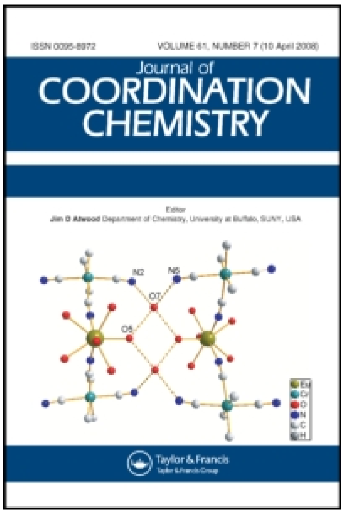

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Syntheses and structures of three manganese coordination polymers with 1,4-<i>bis</i>(imidazol-1-yl)butane

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Syntheses and structures of three manganese coordination polymers with 1,4-*bis*(imidazol-1-yl)butane

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Three manganese coordination polymers $[Mn(bimb)_2(NCS)_2]_n$ (**1**), $[Mn(bimb)_2(dca)_2]_n$ (**2**) and $[Mn(bimb)_2(N_3)_2]_n$ (**3**) (bimb = 1,4-*bis*(imidazol-1-yl)butane, dca = dicyanamide) were synthesized and characterized by X-ray crystallography, IR and thermogravimetric analysis. In **1** and **2**, each Mn(II) links two Mn(II) atoms by double bimb ligands and extends to form a one-dimensional double chain structure containing the $Mn_2(bimb)_2$ 22-member metallocycle. **3** constructs a two-dimensional (4,4) network linked by bimb bridges.

Keywords: Manganese complex; *Bis*(imidazol-1-yl)butane; Crystal structure; Coordination polymers

1. Introduction

Coordination polymers have intriguing structures and potential application as functional materials [1–6]. In contrast to rigid ligands with little or no conformational change when they interact with the metal ions, flexible ligands have more possible coordination modes because they can adopt different conformations according to the geometric needs of the different metal ions [7–11].

The flexible *bis*(imidazole) ligands 1,4-*bis*(imidazol-1-ylmethyl)benzene [9–11] and 1,2-*bis*(imidazol-1-yl)ethane [12–14] have been employed to obtain novel topologies. 1,4-*bis*(imidazol-1-yl)butane (bimb) is a very effective bridging ligand for construction of coordination polymers. Several bimb coordination polymers with transition metal were synthesized [15–19]. Pseudohalides, thiocyanate (SCN^-) [20, 21], azide (N_3^-) [22, 23] and dicyanamide (dca) ($[N(CN)_2]^-$) [24, 25], are widely used to construct coordination polymers because of their versatile coordination modes and ability to mediate strong magnetic coupling.

Previously we synthesized a number of coordination polymers with the flexible *bis*(triazole) ligands such as 1,2-*bis*(1,2,4-triazol-1-yl)ethane (bte) [13, 14, 26, 27], 1,4-*bis*(1,2,4-triazol-1-yl)butane (btb) [28] and 1,4-*bis*(1,2,4-triazol-1-ylmethyl)benzene (bbtz) [29, 30] and the *bis*(imidazole) 1,2-*bis*(imidazol-1-yl)ethane (bim) [13, 14].

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The ligand bimb is longer and more flexible than bim. The combination of the long flexible ligand bimb and the short anion ligands (SCN^-, N_3^- and $[N(CN)_2]^-$) can give novel topologies. Three new Mn(II) coordination polymers $[Mn(bimb)_2(NCS)_2]_n$ (**1**), $[Mn(bimb)_2(dca)_2]_n$ (**2**) and $[Mn(bimb)_2(N_3)_2]_n$ (**3**) were synthesized and structurally characterized.

2. Experimental

2.1. *Materials and physical measurements*

All reagents were analytical grade and used without further purification. 1,4-*Bis*(imidazol-1-yl)butane (bimb) was synthesized according to the literature method [16]. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. IR spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 4000–400 cm^{-1} region. TG and DSC analysis was measured on a Thermal Analyst 2100 TA Instrument and SDT 2960 Simultaneous TGA-DTA Instrument in flowing dinitrogen at a heating rate of 10°C min^{-1}.

2.2. *Synthesis of $[Mn(bimb)_2(NCS)_2]_n$ (1)*

A methanolic solution (20 mL) of bimb (0.190 g, 1.0 mmol) was added to an aqueous solution (20 mL) of $MnCl_2 \cdot 4H_2O$ (0.099 g, 0.5 mmol) and KNCS (0.097 g, 1.0 mmol) with stirring. The colorless single crystals **1** were obtained after the mixture was allowed to stand at room temperature for two weeks. Yield: 82%. Anal. Calcd for $C_{22}H_{28}MnN_{10}S_2$: C, 47.90; H, 5.12; N, 25.40. Found: C, 47.78; H, 5.07; N, 25.34%. IR data (cm^{-1}): 3426m, 3106w, 2072vs, 1520m, 1454w, 1285w, 1235w, 1107m, 1088m, 934w, 887w, 830w, 756w, 660w, 646w, 478w.

2.3. *Synthesis of $[Mn(bimb)_2(dca)_2]_n$ (2)*

The synthetic procedure was similar to the synthesis of **1**, except that $Na[N(CN)_2]$ (Na[dca]) was used instead of KNCS. Yield: 78%. Anal. Calcd for $C_{24}H_{28}MnN_{14}$: C, 50.79; H, 4.97; N, 34.56. Found: C, 50.68; H, 4.88; N, 34.42%. IR data (cm^{-1}): 3118m, 2277s, 2223m, 2161vs, 1621w, 1513m, 1443w, 1351m, 1281w, 1227m, 1088m, 1034w, 934m, 888w, 841w, 756m, 664m, 633w, 509w, 417w.

2.4. *Synthesis of $[Mn(bimb)_2(N_3)_2]_n$ (3)*

The synthetic procedure was similar to the synthesis of **1**, except that NaN_3 was used instead of KNCS. Yield: 78%. Anal. Calcd for $C_{20}H_{28}MnN_{14}$: C, 46.24; H, 5.43; N, 37.76. Found: C, 46.11; H, 5.40; N, 37.71%. IR data (cm^{-1}): 3410w, 2045vs, 1621w, 1513m, 1466w, 1382m, 1327w, 1227m, 1088m, 1034w, 934w, 841m, 741m, 664m, 625w, 548w, 417m.

2.5. *Crystal structure determination*

Suitable single crystals of **1**, **2** and **3** were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å).

Table 1. Crystallographic data for **1**, **2** and **3**.

	1	**2**	**3**
Formula	$C_{22}H_{28}MnN_{10}S_2$	$C_{24}H_{28}MnN_{14}$	$C_{20}H_{28}MnN_{14}$
Fw	551.60	567.54	519.50
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
Temp (K)	173(2)	193(2)	173(2)
a (Å)	9.0108(15)	7.5605(19)	7.6639(13)
b (Å)	9.5953(16)	10.270(3)	18.049(3)
c (Å)	14.481(2)	10.383(3)	9.1059(15)
α (°)	90	110.145(3)	90
β (°)	90.652(4)	102.818(3)	112.137(3)
γ (°)	90	107.748(3)	90
V (Å^3)	1252.0(4)	671.0(3)	1166.8(3)
Z	2	1	2
ρ_{Calcd} (g cm^3)	1.463	1.405	1.479
μ (mm^{-1})	0.727	0.535	0.607
F(000)	574	295	542
Reflections collected	13390	6596	11279
Unique reflections	2866 [$R_{(\text{int})}=0.0266$]	2441 [$R_{(\text{int})}=0.0176$]	2133 [$R_{(\text{int})}=0.0355$]
Parameters	161	179	161
Goodness of fit	1.089	1.113	1.075
R_1 [$I>2\sigma(I)$]	0.0333	0.0291	0.0386
wR_2 (all data)	0.0814	0.0675	0.0880

Intensities were collected by the ω scan technique. The structures were solved by direct methods and refined with full-matrix least-squares technique (SHELXTL-97) [31]. The positions of hydrogen atoms were determined with theoretical calculation. The parameters of the crystal data collection and refinement of **1**, **2** and **3** are given in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

IR spectra show that the imidazole ring vibrations in **1**, **2** and **3** are at 1520 and 1285, 1513 and 1281, 1513 and 1279 cm^{-1}, respectively [14]. The strong absorption at 2072 cm^{-1} for **1** indicates the C=N stretching vibration of the thiocyanate group, consistent with thiocyanate-N coordination [14, 20, 21]. The strong absorptions at 2277, 2223 and 2161 cm^{-1} for **2** are assigned to the C≡N symmetric stretch band (ν_{sym}), the asymmetric stretch band (ν_{asym}) and the combination band of ν_{sym} and ν_{asym} of dca [14, 22, 23]. The smaller shift (2277 cm^{-1}) for **2** towards high frequencies, compared with those of free dca in $Na[N(CN)_2]$ (2232 and 2179 cm^{-1}), indicates that dca is monodentate to the metal. The very strong absorption band at 2045 cm^{-1} for **3** is attributed to terminal coordination of azide [24, 25].

1 and **2** have similar double chain structures [figure 1a and 2a] [14, 26, 27]. Each Mn(II) in **1** and **2** is coordinated to four imidazole nitrogen atoms from four different bimb ligands in the equatorial plane [Mn(1)–N(2) 2.2807(13) Å, Mn(1)–N(4B) 2.2439(13) Å for **1**; Mn(1)–N(2) 2.2550(13) Å, Mn(1)–N(4B) 2.2715(14) Å for **2**], and two nitrogen atoms from two thiocyanates for **1** [Mn(1)–N(5) 2.2196(15) Å] and from two dicyanamides for **2** [Mn(1)–N(6) 2.2300(15) Å], in the axial positions. The Mn–N bond lengths of **1** and **2** are similar.

Table 2. Selected bond lengths (Å) and angles (°) for **1**, **2** and **3**.

1			
Mn(1)–N(2)	2.2807(13)	Mn(1)–N(4B)	2.2439(13)
Mn(1)–N(5)	2.2196(15)		
N(2)–Mn(1)–N(4B)	89.83(5)	N(2)–Mn(1)–N(5)	89.46(5)
N(4B)–Mn(1)–N(5)	89.67(5)	N(5)–C(11)–S(1)	179.23(16)
Mn(1)–N(5)–C(11)	155.43(13)		
2			
Mn(1)–N(2)	2.2550(13)	Mn(1)–N(4B)	2.2715(14)
Mn(1)–N(6)	2.2300(15)	N(5)–C(11)	1.301(2)
N(5)–C(12)	1.308(2)	N(6)–C(11)	1.152(2)
N(7)–C(12)	1.152(2)		
N(2)–Mn(1)–N(4B)	89.71(5)	N(2)–Mn(1)–N(6)	89.69(5)
N(4B)–Mn(1)–N(6)	90.26(5)	Mn(1)–N(6)–C(11)	171.96(14)
C(11)–N(5)–C(12)	123.44(15)	N(5)–C(11)–N(6)	172.23(18)
N(5)–C(12)–N(7)	171.81(18)		
3			
Mn(1)–N(2)	2.2465(17)	Mn(1)–N(4B)	2.2786(17)
Mn(1)–N(5)	2.2305(19)		
N(2)–Mn(1)–N(4B)	89.14(6)	N(2)–Mn(1)–N(5)	87.62(7)
N(4B)–Mn(1)–N(5)	86.77(7)	N(5)–N(6)–N(7)	178.7(2)
Mn(1)–N(5)–N(6)	132.71(16)		

Symmetry codes: **1** A $-x, -y+1, -z+1$; B $-x+1, -y+1, -z+1$; C $x-1, y, z$; **2** A $-x, -y+1, -z+1$; B $x, y-1, z$; C $-x, -y+2, -z+1$; **3** A $-x+1, -y+1, -z+1$; B $-x, y-1/2, -z+3/2$; C $x+1, -y+3/2, z-1/2$.

Each Mn(II) connects to other Mn(II) ions by two bimb ligands, resulting in the 22-member $Mn_2(bimb)_2$ metallocycle. Two strands of bimb ligands are wrapped around each other and held together by metal atoms, forming a double chain structure along the *a* axis for **1** (figure 1b) and along the *b* axis for **2** (figure 2b). The one-dimensional chains are stacked parallel along the *b* axis for **1** and along the *a* axis for **2**. The parallel chains in **1** extend along the *c* axis. But the parallel chains in **2** extend along the *c* axis, offset by $1/2b$ axis translation so that the dca anions of one chain can project into the voids of the adjacent chain (figure 2b).

The bimb ligands exhibit the *gauche*-*anti*-*gauche* conformation in **1** and **2**. The dihedral angles between two imidazole planes for **1** and **2** are 102.6 and 71.9°, respectively. The plane of the $N(CH_2)_4N$ chain is steeply inclined, by 72.6 and 102.6° for **1**, 54.4 and 71.9° for **2**, to the two imidazole ring planes. The torsion angles of the butane are 83.50(18) and 77.12(18) for **1** and **2**, respectively. The Mn $\cdots$ Mn distances separated via the bridging bimb are 9.011 and 10.270 Å for **1** and **2**. The parameters of the bimb ligand in **1**, **2** and **3** are listed in table 3 for comparison.

The structure of **3** is completely different from the structures of **1** and **2** although the Mn/bimb molar ratio in **1**, **2** and **3** all are 1 : 2. Complex **3** forms a neutral two-dimensional (4,4) network while **1** and **2** are double chain structures. The key factor is that two bimb molecules link the same two Mn(II) ions in **1** and **2**, and only one bimb bonds to the same two Mn(II) ions in **3**. As shown in figure 3a, the Mn(II) occupies the inversion center and is six-coordinate by four nitrogen atoms from four bimb ligands [Mn(1)–N(2) 2.2465(17) Å, Mn(1)–N(4B) 2.2786(17) Å] and two nitrogen atoms from two azide ligands [Mn(1)–N(5) 2.2305(19) Å]. The Mn–N bond lengths are similar to those for **1** and **2**. Each azide is monodentate terminal N-coordination.

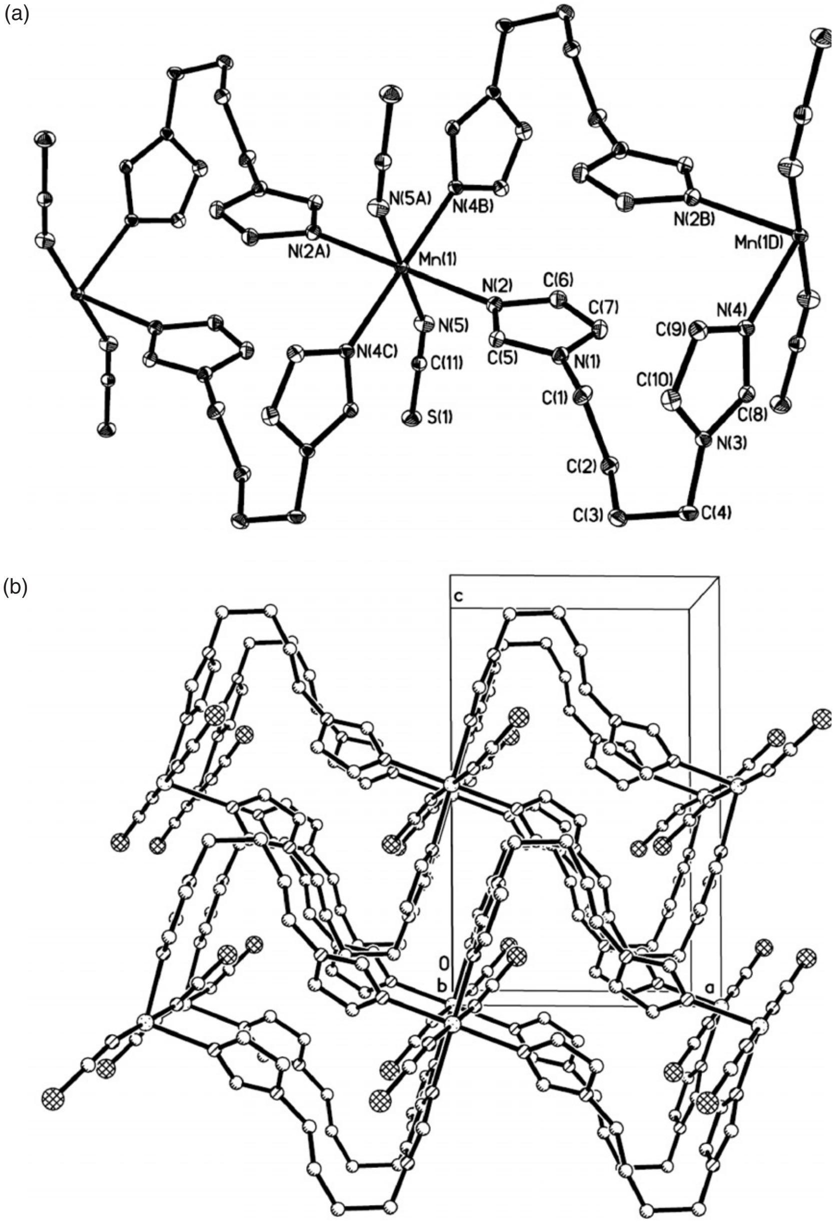

Figure 1. (a) The one-dimensional double chain structure along the *a* direction in **1** (Symmetry codes: A $-x$, $1-y$, $1-z$; B $1-x$, $1-y$, $1-z$; C $-1+x$, y, z; D $x+1$, y, z). The hydrogen atoms are omitted for clarity. (b) The packing of the one-dimensional chains in **1**.

Each bimb ligand shows the *anti* conformation (*anti*-*anti*-*anti*) in **3**. The dihedral angle between two imidazole planes is 127.4°. The plane of the $N(CH_2)_4N$ chain is steeply inclined, by 40.0 and 89.0°, to the two imidazole ring planes. The torsion angle of the butane chain is 177.21(19)°.

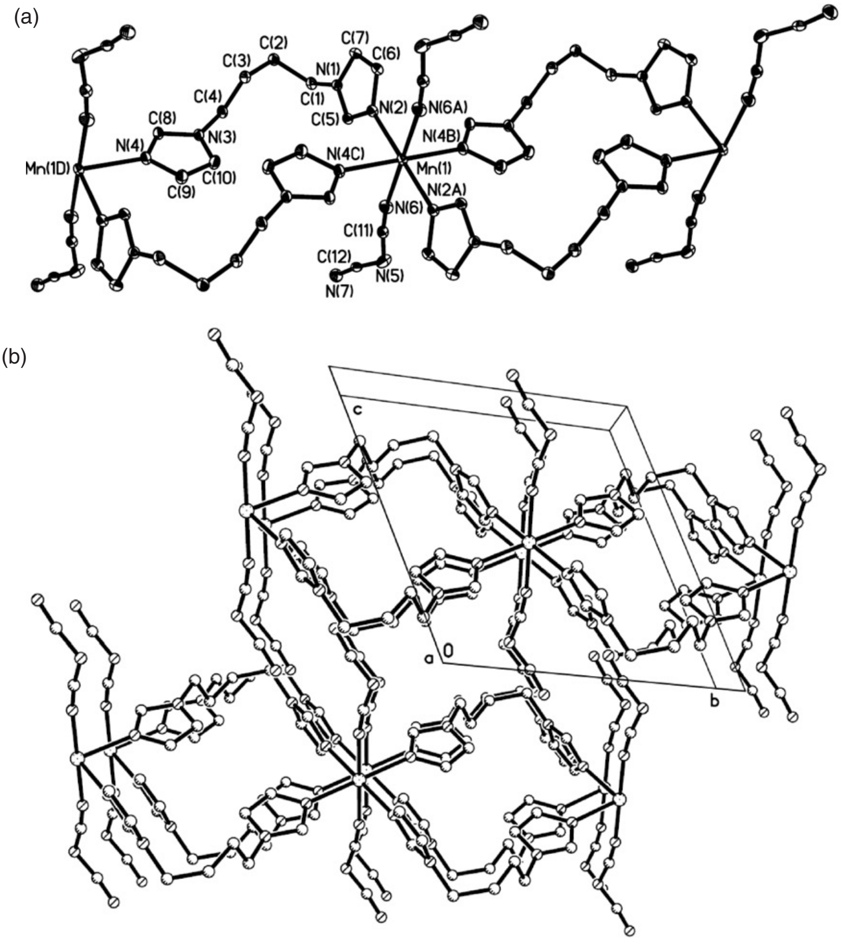

Figure 2. (a) The one-dimensional double chain structure along the *b* direction in **2** (Symmetry codes: A $-x$, $1-y$, $1-z$; B x, $1-y$, z; C $-1+x$, $2-y$, $1-z$; D x, $1+y$, z). The hydrogen atoms are omitted for clarity. (b) The packing of the one-dimensional chains in **2**.

Each Mn(II) is bridged by four bimb ligands to form a two-dimensional neutral (4,4) network (figure 3b). The networks contain square grids (44-membered ring), with a Mn(II) atom at each corner and a bimb molecule at each edge connecting two Mn(II) atoms. Due to the symmetry of the crystal structure, the edge lengths are equal at 13.682 Å, obviously longer than the corresponding Mn $\cdots$ Mn separation [9.011 and 10.270 Å] by the *gauche*-*anti*-*gauche* conformation for **1** and **2**. The two-dimensional networks in **3** are stacked in an offset fashion parallel to the C direction. The azide anions of one network project into the holes of the next network. In the superposition structure, the networks are arranged in the sequence $\cdots$ A–B–A–B $\cdots$ (figure 3c).

The reaction of the flexible *bis*(imidazole) ligand 1,4-*bis*(imidazol-1-yl)butane (bimb) with Mn(II) and non-coordinating anions BF_4^-, ClO_4^-, PF_6^- gives three-dimensional network coordination polymers $[Mn(bimb)_3](BF_4)_2$ [15], $[Mn(bimb)_3](ClO_4)_2$ and the

Table 3. The parameters of the bimb ligand in **1**, **2** and **3**.

Complex	Conformation	Two coordination nitrogen atoms distance (Å)	Mn · · · Mn distance separation by bimb ligand (Å)	Torsion angle of the butane chain (°)	Dihedral angle between two imidazole planes (°)	Dihedral angles between imidazole planes and butane chain (°)
1	*gauche-anti-gauche*	6.571	9.011	83.50(18)	102.9	72.6, 102.6
2	*gauche-anti-gauche*	7.498	10.270	77.12(18)	71.9	54.4, 71.9
3	*anti-anti-anti*	10.071	13.682	174.25(19)	127.4	40.0, 89.0

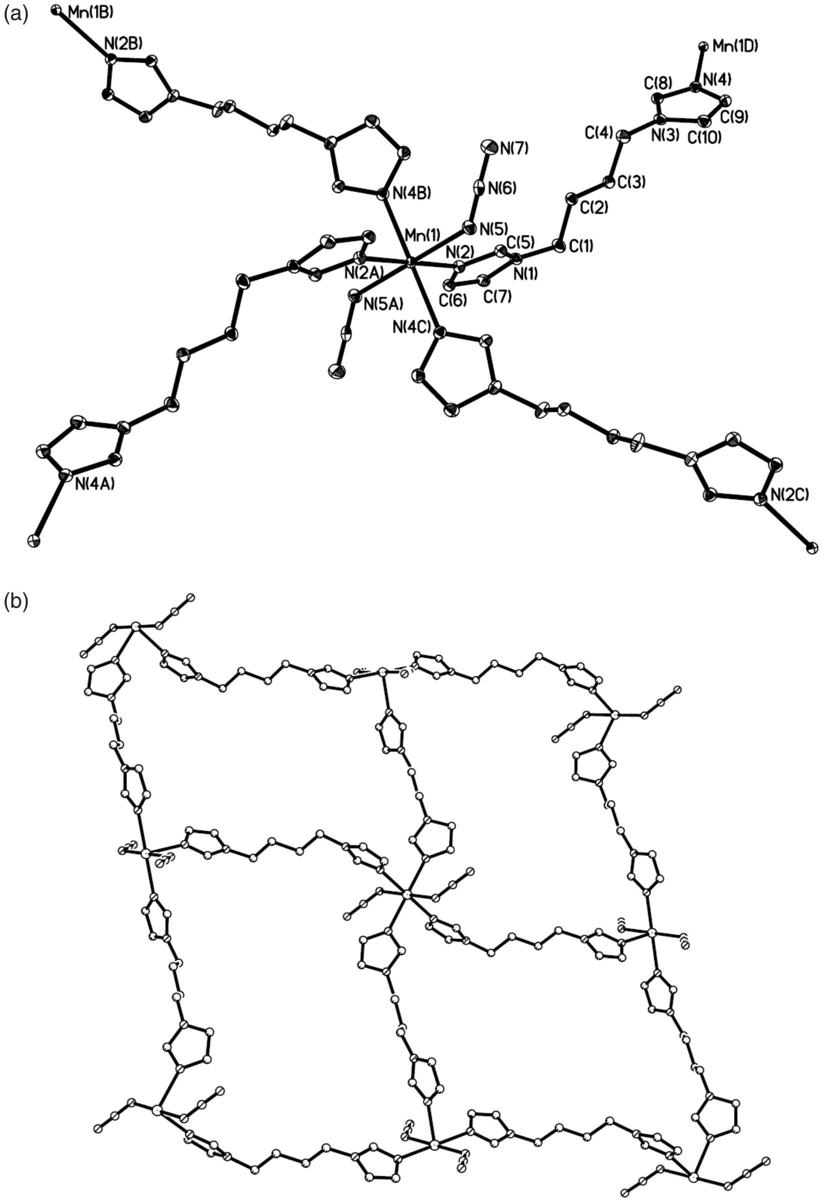

Figure 3. (a) The coordination environment of Mn1 in **3** (Symmetry code: A $1-x$, $1-y$, $1-z$; B $-x$, $-0.5+y$, $1.5-z$; C $1+x$, $1.5-y$, $-0.5+z$; D $-x$, $0.5+y$, $1.5-z$). The hydrogen atoms are omitted for clarity. (b) The two-dimensional (4,4) network in **3**. (c) The packing of the two-dimensional networks in **3**.

analogous compounds containing combinations of ClO_4^-/PF_6^- or ClO_4^-/AsF_6^- [16], which comprise two equivalent, mutually interpenetrating three-dimensional networks. The reaction of bimb with Mn(II) and anion co-ligands (NCS^-, dca, N_3^-) yields three new Mn(II) coordination polymers $[Mn(bimb)_2(NCS)_2]_n$ (**1**), $[Mn(bimb)_2(dca)_2]_n$ (**2**) and $[Mn(bimb)_2(N_3)_2]_n$ (**3**). **1** and **2** form a one-dimensional (1D) double chain;

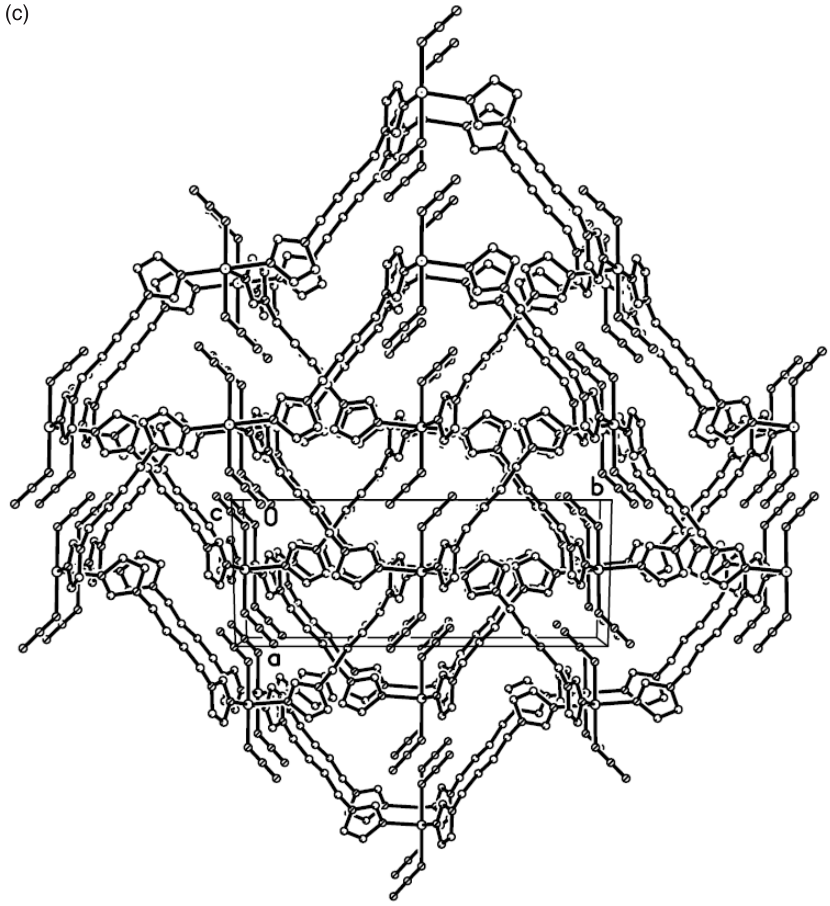

Figure 3. Continued.

3 has a two-dimensional (2D) (4,4) network. The anions play a key role in structural assembly. Further designation and synthesis of new motifs with bimb and different metal salts are under way in our lab.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) (Email: deposit@ccdc.cam.ac.uk) as supplementary materials and the CCDC reference numbers for **1**, **2** and **3** are 612537, 612538 and 612539, respectively.

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