see Fig. 8). This bridging oxygen is therefore four coordinate. Contributions from the three manganese atoms gives O(3) a bond valence sum of 1.14, a value normally suggesting a hydroxide group. The full three-dimensional framework is constructed by pillaring of these layers by oxalate groups, illustrated in Fig. 9.

Iron and nickel bipyridyl complexes act as the counterions in manganese oxalate frameworks, $[\text{Mn}_2^{\text{II}}$

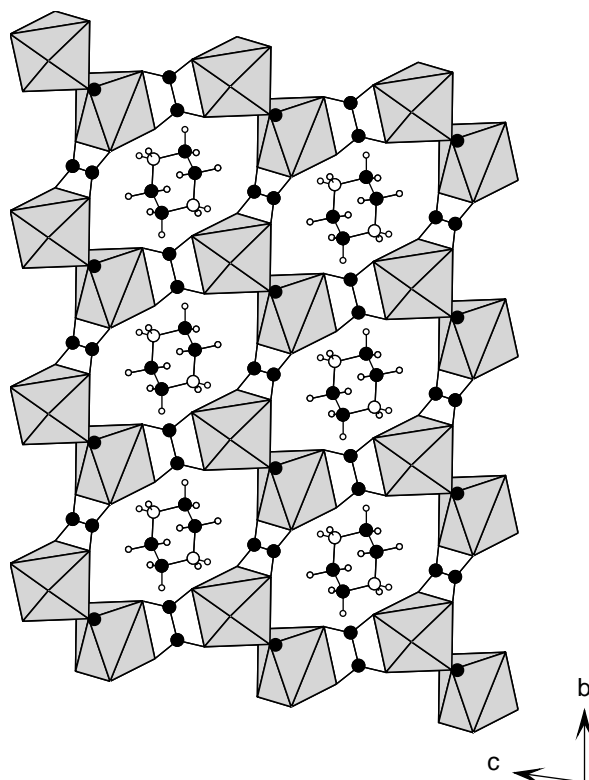


Fig. 6. Framework of $[\text{C}_4\text{H}_8(\text{NH}_2)_2][\text{Mn}_2(\text{C}_2\text{O}_4)_3]$ (**II**) in the *bc* plane, showing diprotonated piperazine cations in channels. Shading as before, N, large white spheres.

Table 6
Atomic coordinates and equivalent isotropic temperature factors for $\text{Mn}_2(\text{C}_2\text{O}_4)(\text{OH})_2$ (**III**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (iso)
Mn(1)	0.4062(3)	0.2650(3)	0.3945(3)	0.0130(7)
O(1)	0.717(1)	0.065(1)	0.461(1)	0.017(2)
C(1)	0.926(2)	0.092(2)	0.456(2)	0.009(3)
O(2)	1.020(1)	0.267(2)	0.382(1)	0.019(2)
O(3)	0.614(2)	0.569(2)	0.345(1)	0.017(2)

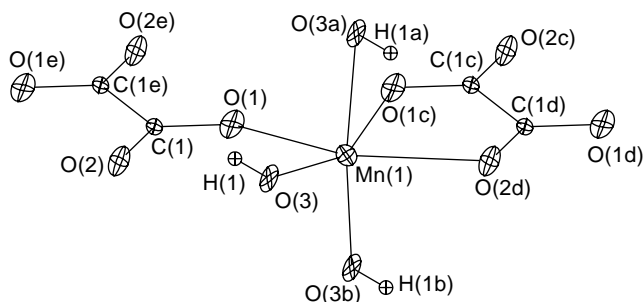


Fig. 7. Building unit of $\text{Mn}_2(\text{C}_2\text{O}_4)(\text{OH})_2$ (**III**) showing the atom labelling scheme, with thermal ellipsoids at 50%. Symmetry labels: (a) $1-x, 1-y, 1-z$; (b) $1-x, -1/2+y, 1/2-z$; (c) $1-x, -y, 1-z$; (d) $-1+x, y, z$; (e) $2-x, -y, 1-z$.

Table 7
Selected bond lengths (Å) and angles (°) for $\text{Mn}_2(\text{C}_2\text{O}_4)(\text{OH})_2$ (**III**)

Mn(1)	O(1)	2.214(8)	Mn(1)	O(3)	2.17(1)		
Mn(1)	O(1)	2.296(8)	C(1)	O(1)	1.25(1)		
Mn(1)	O(2)	2.291(8)	C(1)	O(2)	1.27(1)		
Mn(1)	O(3)	2.12(1)	C(1)	C(1)	1.52(2)		
Mn(1)	O(3)	2.16(1)					
O(1)	Mn(1)	O(3)	87.4(4)	O(1)	Mn(1)	O(2)	72.3(3)
O(1)	Mn(1)	O(3)	88.6(3)	O(2)	Mn(1)	O(3)	85.9(3)
O(1)	Mn(1)	O(3)	94.6(4)	O(2)	Mn(1)	O(3)	124.2(4)
O(1)	Mn(1)	O(3)	87.5(3)	O(2)	Mn(1)	O(3)	87.8(3)
O(1)	Mn(1)	O(3)	157.6(4)	O(3)	Mn(1)	O(3)	107.5(2)
O(1)	Mn(1)	O(3)	84.7(3)	O(3)	Mn(1)	O(3)	171.1(4)
O(1)	Mn(1)	O(1)	75.1(3)	O(3)	Mn(1)	O(3)	81.2(4)
O(1)	Mn(1)	O(2)	146.9(3)				

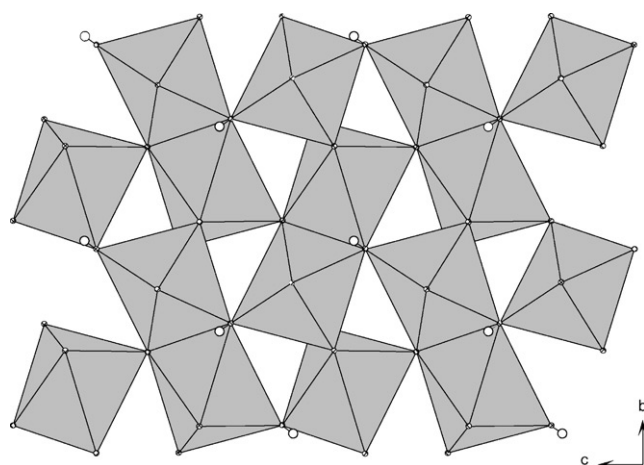


Fig. 8. *cis*-edge-sharing chains of MnO_6 form layers via the three coordinate hydroxide groups in $\text{Mn}_2(\text{C}_2\text{O}_4)(\text{OH})_2$ (**III**). Shading as before.

$(\text{C}_2\text{O}_4)_3](M^{\text{II}}(\text{bpy})_3)$ ($M = \text{Fe}, \text{Ni}$; $\text{bpy} = 2,2'$ -bipyridine) synthesized by Decurtins et al. The manganese is coordinated to three bisbidentate oxalate anions to form a three-dimensional structure with the bipyridyl complexes located in the void space [15]. Many bimetallic oxalate structures have been reported containing manganese. The honeycomb layer structure mentioned above is often seen in these systems, for example $A\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3$ (where A is one of a variety of amines or phosphines) [16].

No other amine-containing manganese oxalates have been reported in the literature, however two zinc oxalates containing amines have been synthesized by Rao et al. [17]. $[\text{Zn}_2(\text{C}_2\text{O}_4)_3](\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3)(\text{H}_2\text{O})_3$ is a layered honeycomb structure with amines found between the layers. Each zinc is octahedrally coordinated to three oxalate anions, and each oxalate is coordinated to two zinc centers. Changing the amine to *n*-propylamine results in $[\text{Zn}_2(\text{C}_2\text{O}_4)_3](\text{C}_3\text{H}_7\text{NH}_3)_2(\text{H}_2\text{O})_3$ which shows similar coordination around the

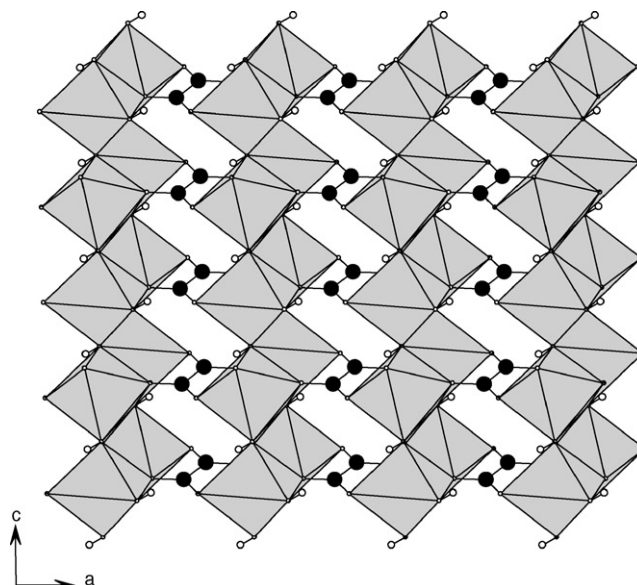


Fig. 9. Oxalate groups act as pillars to join the layers in $\text{Mn}_2(\text{C}_2\text{O}_4)(\text{OH})_2$ (**III**). Shading as before.

zinc, but in this case, the honeycomb layers are 'interrupted' and form a three-dimensional framework with two channel systems.

The oxalates discussed above, and **I** and **III**, contain manganese in six-fold coordination, which is by far the most common coordination number, in contrast to the seven-fold coordination of **II**. Oxalate materials exist with eight coordinate manganese: $\text{K}_2\text{MnU}(\text{C}_2\text{O}_4)_4 \cdot 9\text{H}_2\text{O}$ [18] and $[\text{MnCr}_2(\text{bpy})_2(\text{C}_2\text{O}_4)_4]$ [19]. A search of the Cambridge Structural Database (CSD) using the QUEST program [20] shows no structures with seven coordinate manganese where oxalate is one of the ligands, however a seven coordinate manganese is seen in the three-dimensional framework $\text{Mn}(\text{O}_2\text{CCH}_3)_2$ [21]. This material is built up from trimers of acetate-bridged manganese polyhedra, one of which is seven coordinate (the other two being six coordinate).

Acknowledgments

We thank the SRS, Daresbury for beamtime, and EPSRC and the University of St. Andrews for funding. We also thank the Carnegie Trust for the award of a Summer Scholarship (A. F. C.).

References

- [1] A.K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem. Int. Ed.* 38 (1999) 3268–3292.
- [2] P. Lightfoot, Z.A.D. Lethbridge, R.E. Morris, D.S. Wragg, P.A. Wright, Å. Kvik, G.B.M. Vaughan, *J. Solid State Chem.* 143 (1999) 74–76.

- [3] Z.A.D. Lethbridge, P. Lightfoot, *J. Solid State Chem.* 143 (1999) 58–61.
- [4] Z.A.D. Lethbridge, A.D. Hillier, R. Cywinski, P. Lightfoot, *J. Chem. Soc., Dalton Trans.* (2000) 1595–1599.
- [5] Z.A.D. Lethbridge, S.K. Tiwary, A. Harrison, P. Lightfoot, *J. Chem. Soc., Dalton Trans.* (2001) 1904–1910.
- [6] A. Huizing, H.A.M. van Hal, W. Kwestroo, C. Langereis, P.C. van Loosdregt, *Mater. Res. Bull.* 12 (1977) 605–611.
- [7] A. Altomare, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Gugliardi, G. Polidori, *J. Appl. Crystallogr.* 26 (1993) 343–350.
- [8] TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1992.
- [9] W.T. Robinson, G.M. Sheldrick, in: N.W. Isaacs, M.R. Taylor (Eds.), *Crystallographic Computing 4. Techniques and New Technologies*, IUCr, Oxford University Press, Oxford, 1988, pp. 366–377.
- [10] G.M. Sheldrick, Release 97–2, University of Goettingen, Germany, 1997.
- [11] I.D. Brown, D. Altermatt, *Acta Crystallogr. B* 41 (1985) 244–247.
- [12] M. Hernández-Molina, P.A. Lorenzo-Luis, C. Ruiz-Pérez, *Cryst. Eng. Comm.* (2001), art. no. 16.
- [13] I. Śledzińska, A. Murasik, P. Fischer, *J. Phys. C: Solid State Phys.* 20 (1987) 2247–2259.
- [14] M. Molinier, D.J. Price, P.T. Wood, A.K. Powell, *J. Chem. Soc., Dalton Trans.* (1997) 4061–4068.
- [15] S. Decurtins, H.W. Schmalle, P. Schneuwly, J. Ensling, P. Gütlich, *J. Am. Chem. Soc.* 116 (1994) 9521–9528.
- [16] C. Mathonière, C.J. Nuttall, S.G. Carling, P. Day, *Inorg. Chem.* 35 (1996) 1201–1206.
- [17] R. Vaidyanathan, S. Natarajan, A.K. Cheetham, C.N.R. Rao, *Chem. Mater.* 11 (1999) 3636–3642.
- [18] K.P. Mörtl, J.-P. Sutter, S. Golhen, L. Ouahab, O. Kahn, *Inorg. Chem.* 39 (2000) 1626–1627.
- [19] F.D. Rochon, R. Melanson, M. Andruh, *Inorg. Chem.* 53 (1996) 6085–6092.
- [20] F.H. Allen, O. Kennard, *Chem. Design Automat News* 8 (1993) 1 and 31–37; D.A. Fletcher, R.F. McMeeking, D. Parkin, *J. Chem. Inf. Comput. Sci.* 36 (1996) 746–749.
- [21] J.D. Martin, R.F. Hess, *Chem. Commun.* (1996) 2419–2420.