A two-dimensional coordination network assembled from manganese(II) and 1,4-phenylenediacetate

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Key indicators

Single-crystal X-ray study

$T = 298$ K

Mean σ(C–C) = 0.006 Å

R factor = 0.045

wR factor = 0.136

Data-to-parameter ratio = 13.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The manganese(II) coordination polymer, poly[bis(2,2'-bipyridine)tris(μ-1,4-phenylenediacetato-$\kappa^4 O,O':O'',O'''$)trimanganese(II)], [Mn$_3$(C$_{10}$H$_8$O$_4$)$_3$(C$_{10}$H$_8$N$_2$)$_2$]$_n$, consists of linear trinuclear building blocks with two crystallographically unique Mn atoms. One Mn^{II} ion and the geometric centre of one 1,4-phenylenediacetate ligand in the trinuclear unit both lie on inversion centres. Trinuclear units are bridged by 1,4-phenylenediacetate ligands to yield a two-dimensional network which stacks into a three-dimensional supramolecular structure *via* π–π stacking interactions.

Comment

To achieve the desired structure and properties of porous metal-organic frameworks, rigid ligands are usually chosen as the linker molecules in preference to flexible ligands because they enable easier control of the shape and size of the resulting pores (Stepanow *et al.*, 2004; Rosi *et al.*, 2003; Zhao *et al.*, 2004). However, metal-organic frameworks assembled from flexible ligands may show some unusual advantages over those assembled from rigid ligands. Therefore, we report here the synthesis and crystal structure of the complex [Mn$_3$(2,2'-bpy)$_2$(PDA)$_3$]$_n$ containing the flexible ligand 1,4-phenylenediacetic acid (H$_2$PDA).
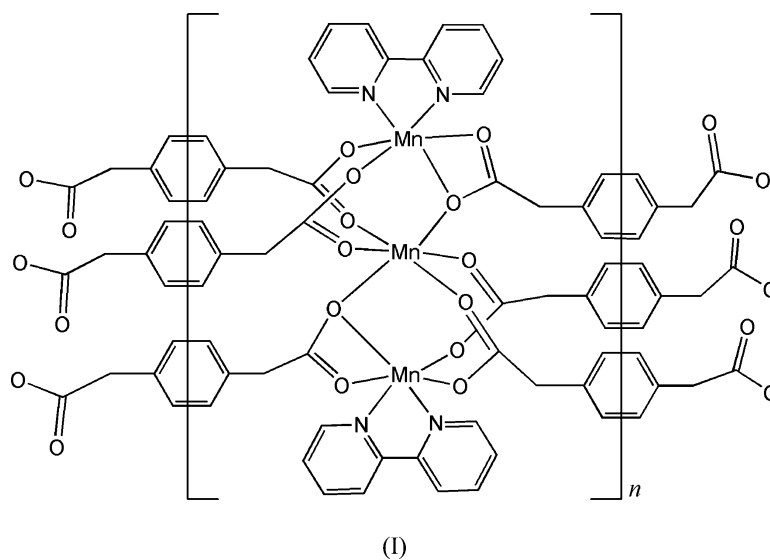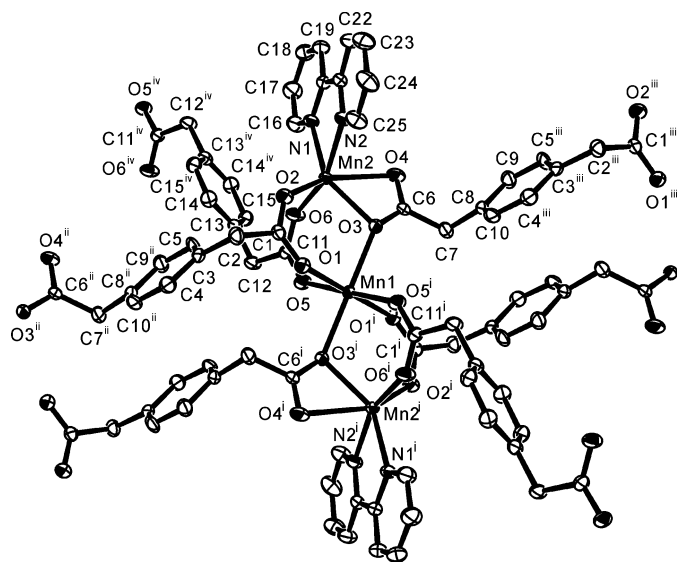

(I)

Fig. 1 shows the trinuclear building block for compound (I), which has inversion centres located both on the centre of the benzene ring of one 1,4-phenylenediacetate ligand and on atom Mn1, such that there are two crystallographically unique Mn^{II} centres. One Mn^{II} centre (Mn2) is coordinated in a
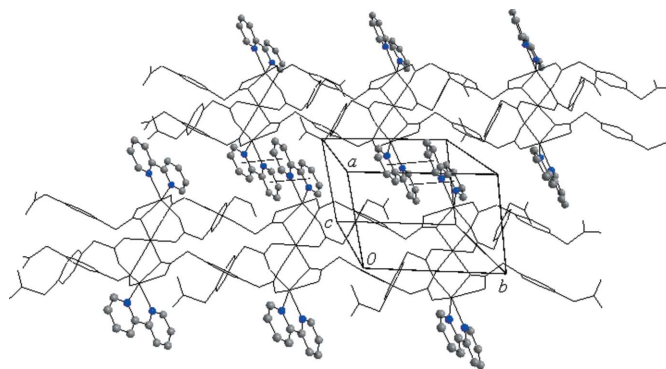
Figure 1
A view of part of the structure of (I), with the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 1$, $-y + 1$, $-z + 1$; (ii) x, $-1 + y$, z; (iii) x, $1 + y$, z; (iv) $1 - x$, $-y$, $-z$.]
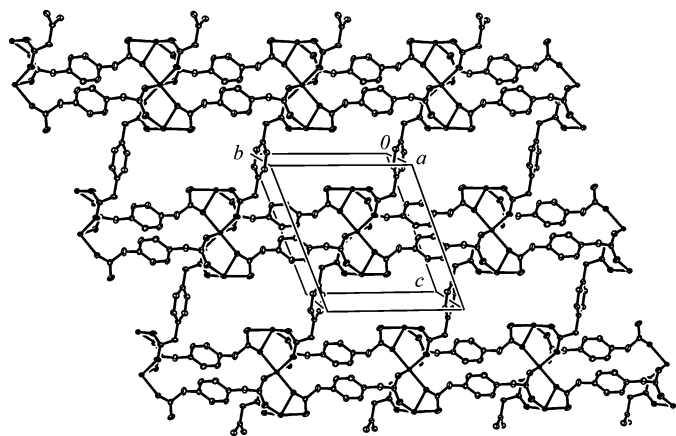
Figure 2
The two-dimensional network in (I) viewed down the a axis. H atoms and 2,2′-bipyridine molecules have been omitted for clarity.

severely distorted octahedral geometry by two N atoms from one 2,2′-bipyridine molecule and four O atoms from three carboxylate groups. The other Mn^{II} centre (Mn1) is linked to six O atoms from six carboxylate groups in a slightly distorted octahedral geometry. The two Mn^{II} centres are bridged by three carboxylate groups to form a linear trinuclear building block, which is similar to a previously reported case (Chen *et al.*, 2006). Adjacent trinuclear building blocks are connected by two 1,4-phenylenediacetate ligands to yield a one-dimensional chain along the b axis. Each trinuclear building block in the chain is further linked to another one in the neighbouring chain by another 1,4-phenylenediacetate ligand, resulting in the construction of a step-like two-dimensional coordination network parallel to the bc plane (Fig. 2). As shown in Fig. 3, the corresponding pyridyl rings of 2,2′-bipyridine from

Figure 3
The stacking of the two-dimensional sheets into a three-dimensional supramolecular structure by π–π stacking interactions, viewed approximately down the c axis. H atoms have been omitted. The dashed lines indicate π–π stacking interactions.

neighbouring two-dimensional sheets overlap with each other with a centroid-to-centroid distance of 3.892 (1) Å and a dihedral angle of 6.9 (1)°. This indicates the existence of π–π stacking effects between these pyridyl rings. These π–π stacking interactions connect the two-dimensional sheets into a three-dimensional supramolecular architecture.

Experimental

To a mixture of MnCl$_2$·4H$_2$O (0.0792 g, 0.4 mmol), 1,4-phenylenediacetic acid (0.0777 g, 0.4 mmol), NaOH (0.032 g, 0.8 mmol) and 2,2′-bipyridine (0.0624 g, 0.4 mmol) placed in a 23 ml Teflon-lined autoclave were added 7 ml of distilled water and 3 ml of methanol. The autoclave was heated at 373 K for 160 h and then cooled over a period of 48 h. Yellow crystals of (I) were separated from the solution and dried. Elemental analysis for C$_{50}$H$_{40}$Mn$_3$N$_4$O$_{12}$, calculated: C 56.45, H 3.86, N 4.88%; found: C 55.94, H 4.49, N 4.09%.

Crystal data

[Mn$_3$(C$_{10}$H$_8$O$_4$)$_3$(C$_{10}$H$_8$N$_2$)$_2$]	$V = 1168.4\ (6)$ Å^3
$M_r = 1053.68$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.498$ Mg m^{-3}
$a = 8.604\ (3)$ Å	Mo $K\alpha$ radiation
$b = 11.207\ (3)$ Å	$\mu = 0.87$ mm^{-1}
$c = 13.444\ (4)$ Å	$T = 298\ (2)$ K
$\alpha = 111.958\ (3)°$	Block, yellow
$\beta = 100.522\ (4)°$	$0.28 \times 0.15 \times 0.13$ mm
$\gamma = 94.042\ (4)°$	

Data collection

Bruker SMART CCD area-detector diffractometer	6109 measured reflections
	4060 independent reflections
φ and ω scans	2912 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	$R_{int} = 0.021$
	$\theta_{max} = 25.0°$
$T_{min} = 0.793$, $T_{max} = 0.896$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 0.5301P]$
$wR(F^2) = 0.136$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
4060 reflections	$\Delta\rho_{max} = 1.27$ e Å^{-3}
313 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Mn1—O5	2.158 (2)	Mn2—O3	2.188 (2)
Mn1—O1	2.183 (3)	Mn2—N2	2.238 (3)
Mn1—O3	2.227 (2)	Mn2—N1	2.256 (3)
Mn2—O6	2.078 (3)	Mn2—O4	2.428 (3)
Mn2—O2	2.092 (3)		
O5—Mn1—O5^i	180.00 (12)	O6—Mn2—N2	158.67 (11)
O5—Mn1—O1^i	90.43 (11)	O2—Mn2—N2	87.72 (12)
O5—Mn1—O1	89.57 (11)	O3—Mn2—N2	107.08 (11)
O1^i—Mn1—O1	180.000 (1)	O6—Mn2—N1	88.13 (11)
O5—Mn1—O3	92.58 (10)	O2—Mn2—N1	121.26 (12)
O5^i—Mn1—O3	87.42 (9)	O3—Mn2—N1	141.87 (11)
O1^i—Mn1—O3	91.70 (10)	N2—Mn2—N1	72.56 (12)
O1—Mn1—O3	88.30 (10)	O6—Mn2—O4	99.96 (12)
O3—Mn1—O3^i	180.000 (1)	O2—Mn2—O4	149.27 (11)
O6—Mn2—O2	94.96 (13)	O3—Mn2—O4	56.02 (9)
O6—Mn2—O3	93.67 (11)	N2—Mn2—O4	87.96 (11)
O2—Mn2—O3	96.55 (11)	N1—Mn2—O4	86.14 (11)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

H atoms were placed in calculated positions, with C—H = 0.93 Å in aromatic rings and C—H = 0.97 Å for other H atoms, and refined in riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$. The position of the highest peak is at (0.1107, 0.6101, 0.5168), which is 2.44 Å from H25. Modelling of either a water or a methanol solvent molecule at the position of the peak of highest electron density was unsuccessful.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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