Thiophene-2,5-dicarboxylic acid incorporated self-assembly of one-, two- and three-dimensional coordination polymers

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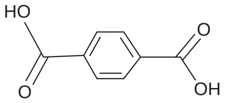
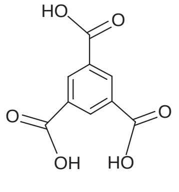
Six thiophene-2,5-dicarboxylic acid incorporated and self-assembled zinc(II), cobalt(II) and manganese(II) coordination polymers [Zn(Tda)(py)]$_n$ (**1**), [Zn(Tda)(bipy)(H_2O) · 1.5H_2O]$_n$ (**2**), [Zn(Tda)(phen)(H_2O)]$_n$ (**3**), [Co(Tda)(phen)(H_2O)]$_n$ (**4**), [Mn(Tda)(phen)]$_n$ (**5**) and [Mn(Tda)(H_2O)$_2$]$_n$ (**6**) have been synthesised and structurally characterised. Complex **1** is characterised as a two-dimensional parallelogram with a cavity of about 10.4 × 10.4 Å, while complexes **2** and **3** (**4**) are one-dimensional linear and zig-zag coordination polymers with mainly hydrogen-bonding and stacking interactions contributing to their crystal packing, respectively. Complex **5** is a two-dimensional porous sheet with alternating 16- and 8-membered rings, while complex **6** is a three-dimensional porous coordination polymer. The diverse coordination properties of thiophene-2,5-dicarboxylate make it a good building block for the construction of coordination polymers of different architectures, which are dependent on both the end-capping ligand and the coordination geometry of the metal ions. Physical and thermal properties of these complexes have also been studied.

There has been increasing interest in the syntheses, structures and properties of coordination polymers because of their potential applications in materials science,[1] and polybasic carboxylic acids have been well established to be useful building blocks for the construction of diverse coordination polymers.[2–10] Of particular interest is the recent research by Yaghi and coworkers on the selective inclusion properties of some zinc(II) coordination polymers with 1,4-benzenedicarboxylic acid[2] (H_2BDC, **A**) and 1,3,5-benzenetricarboxylic acid[3] (H_2BTC, **B**), which may contribute to their development in areas such as separations, catalysis and sensors.



(A)



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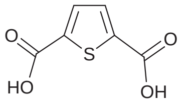


(C)

The structural architecture of diverse coordination polymers is dependent on a number of factors such as ligand donor group geometry, tether length and stereochemistry, solvent, metal coordination preferences and oxidation state, and the identity of the counterion. It is difficult to control the orientation and stereochemistry of the building blocks in the solid state in order to achieve a given target molecular topology and architecture,[1a,b] thus much efforts are needed on the rational design of coordination polymers. Our research on the coordination properties of thiophene-2,5-dicarboxylic acid (H_2Tda, **C**) has shown that the thiophene-2,5-dicarboxylate dianion (Tda^{2-}) is capable of diverse binding modes such as monodentate, bridging bidentate and bridging tridentate in its copper(II) complexes, which make it also a useful building block in the construction of coordination polymers.[11] As an extension of our studies on the application of this ligand in the construction of diverse low-dimensional coordination polymers, we report here the syntheses and crystal structures of the thiophene-2,5-dicarboxylic acid incorporated and self-assembled one-, two- and three-dimensional zinc(II), cobalt(II) and manganese(II) coordination polymers [Zn(Tda)(py)]$_n$ (**1**), [Zn(Tda)(bipy)(H_2O) · 1.5H_2O]$_n$ (**2**), [Zn(Tda)(phen)(H_2O)]$_n$ (**3**), [Co(Tda)(phen)(H_2O)]$_n$ (**4**), [Mn(Tda)(phen)]$_n$ (**5**) and [Mn(Tda)(H_2O)$_2$]$_n$ (**6**). They have diverse architectures that apparently are dependent on both the end-capping ligand and the coordination geometry of the metal ions.

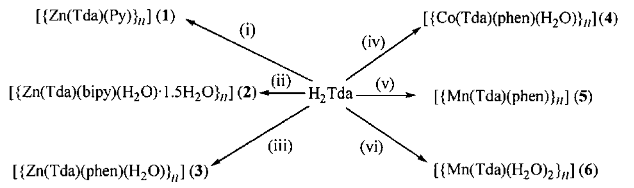
Results and discussion

Syntheses

Reaction of suitable metal salts with thiophene-2,5-dicarboxylic acid in the presence of secondary nitrogen-containing ligands such as pyridine, 2,2′-bipyridine or 1,10-phenanthroline at a suitable pH value at room or higher temperatures readily produced the different coordination polymers as shown in Scheme 1. Single crystals suitable for X-ray crystallographic determination were obtained directly from the reaction mixture. A summary of their crystallographic data is given in Table 1.

One-dimensional coordination polymers: structures of [Zn(Tda)(bipy)(H_2O) · 1.5H_2O]$_n$ (2), [Zn(Tda)(phen)(H_2O)]$_n$ (3) and [Co(Tda)(phen)(H_2O)]$_n$ (4)

The structure of **2** consists of one-dimensional linear polymers in which the mononuclear [Zn(bipy)(H_2O)] subunits are bridged by *syn-syn* bis-monodentate Tda^{2-} with a ZnA· · ·ZnB separation of about 10.09 Å. Hydrogen bonding interactions between the carboxylate oxygen atoms with coordinated water molecules, at distances of 2.695 Å for O5· · ·O1D, and 2.731 Å for O5· · ·O4E, bind a pair of neighbouring [Zn(Tda)(bipy)(H_2O)]$_n$ chains in close proximity with



Scheme 1 (*i*) $Zn(NO_3)_2$–pyridine, 65 °C, 24 h (pH 4.46); (*ii*) $Zn(NO_3)_2$–bipy–NaOH, rt, several days (pH 4.38); (*iii*) $Zn(NO_3)_2$–phen–NaOH, rt, several days (pH 4.34); (*iv*) $CoSO_4$–phen–NaOH, 75 °C, 24 h (pH 4.53); (*v*) $Mn(ClO_4)_2$–phen–NaOH, 75 °C, 24 h (pH 4.96); (*vi*) $Mn(ClO_4)_2$–pyridine, 75 °C, 24 h (pH 4.68).

an inter-chain Zn···Zn separation of about 4.80 Å, as shown in Fig. 1. Selected bond distances and angles are given in Table 2.

3 and **4** are also one-dimensional coordination polymers. However, unlike **2**, they are zig-zag polymers in which the mononuclear [M(phen)(H_2O)] subunits are bridged by *syn-syn* bis-monodentate Tda^{2-} with an M···M separation of approximately 10.54 and 10.57 Å for complexes **3** (M = Zn) and **4** (M = Co), respectively. Stacking interactions between parallel phenanthroline molecules with a separation of *ca.* 3.51 Å make the main contribution to the crystal packing as shown in Fig. 2 and 3 for complexes **3** and **4**. The crystal packing, to some extent, is also stabilised by partial stacking interactions between the thiophene plane and the phenanthroline plane with a tilt angle of about 14.6°. The thiophene S1 atom is about 3.82 Å from the nearest phenanthroline plane in complex **3** and about 3.81 Å away from an immediate phenanthroline plane in complex **4**. Selected bond distances and angles are given in Table 2.

Although each zinc atom is five-coordinated by three oxygen atoms and two nitrogen atoms in **2** and **3**, the coordination geometry is slightly different in the two complexes. In **2** the zinc atom is best described as being in a highly distorted square-pyramidal geometry with the apical position being occupied by O3, while in **3** it is in a highly distorted trigonal-bipyramidal geometry with the axial positions being occupied by O3 and N1; O3–Zn–N1 is equal to 166.66(6)°. The calculated τ values [0.483 and 0.637 for **2** and **3**, respectively, relative to 0 for a regular square pyramid (*SPY*) and 1 for a regular trigonal bipyramid (*TBPY*)][12] clearly indicates the substantial deviation from the *SPY* form for **2** and from the *TBPY* form for **3**. In **4**, each cobalt atom is in a highly distorted trigonal-bipyramidal CoO_3N_2 coordination geometry

Table 1 Crystal data at 298 K and refinement details for complexes **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{11}H_7NO_4SZn$	$C_{16}H_{15}N_2O_{6.5}SZn$	$C_{18}H_{12}N_2O_5SZn$	$C_{18}H_{12}CoN_2O_5S$	$C_{18}H_{10}MnN_2O_4S$	$C_6H_6MnO_6S$
Formula weight	314.61	436.73	433.73	427.29	405.28	261.11
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	*Pbca*	*Pnma*
a/Å	7.853(1)	8.595(3)	10.977(2)	10.917(2)	8.031(2)	7.349(1)
b/Å	15.937(1)	9.491(3)	15.558(2)	15.711(2)	18.113(6)	18.165(1)
c/Å	9.993(1)	12.748(6)	11.376(3)	11.330(2)	21.755(6)	6.721(1)
α/°		69.31(3)				
β/°	95.65(1)	85.99(3)	116.36(3)	116.01(3)		
γ/°		67.59(2)				
U/Å^3	1244.6(1)	896.9(6)	1740.7(6)	1746.5(5)	3165(2)	897.3(1)
Z	4	2	4	4	8	4
μ/mm^{-1}	2.144	1.524	1.564	1.136	0.995	1.703
Unique. obs reflections.	2517; 2147	3850; 3044	2990; 2770	2272; 1629	3233; 2192	947; 873
R_1[a]; wR_2[b]	0.0250; 0.0650	0.0389; 0.0984	0.0235; 0.0647	0.0419; 0.0865	0.0428; 0.0874	0.0238; 0.0602

[a] $R_1 = \sum w|F_o - F_c|/\sum (F_o)$; [b] $wR_2 = \{\sum w[(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$.

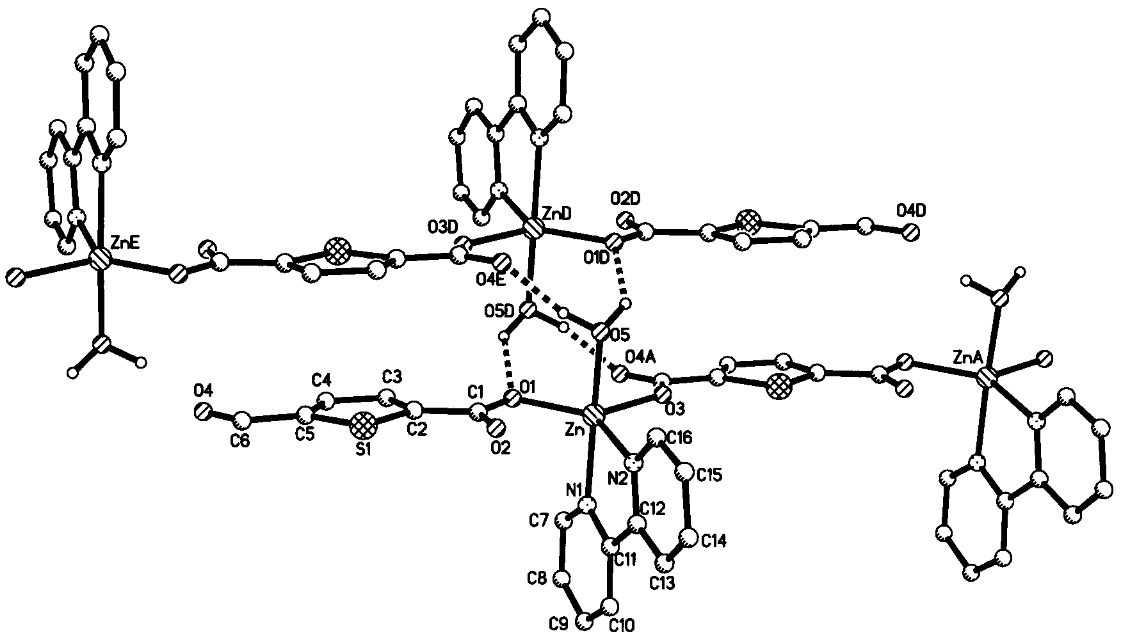


Fig. 1 Partial packing diagram of **2**, with atom labelling scheme, showing hydrogen bonding between two adjacent chains.

Table 2 Selected bond distances (Å) and angles (°) for **2**, **3** and **4**

$[Zn(Tda)(bipy)(H_2O)\cdot 1.5H_2O]_n$ (**2**)			
Zn–O1	2.075(2)	Zn–N1	2.135(3)
Zn–N2	2.106(3)	Zn–O3	2.015(2)
Zn–O5	2.086(2)		
N1–Zn–N2	76.8(1)	N1–Zn–O1	90.3(1)
N2–Zn–O1	139.8(1)	N1–Zn–O3	96.8(1)
N2–Zn–O3	102.4(1)	O1–Zn–O3	117.0(1)
N1–Zn–O5	168.7(1)	N2–Zn–O5	93.0(1)
O1–Zn–O5	94.6(1)	O3–Zn–O5	90.1(1)
$[Zn(Tda)(phen)(H_2O)]_n$ (**3**)			
Zn1–O1	1.987(2)	Zn1–O5	2.041(2)
Zn1–N1	2.171(2)	Zn1–N10	2.098(2)
Zn1–O3	2.064(2)		
O1–Zn1–O5	129.07(6)	O1–Zn1–O3	95.55(6)
O5–Zn1–O3	88.50(1)	O1–Zn1–N10	104.40(6)
O5–Zn1–N10	126.24(6)	O3–Zn1–N10	91.82(6)
O1–Zn1–N1	95.46(6)	O5–Zn1–N1	90.39(7)
O3–Zn1–N1	166.66(6)	N10–Zn1–N1	78.15(6)
$[Co(Tda)(phen)(H_2O)]_n$ (**4**)			
Co1–O1	2.000(3)	Co1–O5	2.038(4)
Co1–N1	2.082(4)	Co1–N10	2.152(4)
Co1–O3	2.042(3)		
O1–Co1–O5	130.53(15)	O1–Co1–O3	96.56(13)
O5–Co1–O3	89.75(16)	O3–Co1–N1	102.67(14)
O5–Co1–N1	125.89(15)	O1–Co1–N1	93.77(14)
O3–Co1–N10	91.37(14)	O5–Co1–N10	89.89(16)
O1–Co1–N10	169.85(14)	N1–Co1–N10	78.26(15)

with a O3–Co–N10 angle of 169.85(14)° and calculated τ value of 0.733.

Two-dimensional coordination polymers: structures of $[Zn(Tda)(py)]_n$ (1) and $[Mn(Tda)(phen)]_n$ (5)

The structure of $[Zn(Tda)(py)]_n$ (**1**) possesses a dimeric subunit in which a pair of zinc atoms are bridged by four *syn,syn*-μ-carboxylato-O,O′ groups of Tda^{2-} as shown in Fig. 4(a) together with the atom labelling scheme. Selected bond distances and angles are given in Table 3. Each zinc(II) atom in **1** is in a five-coordinate, square-pyramidal environment with four carboxylate oxygen atoms forming the basal plane and the pyridine nitrogen atom in the apical position. Pyridine molecules are in a trans geometry in the dimeric subunit. The Zn1···Zn1A separation of 3.030(1) Å is a little longer than the 2.940(3) Å in $[Zn(BDC)\cdot(DMF)(H_2O)]_n$ (BDC = 1,4-benzenedicarboxylate and DMF = *N,N′*-dimethylformamide),[2] indicating there is at best very little Zn···Zn bonding interactions. The dimeric subunits are further inter-linked *via* bridging of *syn,syn,syn,syn*-tetradentate thiophene-2,5-dicarboxylate to

Table 3 Selected bond distances (Å) and angles (°) for **1** and **5**

$[Zn(Tda)(py)]_n$ (**1**)			
Zn1–O1	2.062(2)	Zn1–O2	2.069(2)
Zn1–O3	2.038(2)	Zn1–O4	2.032(2)
Zn1–N1	2.035(2)		
O4–Zn1–N1	101.68(7)	O4–Zn1–O3	157.80(7)
N1–Zn1–O3	100.49(7)	O4–Zn1–O1	88.87(7)
N1–Zn1–O1	103.17(7)	O3–Zn1–O1	87.43(7)
O4–Zn1–O2	85.38(7)	N1–Zn1–O2	98.91(7)
O3–Zn1–O2	89.87(8)	O1–Zn1–O2	157.88(7)
$[Mn(Tda)(phen)]_n$ (**5**)			
Mn–O1	2.183(2)	Mn–O2	2.111(2)
Mn–O3	2.214(2)	Mn–O4	2.124(2)
Mn–N1	2.332(3)	Mn–N10	2.317(3)
O2–Mn–O4	113.36(9)	O2–Mn–O1	85.64(9)
O4–Mn–O1	99.18(9)	O2–Mn–O3	97.67(9)
O4–Mn–O3	88.13(9)	O1–Mn–O3	170.08(8)
O2–Mn–N10	157.82(9)	O4–Mn–N10	87.35(9)
O1–Mn–N10	83.14(9)	O3–Mn–N10	90.56(9)
O2–Mn–N1	89.88(9)	O4–Mn–N1	155.03(9)
O1–Mn–N1	91.25(9)	O3–Mn–N1	79.45(9)
N10–Mn–N1	71.35(9)		

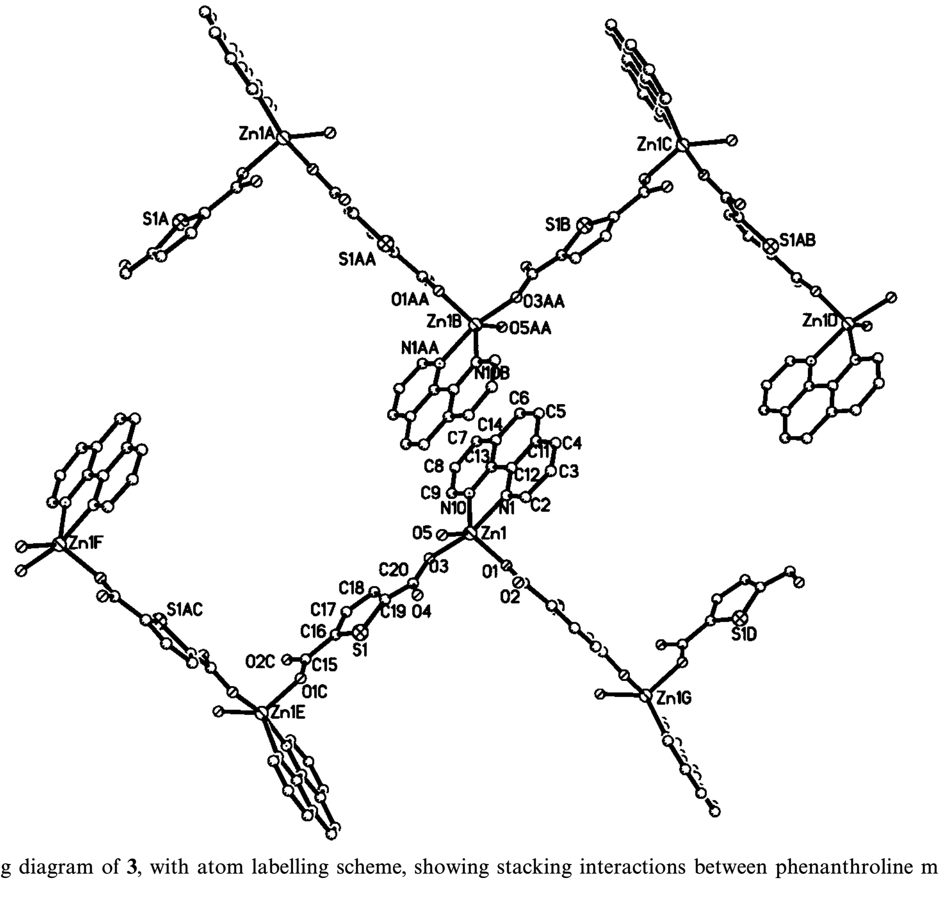


Fig. 2 Partial packing diagram of **3**, with atom labelling scheme, showing stacking interactions between phenanthroline molecules in adjacent chains.

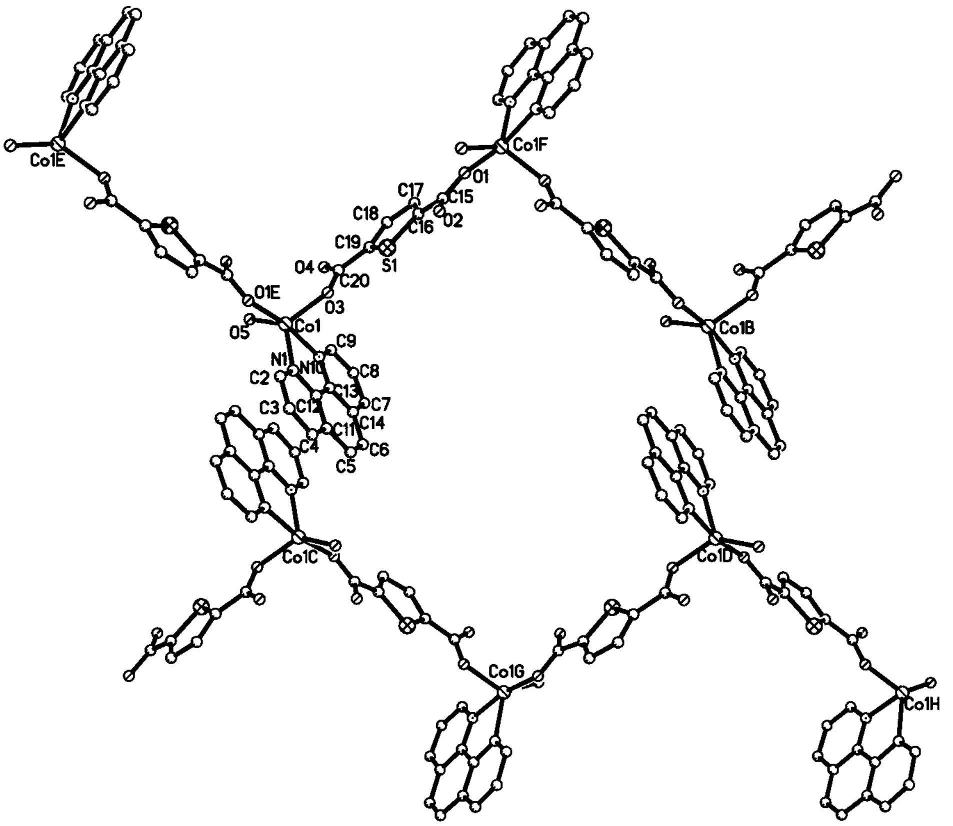


Fig. 3 Partial packing diagram of **4**, with atom labelling scheme, showing stacking interactions between phenanthroline molecules in adjacent chains.

form a two-dimensional framework. As illustrated in Fig. 4(b), each layer consists of parallelograms with corners at the mid-point separating the two zinc(II) (*i.e.*, Zn1 and Zn1A) and bridging thiophene-2,5-dicarboxylates forming the sides. Each parallelogram has angles of 100.3 and 79.7° and a cavity of approximate dimensions 10.4 × 10.4 Å. The pyridine molecules are above and below the plane of the parallelogram. Stacking of the layers is such that the interlayer distance is minimised while at the same time accommodating the protruding pyridine molecules as shown in Fig. 4(c).

The manganese(II) centre in complex **5** is in a six-coordinate, slightly distorted octahedral environment with the two nitrogen atoms from the phenanthroline molecule in *cis* positions and four oxygen atoms from four different *syn*,skew-μ-carboxylato-*O*,*O*′ groups of Tda^{2-} as shown in Fig. 5(a). Selected bond distances and angles are given in Table 3. The bridging tetradentate *syn*,skew,*syn*,skew-Tda^{2-} thus connects the manganese atoms to form a two-dimensional sheet structure [Fig. 5(b)] with alternating 16-membered rings bridged by two Tda^{2-} dianions and 8-membered rings bridged by two carboxylate oxygen atoms. The Mn⋯Mn separations are 4.72 Å (Mn⋯MnA within the 8-membered ring), 9.06 Å (Mn⋯MnB within the 16-membered ring) and 10.18 Å (Mn⋯MnC along the Tda^{2-} bridge). The Mn⋯Mn separation of 4.72 Å in **5** is within the range of 4.56 to 4.85 Å found in some other carboxylate doubly bridged manganese(II) compounds.[5,13] Fig. 5(c) shows the stacking of two adjacent layers as viewed along the *a* axis; the importance of stacking interactions between phenanthroline molecules is quite evident.

Three-dimensional coordination polymers: structure of $[Mn(Tda)(H_2O)_2]_n$ (6)

The manganese(II) centre in complex **6** is in a six-coordinate, slightly distorted octahedral environment with two oxygen atoms from two water molecules in *trans* positions and four oxygen atoms from four different skew,skew-μ-carboxylato-O,O′ groups of Tda^{2-} as shown in Fig. 6(a). Selected bond distances and angles are given in Table 4. The Mn⋯Mn distances are 4.98 Å (Mn1⋯Mn1B), 9.08 Å (Mn1⋯Mn1A) and 10.36 Å (Mn1⋯Mn1E). The bridging tetradentate skew,skew, skew,skew-Tda^{2-} connects the manganese atoms to form a three-dimensional coordination polymer as shown in Fig. 6(b). The Mn1⋯Mn1A separation of 4.98 Å in **6** is significantly shorter than those found in Mn(II) compounds with singly bridged carboxylates,[14–17] possibly because of the constraint of the infinite framework. The pyridine molecule does not appear to coordinate to manganese under the experimental conditions employed.

The different structural frameworks for complexes **1**, **2** and **3** with pyridine, 2,2′-bipyridine and 1,10-phenanthroline as the end-capping ligand, respectively, and for complexes **5** and **6** with 1,10-phenanthroline and water as the end-capping ligand, clearly indicate that the end-capping ligand plays an important role in the construction of coordination polymers. This has previously been established in manganese(II) complexes with 1,4-benzenedicarboxylate (BDC) by Hong and Do.[9,10] It was found that the 4-methylpyrazole manganese(II) complex with BDC, $[Mn(4\text{-methylpyrazole})_3(H_2O)(BDC)]_n$, is a one-dimensional polymer, the 3(5)-methylpyrazole analogue, $[Mn(5\text{-methylpyrazole})_2(BDC)]_n$, is a

Table 4 Selected bond distances (Å) and angles (°) for **6**

Mn1–O1	2.167(2)	Mn1–O1A	2.167(2)
Mn1–O3	2.178(2)	Mn1–O3A	2.178(2)
Mn1–O2	2.193(2)	Mn1–O2A	2.193(2)
O1–Mn1–O1A	180.0	O1–Mn1–O3	93.35(4)
O1A–Mn1–O3	86.65(4)	O1–Mn1–O3A	86.65(4)
O1A–Mn1–O3A	93.35(4)	O3–Mn1–O3A	180.0
O1–Mn1–O2	87.90(5)	O1A–Mn1–O2	92.10(5)
O3–Mn1–O2	87.17(5)	O3A–Mn1–O2	92.83(5)
O1–Mn1–O2A	92.10(5)	O1A–Mn1–O2A	87.90(5)
O3–Mn1–O2A	92.83(5)	O3A–Mn1–O2A	87.17(5)
O2–Mn1–O2A	180.0		

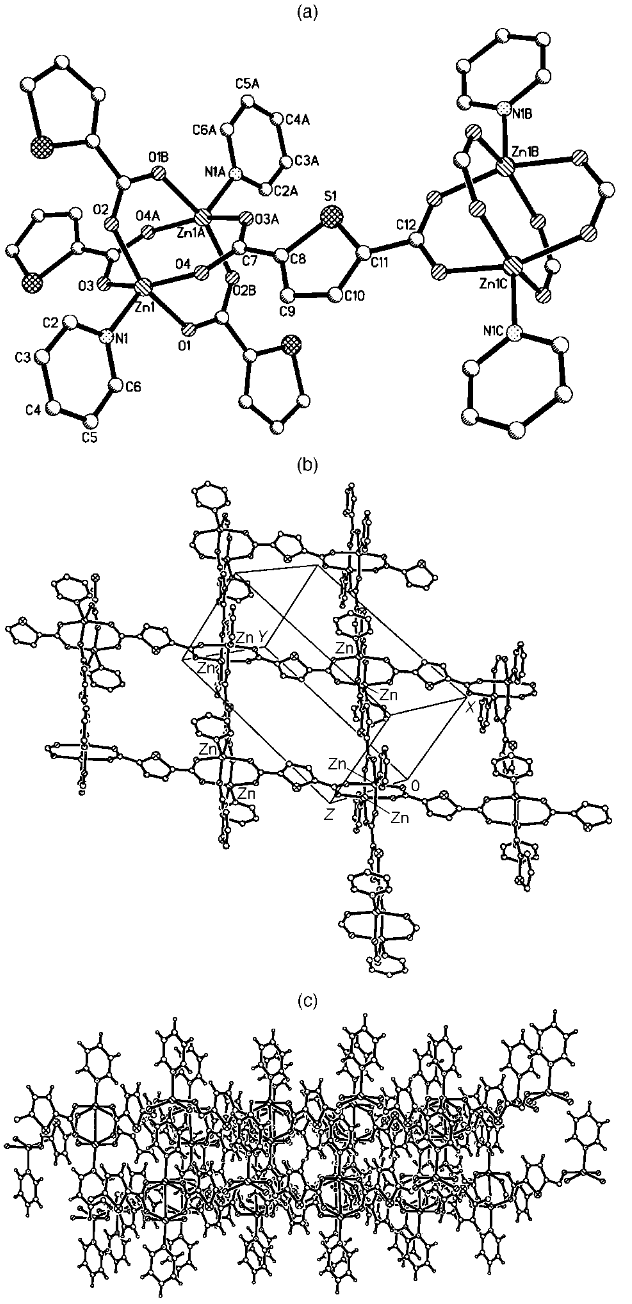


Fig. 4 (a) Dimeric subunit structure of complex **1** showing the atom labelling scheme. (b) Two-dimensional polymeric structure of **1**. (c) Stacking of two layers of complex **1** as viewed along the *b* axis.

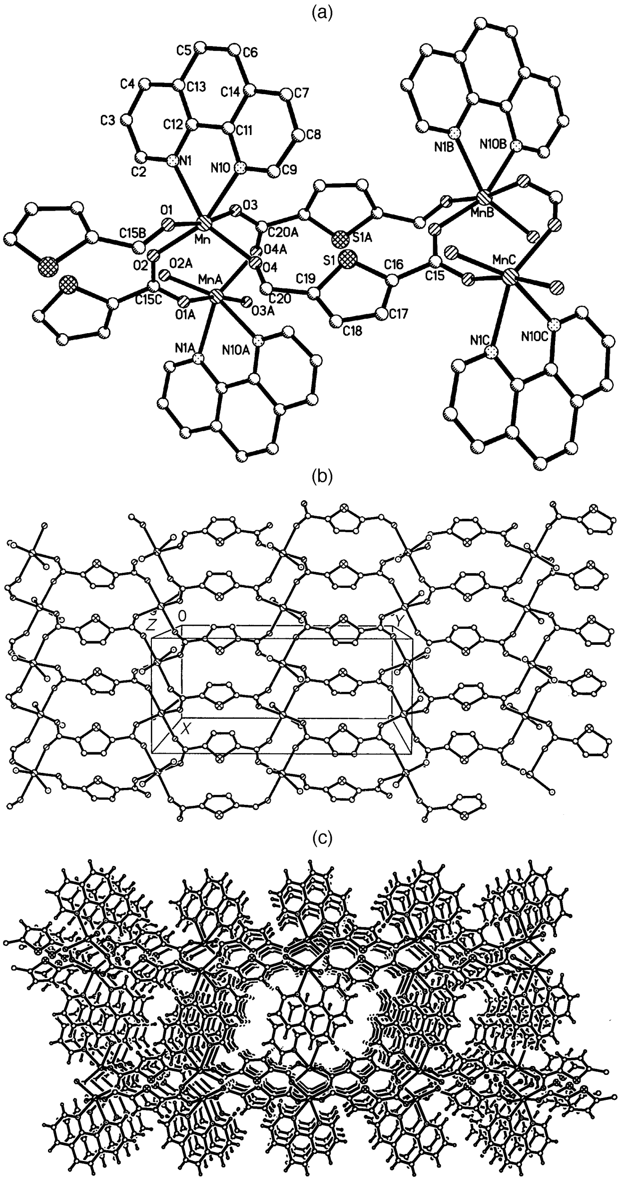


Fig. 5 (a) Part of the structure of **5** showing the atom labelling scheme. (b) Two-dimensional polymeric structure of **5**. For clarity, only nitrogen atoms of the phenanthroline ligands are shown. (c) Stacking of two layers of complex **5** as viewed along the *a* axis.

three-dimensional polymer,[9] while the 1,2-bis(4-pyridyl)-ethane (bpe) manganese(II) complex with BDC, $[Mn(bpe)(H_2O)_4]_{0.5n}(BDC)_{0.5n}(bpe)_n$, is a hydrogen- and covalent-bond-linked three-dimensional polymer.[10] Another important factor acting on the structural framework of coordination polymers is the coordination geometry preference of the metal ion. This was observed in the different structural frameworks of $[Cu(Tda)(py)_2]_n$ [11b] and $[Zn(Tda)(py)]_n$ (**1**), the former is a one-dimensional chain polymer, while the latter is a two-dimensional parallelogram sheet, and of $[Zn(Tda)(phen)(H_2O)]_n$ (**3**) and $[Mn(Tda)(phen)]_n$ (**5**), which are one-dimensional zig-zag and two-dimensional porous polymers, respectively, because of the six-coordinate preference of manganese(II).

Physical and thermal properties

Complexes **1**–**6** are stable solids that are insoluble in common solvents. As a result of complex formation the strong IR absorption of thiophene-2,5-dicarboxylic acid at 1665 cm^{-1}, characteristic of the acid carbonyl groups, disappears and is replaced by very strong and broad bands in the 1537–1595 and 1363–1382 cm^{-1} regions, corresponding to the asymmetric and symmetric vibrations of the carboxylate moiety, respectively. The comparatively low Δ value [155 cm^{-1}, $\Delta = \nu_{as}(COO^-) - \nu_s(COO^-)$] for complex **1** possibly indicates that Tda^{2-} is coordinated to four zinc(II) ions in a tetradentate bridging fashion, while the Δ values of 213, 216 and 223 cm^{-1} are indicative of the existence of non-coordinated Tda^{2-} oxygen atoms in **2**, **3** and **4**,[18] which are consistent with the X-ray structures of **1**–**4** in which Tda^{2-} are *syn,syn,syn,syn*-bridging tetradentate for **1** and *syn,syn*-bridging bidentate for **2**–**4**. The Δ values of 183 and 176 cm^{-1} for complexes **5** and **6**, comparable to those in $[Mn_2(bipy)_4(BDC)][ClO_4]_2$ ($\Delta = 185$ cm^{-1}),[5] $[Mn_2(phen)_4(BDC)][ClO_4]_2$ ($\Delta = 185$ cm^{-1}) and $[Mn_2(phen)_4(H_2O)_2(BDC)][ClO_4]_2$ ($\Delta = 185$ cm^{-1}),[19] indicate that all oxygen atoms of both carboxylate groups of Tda^{2-} are coordinated to manganese(II) ions, consistent with the X-ray structure.

TGA results show complex **1** loses the coordinated pyridine molecule between 220 and 320 °C (calcd. weight loss: 25.1%;

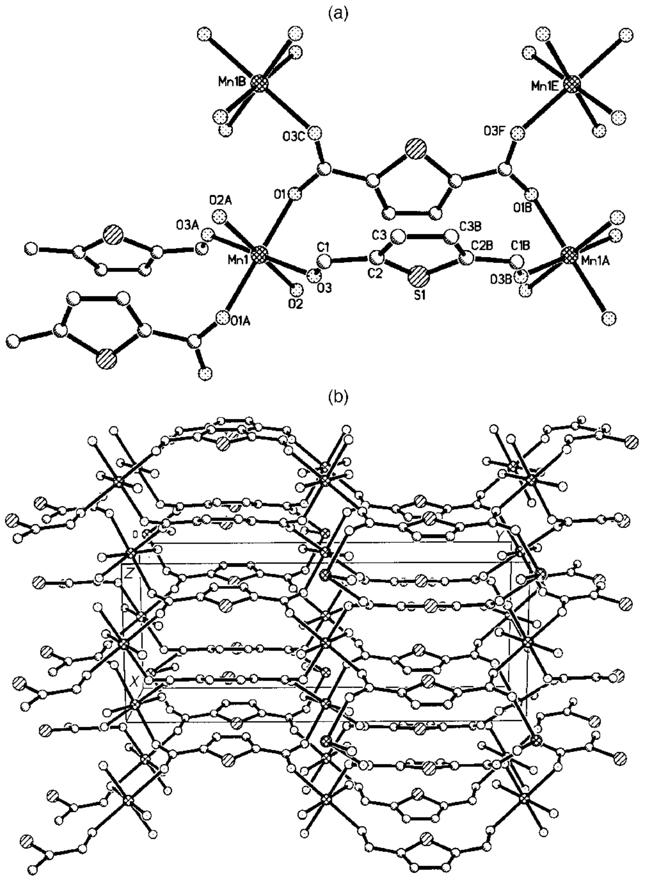
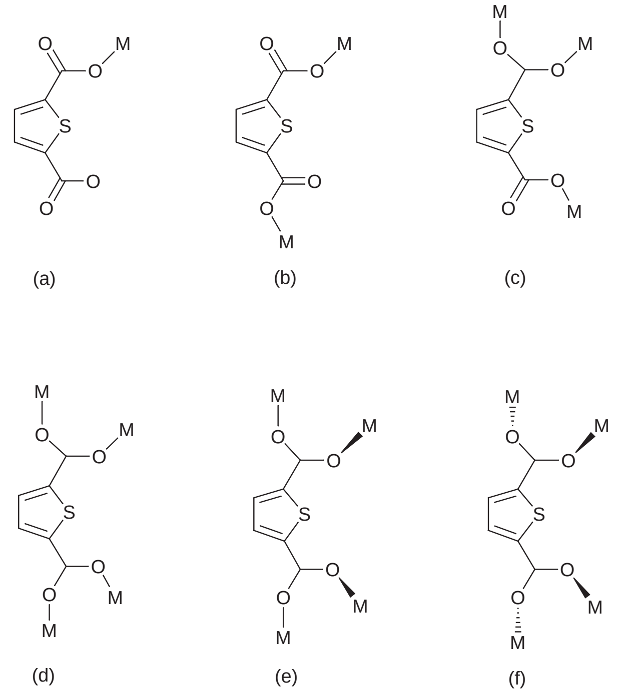


Fig. 6 (a) Part of the structure of **6** showing the atom labelling scheme. (b) Three-dimensional polymeric structure of **6**. Hydrogen atoms are omitted for clarity.

found: 24.9%). Complex **2** first loses water of crystallisation between 100 and 142 °C, with a total loss of one and half water molecules (calcd. weight loss: 12.5%; found: 13.0%). The complex began losing the coordinated water molecule at 142 °C. In complex **3** the coordinated water molecule is lost in the 125–150 °C range (calcd. weight loss: 4.1%, found: 4.5%). Complex **4** loses the coordinated water at 132–153 °C (calcd. weight loss: 4.2%; found: 4.6%). In complex **6** the two coordinated water molecules are lost in the 130–185 °C range (calcd. weight loss: 13.8%; found: 14.6%). There is no further weight loss in the 185–350 °C temperature range, indicating the formation of a stable phase formulated as Mn(Tda).



Scheme 2 Diverse coordination modes of Tda^{2-} in its metal complexes.

Conclusions

Our studies on the coordination properties of thiophene-2,5-dicarboxylic acid establishes that the thiophene-2,5-dicarboxylate dianion shows a variety of coordination modes in its transition metal complexes, that is as a *syn*-monodentate (*a*), *syn,syn*-bridging bidentate (*b*), *syn,syn,syn*-bridging tridentate (*c*),[11] *syn,syn,syn,syn*-bridging tetradentate (*d*), *syn*,skew,*syn*, skew-bridging tetradentate (*e*) and skew,skew,skew,skew-bridging tetradentate (*f*) ligand, as shown in Scheme 2. The diverse bridging properties of Tda^{2-} make it a useful building block in the construction of coordination polymers of different architectures, which are dependent on both the end-capping ligand and the coordination geometry of the metal ions.

Experimental

Materials and methods

All chemicals were reagent grade and used without further purification. Elemental analyses were carried out by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore. Solution pH values of the reaction mixtures was measured using a Metrohm 691 pH Meter. IR spectra were recorded as KBr discs using a Perkin Elmer 1600 Fourier transform IR spectrometer (4400–450 cm^{-1}). Thermogravimetric data were obtained on a Universal V1.5B TA instrument in air flux with a heating rate of 10 °C min^{-1}. Thiophene-2,5-dicarboxylic acid was synthesised by a modified literature method.[20]

Safety note! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Preparations

[Zn(Tda)(py)]$_n$ (1). An aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 M, 3 ml) and an ethanol solution of H_2Tda (0.1 M, 3 ml) were mixed in a 15 ml test tube, then pyridine (0.5 ml) was added. The resulting solution with a pH of 4.46 was heated in a water bath at 65 °C for 24 h to obtain complex **1** (61 mg, yield 65% based on Zn). Anal. calcd. for $C_{11}H_7NO_4SZn$: C, 41.97; H, 2.23; N, 4.45; S, 10.17%. Found: C, 41.84; H, 2.03; N, 4.38; S, 10.25%. IR (KBr disc, cm^{-1}): 1537 $\nu_{as}(COO^-)$, 1382 $\nu_s(COO^-)$.

[Zn(Tda)(bipy)(H$_2$O)·1.5H$_2$O]$_n$ (2). An aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 M, 2 ml) and an ethanol solution of H_2Tda–bipy (1 : 1 molar ratio, 0.1 M, 2 ml) were mixed in a 10 ml capped bottle (vial), then an aqueous NaOH solution (0.1 M, 4 ml) was added. The resulting solution with a pH of 4.38 was put aside. After several days, colourless crystals were formed and collected as **2** (25 mg, yield 29% based on Zn). Anal. calcd for $C_{16}H_{15}N_2O_{6.5}SZn$: C, 43.97; H, 3.43; N, 6.41; S, 7.34%. Found: C, 43.98; H, 3.95; N, 6.28; S, 6.98%. IR (KBr disc, cm^{-1}): 1576 $\nu_{as}(COO^-)$, 1363 $\nu_s(COO^-)$.

[Zn(Tda)(phen)(H$_2$O)]$_n$ (3). An aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 M, 2 ml) and an ethanol solution of H_2Tda–phen (1 : 1 molar ratio, 0.1 M, 2 ml) were mixed in a 10 ml capped bottle (vial), then an aqueous NaOH solution

(0.1 M, 4 ml) was added. The resulting solution with a pH of 4.34 was put aside. After several days, colourless crystals were formed and were collected as **3** (28 mg, yield 33% based on Zn). Anal. calcd for $C_{18}H_{12}N_2O_5SZn$: C, 49.82; H, 2.77; N, 6.46; S, 7.38%. Found: C, 49.97; H, 2.50; N, 6.94; S, 7.04%. IR (KBr disc, cm^{-1}): 1595 $\nu_{as}(COO^-)$, 1363 $\nu_s(COO^-)$.

$[Co(Tda)(phen)(H_2O)]_n$ (4). An aqueous solution of $CoSO_4 \cdot 7H_2O$ (0.1 M, 2 ml) and an ethanol solution of H_2Tda–phen (1 : 1 molar ratio, 0.1 M, 2 ml) were mixed in a test tube (15 ml); then an aqueous solution of NaOH (0.1 M, 4 ml) was added. The resulting solution with a pH of 4.53 was heated in a water bath at 75 °C for 24 h. Evaporation of solvent at room temperature for several days produced purple crystals as complex **4** (13 mg, yield 15% based on Co). Anal. calcd for $C_{18}H_{12}CoN_2O_5S$: C, 50.59; H, 2.81; N, 6.55; S, 7.50%. Found: C, 50.39; H, 2.73; N, 6.55; S, 6.84%. IR (KBr disc, cm^{-1}): 1587 $\nu_{as}(COO^-)$, 1364 $\nu_s(COO^-)$.

$[Mn(Tda)(phen)]_n$ (5). An aqueous solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.1 M, 2 ml) and an ethanol solution of H_2Tda–phen (1 : 1 molar ratio, 0.1 M, 2 ml) were mixed in a 15 ml test tube, then an aqueous NaOH solution (0.1 M, 4.0 ml) was added. The resulting solution with a pH of 4.96 was heated in a water bath at 75 °C for 24 h to obtain complex **5** as light yellow crystals (20 mg, yield 25% based on Mn). Anal. calcd. for $C_{18}H_{10}N_2O_4SMn$: C, 53.34; H, 2.47; N, 6.91; S, 7.91%. Found: C, 53.18; H, 2.35; N, 6.26; S, 7.48%. IR (KBr disc, cm^{-1}): 1558 $\nu_{as}(COO^-)$, 1375 $\nu_s(COO^-)$.

$[Mn(Tda)(H_2O)_2]_n$ (6). An aqueous solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.1 M, 2 ml) and an ethanol solution of H_2Tda (0.1 M, 2 ml) were mixed in a 15 ml test tube, then pyridine (0.4 ml) was added. The resulting solution with a pH of 4.68 was heated in a water bath at 75 °C for 24 h to obtain complex **6** as light yellow crystals (19 mg, yield 36% based on Mn). Anal. calcd. for $C_6H_6O_6SMn$: C, 27.60; H, 2.30; S, 12.28%. Found: C, 27.74; H, 1.90; S, 12.09%. IR (KBr disc, cm^{-1}): 1544 $\nu_{as}(COO^-)$, 1368 $\nu_s(COO^-)$.

Crystallography

X-Ray diffraction data for **1**, **5** and **6** were collected on a Siemens CCD SMART System, data for **2** were obtained on a Siemens R3m/V diffractometer and data for **3** and **4** were collected on a MAR Research image plate system, all using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). SADABS absorption correction program was used on **1**, **5** and **6**, semi-empirical absorption corrections were applied on **2** and no absorption corrections were made on **3** and **4**. All the structures were solved by direct methods with remaining non-hydrogen atoms located from Fourier difference maps. All non-hydrogen atoms were refined anisotropically using the SHELXL 93[21] software package.

CCDC reference number 440/118. See http://www.rsc.org/suppdata/nj/1999/877/ for crystallographic files in .cif format.

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