

# Zinc dicarboxylate polymers and dimers: thiourea substitution as a tool in supramolecular synthesis †

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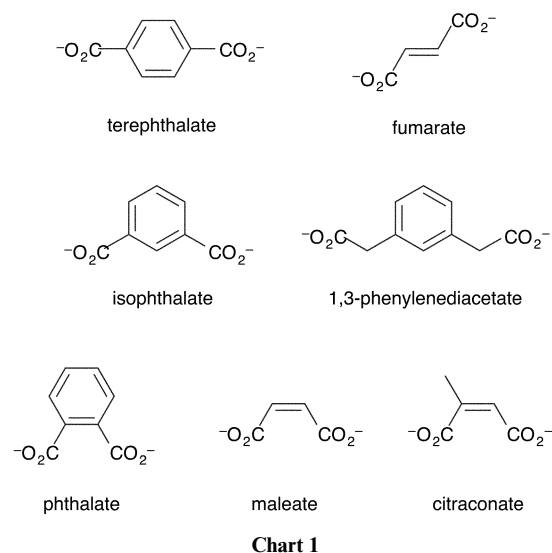
The reactions of the zinc thiourea complexes  $[\text{Zn}\{\text{SC}(\text{NHR})(\text{NHR}')\}_4]\text{Cl}_2$  ( $\text{L} = \text{L}^1$ ,  $\text{R} = \text{H}$ ,  $\text{R}' = \text{Me}$ ;  $\text{L} = \text{L}^2$ ,  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Me}$ ) with a range of dicarboxylates have been investigated. From these reactions eleven products –  $[\text{Zn}(\text{L}^1)_2(\mu\text{-terephthalate})]_n$ ,  $[\text{Zn}(\text{L}^1)_2(\mu\text{-fumarate})]_n$ ,  $\{[\text{Zn}(\text{L}^1)_2(\mu\text{-isophthalate})]\cdot\text{H}_2\text{O}\}_n$ ,  $[\text{Zn}(\text{L}^1)_2(\mu\text{-1,3-phenylenediacetate})]_n$ ,  $[\text{Zn}(\text{L}^1)_2(\mu\text{-phthalate})]_2\cdot 4\text{H}_2\text{O}$ ,  $\{[\text{Zn}(\text{L}^2)_2(\mu\text{-terephthalate})]\cdot 0.5\text{H}_2\text{O}\}_n$ ,  $[\text{Zn}(\text{L}^2)_2(\mu\text{-fumarate})]_n$ ,  $[\text{Zn}(\text{L}^2)_2(\mu\text{-isophthalate})]_2\cdot 2\text{H}_2\text{O}$ ,  $[\text{Zn}(\text{L}^2)_2(\mu\text{-phthalate})]_n$ ,  $[\text{Zn}(\text{L}^2)_2(\mu\text{-maleate})]_2\cdot 2\text{H}_2\text{O}$  and  $[\text{Zn}(\text{L}^2)_2(\mu\text{-citraconate})]_2\cdot 2\text{H}_2\text{O}$  – have been crystallographically characterised. The structural characterisation of these compounds demonstrates that by increasing the number of methyl substituents on the thiourea ligand, the likelihood of forming a dimer as opposed to a coordination polymer also increases. Moreover, dimer formation is only favoured for non-linear dicarboxylates – those in which the angle between the carboxylate groups is less than  $180^\circ$ .

## Introduction

Coordination bonds<sup>1</sup> and hydrogen bonds<sup>2</sup> can be employed in the design and preparation of extended solid-state structures, with the products having a wide range of potential applications including use as porous<sup>3</sup> and polar<sup>4</sup> materials. Systems in which there is competition between the two types of interaction are therefore of considerable interest,<sup>5</sup> and we have demonstrated how changing the lability of ligands containing hydrogen bonding faces can change the mode of aggregation observed.<sup>6</sup>

We have previously reported<sup>7</sup> that the reaction of  $[\text{Zn}(\text{tu})_4]^{2+}$  [ $\text{tu} = \text{thiourea}$ ,  $\text{H}_2\text{NC}(\text{S})\text{NH}_2$ ] with a sodium dicarboxylate typically leads to the formation of coordination polymers of the general formula  $[\text{Zn}(\text{tu})_2(\mu\text{-dicarboxylate})]_n$ . Indeed, of the fourteen compounds crystallographically characterised from this general reaction<sup>7–9</sup> only two exceptions have been observed; the reaction of  $[\text{Zn}(\text{tu})_4](\text{NO}_3)_2$  with terephthalate leads to double-stranded polymers  $[\text{Zn}_2(\mu\text{-tu})(\text{tu})_2(\mu\text{-dicarboxylate})_2]_n$ , whereas the reaction of  $[\text{Zn}(\text{tu})_4]\text{Cl}_2$  with homophthalate  $[\text{O}_2\text{CC}_6\text{H}_4\text{CH}_2\text{CO}_2\text{--}]$  leads to  $[\text{Zn}(\text{tu})_2(\mu\text{-homophthalate})]_2$  dimers.

In all of the  $[\text{Zn}(\text{tu})_2(\mu\text{-dicarboxylate})]_n$  coordination polymers characterised, intra-chain hydrogen bonds between the thiourea ligands and either carboxylate oxygen atoms or thiourea sulfur atoms are observed. In addition,  $\text{N-H}\cdots\text{O}$  hydrogen bonds serve to link the chains together, with interactions involving the thiourea face containing two parallel hydrogen bond donors (DD) particularly important. We have previously shown that simple substitutions on ligands can have profound effects on the manner in which hydrogen-bonded tapes aggregate to give extended structures, and that the intermolecular hydrogen bonding can influence coordination geometry.<sup>10</sup> We were therefore interested to determine what effects substitution on the thiourea ligands would have on both the molecular and supramolecular structures of zinc-thiourea-dicarboxylates. In this paper we report the reactions of the substituted thiourea complexes  $[\text{Zn}(\text{L}^{1-3})_4]^{2+}$  [ $\text{L}^1 = N\text{-methylthiourea}$ ,  $\text{H}_2\text{NC}(\text{S})\text{NHMe}$ ;  $\text{L}^2 = N,N'\text{-dimethylthiourea}$ ,  $\text{MeHNC}(\text{S})\text{NHMe}$ ; and  $\text{L}^3 = N,N,N'\text{-trimethylthiourea}$ ,  $\text{Me}_2\text{NC}(\text{S})\text{NHMe}$ ] with the range of dicarboxylates shown in Chart 1. All the dicarboxylates used had previously yielded

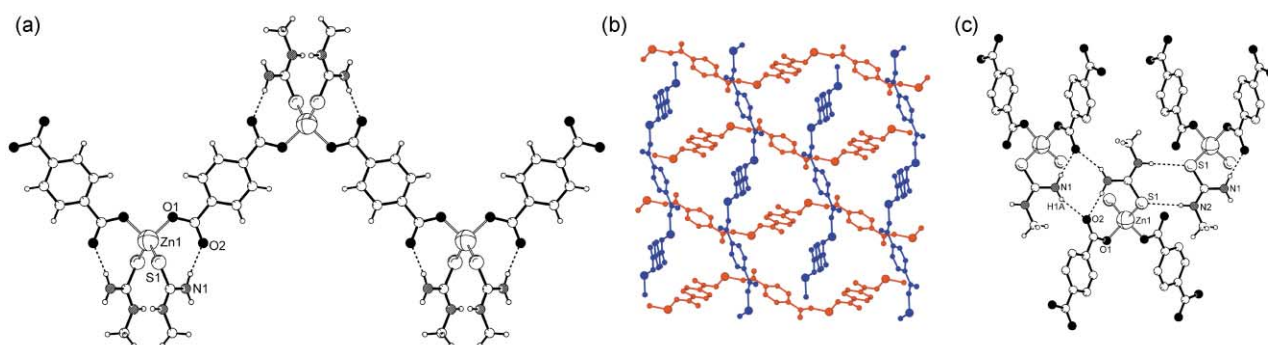


structurally characterised products on reaction with  $[\text{Zn}(\text{tu})_4]\text{Cl}_2$ . The results reported below demonstrate that the number of methyl substituents on the thiourea ligands has a major effect not just on the supramolecular structure, but also on the molecular structure. Increasing the number of substituents by using  $N,N'$ -dimethylthiourea in place of  $N$ -methylthiourea increases the propensity to form dimers as opposed to coordination polymers. However, an additional increase through use of  $N,N,N'$ -trimethylthiourea does not lead to products containing both thiourea and dicarboxylate ligands.

## The reaction of $[\text{Zn}(\text{L}^{1-3})_4]\text{Cl}_2$ with sodium dicarboxylates

The compounds  $[\text{Zn}(\text{L}^{1-3})_4]\text{Cl}_2$  were prepared from the reactions of  $\text{ZnCl}_2$  and the appropriate thiourea in ethanol.<sup>11</sup> The reactions of  $[\text{Zn}(\text{L}^1)_4]\text{Cl}_2$  with one equivalent of the dicarboxylates shown in Chart 1, as sodium salts in water, gave crystalline materials in the cases of terephthalate, fumarate, isophthalate, 1,3-phenylenediacetate and phthalate. Analysis of these products by single crystal X-ray diffraction revealed their structures to be  $[\text{Zn}(\text{L}^1)_2(\mu\text{-terephthalate})]_n$  **1**,  $[\text{Zn}(\text{L}^1)_2(\mu\text{-fumarate})]_n$  **2**,  $\{[\text{Zn}(\text{L}^1)_2(\mu\text{-isophthalate})]\cdot\text{H}_2\text{O}\}_n$  **3**,  $[\text{Zn}(\text{L}^1)_2(\mu\text{-1,3-phenylenediacetate})]_n$  **4** and  $[\text{Zn}(\text{L}^1)_2(\mu\text{-phthalate})]_2\cdot 4\text{H}_2\text{O}$  **5**. Compounds **1–4** exist as coordination polymers whilst **5** exists as discrete

† Electronic supplementary information (ESI) available: Rotatable 3D versions of all the figures. See <http://www.rsc.org/suppdata/dt/b3/037420j/>



**Fig. 1** Structure of compound **1**. (a) Part of the coordination polymer formed by **1**. Intra-chain hydrogen bond parameters: N(1)  $\cdots$  O(2) 2.876, H(1B)  $\cdots$  O(2) 2.00 Å, N(1)–H(1B)  $\cdots$  O(2) 174°. (b) Interweaving of coordination polymers. (c) Interactions between the interwoven sheets. Hydrogen bond parameters: N(1)  $\cdots$  O(2) 2.950, H(1A)  $\cdots$  O(2) 2.13 Å, N(1)–H(1A)  $\cdots$  O(2) 158°; and N(2)  $\cdots$  S(1) 3.442, H(2B)  $\cdots$  S(1) 2.59 Å, N(2)–H(2B)  $\cdots$  S(1) 175°.

dimers. In all cases coordination of two dicarboxylates to the zinc occurs with displacement of two  $L^1$  ligands and results in the formation of a distorted tetrahedral metal centre geometry. No crystalline products were observed using citraconate or maleate, the former yielding a glass and the latter a powder. Neither of these compounds was analysed further, as without a crystal structure it was not possible to unambiguously determine their identity as polymers or dimers.

The reactions of  $[Zn(L^3)_4]Cl_2$  with one equivalent of the dicarboxylates shown in Chart 1, as sodium salts in water, gave crystalline materials in the cases of terephthalate, fumarate, isophthalate, phthalate, maleate and citraconate. X-ray diffraction studies revealed their structures to be  $\{[Zn(L^2)_2(\mu\text{-terephthalate})] \cdot 0.5H_2O\}_n$  **6**,  $[Zn(L^2)_2(\mu\text{-fumarate})]_n$  **7**,  $[Zn(L^2)_2(\mu\text{-isophthalate})]_2 \cdot 2H_2O$  **8**,  $[Zn(L^2)_2(\mu\text{-phthalate})]_n$  **9**,  $[Zn(L^2)_2(\mu\text{-maleate})]_2 \cdot 2H_2O$  **10** and  $[Zn(L^2)_2(\mu\text{-citraconate})]_2 \cdot 2H_2O$  **11**. The reaction with 1,3-phenylenediacetate gave crystals, though these did not prove suitable for a single crystal determination and hence were not examined further.

The reactions of  $[Zn(L^3)_4]Cl_2$  with one equivalent of the dicarboxylates gave crystalline materials in the cases of fumarate, isophthalate, maleate and citraconate. The products were shown to be identical, with all reactions yielding  $[Zn(L^3)_2Cl_2]$  as confirmed crystallographically. In an effort to eliminate the competitive chloride coordination,  $[Zn(L^3)_4](NO_3)_2$  was prepared from the reaction of  $Zn(NO_3)_2$  and  $L^3$  in ethanol. However, the reactions of  $[Zn(L^3)_4](NO_3)_2$  with dicarboxylates only yielded a zinc-containing crystalline product in the case of terephthalate, which was crystallographically confirmed as being the previously characterised coordination polymer  $[Zn(OH)_2(\mu\text{-terephthalate})]_n$ .<sup>12</sup>

**The structure of  $[Zn(L^1)_2(\mu\text{-terephthalate})]_n$  **1**.** The structure of  $[Zn(L^1)_2(\mu\text{-terephthalate})]_n$  **1** consists of coordination polymers in which  $Zn(L^1)_2$  units are linked by bridging terephthalate anions. Important bond lengths and angles for **1** are given in Table 1. Two intra-chain N–H  $\cdots$  O hydrogen bonds are formed around each zinc centre, each involving one of the N–H bonds from an  $NH_2$  group and a non-coordinated carboxylate oxygen atom to generate eight-membered rings [graph set S(8)] (Fig. 1(a)).

The coordination polymers form zigzag chains which are orientated in two distinct directions, with an angle of approximately 77° between them. These chains are interwoven to form sheets (Fig. 1(b)), though there are no hydrogen bond interactions between the chains in the sheets, and the closest Zn  $\cdots$  Zn distance is 6.5 Å. Both N–H  $\cdots$  O and N–H  $\cdots$  S hydrogen bonds are involved in linking the sheets together to form the gross structure, the former giving rise to eight-membered rings involving two  $NH_2$  groups and two oxygen atoms [graph set  $R_4^2(8)$ ] and the latter to eight-membered rings

involving pairs of thiourea ligands connected in a DA–AD manner [graph set  $R_2^2(8)$ ] (Fig. 1(c)).

The structure of **1** is very different to its thiourea analogue,  $[Zn_2(\mu\text{-tu})(\mu\text{-terephthalate})]_2 \cdot 4H_2O$ <sup>8</sup> in which both bridging thiourea and terephthalate ligands are present. However since this compound represents the only example to date of a double-stranded coordination polymer arising from the reaction between a  $[ZnL_4]^{2+}$  cation and a dicarboxylate it would appear that it is the structure of the thiourea derivative that is anomalous, as opposed to **1**.

**The structure of  $[Zn(L^1)_2(\mu\text{-fumarate})]_n$  **2**.** In a similar manner to **1**, the structure of  $[Zn(L^1)_2(\mu\text{-fumarate})]_n$  **2** consists of coordination polymers in which  $Zn(L^1)_2$  units are linked by bridging dicarboxylates. Selected bond lengths and angles for **2** are given in Table 1. Intra-chain N–H  $\cdots$  O hydrogen bonding is absent in **2**, instead N–H bonds from the symmetry-related  $NH_2$  groups are involved in N–H  $\cdots$  S hydrogen bonds to the coordinated sulfur atoms, giving rise to S(6) rings which, ignoring the presence of the zinc atom, give  $R_2^2(8)$  rings (Fig. 2(a)). This intra-chain hydrogen bonding motif is identical to that observed in the thiourea analogue  $[Zn(tu)_2(\mu\text{-fumarate})]_n$ <sup>7</sup> and has parallels with the interactions observed in the inclusion compound  $[NEt_4]_2[fumarate] \cdot 2tu$ .<sup>13</sup> However, the fumarate coordination modes are different in the two zinc compounds, with coordination in **2** occurring *via* coordination of the *syn* lone pairs, whereas that in  $[Zn(tu)_2(\mu\text{-fumarate})]_n$  occurs through the *anti* lone pairs.

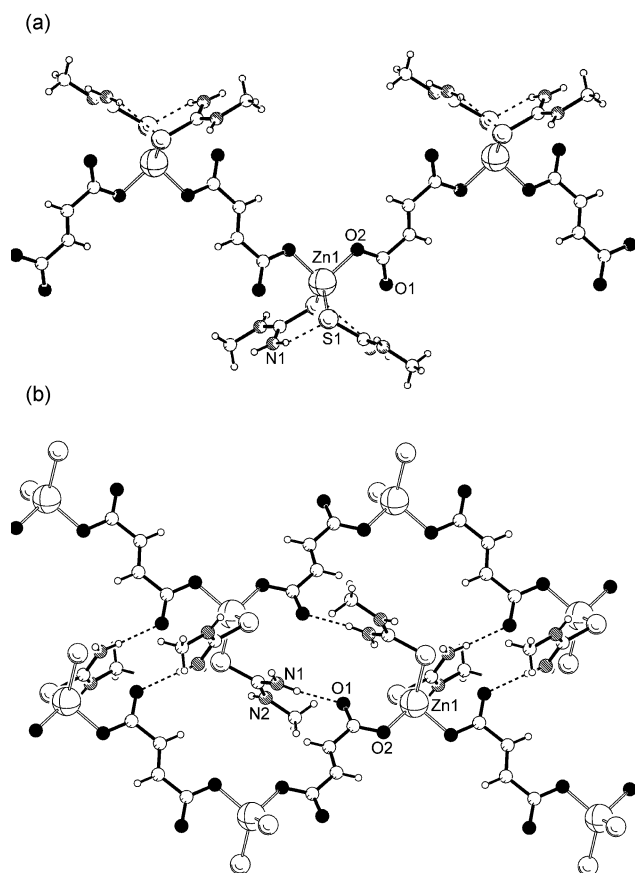
The coordination polymers in **2** form zigzag chains which, in contrast to those in **1**, are all orientated in the same direction. N–H  $\cdots$  O hydrogen bonds to the non-coordinated oxygen atom O(1) connect these chains into sheets (Fig. 2(b)), whereas further N–H  $\cdots$  O hydrogen bonds, this time to the coordinated oxygen atoms connect the sheets into the three-dimensional structure  $[N(2) \cdots O(2) 2.914, H(2) \cdots O(2) 2.08 \text{ Å}, N(2)–H(2) \cdots O(2) 162^\circ]$ . Both hydrogen bonds lead to the formation of  $R_2^2(16)$  motifs. This supramolecular structure is very different from that observed for  $[Zn(tu)_2(\mu\text{-fumarate})]_n$ , where coordination of the *anti* lone pairs means that the carboxylate group contains a hydrogen bonding face containing two parallel lone pairs, and this face is involved in a DD–AA interaction with a thiourea. This interaction is prevented in **2** by blocking of the DD face through substitution, and of the AA face by *syn* coordination.

**The structure of  $\{[Zn(L^1)_2(\mu\text{-isophthalate})] \cdot H_2O\}_n$  **3**.** The structure of  $\{[Zn(L^1)_2(\mu\text{-isophthalate})] \cdot H_2O\}_n$  **3** consists of coordination polymers, in which  $Zn(L^1)_2$  units are bridged by isophthalate ligands, with water molecules also included within the lattice. Significant bond lengths and angles for **3** are given in Table 1. Two intra-chain N–H  $\cdots$  O hydrogen bonds are

**Table 1** Selected bond lengths (Å) and angles (°) for compounds **1–11**

<b>1</b>		<b>2</b>		<b>3</b>		<b>4</b>	
Zn(1)–O(1)	1.9419(10)	Zn(1)–O(2)	1.9876(15)	Zn(1)–O(1)	1.997(2)	Zn(1)–O(1)	1.959(3)
Zn(1)–S(1)	2.3142(4)	Zn(1)–S(1)	2.3287(7)	Zn(1)–O(3)′	1.969(2)	Zn(1)–O(3)′	1.986(3)
				Zn(1)–S(1)	2.3259(9)	Zn(1)–S(1)	2.3378(14)
				Zn(1)–S(2)	2.3249(9)	Zn(1)–S(2)	2.3324(15)
O(1)–Zn(1)–O(1)′	96.08(6)	O(2)–Zn(1)–O(2)′	93.03(9)	O(1)–Zn(1)–O(3)′	94.04(8)	O(1)–Zn(1)–O(3)′	113.83(15)
S(1)–Zn(1)–S(1)′	117.04(2)	S(1)–Zn(1)–S(1)′	114.06(4)	S(1)–Zn(1)–S(2)	114.84(3)	S(2)–Zn(1)–S(1)	112.00(5)
O(1)–Zn(1)–S(1)	110.07(4)	O(2)–Zn(1)–S(1)	111.61(5)	O(1)–Zn(1)–S(1)	116.18(7)	O(1)–Zn(1)–S(1)	117.00(11)
O(1)–Zn(1)–S(1)′	110.80(3)	O(2)–Zn(1)–S(1)′	112.38(5)	O(1)–Zn(1)–S(2)	105.68(7)	O(1)–Zn(1)–S(2)	107.55(11)
O(1)′–Zn(1)–S(1)	110.80(3)	O(2)′–Zn(1)–S(1)	112.38(5)	O(3)′–Zn(1)–S(1)	106.96(7)	O(3)′–Zn(1)–S(1)	94.93(10)
O(1)′–Zn(1)–S(1)′	110.07(4)	O(2)′–Zn(1)–S(1)′	111.61(5)	O(3)′–Zn(1)–S(2)	117.70(7)	O(3)′–Zn(1)–S(2)	111.21(11)
C(1)–S(1)–Zn(1)	103.35(5)	C(1)–S(1)–Zn(1)	103.69(8)	C(1)–S(1)–Zn(1)	102.62(11)	C(1)–S(1)–Zn(1)	101.55(18)
				C(3)–S(2)–Zn(1)	105.93(11)	C(3)–S(2)–Zn(1)	107.66(18)
<b>5 (molecule 1)</b>		<b>5 (molecule 2)</b>		<b>6</b>		<b>7</b>	
Zn(1)–O(2)	1.9557(19)	Zn(2)–O(3)	1.9790(19)	Zn(1)–O(1)	1.9682(12)	Zn(1)–O(1)	1.9815(9)
Zn(1)–O(5)	1.9738(17)	Zn(2)–O(7)	1.954(2)	Zn(1)–O(3)	1.9729(13)	Zn(1)–O(4)	1.9657(9)
Zn(1)–S(1)	2.3064(8)	Zn(2)–S(3)	2.3226(8)	Zn(1)–S(1)	2.3493(5)	Zn(1)–S(1)	2.3090(4)
Zn(1)–S(2)	2.3599(7)	Zn(2)–S(4)	2.3398(8)	Zn(1)–S(2)	2.3156(5)	Zn(1)–S(2)	2.3244(4)
O(2)–Zn(1)–O(5)	103.51(8)	O(7)–Zn(2)–O(3)	105.93(8)	S(2)–Zn(1)–S(1)	108.44(2)	O(4)–Zn(1)–O(1)	89.61(4)
S(1)–Zn(1)–S(2)	108.36(3)	S(3)–Zn(2)–S(4)	116.40(3)	O(1)–Zn(1)–O(3)	100.28(6)	S(1)–Zn(1)–S(2)	115.585(14)
O(2)–Zn(1)–S(1)	114.06(6)	O(3)–Zn(2)–S(3)	107.69(7)	O(1)–Zn(1)–S(1)	105.72(4)	O(1)–Zn(1)–S(1)	110.55(3)
O(2)–Zn(1)–S(2)	119.34(6)	O(3)–Zn(2)–S(4)	89.71(6)	O(1)–Zn(1)–S(2)	108.45(4)	O(1)–Zn(1)–S(2)	112.69(4)
O(5)–Zn(1)–S(1)	109.14(6)	O(7)–Zn(2)–S(3)	113.46(6)	O(3)–Zn(1)–S(1)	111.61(5)	O(4)–Zn(1)–S(1)	119.77(3)
O(5)–Zn(1)–S(2)	101.11(6)	O(7)–Zn(2)–S(4)	119.38(6)	O(3)–Zn(1)–S(2)	121.02(5)	O(4)–Zn(1)–S(2)	105.91(3)
C(1)–S(1)–Zn(1)	104.62(10)	C(7)–S(3)–Zn(2)	107.20(10)	C(1)–S(1)–Zn(1)	107.20(7)	C(1)–S(1)–Zn(1)	102.61(5)
C(3)–S(2)–Zn(1)	104.20(9)	C(5)–S(4)–Zn(2)	109.29(9)	C(4)–S(2)–Zn(1)	107.71(7)	C(4)–S(2)–Zn(1)	104.91(5)
<b>8</b>		<b>9</b>		<b>10</b>		<b>11</b>	
Zn(1)–O(1)	1.9948(13)	Zn(1)–O(1)	2.0250(13)	Zn(1)–O(1)	1.9958(18)	Zn(1)–O(1)	2.0000(18)
Zn(1)–O(3)′	1.9560(12)	Zn(1)–O(4)′	1.9790(13)	Zn(1)–O(3)′	1.9528(19)	Zn(1)–O(4)′	1.9536(18)
Zn(1)–S(1)	2.2863(5)	Zn(1)–S(1)	2.3374(4)	Zn(1)–S(1)	2.3159(8)	Zn(1)–S(1)	2.3160(8)
Zn(1)–S(2)	2.3458(5)	Zn(1)–S(2)	2.3644(5)	Zn(1)–S(2)	2.3287(9)	Zn(1)–S(2)	2.3399(9)
O(1)–Zn(1)–O(3)′	93.03(5)	O(1)–Zn(1)–O(4)′	96.38(6)	O(1)–Zn(1)–O(3)′	97.35(8)	O(1)–Zn(1)–O(4)′	95.87(7)
S(1)–Zn(1)–S(2)	117.065(18)	S(1)–Zn(1)–S(2)	95.181(16)	S(1)–Zn(1)–S(2)	105.34(3)	S(1)–Zn(1)–S(2)	105.91(3)
O(1)–Zn(1)–S(1)	110.95(4)	O(1)–Zn(1)–S(1)	121.91(4)	O(1)–Zn(1)–S(1)	110.05(5)	O(1)–Zn(1)–S(1)	108.30(5)
O(1)–Zn(1)–S(2)	106.34(4)	O(1)–Zn(1)–S(2)	104.13(4)	O(1)–Zn(1)–S(2)	106.06(6)	O(1)–Zn(1)–S(2)	107.67(6)
O(3)′–Zn(1)–S(1)	120.92(4)	O(4)′–Zn(1)–S(1)	130.91(4)	O(3)′–Zn(1)–S(1)	118.47(6)	O(4)′–Zn(1)–S(1)	121.24(6)
O(3)′–Zn(1)–S(2)	105.24(4)	O(4)′–Zn(1)–S(2)	104.56(4)	O(3)′–Zn(1)–S(2)	118.54(6)	O(4)′–Zn(1)–S(2)	116.49(6)
C(1)–S(1)–Zn(1)	103.59(6)	C(1)–S(1)–Zn(1)	111.21(6)	C(1)–S(1)–Zn(1)	108.72(9)	C(1)–S(1)–Zn(1)	109.01(9)
C(4)–S(2)–Zn(1)	103.72(6)	C(4)–S(2)–Zn(1)	103.31(6)	C(4)–S(2)–Zn(1)	110.00(9)	C(4)–S(2)–Zn(1)	108.89(9)

Primed atoms given by the symmetry operations  $-x, y, -z + 1/2$  (**1**);  $-x + 1, y, -z + 3/2$  (**2**);  $x - y + 1/2, z - 1/2$  (**3** and **4**);  $-x + 1, -y + 1, -z + 1$  (**8**);  $x, y, z - 1$  (**9**),  $-x, -y, -z + 1$  (**10** and **11**).

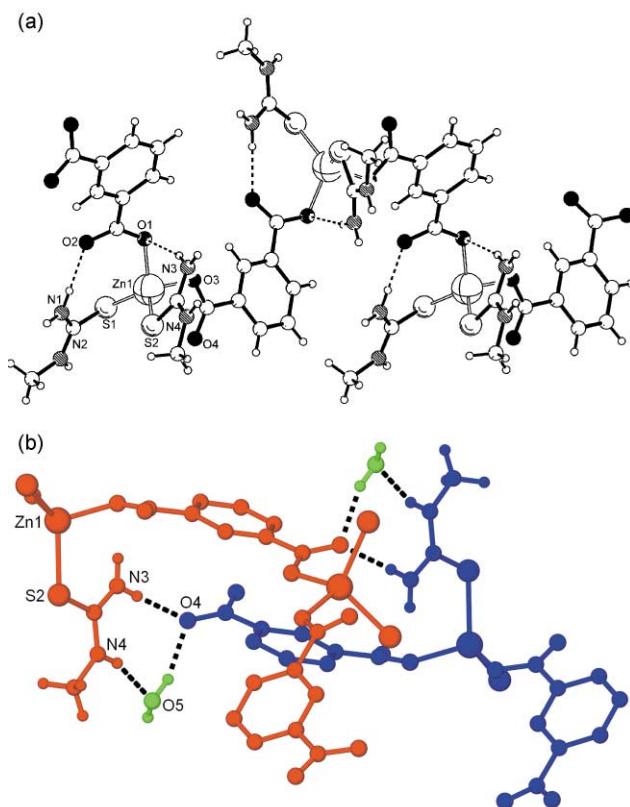


**Fig. 2** Structure of compound **2**. (a) Part of the coordination polymer formed by **2**. Intra-chain hydrogen bond parameters: N(1)  $\cdots$  S(1) 3.581, H(1B)  $\cdots$  S(1) 2.76 Å, N(1)–H(1B)  $\cdots$  S(1) 159°. (b) Interactions between the coordination polymers to form sheets. Hydrogen bond parameters: N(1)  $\cdots$  O(1) 2.845, H(1A)  $\cdots$  O(1) 1.98 Å, N(1)–H(1A)  $\cdots$  O(1) 167°.

formed around each zinc centre, each involving one of the N–H bonds from an NH<sub>2</sub> group, with the acceptors either a co-ordinated carboxylate oxygen atom [O(1), graph set S(6)] or a non-coordinated carboxylate oxygen atom [O(2), graph set S(8)]. Consequently one of the two independent carboxylate groups is not involved in intra-chain hydrogen bonding (Fig. 3(a)).

The zigzag coordination polymers formed in **3** are reminiscent of those formed in the thiourea analogue  $\{[\text{Zn}(\text{tu})_2(\mu\text{-isophthalate})]\cdot\text{H}_2\text{O}\}_n$  with similar carboxylate coordination and intra-chain hydrogen bonding.<sup>7</sup> The two independent L<sup>1</sup> ligands in **3** have different orientations of the NHMe groups, with that containing S(1) having the methyl group *anti* to the sulfur and that in S(2) having the methyl group *syn* to the sulfur. This leads to the potential for different hydrogen bonding patterns, since only the latter conformation contains a DD face.

The chains are linked into bilayers through a N–H  $\cdots$  O hydrogen bond involving one of the parallel NH groups of the DD face and the non-coordinated carboxylate oxygen atom O(4). The other NH group from this face hydrogen bonds to the included water molecule, and together with an O–H  $\cdots$  O hydrogen bond these generate a R<sub>3</sub><sup>2</sup>(8) motif (Fig. 3(b)). The bilayers are connected into the overall three-dimensional structure only through interactions involving the included water, with the second L<sup>1</sup> ligand involved in an N–H  $\cdots$  O hydrogen bond to this molecule and further O–H  $\cdots$  O hydrogen bonds also present [N(1)  $\cdots$  O(5) 2.938, H(1A)  $\cdots$  O(5) 2.07 Å, N(1)–H(1A)  $\cdots$  O(5) 167°; O(5)  $\cdots$  O(2) 2.853, H(5A)  $\cdots$  O(2) 1.98 Å, O(5)–H(5A)  $\cdots$  O(2) 173°]. It is noticeable that one of the NH groups [N(2)–H(2)] does not form a close contact to any other atom.



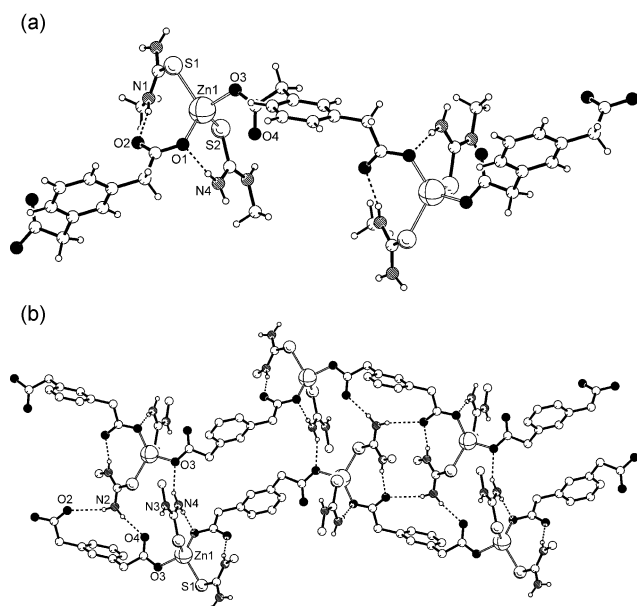
**Fig. 3** Structure of compound **3**. (a) Part of the coordination polymer formed by **3**. Intra-chain hydrogen bond parameters: N(1)  $\cdots$  O(2) 2.859, H(1B)  $\cdots$  O(2) 1.98 Å, N(1)–H(1B)  $\cdots$  O(2) 176°; and N(3)  $\cdots$  O(1) 2.893, H(3B)  $\cdots$  O(1) 2.05 Å, N(3)–H(3B)  $\cdots$  O(1) 160°. (b) Interactions between the coordination polymers. Hydrogen bond parameters: N(3)  $\cdots$  O(4) 2.826, H(3A)  $\cdots$  O(4) 1.96 Å, N(3)–H(3A)  $\cdots$  O(4) 169°; N(4)  $\cdots$  O(5) 2.934, H(4)  $\cdots$  O(5) 2.09 Å, N(4)–H(4)  $\cdots$  O(5) 163°; and O(5)  $\cdots$  O(4) 2.747, H(5B)  $\cdots$  O(4) 1.95 Å, O(5)–H(5B)  $\cdots$  O(4) 155°.

Like **3**, the thiourea analogue also crystallises with a molecule of water, though in that case the water is disordered and fills channels within the structure. Similar channels are absent in **3**, and the included water is not disordered.

**The structure of  $[\text{Zn}(\text{L}^1)_2(\mu\text{-1,3-phenylenediacetate})]_n$ , **4**.** In a similar manner to those of **1–3**, the structure of **4** consists of Zn(L<sup>1</sup>)<sub>2</sub> units which are interconnected by dicarboxylate anions into coordination polymers. Important bond lengths and angles for **4** are given in Table 1. The intra-chain hydrogen bonding is comparable to that in **3**, with one S(6) and one S(8) ring formed, though in this instance the hydrogen bond to the non-coordinated carboxylate oxygen atom O(2) involves an NH bond from a NHMe group rather than a NH<sub>2</sub> group (Fig. 4(a)).

The coordination polymers in **4** are less puckered than those in the thiourea analogue  $[\text{Zn}(\text{tu})_2(\mu\text{-1,3-phenylenediacetate})]_n$ ,<sup>9</sup> which is a consequence of the methyl substituent preventing formation of hydrogen bonds between L<sup>1</sup> ligands and remote carboxylates within the same chain. This leads to the Zn  $\cdots$  Zn  $\cdots$  Zn angle increasing from 74° in  $[\text{Zn}(\text{tu})_2(\mu\text{-1,3-phenylenediacetate})]$  to 132° in **4**. The coordination polymers in **4** are cross-linked into sheets *via* three independent N–H  $\cdots$  O hydrogen bonds, with the NH<sub>2</sub> group not involved in intra-chain hydrogen bonding forming hydrogen bonds to the two uncoordinated oxygen atoms O(2) and O(4) of the same 1,3-phenylenediacetate ligand (Fig. 4(b)). A further N–H  $\cdots$  O hydrogen bond connects these sheets into the three-dimensional gross structure [N(3)  $\cdots$  O(4) 2.931, H(3)  $\cdots$  O(4) 2.14 Å, N(3)–H(3)  $\cdots$  O(4) 148°].

**The structure of  $[\text{Zn}(\text{L}^1)_2(\mu\text{-phthalate})]_2\cdot 4\text{H}_2\text{O}$  **5**.** In contrast to **1–4**, the Zn(L<sup>1</sup>)<sub>2</sub> units in **5** are connected by bridging dicarb-



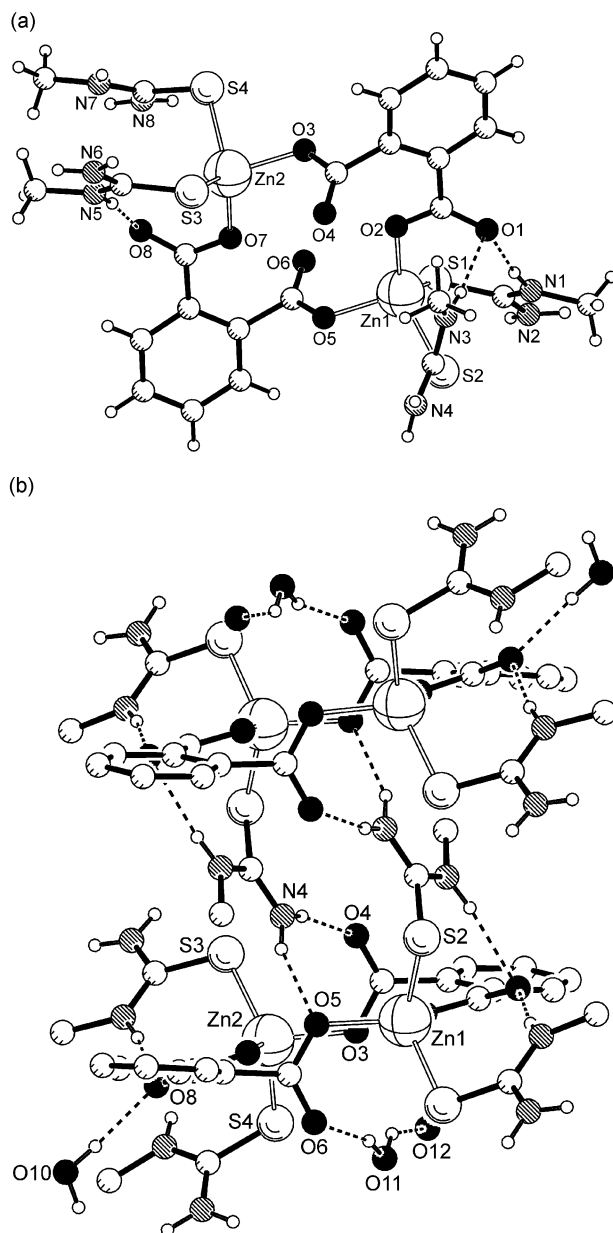
**Fig. 4** Structure of compound **4**. (a) Part of the coordination polymer formed by **4**. Intra-chain hydrogen bond parameters: N(1)  $\cdots$  O(2) 2.891(7), H(1)  $\cdots$  O(2) 2.07 Å, N(1)–H(1)  $\cdots$  O(2) 169°; and N(4)  $\cdots$  O(1) 2.910(6), H(4B)  $\cdots$  O(1) 2.04 Å, N(4)–H(4B)  $\cdots$  O(1) 176°. (b) Interactions between the coordination polymers. Hydrogen bond parameters: N(2)  $\cdots$  O(2) 3.160(7), H(2A)  $\cdots$  O(2) 2.38 Å, N(2)–H(2A)  $\cdots$  O(2) 148°; N(2)  $\cdots$  O(4) 2.921(7), H(2B)  $\cdots$  O(4) 2.05 Å, N(2)–H(2B)  $\cdots$  O(4) 177°; and N(4)  $\cdots$  O(3) 2.931(6), H(4A)  $\cdots$  O(3) 2.10 Å, N(4)–H(4A)  $\cdots$  O(3) 159°.

oxylates into  $[\text{Zn}(\text{L}^1)_2(\mu\text{-phthalate})]_2$  dimers, which crystallise with four molecules of water. Important bond lengths and angles for **5** are given in Table 1. The dimers contain two independent zinc centres, and there are differences in the intramolecular hydrogen bonding around each of these. The non-coordinated dicarboxylate oxygen atom O(1) acts as the hydrogen bond acceptor to two N–H  $\cdots$  O interactions around Zn(1), forming two S(8) rings. In contrast, only one hydrogen bond is present around Zn(2), with an S(8) ring formed *via* an N–H  $\cdots$  O interaction (Fig. 5(a)). The second N–H group which might have been expected to participate in an intramolecular hydrogen bond around this atom is involved instead in a N–H  $\cdots$  O interaction with an included water molecule, forming a  $\text{R}_3^3(15)$  ring in conjunction with further water molecules. In all cases the intramolecular hydrogen bonds involve NH bonds on the NHMe groups.

The dimers in **5** themselves dimerise *via* two pairs of N–H  $\cdots$  O interactions involving both NH bonds of an  $\text{NH}_2$  group, which form hydrogen bonds with the coordinated and non-coordinated carboxylate oxygen atoms, O(5) and O(4), respectively, of another molecule. The two ends of these ‘dimers of dimers’ are capped by water molecules, which form O–H  $\cdots$  O hydrogen bonds (Fig. 5(b)). These ‘dimer of dimer’ units are connected into the gross structure *via* hydrogen bonds involving the included water molecules, with a N(6)–H(6B)  $\cdots$   $\pi$  interaction also present. ‡

The structure of **5** contrasts markedly with that of the thiourea analogue, which is a coordination polymer.<sup>7</sup> A comparison

‡ Additional hydrogen bond parameters in **5**: N(2)  $\cdots$  S(2) 3.327, H(2A)  $\cdots$  S(2) 2.51 Å, N(2)–H(2A)  $\cdots$  S(2) 154°; N(2)  $\cdots$  O(4) 2.808, H(2B)  $\cdots$  O(4) 1.98 Å, N(2)–H(2B)  $\cdots$  O(4) 154°; N(6)  $\cdots$  O(9) 2.849, H(6A)  $\cdots$  O(9) 2.01 Å, N(6)–H(6A)  $\cdots$  O(9) 159°; N(7)  $\cdots$  S(4) 3.457, H(7)  $\cdots$  S(4) 2.62 Å, N(7)–H(7)  $\cdots$  S(4) 163°; N(8)  $\cdots$  O(11) 2.969, H(8A)  $\cdots$  O(11) 2.09 Å, N(8)–H(8A)  $\cdots$  O(11) 165°; N(8)  $\cdots$  O(10) 2.892, H(8B)  $\cdots$  O(10) 2.03 Å, N(8)–H(8B)  $\cdots$  O(10) 172°; O(9)  $\cdots$  O(6) 2.801, H(9A)  $\cdots$  O(6) 1.95 Å, O(9)–H(9A)  $\cdots$  O(6) 170°; O(9)  $\cdots$  O(10) 2.850, H(9B)  $\cdots$  O(10) 2.01 Å, O(9)–H(9B)  $\cdots$  O(10) 158°; O(10)  $\cdots$  O(11) 2.867, H(10A)  $\cdots$  O(11) 2.01 Å, O(10)–H(10A)  $\cdots$  O(11) 165°.

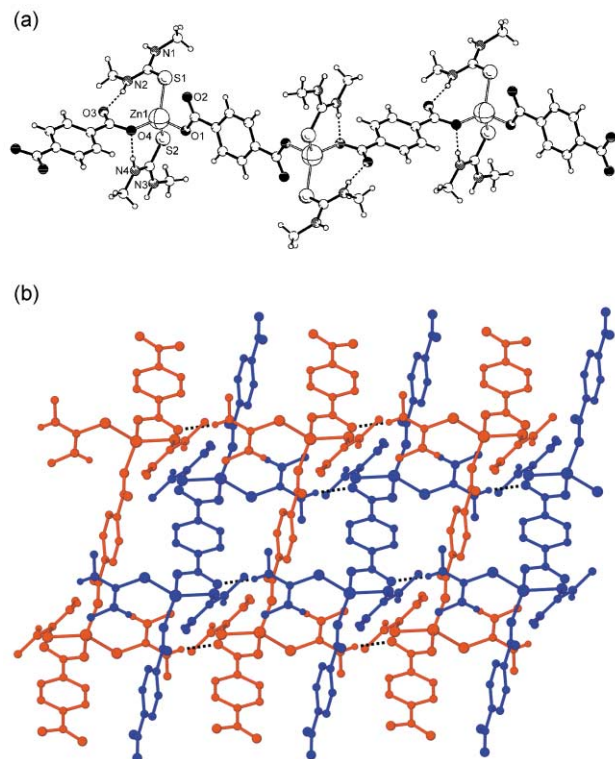


**Fig. 5** Structure of compound **5**. (a) Dimers formed by **5**. Intramolecular hydrogen bond parameters: N(1)  $\cdots$  O(1) 2.858, H(1)  $\cdots$  O(1) 2.00 Å, N(1)–H(1)  $\cdots$  O(1) 171°; N(3)  $\cdots$  O(1) 3.002, H(3)  $\cdots$  O(1) 2.14 Å, N(3)–H(3)  $\cdots$  O(1) 172°; and N(5)  $\cdots$  O(8) 2.818, H(5)  $\cdots$  O(8) 1.95 Å, N(5)–H(5)  $\cdots$  O(8) 172°. (b) Interactions linking the molecules of **5** into ‘dimers of dimers’. Hydrogen bond parameters: N(4)  $\cdots$  O(5) 2.938, H(4A)  $\cdots$  O(5) 2.11 Å, N(4)–H(4A)  $\cdots$  O(5) 156°; N(4)  $\cdots$  O(4) 2.925, H(4B)  $\cdots$  O(4) 2.06 Å, N(4)–H(4B)  $\cdots$  O(4) 166°; O(10)  $\cdots$  O(8) 2.806, H(10B)  $\cdots$  O(8) 1.93 Å, O(10)–H(10B)  $\cdots$  O(8) 176°; O(11)  $\cdots$  O(6) 2.862, H(11A)  $\cdots$  O(6) 2.03 Å, O(11)–H(11A)  $\cdots$  O(6) 162°; and O(11)  $\cdots$  O(12) 2.708, H(11B)  $\cdots$  O(12) 1.96 Å, O(11)–H(11B)  $\cdots$  O(12) 143°.

of the two structures reveals that in **5**, from the carboxylate group co-planar with the benzene ring it is the oxygen proximal to the second carboxylate that coordinates to the metal, whereas it is the distal oxygen that coordinates in  $[\text{Zn}(\text{tu})_2(\mu\text{-phthalate})]_n$  – this reduces the Zn  $\cdots$  Zn distance from 8.0 Å in  $[\text{Zn}(\text{tu})_2(\mu\text{-phthalate})]_n$  to 5.4 Å in **5**.

**The structure of  $\{[\text{Zn}(\text{L}^2)_2(\mu\text{-terephthalate})] \cdot 0.5\text{H}_2\text{O}\}_n$  **6**.** The structure of  $\{[\text{Zn}(\text{L}^2)_2(\mu\text{-terephthalate})] \cdot 0.5\text{H}_2\text{O}\}_n$  **6** consists of coordination polymers in which  $\text{Zn}(\text{L}^2)_2$  units are linked by bridging terephthalate ligands, with included water molecules also present in the lattice. Selected bond lengths and angles for **6** are given in Table 1. The thiourea ligands both adopt *syn,anti*

conformations with one of the two NH groups on each ligand involved in intra-chain hydrogen bonding around the zinc centre. These involve the coordinated and non-coordinated carboxylate oxygen atoms O(3) and O(4), generating S(6) and S(8) graph sets respectively, and since there are two independent dicarboxylates within each chain only alternate terephthalates within each coordination polymer are involved in intra-chain hydrogen bonding (Fig. 6(a)).

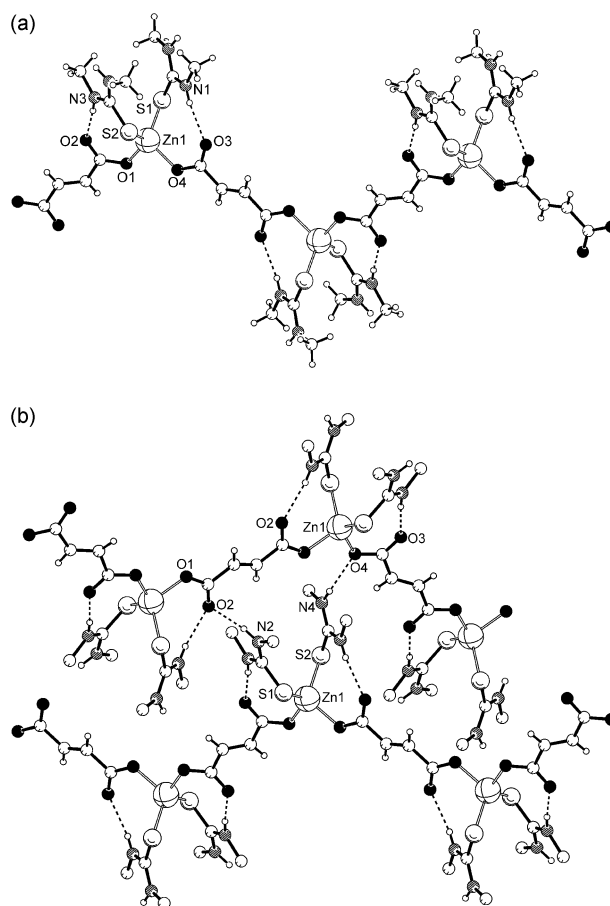


**Fig. 6** Structure of compound 6. (a) Part of the coordination polymer formed by 6. Intra-chain hydrogen bond parameters: N(2)  $\cdots$  O(3) 2.943, H(2)  $\cdots$  O(3) 2.06 Å, N(2)–H(2)  $\cdots$  O(3) 174°; and N(4)  $\cdots$  O(4) 2.828, H(4)  $\cdots$  O(4) 1.99 Å, N(4)–H(4)  $\cdots$  O(4) 165°. (b) Linking of the coordination polymers into sheets. Hydrogen bond parameters: N(1)  $\cdots$  O(2) 2.824, H(1)  $\cdots$  O(2) 1.99 Å, N(1)–H(1)  $\cdots$  O(2) 161°.

The terephthalates connect the zinc centres into zigzag chains, which all run in the same direction and are cross-linked by N–H  $\cdots$  O hydrogen bonds involving non-coordinated oxygen atom O(2). These hydrogen bonds connect each chain not with its neighbours, but with the next-nearest neighbours. This generates sheets that consist of two interpenetrating networks (Fig. 6(b)). Interactions involving the half-occupancy water molecule connect these sheets together into the gross structure [N(3)  $\cdots$  O(5) 2.914, H(3)  $\cdots$  O(5) 2.17 Å, N(3)–H(3)  $\cdots$  O(5) 147°].

The intra-chain Zn  $\cdots$  Zn distances and Zn  $\cdots$  Zn  $\cdots$  Zn angles are very similar in 6 and 1, though in 1 neighbouring terephthalates are close to being co-planar, with an angle between mean terephthalate planes of 17°, whereas those in 6 are almost perpendicular, as witnessed by an angle between mean terephthalate planes of 85°.

**The structure of [Zn(L<sup>2</sup>)<sub>2</sub>(μ-fumarate)]<sub>n</sub> 7.** The structure of [Zn(L<sup>2</sup>)<sub>2</sub>(μ-fumarate)]<sub>n</sub> 7 consists of coordination polymers in which Zn(L<sup>2</sup>)<sub>2</sub> units are linked by bridging fumarate ligands. Important bond lengths and angles for 7 are given in Table 1. As in 6, the thiourea ligands adopt *syn,anti* conformations with one of the two NH groups on each ligand involved in hydrogen bonding around the zinc centre. In contrast to [Zn(tu)<sub>2</sub>(μ-fumarate)]<sub>n</sub> and 2, sulfur atoms do not act as acceptors for these intra-chain hydrogen bonds – instead the



**Fig. 7** Structure of compound 7. (a) Part of the coordination polymer formed by 7. Intra-chain hydrogen bond parameters: N(1)  $\cdots$  O(3) 2.716, H(1)  $\cdots$  O(3) 1.90 Å, N(1)–H(1)  $\cdots$  O(3) 175°; and N(3)  $\cdots$  O(2) 2.971, H(3)  $\cdots$  O(2) 2.14 Å, N(3)–H(3)  $\cdots$  O(2) 170°. Interactions between the coordination polymers. Hydrogen bond parameters: N(2)  $\cdots$  O(2) 2.833, H(2)  $\cdots$  O(2) 1.99 Å, N(2)–H(2)  $\cdots$  O(2) 156°; and N(4)  $\cdots$  O(4) 2.896, H(4)  $\cdots$  O(4) 2.12 Å, N(4)–H(4)  $\cdots$  O(4) 151°.

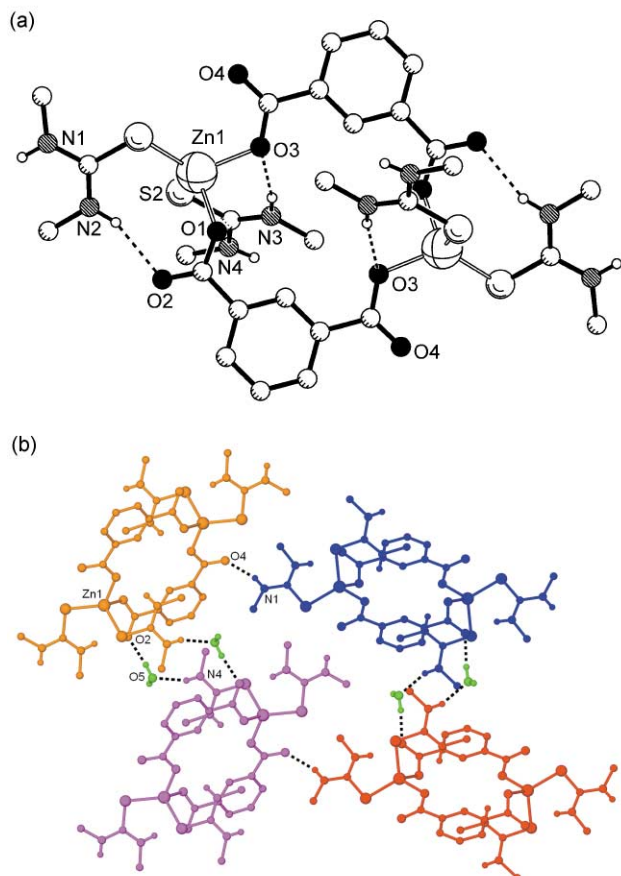
acceptors are the non-coordinated carboxylate oxygen atoms O(2) and O(3), giving rise to two S(8) motifs (Fig. 7(a)).

The zigzag polymer chains formed in compound 7 run in two directions, with an angle of approximately 56° between them. There are no strong interactions between parallel chains, which lie flat to give sheets, though two independent N–H  $\cdots$  O interactions occur between neighbouring non-parallel chains, involving one N–H group of each L<sup>2</sup> ligand and both coordinated and non-coordinated dicarboxylate oxygen atoms. These interactions lead to the formation of R<sup>2</sup><sub>2</sub>(17) rings (Fig. 7(b)).

The coordination polymers are somewhat more unfurled in 7 with respect to those in 2 and [Zn(tu)<sub>2</sub>(μ-fumarate)]<sub>n</sub>, as evidenced by the Zn  $\cdots$  Zn distances (9.5 Å for 7, 8.9 Å for 2 and 7.0 Å for [Zn(tu)<sub>2</sub>(μ-fumarate)]<sub>n</sub>) and Zn  $\cdots$  Zn  $\cdots$  Zn angles (122° for 7, 110° for 2 and 108° for [Zn(tu)<sub>2</sub>(μ-fumarate)]<sub>n</sub>). This is mainly due to the conformation of the fumarate ligands which is sufficiently flexible to adapt to the demands of the supramolecular structure.

**The structure of [Zn(L<sup>2</sup>)<sub>2</sub>(μ-isophthalate)]<sub>2</sub>·2H<sub>2</sub>O 8.** The Zn(L<sup>2</sup>)<sub>2</sub> units in 8 are connected by bridging dicarboxylates into [Zn(L<sup>2</sup>)<sub>2</sub>(μ-isophthalate)]<sub>2</sub> dimers, which crystallise with two molecules of water. Significant bond lengths and angles for 8 are given in Table 1. As in 6 and 7, the L<sup>2</sup> ligands adopt *syn,anti* conformations, and one N–H group on each ligand is involved in an intramolecular hydrogen bond. In this case, both coordinated and non-coordinated oxygen atoms act as

acceptors with the generation of S(6) and S(8) motifs respectively (Fig. 8(a)). These motifs are identical to those observed on the  $L^1$  and thiourea analogues of **8**, despite the fact that both of these compounds form coordination polymers.

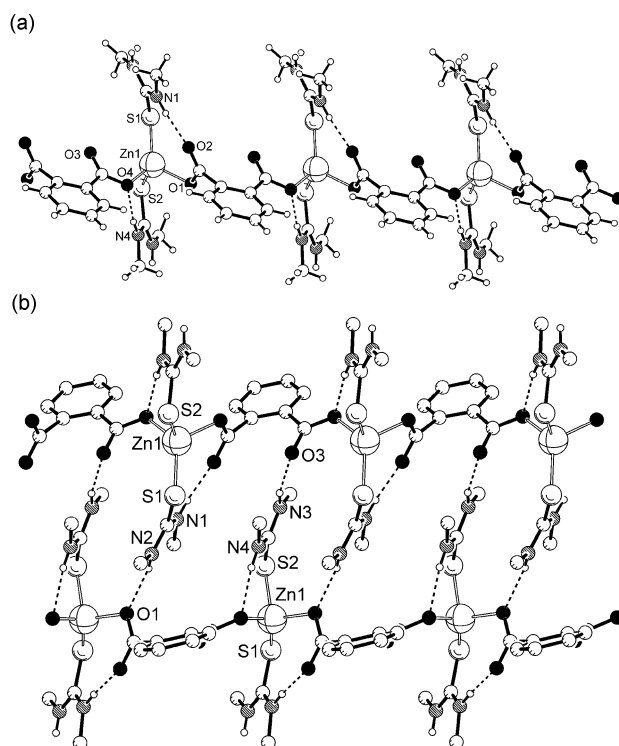


**Fig. 8** Structure of compound **8**. (a) Dimers formed by **8**. Intramolecular hydrogen bond parameters: N(2)  $\cdots$  O(2) 2.942, H(2)  $\cdots$  O(2) 2.11 Å, N(2)–H(2)  $\cdots$  O(2) 160°; N(3)  $\cdots$  O(3) 2.892, H(3)  $\cdots$  O(3) 2.05 Å, N(3)–H(3)  $\cdots$  O(3) 166°. (b) Interactions linking dimers into sheets. Hydrogen bond parameters: N(1)  $\cdots$  O(4) 2.796, H(1)  $\cdots$  O(4) 1.99 Å, N(1)–H(1)  $\cdots$  O(4) 155°; N(4)  $\cdots$  O(5) 2.851, H(4)  $\cdots$  O(5) 2.03 Å, N(4)–H(4)  $\cdots$  O(5) 160°; and O(5)  $\cdots$  O(2) 2.780, H(5WA)  $\cdots$  O(2) 1.93 Å, O(5)–H(5WA)  $\cdots$  O(2) 172°.

N–H  $\cdots$  O hydrogen bonds connect the dimers into sheets (Fig. 8(b)), which are interconnected into the gross structure by N–H  $\cdots$  O and O–H  $\cdots$  O hydrogen bonds, both of which involve the included water molecules [O(5)  $\cdots$  O(1) 2.958, H(5WB)  $\cdots$  O(1) 2.13 Å, O(5)–H(5WB)  $\cdots$  O(1) 167°]. The isophthalate ligands in **8** coordinate using the proximal oxygen atoms, which leads to a Zn  $\cdots$  Zn distance of 7.4 Å. This is significantly shorter than the equivalent distance, 9.5 Å, observed in **3** for which one of the distal oxygen atoms is coordinated.

**The structure of [Zn(L<sup>2</sup>)<sub>2</sub>(μ-phthalate)]<sub>n</sub> **9**.** In contrast to observations with  $L^1$ , the reaction of [Zn(L<sup>2</sup>)<sub>4</sub>]Cl<sub>2</sub> with sodium phthalate leads to coordination polymers of [Zn(L<sup>2</sup>)<sub>2</sub>(μ-phthalate)]<sub>n</sub> **9** in which Zn(L<sup>2</sup>)<sub>2</sub> units are connected by bridging phthalate ligands. Important bond lengths and angles for **9** are given in Table 1. The  $L^2$  ligands adopt *syn,anti* conformations, and intra-chain hydrogen bonds are observed to coordinated and non-coordinated oxygen atoms, generating both S(6) and S(8) motifs (Fig. 9(a)).

The chains all lie parallel, with two independent N–H  $\cdots$  O hydrogen bonds connecting the chains into sheets (Fig. 9(b)). There are no strong interactions between sheets. The polymeric

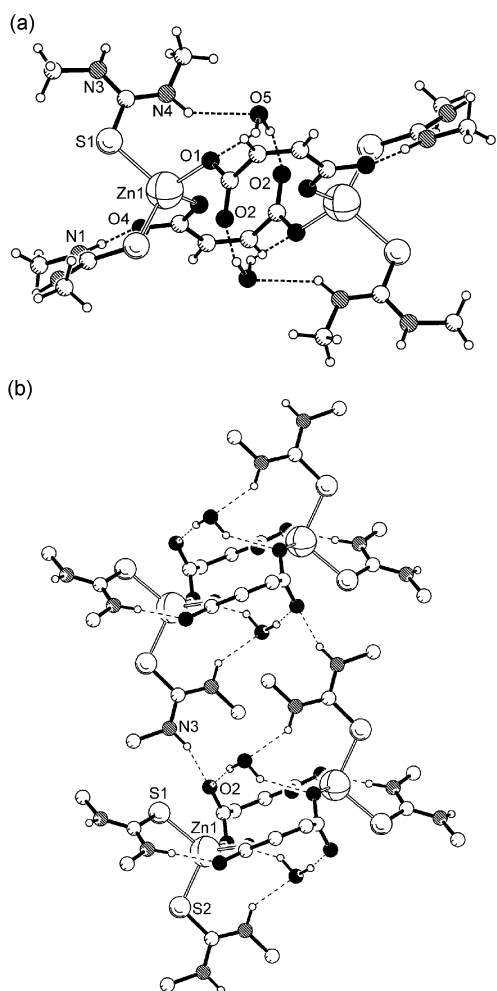


**Fig. 9** Structure of compound **9**. (a) Part of the coordination polymer formed by **9**. Intra-chain hydrogen bond parameters: N(1)  $\cdots$  O(2) 2.768, H(1)  $\cdots$  O(2) 1.89 Å, N(1)–H(1)  $\cdots$  O(2) 175°; and N(4)  $\cdots$  O(4) 2.935, H(4)  $\cdots$  O(4) 2.06 Å, N(4)–H(4)  $\cdots$  O(4) 168°. (b) Interactions connecting the coordination polymers into sheets. Hydrogen bond parameters: N(2)  $\cdots$  O(1) 3.020, H(2)  $\cdots$  O(1) 2.20 Å, N(2)–H(2)  $\cdots$  O(1) 155°; and N(3)  $\cdots$  O(3) 2.864, H(3)  $\cdots$  O(3) 2.02 Å, N(3)–H(3)  $\cdots$  O(3) 158°.

structure of **9** contains a number of differences with respect to that of [Zn(tu)<sub>2</sub>(μ-phthalate)]<sub>n</sub>. In the thiourea compound the chains are helical, with hydrogen bonds connecting them into a three-dimensional structure, whereas in **9** the chains lie flat, and as described above the hydrogen bonds connect the chains only into two-dimensional sheets.

**The structures of [Zn(L<sup>2</sup>)<sub>2</sub>(μ-maleate)]<sub>2</sub>·2H<sub>2</sub>O **10** and [Zn(L<sup>2</sup>)<sub>2</sub>(μ-citraconate)]<sub>2</sub>·2H<sub>2</sub>O **11**.** The compounds [Zn(L<sup>2</sup>)<sub>2</sub>(μ-maleate)]<sub>2</sub>·2H<sub>2</sub>O **10** and [Zn(L<sup>2</sup>)<sub>2</sub>(μ-citraconate)]<sub>2</sub>·2H<sub>2</sub>O **11** display very similar structural features and can be discussed together. As for **8**, reaction with the dicarboxylate has led to the formation of dimers, which crystallise with two equivalents of water. Selected bond lengths and angles for **10** and **11** are given in Table 1. In common with other structures of  $L^2$ , the ligands adopt *syn,anti* conformations. There is only one strong intramolecular interaction around each zinc centre, with an N–H  $\cdots$  O hydrogen bond to a non-coordinated oxygen atom giving rise to an S(8) ring. § The second anticipated intramolecular interaction is replaced by an N–H  $\cdots$  O hydrogen bond to an included water molecule. The water molecules cap the open faces of the dimers, forming O–H  $\cdots$  O hydrogen bonds to coordinated and non-coordinated oxygen atoms on either side of the 14-membered metallacyclic ring (Fig. 10(a)). Pairs of N–H  $\cdots$  O hydrogen bonds link the rings into columns (Fig. 10(b)), which are linked together into sheets through

§ Intramolecular hydrogen bond parameters for **11**: N(1)  $\cdots$  O(3) 2.776, H(1)  $\cdots$  O(3) 1.92 Å, N(1)–H(1)  $\cdots$  O(3) 169°. Intermolecular hydrogen bond parameters for **11**: N(2)  $\cdots$  O(5) 3.020, H(2)  $\cdots$  O(5) 2.23 Å, N(2)–H(2)  $\cdots$  O(5) 155°; N(3)  $\cdots$  O(5) 3.052, H(3)  $\cdots$  O(5) 2.39 Å, N(3)–H(3)  $\cdots$  O(5) 131°; N(4)  $\cdots$  O(2) 2.878, H(4)  $\cdots$  O(2) 2.06 Å, N(4)–H(4)  $\cdots$  O(2) 153°; O(5)  $\cdots$  O(1) 2.909, H(5A)  $\cdots$  O(1) 2.07 Å, O(5)–H(5A)  $\cdots$  O(1) 160°; O(5)  $\cdots$  O(2) 2.866, H(5B)  $\cdots$  O(2) 1.99 Å, O(5)–H(5B)  $\cdots$  O(2) 175°.



**Fig. 10** Structure of compound **10**. (a) Dimers formed by **10**. Hydrogen bond parameters: N(1)  $\cdots$  O(4) 2.802, H(1)  $\cdots$  O(4) 1.88 Å, N(1)–H(1)  $\cdots$  O(4) 170°; N(4)  $\cdots$  O(5) 3.017, H(4)  $\cdots$  O(5) 2.23 Å, N(4)–H(4)  $\cdots$  O(5) 140°; O(5)  $\cdots$  O(2) 2.891, H(5A)  $\cdots$  O(2) 1.97 Å, O(5)–H(5A)  $\cdots$  O(2) 167°; and O(5)  $\cdots$  O(1) 2.902, H(5B)  $\cdots$  O(1) 2.10 Å, O(5)–H(5B)  $\cdots$  O(1) 144°. (b) Linking of the dimers into columns. Hydrogen bond parameters: N(3)  $\cdots$  O(2) 2.826, H(3)  $\cdots$  O(2) 1.96 Å, N(3)–H(3)  $\cdots$  O(2) 151°.

hydrogen bonds involving the water molecule [N(2)  $\cdots$  O(5) 3.020, H(2)  $\cdots$  O(5) 2.23 Å, N(2)–H(2)  $\cdots$  O(5) 155°].

Compounds **10** and **11** have very similar lattice parameters, with the largest difference a lengthening of *a* for the citraconate compound **11**. There are no hydrogen bond interactions in this direction, though the additional presence of the methyl group in **11** pushes the sheets further apart.

## Discussion

The structural results described above suggest that both the dicarboxylate shape and the degree of thiourea substitution are major factors influencing whether the reaction between a tetra(thiourea)zinc(2+) cation and a dicarboxylate results in a coordination polymer or a dimer. Linear dicarboxylates such as terephthalate and fumarate, in which the angle  $\theta^{14}$  between the carboxylate groups is 180°, always appear to favour polymers, and there are significant steric reasons for this. Utilisation of the carboxylate *syn* lone pairs in coordination would lead to steric repulsions between the two bridging ligands in a dimer, and although *anti* coordination has been observed in [Zn(tu)<sub>2</sub>(μ-fumarate)]<sub>n</sub>, this is generally a less favourable coordination mode for carboxylates.

For non-linear dicarboxylates such as maleate, citraconate, phthalate and isophthalate, with  $\theta$  less than 120°, the probability of dimer formation increases with substitution, with

dimers being more favourable than polymers for complexes of **L**<sup>2</sup>. Thus for these four dicarboxylates all of the thiourea products are polymers, whereas three of the four **L**<sup>2</sup> derivatives are dimers. This provides a degree of structural predictability, though the observation of polymers for [Zn(tu)<sub>2</sub>(μ-phthalate)]<sub>n</sub> and [Zn(**L**<sup>2</sup>)<sub>2</sub>(μ-phthalate)]<sub>n</sub> **9** in addition to dimers for [Zn(**L**<sup>1</sup>)<sub>2</sub>(μ-phthalate)]<sub>2</sub>·4H<sub>2</sub>O **5** suggests there are limits to using this predictability in specific cases.

In all of the compounds **1–11**, the zinc adopts a distorted tetrahedral ZnS<sub>2</sub>O<sub>2</sub> coordination geometry, so compounds of the stoichiometry ZnL<sub>2</sub>(dicarboxylate) are formed with excellent predictability. An analysis of the structural parameters around the zinc centres (Table 1) reveals few differences between the bond lengths and angles observed for polymers and dimers, though the range is larger for the former. For example, the O–Zn–O angles for polymeric derivatives of **L**<sup>1</sup> or **L**<sup>2</sup> range from 89.6 to 113.8° whereas those for dimers range from 93.0 to 105.9°.

A dimer or polymer of stoichiometry Zn(**L**<sup>1</sup>)<sub>2</sub>(μ-dicarboxylate) nominally contains six hydrogen bond donors and six hydrogen bond acceptors per zinc centre, assuming that carboxylate oxygen atoms accept one hydrogen bond when coordinated and two when not. Introduction of water increases the number of both donors and acceptors by an equal amount. Of the **L**<sup>1</sup> compounds, all donors and acceptors are satisfied only in **4**. Compounds **1** and **2** contain weaker N–H  $\cdots$  S hydrogen bonds which results in non-saturation of some oxygen atoms, whereas in **3** and **5** there are N–H groups that do not form any hydrogen bonds. A dimer or polymer of stoichiometry Zn(**L**<sup>2</sup>)<sub>2</sub>(μ-dicarboxylate) contains 4 hydrogen bond donors and 6 hydrogen bond acceptors per zinc centre. In compounds **6–11**, all N–H donors are satisfied, though some acceptors are not. The excess of acceptors therefore introduces a level of flexibility not present in compounds containing **L**<sup>1</sup>, thus enabling all donors to form hydrogen bonds to good acceptors.

The intramolecular and intra-chain hydrogen bonding motifs observed in compounds **1–11** are summarised in Table 2. The majority of the compounds contain two intramolecular or intra-chain N–H  $\cdots$  O hydrogen bonds with those to coordinated carboxylate oxygen atoms giving rise to six-membered rings [graph set S(6)], and those to non-coordinated carboxylate oxygen atoms giving rise to eight-membered rings [graph set S(8)]. The exceptions are [Zn(**L**<sup>1</sup>)<sub>2</sub>(μ-fumarate)]<sub>n</sub> **2** where two intra-chain N–H  $\cdots$  S hydrogen bonds, similar to those observed in [Zn(tu)<sub>2</sub>(μ-fumarate)], are present, [Zn(**L**<sup>1</sup>)<sub>2</sub>(μ-phthalate)]<sub>2</sub>·4H<sub>2</sub>O **5**, where there is only one such interaction around one of the two crystallographically independent zinc atoms, and [Zn(**L**<sup>2</sup>)<sub>2</sub>(μ-maleate)]<sub>2</sub>·2H<sub>2</sub>O **10** and [Zn(**L**<sup>2</sup>)<sub>2</sub>(μ-citraconate)]<sub>2</sub>·2H<sub>2</sub>O **11** where there is also only one such interaction. In compounds **5**, **10** and **11** one of the N–H groups anticipated to be involved in intra-chain hydrogen bonding is employed instead in an N–H  $\cdots$  O interaction with an included water molecule. Comparison of the intramolecular or intra-chain hydrogen bonding for compounds of **L**<sup>1</sup> and **L**<sup>2</sup> reveals an increase in the formation of S(8) rings with increasing degree of substitution.

Interactions between polymeric chains in the thiourea compounds are dominated by hydrogen bonds involving the parallel NH groups. The orientation of the **L**<sup>1</sup> ligands in compounds **1–5** is such that parallel NH groups are present in only one of the crystallographically independent **L**<sup>1</sup> ligands of **3** and these are involved in N–H  $\cdots$  O hydrogen bonds to a dicarboxylate oxygen atom and an included water molecule [graph set R<sub>3</sub><sup>2</sup>(8)]. The presence of intra-chain or intramolecular hydrogen bonds in compounds **6–11** results in only one N–H group per **L**<sup>2</sup> ligand being available for inter-chain or intermolecular hydrogen bonding. In addition to decreasing the number of hydrogen bonding groups, substitution on the thiourea also has a steric effect. The presence of the methyl groups would affect the packing of both coordination polymers and dimers, though the



**Table 2** Intramolecular and intra-chain hydrogen bonding motifs in compounds 1–11 and their thiourea analogues.

	Dicarboxylate	Thiourea	L <sup>1</sup>	L <sup>2</sup>
	Terephthalate	S(8), S(8), S(8)	S(8), S(8) [1]	S(6), S(8) [6]
	Fumarate	2 S(6) (NH...S)	2 S(6) (NH...S) [2]	S(8), S(8) [7]
	Isophthalate	S(6), S(8)	S(6), S(8) [3]	S(6), S(8) [8]
	1,3-Phenylenediacetate	S(6), S(8)	S(6), S(8) [4]	
	Phthalate	S(6), S(6)	S(8), S(8) [5] S(8), R <sub>3</sub> (15) [5]	S(6), S(8) [9]
	Maleate	S(6), S(8)		S(8), R <sub>3</sub> (8) [10]
	Citraconate	S(6), S(6)		S(8), R <sub>3</sub> (8) [11]

**Table 3** Crystallographic data for compounds 1–11

Compound	1	2	3	4	5	6
Empirical formula	C <sub>12</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub> Zn	C <sub>8</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub> Zn	C <sub>12</sub> H <sub>18</sub> N <sub>4</sub> O <sub>5</sub> S <sub>2</sub> Zn	C <sub>14</sub> H <sub>20</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub> Zn	C <sub>24</sub> H <sub>39</sub> N <sub>8</sub> O <sub>11.5</sub> S <sub>4</sub> Zn <sub>2</sub>	C <sub>14</sub> H <sub>21</sub> N <sub>4</sub> O <sub>4.5</sub> S <sub>2</sub> Zn
<i>M</i>	409.78	359.72	427.79	437.83	882.61	446.84
<i>T</i> /K	150(2)	293(2)	150(2)	150(2)	150(2)	296(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>Ccca</i>	<i>C2/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P1</i>
<i>a</i> /Å	11.08100(10)	14.817(4)	10.3830(3)	6.5790(2)	17.9560(3)	8.55500(10)
<i>b</i> /Å	22.7150(3)	9.1050(10)	10.4260(3)	13.3430(5)	10.7140(2)	9.6180(2)
<i>c</i> /Å	13.8470(2)	12.430(3)	16.5870(4)	21.2060(9)	20.4420(4)	13.0360(2)
<i>a</i> <sup>o</sup>	90	90	90	90	90	98.2960(10)
<i>β</i> <sup>o</sup>	90	115.84(2)	94.1980(10)	97.9270(17)	110.6040(10)	106.8340(10)
<i>γ</i> <sup>o</sup>	90	90	90	90	90	100.0610(10)
<i>U</i> /Å <sup>3</sup>	3485.36(8)	1509.2(6)	1790.78(8)	1843.75(12)	3681.09(12)	989.03(3)
<i>Z</i>	8	4	4	4	4	2
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.562	1.583	1.587	1.577	1.593	1.500
<i>μ</i> /mm <sup>-1</sup>	1.671	1.917	1.634	1.585	1.595	1.481
Crystal size/mm	0.45 × 0.43 × 0.10	0.30 × 0.20 × 0.10	0.10 × 0.10 × 0.10	0.10 × 0.05 × 0.03	0.25 × 0.10 × 0.10	0.20 × 0.20 × 0.10
Reflections collected	34384	1427	19197	19001	38257	20647
Independent reflections	2558	1328	4086	4048	8381	4510
<i>R</i> <sub>int</sub>	0.0658	0.0104	0.0923	0.1249	0.0802	0.0359
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0257, 0.0622	0.0268, 0.0711	0.0392, 0.0815	0.0498, 0.0901	0.0379, 0.0705	0.0303, 0.0831
<i>R</i> indices (all data)	0.0311, 0.0645	0.0306, 0.0729	0.0691, 0.0941	0.1011, 0.1090	0.0687, 0.0807	0.0337, 0.0854

Compound	7	8	9	10	11
Empirical formula	C <sub>10</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub> Zn	C <sub>28</sub> H <sub>44</sub> N <sub>8</sub> O <sub>10</sub> S <sub>4</sub> Zn <sub>2</sub>	C <sub>14</sub> H <sub>20</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub> Zn	C <sub>20</sub> H <sub>40</sub> N <sub>8</sub> O <sub>10</sub> S <sub>4</sub> Zn <sub>2</sub>	C <sub>22</sub> H <sub>44</sub> N <sub>8</sub> O <sub>10</sub> S <sub>4</sub> Zn <sub>2</sub>
<i>M</i>	387.77	911.70	437.83	811.58	839.63
<i>T</i> /K	170(2)	150(2)	150(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/c</i>	<i>Pna2<sub>1</sub></i>	<i>P1</i>	<i>P1</i>
<i>a</i> /Å	7.7910(2)	10.3390(2)	15.9784(3)	8.264(2)	9.011(2)
<i>b</i> /Å	14.6240(2)	11.5500(2)	15.1177(2)	9.642(2)	9.701(2)
<i>c</i> /Å	15.1050(4)	16.6330(3)	7.4566(1)	11.199(2)	11.141(2)
<i>a</i> <sup>o</sup>	90	90	90	78.46(2)	77.79(2)
<i>β</i> <sup>o</sup>	94.1120(11)	90.6080(7)	90	76.48(2)	77.94(2)
<i>γ</i> <sup>o</sup>	90	90	90	83.750(10)	85.63(2)
<i>U</i> /Å <sup>3</sup>	1716.57(7)	1986.13(6)	1801.19(5)	848.3(3)	930.4(3)
<i>Z</i>	4	2	4	1	1
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.500	1.524	1.615	1.589	1.499
<i>μ</i> /mm <sup>-1</sup>	1.691	1.478	1.622	1.719	1.570
Crystal size/mm	0.33 × 0.25 × 0.20	0.25 × 0.25 × 0.25	0.25 × 0.20 × 0.20	0.20 × 0.20 × 0.10	0.20 × 0.15 × 0.10
Reflections collected	19067	20408	20298	3329	12787
Independent reflections	3920	4547	4116	2985	4250
<i>R</i> <sub>int</sub>	0.0279	0.0439	0.0333	0.0116	0.0494
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0232, 0.0827	0.0282, 0.0649	0.0212, 0.0552	0.0293, 0.0703	0.0376, 0.0902
<i>R</i> indices (all data)	0.0252, 0.0854	0.0368, 0.0691	0.0225, 0.0561	0.0386, 0.0730	0.0631, 0.0994

former would be expected to be affected by a greater extent due to the constraints already imposed by polymer formation.

It has been previously shown that dimer formation is less favourable than polymer formation for the thiourea compounds [Zn(tu)<sub>2</sub>(μ-dicarboxylate)]<sub>n</sub>,<sup>7,15</sup> so it is likely that packing problems raise the energy of many Zn–L<sup>2</sup>-dicarboxylate polymers, thus favouring formation of dimers with substituted ligands.

## Experimental

### General experimental

Microanalyses (C, H and N) were carried out by Mr. Alan

Carver (University of Bath Microanalytical Service). Despite repeated attempts the microanalysis for 7 was always low in carbon, though satisfactory for nitrogen and hydrogen. The compounds [Zn(L<sup>1</sup>)<sub>4</sub>]Cl<sub>2</sub>, [Zn(L<sup>2</sup>)<sub>4</sub>]Cl<sub>2</sub>, [Zn(L<sup>3</sup>)<sub>4</sub>]Cl<sub>2</sub> and [Zn(L<sup>3</sup>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> were prepared following the literature methods.<sup>11</sup> Sodium dicarboxylates were prepared by reaction of the appropriate dicarboxylic acid with either sodium hydroxide or sodium hydrogen carbonate where not available from commercial sources. Crystals chosen for structural analyses were shown to be representative of the bulk samples either by comparing their powder diffraction pattern with that calculated from the single crystal structure or by determining the unit cells of several single crystals.

**Synthesis of  $[\text{Zn}(\text{L}^1)_2(\mu\text{-terephthalate})]_n$ , **1**.** An aqueous solution of sodium terephthalate (0.038 g, 0.18 mmol) was added to an aqueous solution of  $[\text{Zn}(\text{L}^1)_4]\text{Cl}_2$  (0.100 g, 0.18 mmol), with no discernable change. After approximately 72 h a colourless crystalline precipitate was observed which was separated by filtration. Yield 0.047 g (78%). Microanalysis. Found: C, 35.3; H, 3.86; N, 13.7.  $\text{C}_{12}\text{H}_{14}\text{N}_4\text{O}_4\text{S}_2\text{Zn}$  requires: C, 35.2; H, 3.91; N, 13.7%. Single crystals suitable for X-ray analysis were obtained by repeating the reaction on a smaller scale in a more dilute solution, allowing the crystals to grow over a longer time period.

Compounds **2–5** were synthesised in an analogous manner to **1** using  $[\text{Zn}(\text{L}^1)_4]\text{Cl}_2$  (0.100 g) and one equivalent of the appropriate sodium dicarboxylate. In each case the synthesis was repeated on a smaller scale in order to obtain higher quality crystals.  $[\text{Zn}(\text{L}^1)_2(\mu\text{-fumarate})]_n$ , **2**: yield 0.052 g (74%). Microanalysis. Found: C, 26.6; H, 3.93; N, 15.5.  $\text{C}_8\text{H}_{14}\text{N}_4\text{O}_4\text{S}_2\text{Zn}$  requires C, 26.7; H, 3.90; N, 15.6%.  $\{[\text{Zn}(\text{L}^1)_2(\mu\text{-isophthalate})]\cdot\text{H}_2\text{O}\}_n$ , **3**: yield 0.048 g (63%). Microanalysis. Found: C, 33.5; H, 4.21; N, 12.9.  $\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}_5\text{S}_2\text{Zn}$  requires C, 33.7; H, 4.21; N, 13.1%.  $[\text{Zn}(\text{L}^1)_2(\mu\text{-1,3-phenylenediacetate})]_n$ , **4**: yield 0.061 g (78%). Microanalysis. Found: C, 38.7; H, 4.57; N, 12.5.  $\text{C}_{14}\text{H}_{20}\text{N}_4\text{O}_4\text{S}_2\text{Zn}$  requires C, 38.4; H, 4.57; N, 12.8%.  $[\text{Zn}(\text{L}^1)_2(\mu\text{-phthalate})]_2\cdot 4\text{H}_2\text{O}$  **5**: yield 0.072 g (89%). Microanalysis. Found: C, 32.6; H, 4.00; N, 12.6.  $\text{C}_{24}\text{H}_{40}\text{N}_8\text{O}_{12}\text{S}_4\text{Zn}_2$  requires C, 32.3; H, 4.49; N, 12.6%.

**Synthesis of  $\{[\text{Zn}(\text{L}^2)_2(\mu\text{-terephthalate})]\cdot 0.5\text{H}_2\text{O}\}_n$ , **6**.** An aqueous solution of sodium terephthalate (0.032 g, 0.15 mmol) was added to an aqueous solution of  $[\text{Zn}(\text{L}^2)_4]\text{Cl}_2$  (0.100 g, 0.15 mmol), with no discernable change. After several hours a colourless crystalline precipitate was observed which was separated by filtration. Yield 0.045 g (67%). Microanalysis. Found: C, 37.1; H, 4.74; N, 12.4%.  $\text{C}_{14}\text{H}_{22}\text{N}_4\text{O}_5\text{S}_2\text{Zn}$  requires C, 37.1; H, 4.74; N, 12.4%.

Compounds **7–11** were synthesised in an analogous manner to **6** using  $[\text{Zn}(\text{L}^2)_4]\text{Cl}_2$  (0.100 g) and one equivalent of the appropriate sodium dicarboxylate.  $[\text{Zn}(\text{L}^2)_2(\mu\text{-fumarate})]_n$ , **7**: yield 0.045 g (67%).  $[\text{Zn}(\text{L}^2)_2(\mu\text{-isophthalate})]_2\cdot 2\text{H}_2\text{O}$  **8**: yield 0.047 g (68%). Microanalysis. Found: C, 37.4; H, 4.84; N, 11.8.  $\text{C}_{14}\text{H}_{22}\text{N}_4\text{O}_5\text{S}_2\text{Zn}$  requires C, 36.9; H, 4.86; N, 12.3%.  $[\text{Zn}(\text{L}^2)_2(\mu\text{-phthalate})]_n$ , **9**: yield 0.052 g (76%). Microanalysis. Found: C, 38.2; H, 4.54; N, 12.8.  $\text{C}_{14}\text{H}_{20}\text{N}_4\text{O}_4\text{S}_2\text{Zn}$  requires C, 38.4; H, 4.60; N, 12.8%.  $[\text{Zn}(\text{L}^2)_2(\mu\text{-maleate})]_2\cdot 2\text{H}_2\text{O}$  **10**: yield 0.049 g (73%). Microanalysis. Found: C, 29.6; H, 4.96; N, 13.6.  $\text{C}_{10}\text{H}_{20}\text{N}_4\text{O}_5\text{S}_2\text{Zn}$  requires C, 29.6; H, 4.97; N, 13.8%.  $[\text{Zn}(\text{L}^2)_2(\mu\text{-citrate})]_2\cdot 2\text{H}_2\text{O}$  **11**: yield 0.052 g (74%). Microanalysis. Found: C, 30.0; H, 5.30; N, 13.0.  $\text{C}_{11}\text{H}_{22}\text{N}_4\text{O}_5\text{S}_2\text{Zn}$  requires C, 30.2; H, 5.53; N, 12.8%.

### Crystallography

Single crystals of compounds **2** and **10** were analysed using an Enraf-Nonius CAD4 automatic four-circle diffractometer whereas single crystals of **1**, **3–9** and **11** were analysed using a Nonius Kappa CCD diffractometer. Details of the data collections, solutions and refinements are given in Table 3. The structures were solved using SHELXS-97 and refined using SHELXL-97.<sup>16</sup>

In compounds **1** and **2** the zinc atoms lie on special positions so the full coordination sphere is generated by rotation about a

crystallographic two-fold axis. Nitrogen-bound hydrogen atoms in addition to water molecule hydrogens were located where possible and refined at a distance of 0.89 Å from the relevant parent atoms throughout, with the exception of compound **10** where a fixed distance of 0.98 Å was employed. Additional H...H constraints (1.45 Å) were included in compounds **2** (H1A...H1B), **4** (H2A...H2B, H4A...H4B) and **8** (H10...H10B, H11A...H11B).

Data were corrected for extinction and absorption on the basis of individual merit. In particular, extinction corrections were universally applied with the sole exception of **10**. A semi-empirical absorption correction based on equivalents was included for compounds **5–7** and **11** (max./min. transmission 0.86/0.81, 0.83/0.77, 0.73/0.61, and 1.02/0.97 respectively). The absolute structure parameter for **9** refined to a value of 0.062(6).

CCDC reference numbers 213865–213875.

See <http://www.rsc.org/suppdata/dt/b3/b307420j/> for crystallographic data in CIF or other electronic format.

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