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The influence of hydrogen bonding on the structure of zinc co-ordination polymers†

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The compounds [Zn(tu)$_2$(μ-fum)] **2** (tu = thiourea, fum = fumarate), [Zn(tu)$_2$(μ-mal)] **3** (mal = malonate), [Zn(tu)$_2$(μ-ipht)]·H$_2$O **4** (ipht = isophthalate), [Zn(tu)$_2$(μ-citr)] **5** (citr = citraconate), [Zn(tu)$_2$(μ-pht)] **6** (pht = phthalate), [Zn(tu)$_2$(μ-male)]·H$_2$O **7** (male = maleate) and [Zn(tu)$_2$(μ-hpht)]$_2$ **8** (hpht = homophthalate) have all been prepared from the reaction of [ZnCl$_2$(tu)$_4$] with the appropriate sodium dicarboxylate. Crystal structure determinations of the seven compounds demonstrate that in **2**–**7** bridging dicarboxylates link the zinc centres into polymeric chains, whereas in **8** bridging homophthalates lead to discrete dimers. Where permitted by the relative orientations of the carboxylates, the chains are linked together by pairs of N–H · · · O hydrogen bonds between thiourea NH groups and carboxylate oxygen atoms in a hydrogen bond donor–donor acceptor–acceptor (DD : AA) arrangement. The hydrogen bonding patterns in the structure of **2** are very similar to those previously observed in [NEt$_4$]$_2$[fum]·2tu, suggesting that incorporation of zinc has little effect on the gross structure. The supramolecular structures of **5** and **6** are very similar to each other, and also to that of the previously reported compound [Zn(tu)$_2$(μ-male)], which reflects the similar dispositions of the carboxylate groups. In contrast, the structure of **7** is very different, illustrating the dramatic effects that inclusion of solvent can have on the supramolecular structure.

Introduction

There are currently two main strategies used in crystal engineering, based on the use of either co-ordinative bonds[1] or of weaker intermolecular interactions. In the latter methodology the hydrogen bond has attracted most interest due to its relative strength and directionality.[2] Although in many instances the two approaches are independent, the presence of hydrogen bonding can influence metal co-ordination geometry,[3] and recently there has been interest in combining both approaches in order to determine the effects of intermolecular interactions on the structure of co-ordination polymers.[4]

Dicarboxylates constitute an important class of ligands in the formation of co-ordination polymers. These ligands are able to bridge between metal centres in a number of different manners involving, for example, one carboxylate bound to each metal which links the metal centres into dimers,[5,6] or two carboxylates per metal which link the metal centres into either infinite chains[7] or smaller cyclic oligomers.[6,8]

Recently[9] we demonstrated that [Zn(tu)$_4$][NO$_3$]$_2$ (tu = thiourea) reacts with sodium terephthalate, Na$_2$tpht, to generate a double stranded co-ordination polymer [Zn$_2$(μ-tu)(tu)$_2$(μ-tpht)$_2$] **1** in which two {Zn(μ-tpht)}$_n$ chains are linked by bridging thiourea ligands. In addition to the potential to bridge between chains, thioureas contain hydrogen bond donors that may serve to link the chains through N–H · · · O hydrogen bonds. We sought to investigate how the structures of zinc dicarboxylate polymers containing thioureas as co-ligands are affected by changing the terephthalate anion to an alternative dicarboxylate. This substitution changes the relative orientation of the carboxylate groups, which was thought likely to influence the hydrogen bonding patterns. It has recently been shown by Guilera and Steed[10] that single-stranded zinc terephthalate polymers containing either two waters or an ethylenediamine as co-ligands can be formed, and that both the orientation of the terephthalates and the zinc co-ordination geometry are influenced by the hydrogen bonding of the terephthalates with the co-ligands.

Results and discussion

Reaction of [ZnCl$_2$(tu)$_4$], in aqueous solution, with the sodium salts of the dicarboxylates depicted in Chart 1 gave rise to products that analysed correctly for either [Zn(tu)$_2$(dicarboxylate)] or [Zn(tu)$_2$(dicarboxylate)]·H$_2$O. There was no evidence in any of the reactions for the formation of compounds analogous to **1** which contains bridging thiourea, concomitant with a zinc : thiourea ratio less than 1 : 2. Indeed, in all cases the reactions appear to be highly selective, and the compounds described below were the only ones observed in the syntheses. Single crystal structure analyses were carried out on [Zn(tu)$_2$(μ-fum)] **2** (fum = fumarate), [Zn(tu)$_2$(μ-mal)] **3** (mal = malonate), [Zn(tu)$_2$(μ-ipht)]·H$_2$O **4** (ipht = isophthalate), [Zn(tu)$_2$(μ-citr)] **5** (citr = citraconate), [Zn(tu)$_2$(μ-pht)] **6** (pht = phthalate), [Zn(tu)$_2$(μ-male)]·H$_2$O **7** (male = maleate) and [Zn(tu)$_2$(μ-hpht)]$_2$ **8** (hpht = homophthalate). In all cases, two of the thiourea ligands have been displaced from the zinc co-ordination sphere by two unidentate carboxylates, leading to distorted tetrahedral geometry around the metal centre. In complexes **2**–**7**, this results in polymerisation, and the formation of one-dimensional chains, whereas in **8** it results in the formation of dimers. Although the gross co-ordination geometry in **2**–**7** is similar, there are considerable differences in the supramolecular structures, resulting from the manner in which the chains are linked by hydrogen bonding.

Structure of [Zn(tu)$_2$(μ-fum)], 2

The asymmetric unit of compound **2**, as illustrated by the labelled unprimed atoms of Fig. 1, consists of one zinc centre,

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Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b003210g/

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Table 1 Selected bond distances (Å) and angles (°) for compounds **2**–**8**

2		**3**		**4**		**5**	
Zn(1)–S(1)	2.3292(6)	Zn(1)–S(1)	2.3194(7)	Zn(1)–S(1)	2.3451(10)	Zn(1)–S(1)	2.295(2)
		Zn(1)–S(2)	2.3205(7)	Zn(1)–S(2)	2.2943(10)	Zn(1)–S(2)	2.334(2)
Zn(1)–O(1)	1.9490(14)	Zn(1)–O(1)	1.977(2)	Zn(1)–O(1)	2.000(3)	Zn(1)–O(1)′	1.948(4)
		Zn(1)–O(3)′	1.993(2)	Zn(1)–O(3)′	1.976(2)	Zn(1)–O(3)	1.982(4)
O(1)–Zn(1)–O(1)′	107.72(9)	O(1)–Zn(1)–O(3)′	97.22(7)	O(1)–Zn(1)–O(3)′	91.34(9)	O(1)′–Zn(1)–O(3)	113.3(2)
S(1)–Zn(1)–S(1)′	113.23(3)	S(1)–Zn(1)–S(2)	107.05(3)	S(1)–Zn(1)–S(2)	118.31(3)	S(1)–Zn(1)–S(2)	122.08(9)
O(1)–Zn(1)–S(1)	104.46(4)	O(1)–Zn(1)–S(1)	117.90(5)	O(1)–Zn(1)–S(1)	107.10(8)	O(1)′–Zn(1)–S(1)	113.5(2)
O(1)′–Zn(1)–S(1)	113.54(5)	O(1)–Zn(1)–S(2)	116.16(6)	O(1)–Zn(1)–S(2)	120.41(7)	O(1)′–Zn(1)–S(2)	102.9(1)
		O(3)′–Zn(1)–S(1)	111.15(5)	O(3)′–Zn(1)–S(1)	106.39(8)	O(3)–Zn(1)–S(1)	107.1(1)
		O(3)′–Zn(1)–S(2)	106.48(5)	O(3)′–Zn(1)–S(2)	109.20(7)	O(3)–Zn(1)–S(2)	97.0(1)
C(1)–S(1)–Zn(1)	96.89(7)	C(1)–S(1)–Zn(1)	103.51(8)	C(2)–S(1)–Zn(1)	101.00(11)	C(1)–S(1)–Zn(1)	105.2(2)
		C(2)–S(2)–Zn(1)	106.78(9)	C(1)–S(2)–Zn(1)	109.81(11)	C(2)–S(1)–Zn(1)	106.8(3)
Primed atoms generated by $-x, y, -z + \frac{1}{2}$		Primed atoms generated by $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$		Primed atoms generated by $x, -y + 1, z + \frac{1}{2}$		Primed atoms generated by $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$	
6		**7**		**8** (molecule 1)		**8** (molecule 2)	
Zn(1)–S(1)	2.3339(9)	Zn(1)–S(1)	2.3304(12)	Zn(1)–S(1)	2.3432(12)	Zn(2)–S(2)	2.3051(11)
Zn(1)–S(2)	2.3011(9)	Zn(1)–S(2)	2.294(2)	Zn(1)–S(3)	2.3195(11)	Zn(2)–S(4)	2.3303(12)
Zn(1)–O(1)	1.995(2)	Zn(1)–O(1)	1.959(2)	Zn(1)–O(1)	1.976(3)	Zn(2)–O(5)	1.979(3)
Zn(1)–O(4)′	1.939(2)	Zn(1)–O(3)′	1.965(2)	Zn(1)–O(3)′	1.972(3)	Zn(2)–O(8)′	1.977(3)
O(1)–Zn(1)–O(4)′	110.74(11)	O(1)–Zn(1)–O(3)′	99.57(8)	O(1)–Zn(1)–O(3)′	96.26(11)	O(5)–Zn(2)–O(8)′	94.24(12)
S(1)–Zn(1)–S(2)	122.33(4)	S(1)–Zn(1)–S(2)	117.19(3)	S(1)–Zn(1)–S(3)	110.70(5)	S(2)–Zn(2)–S(4)	113.71(5)
O(1)–Zn(1)–S(1)	97.17(7)	O(1)–Zn(1)–S(1)	107.1(1)	O(1)–Zn(1)–S(1)	116.10(9)	O(5)–Zn(2)–S(2)	110.07(9)
O(1)–Zn(1)–S(2)	105.46(7)	O(1)–Zn(1)–S(2)	119.2(1)	O(1)–Zn(1)–S(3)	114.08(9)	O(5)–Zn(2)–S(4)	110.11(9)
O(4)′–Zn(1)–S(1)	105.26(7)	O(3)′–Zn(1)–S(1)	107.05(9)	O(3)′–Zn(1)–S(1)	107.38(8)	O(8)′–Zn(2)–S(2)	110.53(10)
O(4)′–Zn(1)–S(2)	114.35(9)	O(3)′–Zn(1)–S(2)	104.54(7)	O(3)′–Zn(1)–S(3)	111.22(8)	O(8)′–Zn(2)–S(4)	115.58(10)
C(1)–S(1)–Zn(1)	109.0(1)	C(1)–S(1)–Zn(1)	108.69(9)	C(1)–S(1)–Zn(1)	108.8(2)	C(12)–S(2)–Zn(2)	109.7(1)
C(2)–S(2)–Zn(1)	105.60(11)	C(2)–S(2)–Zn(1)	105.10(9)	C(2)–S(3)–Zn(1)	109.7(1)	C(13)–S(4)–Zn(2)	109.6(2)
Primed atoms generated by $-1 - x, \frac{1}{2} + y, -\frac{1}{2} + z$		Primed atoms generated by $x - \frac{1}{2}, y - \frac{1}{2}, z$		Primed atoms generated by $-x, -y, -z$		Primed atoms generated by $-x + 1, -y + 1, -z + 2$	

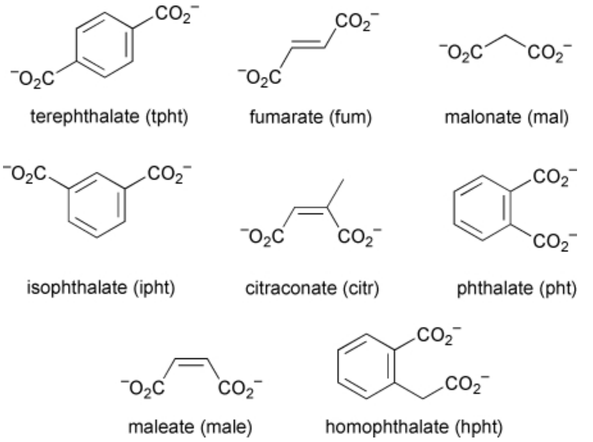

Chart 1 Structures of the dicarboxylates mentioned in the text.

located on a special position with half-site occupancy, to which is co-ordinated a thiourea ligand and one half of a fumarate anion. Selected bond lengths and angles (of all structures) are given in Table 1. The remainder of the zinc co-ordination sphere is generated by transformation through a twofold rotation axis, intrinsic to the space group symmetry (*Pbcn*) while the other half of the fumarate is generated by an inversion centre also implicit in the space group. Looking down the *c* axis, the zinc–fumarate chains appear as ‘figure of eight’ spirals, and since these chains are related by inversion centres both left- and right-handed spirals are present.

Each of the thiourea ligands is involved in intramolecular N–H···S hydrogen bonding with the other. Formation of these hydrogen bonds is facilitated by a reduction of the Zn–S–C bond angle to 96.89(7)°, compared to an average M–S–C bond angle of 108° for thiourea complexes in the Cambridge Structural Database.[11] The presence of these hydrogen bonds is at first sight surprising given the propensity for co-ordinated carboxylate groups to act as hydrogen bond acceptors. Indeed, the four structures of [Zn(tu)$_2$(carboxylate)$_2$] complexes previously reported (carboxylate = acetate,[12] propanoate,[13] trichloroacetate[14] or benzoate[15]) all contain intramolecular N–H···O hydrogen bonds to co-ordinated carboxylate oxygen atoms [graph set[16] S(6)], unco-ordinated carboxylate oxygen atoms [graph set S(8)], or both.

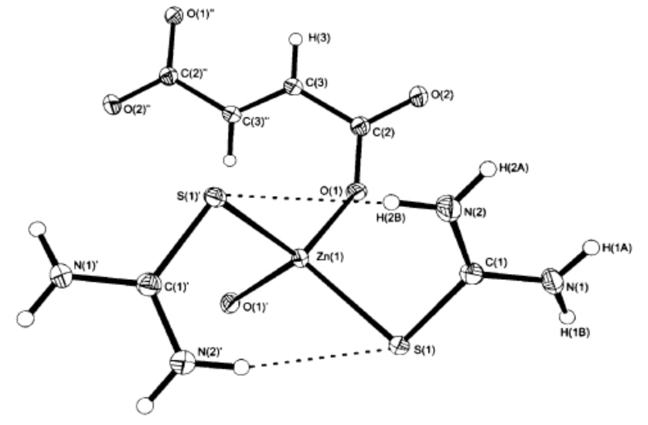

Fig. 1 The zinc co-ordination sphere in compound **2** with thermal ellipsoids represented at the 30% probability level (as in all cases shown). The asymmetric unit is represented by the unprimed atoms, with primed atoms generated by the operation $-x, y, ½-z$, and double-primed atoms by $-x, 1 - y, 1 - z$. The hydrogen bond geometries are N(2)···S(1)′ 3.581(2), H(2B)···S(1)′ 2.76(2) Å, N(2)–H(2B)···S(1)′ 159(3)°.

Study of the inter-chain interactions readily accounts for the absence of intramolecular N–H···O hydrogen bonds. As can

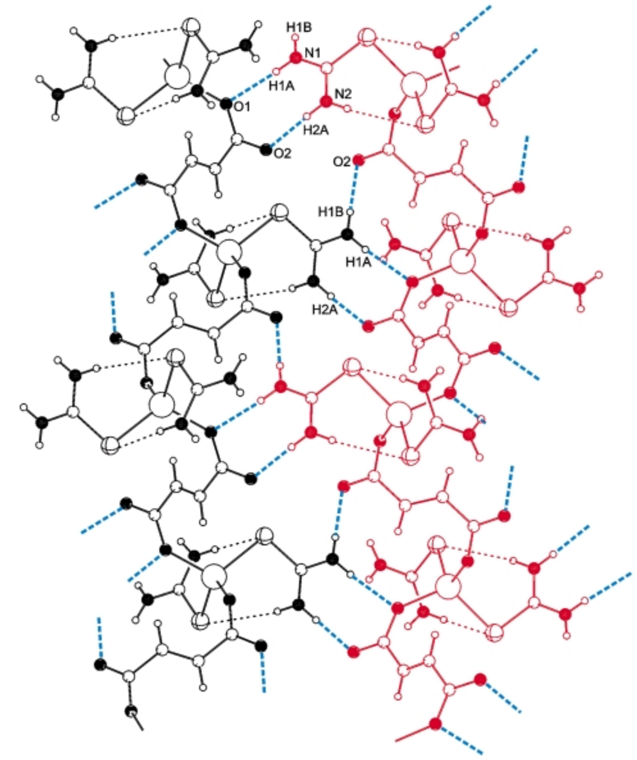

Fig. 2 Inter-chain hydrogen bonding in compound **2**. The hydrogen bond distances (Å) and angles (°) are N(1)···O(1) 2.938(2), H(1A)···O(1) 2.14(2), N(1)–H(1A)···O(1) 163(3); N(2)···O(2) 2.923(2), H(2A)···O(2) 2.12(2), N(2)–H(2A)···O(2) 159(3); and N(1)···O(2) 2.819(3), H(1B)···O(2) 1.96(2), N(1)–H(1B)···O(2) 177(3).

be seen in Fig. 2, thiourea and dicarboxylate ligands are linked by two parallel hydrogen bonds between N(1)–H(1A) and N(2)–H(2A), and co-ordinated oxygen atom O(1) and non-co-ordinated oxygen atom O(2) respectively. These hydrogen bonds occur in a DD:AA orientation[3] [graph set $R^2_2(8)$] so that the hydrogen bonding is enhanced by attractive secondary interactions.[17] This hydrogen bonding pattern leads to cation–anion–cation chains through the gross structure which are coplanar with the zinc–fumarate chains. We have previously observed similar hydrogen bonding motifs in the structures of both zinc[9] and nickel[3,18] bis(thiosemicarbazide) dicarboxylates. Li and Mak[19] observed the same pattern in the structure of $[NEt_4]_2[fum]\cdot 2tu$, where in addition to this DD:AA interaction, the structure also contains $R^2_2(8)$ rings formed from the dimerisation of thioureas through two N–H···S hydrogen bonds, reminiscent of the two S(6) rings observed in **2** but without the zinc centre. Incorporation of zinc in **2** has therefore had very little effect on the interaction between thiourea and fumarate leading to hydrogen bonded chains, though it does influence the manner in which these chains inter-connect by essentially blocking a hydrogen bond acceptor site.

In compound **2** pairs of chains are further linked by a third hydrogen bond between N(1)–H(1B) and the non-co-ordinated oxygen atom O(2) on a neighbouring chain (Fig. 2) which, when combined with the DD:AA interaction, leads to the formation of 11- and 19-membered rings. Since the three intermolecular hydrogen bonds are essentially coplanar, the structure can be considered as consisting of hydrogen bonded layers linked together by zinc ions (Fig. 3). In this structure the NH groups all act as hydrogen bond donors, while co-ordinated oxygen atom O(1) accepts one hydrogen bond and non-co-ordinated oxygen atom O(2) accepts two.

Structure of $[Zn(tu)_2(\mu\text{-mal})]$, 3

The asymmetric unit of compound **3**, as illustrated by the labelled unprimed atoms of Fig. 4, consists of a zinc centre to which two thiourea ligands and one malonate anion are co-ordinated. Co-ordination of the latter serves to link the asymmetric units into infinite spiral chains along the *b* axis, with the malonate bridging the metal centres in a *cis* conformation employing O(1) and O(3).

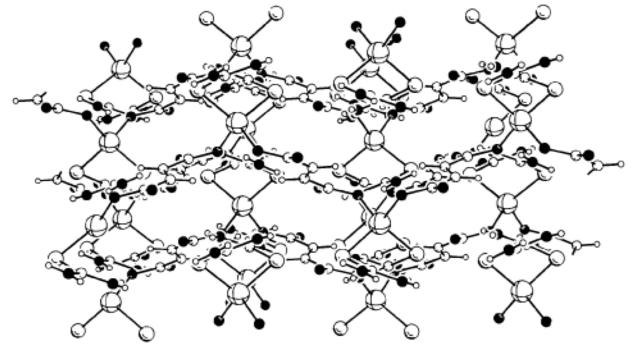

Fig. 3 Layer structure in compound **2**.

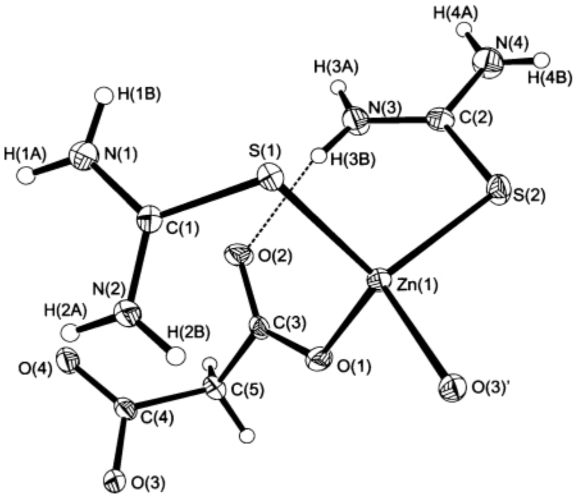

Fig. 4 The zinc co-ordination sphere in compound **3**. The hydrogen bond distances (Å) and angles (°) are N(3)···O(2) 2.834(3), H(3B)···O(2) 2.02(2), N(3)–H(3B)···O(2) 151(3).

Each thiourea hydrogen bonds *via* a N–H···O interaction to an unco-ordinated carboxylate oxygen atom, leading to the presence of two eight-membered hydrogen-bonded rings around each metal centre [graph set S(8)]. Further hydrogen bonds within the spiral chains serve to link one of the thioureas to a malonate through two N–H···O interactions in a DD:AA orientation involving the parallel NH groups N(1)–H(1A) and N(2)–H(2A) and the co-ordinated carboxylate oxygen atoms O(3) and O(1) respectively (Fig. 5).

The inter-chain interactions also involve two hydrogen bonds in a DD:AA orientation, in this case between the parallel NH groups N(3)–H(3A) and N(4)–H(4A) and the unco-ordinated oxygen atoms O(2) and O(4) respectively (Fig. 5). These hydrogen bonds serve to link the chains into sheets. The interactions between sheets are much weaker than those within them, with just one N–H···S hydrogen bond involved [N(1)···S(1) 3.464(2), H(1B)···S(1) 2.61(2) Å, N(1)–H(1B)···S(1) 163(3)°]. N(4)–H(4B) is notable in that it does not act as a hydrogen bond donor.

Compound **3** is the only structure observed in the zinc–thiourea–dicarboxylate system in which DD:AA interactions are observed both within chains and between them. These interactions are possible for **3** as the short methylene linker between the carboxylate groups allows both the co-ordinated oxygen atoms, O(1) and O(3), and the unco-ordinated oxygen atoms, O(2) and O(4), to act as hydrogen bond acceptors to two parallel NH groups from a thiourea ligand.

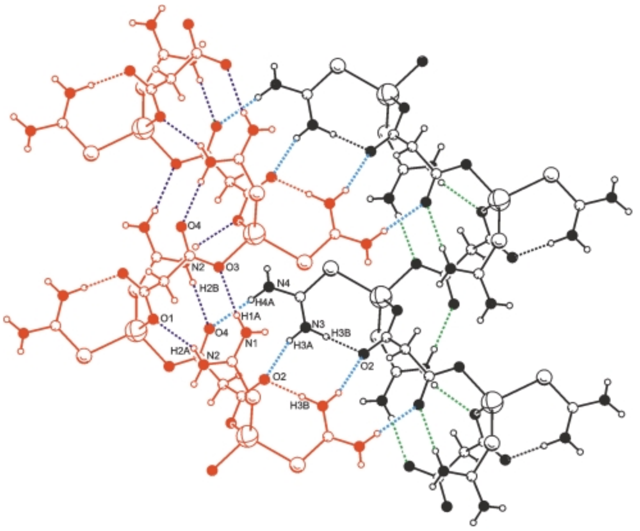

Fig. 5 Hydrogen bonding in compound **3**. The intra-chain hydrogen bonds are depicted in blue or green and have distances (Å) and angles (°) of N(2)···O(4) 2.864(3), H(2B)···O(4) 1.99(2), N(2)–H(2B)···O(4) 172(2); N(1)···O(3) 2.923(3), H(1A)···O(3) 2.08(2), N(1)–H(1A)···O(3) 167(2); and N(2)···O(1) 2.905(3), H(2A)···O(1) 2.09(2), N(2)–H(2A)···O(1) 154(2). The inter-chain hydrogen bonds are depicted in cyan and have distances (Å) and angles (°) of N(3)···O(2) 2.840(3), H(3A)···O(2) 2.02(2), N(3)–H(3A)···O(2) 156(2); and N(4)···O(4) 2.946(3), H(4A)···O(4) 2.06(2), N(4)–H(4A)···O(4) 173(3).

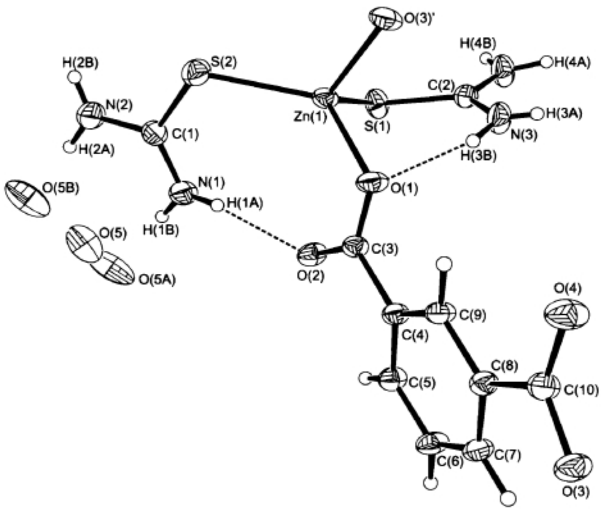

Fig. 6 The zinc co-ordination sphere in compound **4**. The hydrogen bond distances (Å) and angles (°) are N(1)···O(2) 2.817(4), H(1A)···O(2) 2.06(4), N(1)–H(1A)···O(2) 167(4); and N(3)···O(1) 3.079(4), H(3B)···O(1) 2.20(5), N(3)–H(3B)···O(1) 161(4).

Structure of $[Zn(tu)_2(\mu\text{-ipht})]\cdot H_2O$, 4

The asymmetric unit of compound **4**, illustrated in Fig. 6, consists of a zinc centre, to which is co-ordinated two thiourea ligands and one isophthalate ligand, and one water molecule disordered between three sites in a 2:2:1 ratio between O(5), O(5A) and O(5B) respectively. The asymmetric units are linked together *via* the isophthalate to form infinite chains along the crystallographic *c* axis. The isophthalate ligands bridge the metal centres in a *trans* conformation employing O(1) and O(3).

There are intramolecular hydrogen bonds between amino hydrogen atoms and both the co-ordinated and unco-ordinated oxygen atoms of one of the carboxylate groups giving rise to S(6) rings and S(8) rings respectively. The hydrogen bonding motifs are reflected in the marked difference in the two Zn–S distances, with Zn–S(1) 2.3451(10) Å and Zn–S(2) 2.2943(10) Å, and it is consistent with related structures that S(6) rings involve longer Zn–S bonds than S(8) rings.

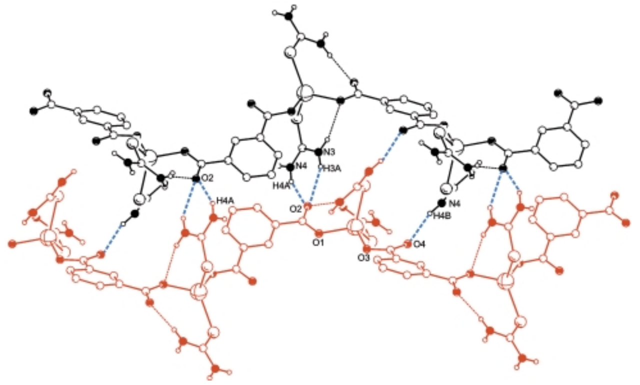

Fig. 7 Inter-chain hydrogen bonding in compound **4**. The hydrogen bond distances (Å) and angles (°) are N(3)···O(2) 2.938(4), H(3A)···O(2) 2.33(4), N(3)–H(3A)···O(2) 151(5); N(4)···O(2) 2.860(4), H(4A)···O(2) 2.05(5), N(4)–H(4A)···O(2) 156(4); and N(4)···O(4) 2.840(4), H(4B)···O(4) 2.08(5), N(4)–H(4B)···O(4) 159(4).

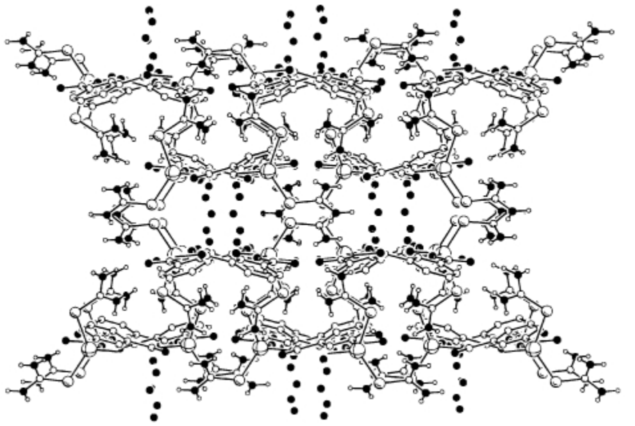

Fig. 8 Packing in compound **4** showing the occupation of the channels by included water molecules.

The chains are linked through three N–H···O hydrogen bonds to non-co-ordinated oxygen atoms, two to O(2) [generating the graph set $R_2^1(6)$] and one to O(4) (Fig. 7). Further linking of the chains occurs through a relatively long DA:AD interaction, involving two N–H···S hydrogen bonds [N(2)···S(2) 3.450(4), H(2B)···S(2) 2.75(5) Å, N(2)–H(2B)···S(2) 146(4)°, graph set $R_2^2(8)$]. These interactions generate a gross structure containing channels of approximate dimensions 4.5 × 6 Å within which the disordered water molecules are included (Fig. 8). The water takes up one of three positions, which presumably indicates a small energy separation between the oxygen atom acting as a hydrogen bond acceptor to N(1)–H(1B) [O(5A)], N(2)–H(2A) [O(5B)] or both of these [O(5)] in an analogous manner to the carboxylate oxygen O(2) [N(1)···O(5) 2.84(1), H(1B)···O(5) 2.08(5) Å, N(1)–H(1B)···O(5) 158(4)°; N(2)···O(5B) 2.71(2), H(2A)···O(5B) 1.76(5) Å, N(2)–H(2A)···O(5B) 176(4)°].

Structure of $[Zn(tu)_2(\mu\text{-citr})]$, 5

The asymmetric unit of compound **5**, as illustrated by the labelled unprimed atoms of Fig. 9, consists of one zinc centre, to which is co-ordinated two thiourea ligands and one citraconate anion. Co-ordination of the citraconate links zinc centres into infinite polymeric spirals along the *b* axis. These spirals are similar to those observed in the recently reported[20] structure of $[Zn(tu)_2(\mu\text{-male})]$ **9** which was prepared from the reaction of zinc sulfate, thiourea and maleic anhydride. The main differences between the structures of **5** and **9** lie in the packing of the spirals: in **9** the spirals are in a square-based array, whereas for **5** they constitute a hexagonal-based array (Fig. 10), the difference at least in part due to the steric effects of the anion methyl

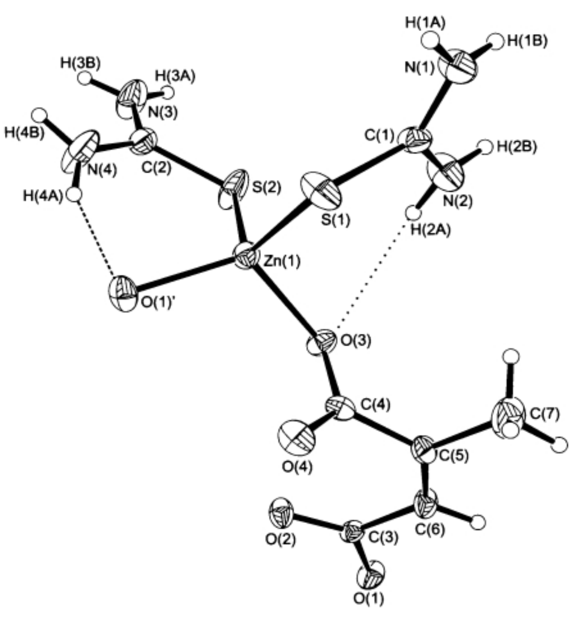

Fig. 9 The zinc co-ordination sphere in compound **5**. The hydrogen bond distances (Å) and angles (°) are N(4)···O(1) 2.856(8), H(4A)···O(1) 2.04(4), N(4)–H(4A)···O(1) 153(6); and N(2)···O(3) 3.405(7), H(2A)···O(3) 2.57(4), N(2)–H(2A)···O(3) 156(7).

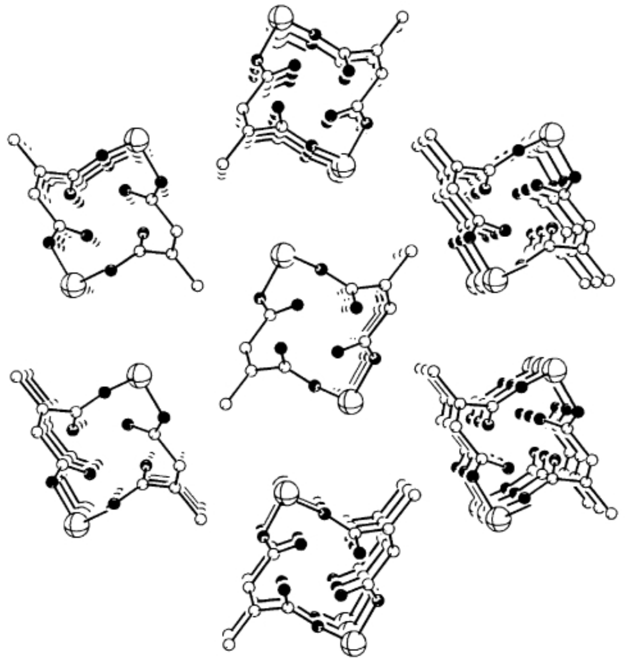

Fig. 10 The hexagonal array of spirals in compound **5**. Thiourea ligands have been omitted for clarity.

groups. In addition, all the spirals in **5** have the same handedness, in contrast to **9**.

The Zn–S distances in compound **5** are markedly different at 2.295(2) and 2.334(2) Å as are the Zn–O distances at 1.948(4) and 1.982(4) Å. The presence of *cis* carboxylates means that one of these groups [C(4)O(3)O(4)] is orientated approximately perpendicular to the plane defined by the carbon atoms in the anion. As in the structure of **3**, there are two intramolecular hydrogen bonds, though in this case both are to the co-ordinated oxygen atoms, O(1) and O(3), and give rise to S(6) rings. The interaction involving H(2A), though reasonably directional and the only hydrogen bond this proton makes, is rather long [N(2)···O(3) 3.405(7), H(2A)···O(3) 2.57(4) Å, N(2)–H(2A)···O(3) 156(7)°].

Hydrogen bonds between the parallel NH groups N(1)–H(1B) and N(2)–H(2B) and the non-co-ordinated oxygen atoms, O(4) and O(2) respectively, serve to link the spiral chains into sheets along the *a* axis *via* the generation of 11-membered hydrogen bonded rings. An additional hydrogen bond between N(1)–H(1A) and co-ordinated oxygen atom O(3) reinforces this interaction (Fig. 11a). The spirals are also linked into sheets along the *c* axis *via* three hydrogen bonds. Again these interactions involve the parallel NH groups on one thiourea ligand, N(3)–H(3B) and N(4)–H(4B), and the non-co-ordinated oxygen atoms O(2) and O(4) respectively, though this time the oxygens are on different citraconate ligands, which leads to the formation of 12-membered rings. The third linking hydrogen bond is between N(3)–H(3A) and co-ordinated oxygen atom O(1) on a third citraconate (Fig. 11b). In contrast to the hydrogen bonds linking the chains along the *a* axis, each chain acts as hydrogen bond donors to citraconates in one neighbouring chain, and hydrogen bond acceptors to thioureas in another. In the structure all NH groups act as hydrogen bond donors and all oxygen atoms accept two hydrogen bonds.

These inter-spiral hydrogen bonding patterns are identical to those observed in compound **9**. However, in **9** there are no intramolecular N–H···O hydrogen bonds leading to S(6) and/or S(8) rings: in contrast the two NH groups not involved in inter-spiral hydrogen bonds form intramolecular N–H···S hydrogen bonds in an analogous manner to those of **2**.

Structure of [Zn(tu)$_2$(μ-pht)], 6

The structure of compound **6** has many similarities to that of **5** both in terms of chain formation and supramolecular structure. The asymmetric unit (Fig. 12) consists of a zinc centre to which is co-ordinated two thioureas and one phthalate, and co-ordination of the latter serves to link the zinc centres into infinite spirals along the *b* axis as in **5**. The steric demands of the two *ortho* carboxylates on the phthalate lead to one of these groups [C(3)O(1)O(2)] being orientated approximately perpendicular to the plane of the benzene ring.

The hydrogen bonding present within the structure of compound **6** is very similar to that observed in **5**. The orientation of the thiourea ligands suggests the presence of two intramolecular N–H···O hydrogen bonds giving rise to 6-membered hydrogen bonded rings as in **5**, though closer inspection reveals the interaction between N(3)–H(3A) and O(1) may be too long to be significant [N(3)···O(1) 3.545(4), H(3A)···O(1) 2.74(2) Å, N(3)–H(3A)···O(1) 151(3)°]. The spirals are linked into sheets along the *a* axis *via* three hydrogen bonds, including two that involve the parallel NH groups N(3)–H(3B) and N(4)–H(4B) and lead to the formation of 11-membered hydrogen bonded rings [N(3)···O(3) 2.927(4), H(3B)···O(3) 2.06(1) Å, N(3)–H(3B)···O(3) 165(3)°; N(4)···O(2) 2.885(4), H(4B)···O(2) 2.001(6) Å, N(4)–H(4B)···O(2) 172(3)°; and N(4)···O(1) 2.954(4), H(4A)···O(1) 2.067(5) Å, N(4)–H(4A)···O(1) 175(3)°]. Further linking of spirals occurs along the *c* axis involving two parallel NH groups hydrogen bonding to non-co-ordinated oxygen atoms on different phthalates, though a possible third hydrogen bond between N(2)–H(2A) and O(4) is too long to be significant [N(1)···O(2) 3.026(4), H(1B)···O(2) 2.17(2) Å, N(1)–H(1B)···O(2) 163(5)°; N(2)···O(3) 3.041(4), H(2B)···O(3) 2.19(2) Å, N(2)–H(2B)···O(3) 160(4)°; and N(2)···O(4) 3.621(5), H(2A)···O(4) 2.76(1) Å, N(2)–H(2A)···O(4) 163(4)°].

Despite the incorporation of an aromatic ring, the intermolecular hydrogen bonding observed in compounds **5**, **6** and **9** is virtually identical. This can be rationalised by consideration of the relative positions of the oxygen atoms which are comparable in the three compounds, as witnessed by the oxygen–oxygen distances [O(1)···O(3) 3.104, O(2)···O(3) 3.124 Å within each phthalate, O(2)···O(3) 3.254 Å between non-co-ordinated oxygen atoms in different phthalates; *cf.* equivalent values for **5** are 3.181, 3.140 and 3.411 Å, and for **9** 3.067, 3.433

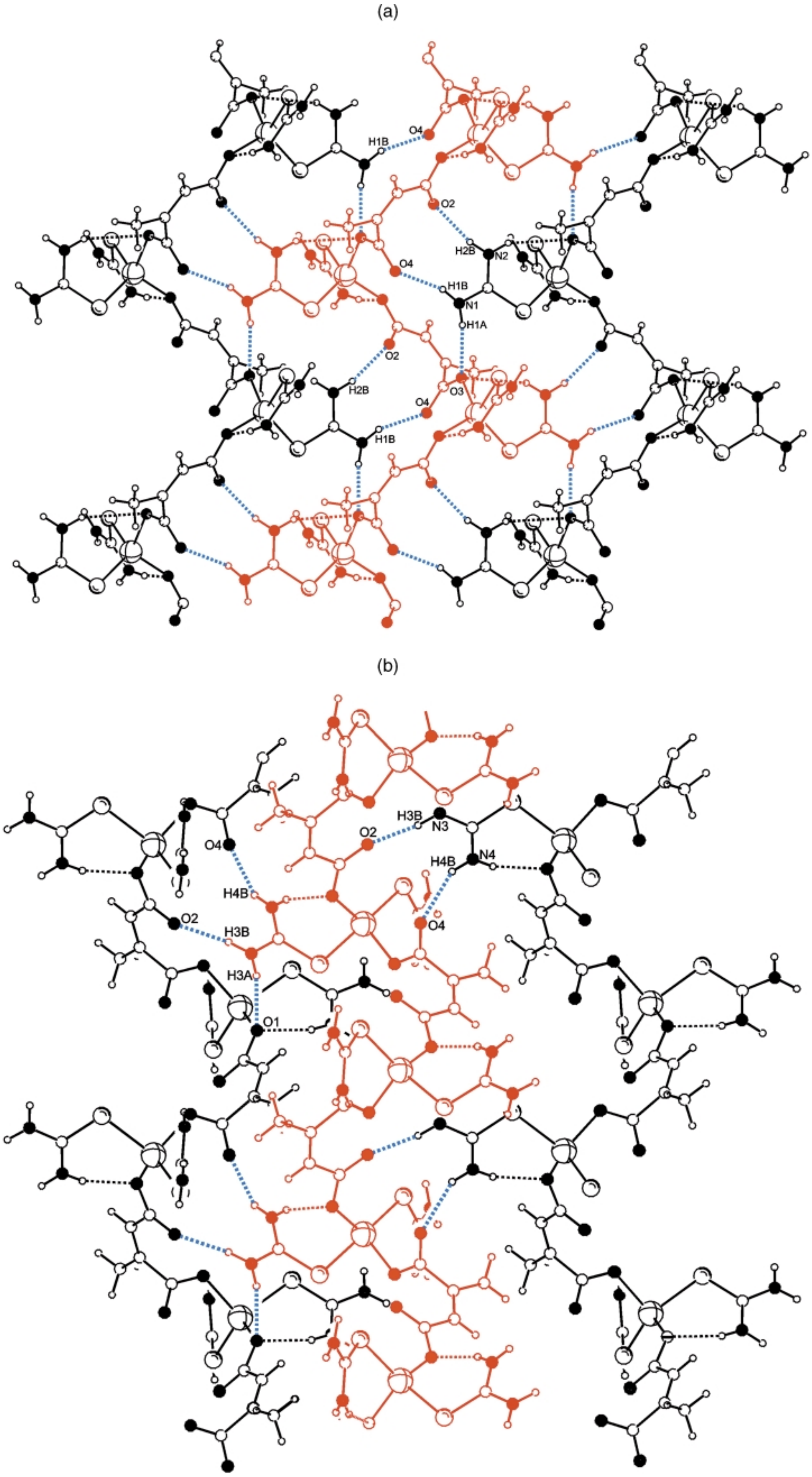

Fig. 11 Inter-chain hydrogen bonding in compound **5** along the *a* (a) and *c* axes (b). The hydrogen bond distances (Å) and angles (°) are for (a) N(1) · · · O(4) 2.913(7), H(1B) · · · O(4) 2.10(4), N(1)–H(1B) · · · O(4) 157(7); N(2) · · · O(2) 2.945(7), H(2B) · · · O(2) 2.07(3), N(2)–H(2B) · · · O(2) 169(6); N(1) · · · O(3) 2.999(8), H(1A) · · · O(3) 2.14(2), N(1)–H(1A) · · · O(3) 173(9); and for (b) N(3) · · · O(2) 2.910(8), H(3B) · · · O(2) 2.03(3), N(3)–H(3B) · · · O(2) 168(6); N(4) · · · O(4) 3.009(9), H(4B) · · · O(4) 2.22(6), N(4)–H(4B) · · · O(4) 148(10); and N(3) · · · O(1) 3.018(10), H(3A) · · · O(1) 2.13(3), N(3)–H(3A) · · · O(1) 174(6).

and 3.531 Å]. The similarities in the relative carboxylate positions within the anion backbones can also be demonstrated by the angle between the carboxylate planes, which is 89.9° in **5** and 91.1° in **6**.

Structure of [Zn(tu)$_2$(μ-male)]·H$_2$O, 7

The asymmetric unit of compound **7**, as illustrated by the labelled unprimed atoms of Fig. 13, consists of one zinc

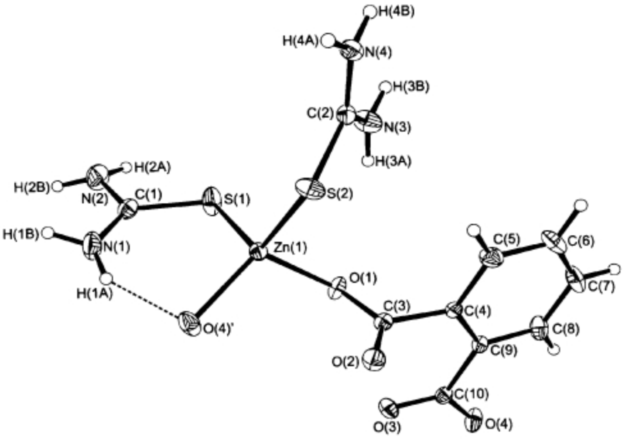

Fig. 12 The zinc co-ordination sphere in compound **6**. The hydrogen bond distances (Å) and angles (°) are N(1)···O(4) 2.864(4), H(1A)···O(4) 2.07(2), N(1)–H(1A)···O(4) 149(3).

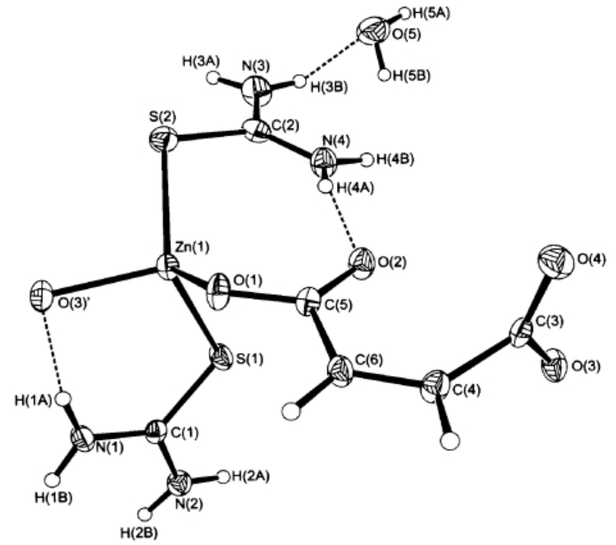

Fig. 13 The zinc co-ordination sphere in compound **7**. The hydrogen bond distances (Å) and angles (°) are N(1)···O(3) 2.813(3), H(1A)···O(3) 1.94(2), N(1)–H(1A)···O(3) 169(2); N(4)···O(2) 2.979(4), H(4A)···O(2) 2.13(2), N(4)–H(4A)···O(2) 165(3); and N(3)···O(5) 3.110(4), H(3B)···O(5) 2.30(2), N(3)–H(3B)···O(5) 157(3).

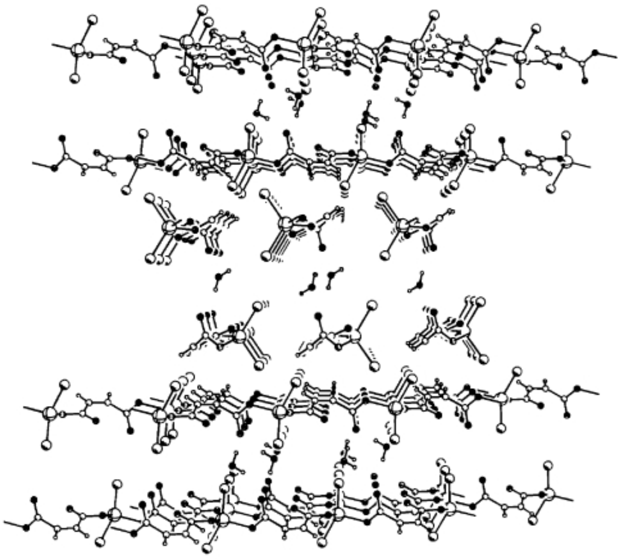

Fig. 14 Packing of the zinc–maleate chains in compound **7**. Only the sulfur atoms of the thioureas have been shown for clarity.

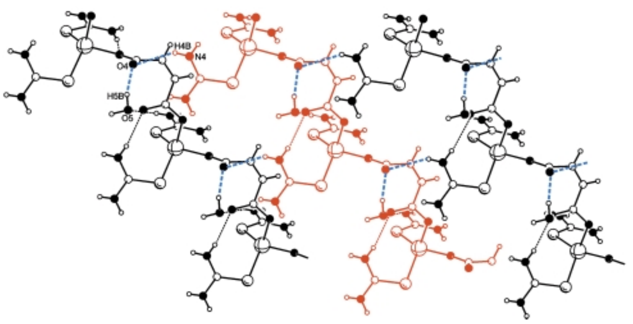

Fig. 15 Inter-chain hydrogen bonding in compound **7** leading to sheet formation. The hydrogen bond distances (Å) and angles (°) are N(4)···O(4) 3.210(3), H(4B)···O(4) 2.44(2), N(4)–H(4B)···O(4) 146(3); and O(5)···O(4) 2.814(4), H(5B)···O(4) 1.99(2), O(5)–H(5B)···O(4) 174(5).

centre, to which is co-ordinated two thiourea ligands and one maleate anion, plus one non-co-ordinated water molecule. Co-ordination of the maleate serves to link the zinc centres into polymeric chains, and as in **5** and **6**, the presence of the *cis* carboxylates leads to one of these groups [C(3)O(3)O(4)] being orientated out of the maleate plane.

The two Zn–S distances are markedly different, with Zn–S(1) 2.3304(12) and Zn–S(2) 2.294(2) Å. As with compound **3**, this can be related to the intramolecular hydrogen bonding, which involves two N–H···O hydrogen bonds to co-ordinated and unco-ordinated oxygen atoms on different carboxylates, leading to the formation of S(6) and S(8) rings. The longer Zn–S bond is, as before, part of the 6-membered hydrogen bonded ring.

The presence of the water molecule has resulted in dramatic changes to the supramolecular structure when compared with that of the anhydrous complex **9**. The chains in **7** do not form spirals, and are orientated in two perpendicular directions (Fig. 14). The chains are linked into sheets that run along the *a* and *b* directions *via* a long N–H···O hydrogen bond, in addition to both N–H···O and O–H···O hydrogen bonds where the water acts as the hydrogen bond acceptor and donor respectively (Fig. 15).

Interactions between the sheets occur in two different manners. Perpendicular chains interdigitate, and are linked through two N–H···O hydrogen bonds, involving non-co-ordinated oxygen atom O(2) and co-ordinated oxygen atom O(1), plus a longer contact to S(2) [N(1)···O(2) 2.941(3), H(1B)···O(2) 2.14(2) Å, N(1)–H(1B)···O(2) 155(3)°; N(2)···O(1) 2.882(3), H(2A)···O(1) 2.02(2) Å, N(2)–H(2A)···O(1) 172(2)°; N(2)···S(2) 3.557(5), H(2B)···S(2) 2.86(3) Å, N(2)–H(2B)···S(2) 139(2)°]. In turn, these pairs of chains are linked along the *c* axis through two hydrogen bonds involving the water molecule [O(5)···O(4) 2.970(5), H(5A)···O(4) 2.59(3) Å, O(5)–H(5A)···O(4) 106(2)°; and N(3)···O(5) 2.871(4), H(3A)···O(5) 2.03(2) Å, N(3)–H(3A)···O(5) 162(3)°]. As such, all NH and OH groups in this structure act as hydrogen bond donors and all oxygen atoms act as hydrogen bond acceptors.

Structure of $[Zn(tu)_2(\mu\text{-hpht})]_2$, 8

In contrast to the structures of compounds **1**–**7**, **8** is not polymeric, but consists of discrete $[Zn(tu)_2(\mu\text{-hpht})]_2$ dimers, in which two homophthalate anions are bridging pairs of zinc atoms. The asymmetric unit consists of two independent fragments each of which straddles a crystallographic inversion centre, transformation through which leads to the generation of two independent rings, which lie approximately perpendicular to each other. One of the rings is shown in Fig. 16.

The orientation around each zinc centre is distorted tetrahedral, with angles ranging from 96.26(11) to 116.10(9) Å about Zn(1) and from 94.24(12) to 115.58(10) Å about Zn(2). There are two intramolecular hydrogen bonds per zinc centre, involving N–H···O hydrogen bonds to co-ordinated and unco-ordinated oxygen atoms on different carboxylates, as in **7**, leading to the formation of S(6) and S(8) rings. As in other compounds, the presence of these motifs is reflected in the Zn–S distances, with the longer Zn–S bond forming part of the 6-membered hydrogen bonded ring.

The cyclic dimers containing Zn(1) and Zn(2) are linked by N–H···O and N–H···S hydrogen bonds into chains lying along the *c* axis in the supramolecular array (Fig. 17). These hydrogen-bonded chains are cross-linked by further N–H···O hydrogen bonds into the three-dimensional structure. It is interesting that the two independent ring systems do not form equivalent hydrogen bonding patterns. Indeed there are five independent hydrogen bonds linking the chains into the three-dimensional structure: two between ring systems both containing Zn(2), one between ring systems both containing Zn(1), and two between rings one of which contains Zn(1) and the other Zn(2). This structure is unusual in that there are two potential hydrogen bond donors in each ring [N(2)–H(2A), N(4)–H(4B), N(5)–H(5B) and N(7)–H(7B)] that are not involved in strong hydrogen bonds. Instead N(2)–H(2A) forms two very long and bent contacts to oxygen atoms, N(4)–H(4B) and N(5)–H(5B) form long N–H···π interactions and N(7)–H(7B) forms a long N–H···N hydrogen bond. Moreover, the co-ordinated oxygen atoms O(1) and O(8) which are directed into the centre of the rings do not accept hydrogen bonds. The distances across the rings, as represented by the O(1)···O(1)′ and O(8)···O(8)′ distances, are 4.9 and 5.3 Å respectively.

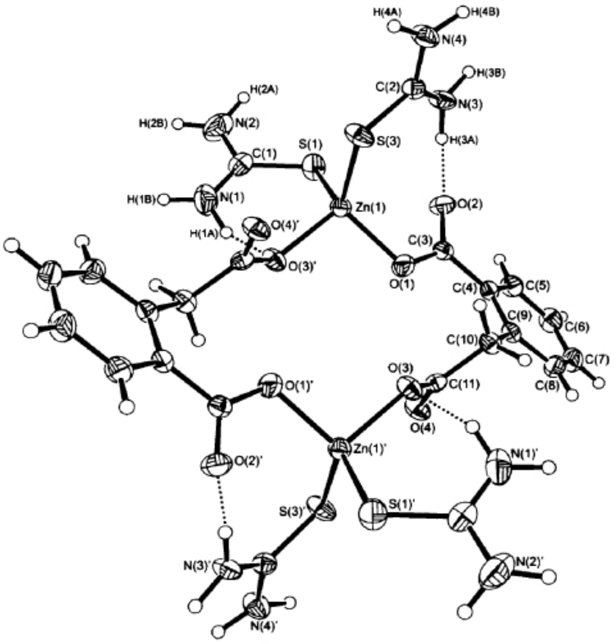

Fig. 16 The molecular structure of one of the independent ring systems present in the structure of compound **8**. Atoms in the asymmetric unit have unprimed labels. The hydrogen bond distances (Å) and angles (°) are N(1)···O(3) 2.971(6), H(1A)···O(3) 2.25(5), N(1)–H(1A)···O(3) 138(6); and N(3)···O(2) 2.881(4), H(3A)···O(2) 1.997(7), N(3)–H(3A)···O(2) 172(4). The analogous distances (Å) and angles (°) in the other ring are N(7)···O(5) 2.911(5), H(7A)···O(5) 2.05(1), N(7)–H(7A)···O(5) 164(5); and N(6)···O(7) 2.998(5), H(6A)···O(7) 2.113(7), N(6)–H(6A)···O(7) 172(3).

In view of the non-participation of potential hydrogen bond donors and acceptors in the supramolecular structure it was thought possible that compound **8** was a kinetic product from the reaction, whereas a chain structure may be thermodynamically favoured. Zhang *et al.*[20] report the isolation of the dimeric species $[Zn(tu)(OH_2)(\mu\text{-male})]_2\cdot 4H_2O$ as a kinetic product in the formation of compound **9**, though it is uncertain whether it is the ring structure or the ligand set that leads to **9** being the thermodynamic product. In order to test whether **8** can be converted into a chain structure, an aqueous solution containing $[ZnCl_2(tu)_4]$ and sodium homophthalate was refluxed for ten minutes before allowing to crystallise. Crystallisation was more rapid than in the initial synthesis, but the unit cell data collected on a suitable crystal indicated categorically that the crystalline product was **8**. Hence it would appear that reflux merely increases the rate of formation of **8** and there is no evidence of the formation of a chain structure.

Comparison of the structures

It is important to note that complexes **2**–**8** were the only products to be isolated from the reaction mixtures, strongly suggesting that the reactions and crystallisations are selective. The most obvious difference in the structures of these compounds is that **2**–**7** form co-ordination polymers whereas **8** forms discrete dimers. It is not readily apparent why this is so, especially given the relative inefficiency of hydrogen bonding in **8**, and although

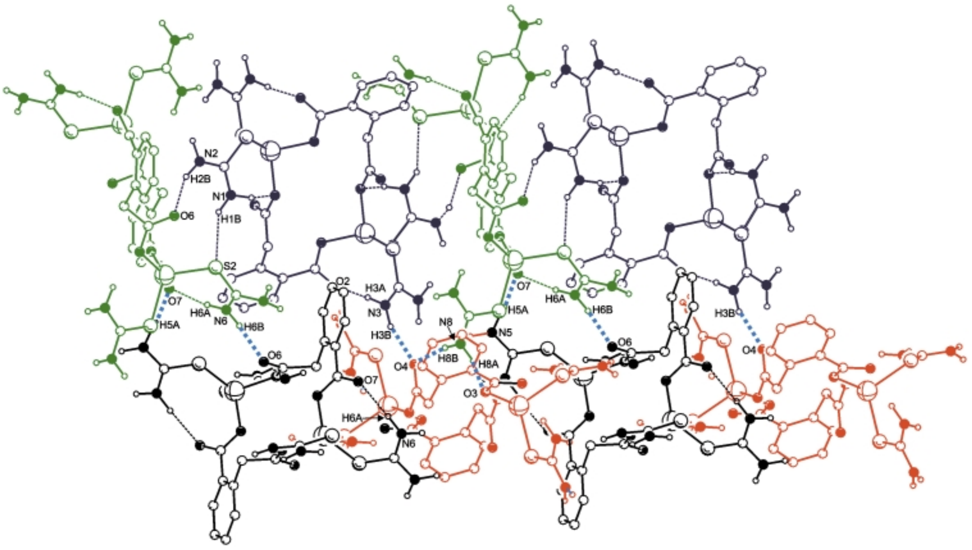

Fig. 17 Interactions between the rings in compound **8**. The hydrogen bond distances (Å) and angles (°) are N(2)···O(6) 2.885(6), H(2B)···O(6) 2.04(2), N(2)–H(2B)···O(6) 159(4); N(1)···S(2) 3.408(4), H(1B)···S(2) 2.62(3), N(1)–H(1B)···S(2) 148(4); N(5)···O(7) 3.065(5), H(5A)···O(7) 2.21(2), N(5)–H(5A)···O(7) 160(4); N(6)···O(6) 2.921(5), H(6B)···O(6) 2.04(1), N(6)–H(6B)···O(6) 169(5); N(3)···O(4) 2.926(4), H(3B)···O(4) 2.07(1), N(3)–H(3B)···O(4) 160(3); N(8)···O(4) 2.964(5), H(8B)···O(4) 2.085(10), N(8)–H(8B)···O(4) 169(4); N(8)···O(3) 3.000(5), H(8A)···O(3) 2.113(7), N(8)–H(8A)···O(3) 174(3).

there are no polymeric structures containing bridging homophthalate in the Cambridge Structural Database[11] there is no obvious reason preventing formation of such chains. Ring systems analogous to that in **8** have previously been observed for both isophthalate[6] and fumarate.[8]

There are three main motifs of intramolecular hydrogen bonds that have been observed in the structures of compounds **1**–**9**. These are S(6) rings, involving hydrogen bonds to co-ordinated carboxylate oxygen atoms (observed in **4**, **5**, **6**, **7** and **8**), S(8) rings, involving hydrogen bonds to non-co-ordinated carboxylate oxygen atoms (observed in **1**, **3**, **4**, **7** and **8**), and $R_2^2(8)$ rings, involving two N–H · · · S hydrogen bonds around the zinc centre (observed in **2** and **9**). Of the two motifs involving N–H · · · O hydrogen bonds, S(8) rings involve relatively short Zn–S bonds (mean Zn–S distance 2.34 Å in unconstrained thiourea complexes) and larger S–Zn–O bond angles, though the motif adopted has little discernible effect on Zn–O bond distances.

Bearing these three motifs in mind, together with the number of ways in which the first two can be combined, there is evidently considerable flexibility in the relative orientation of the thiourea ligands. This flexibility allows the compounds to maximise intermolecular hydrogen bonding between the chains or rings without loss of intramolecular hydrogen bonding. The conformation adopted in compound **2**, considered in isolation, is surprising given Etter's rules[21] and the relative strength of N–H · · · O hydrogen bonds with respect to N–H · · · S hydrogen bonds. However, the weakness of the observed intramolecular interactions is counterbalanced by the inter-chain interactions, especially the DD : AA interactions between the thiourea and fumarate ligands. This supramolecular structure would appear to be unfavourable for isophthalate, citraconate, phthalate, maleate and homophthalate as the relative orientation of the carboxylate groups (given by the C–CO_2 bond vectors) is not 180°. In the structures of compounds **3**–**8** DD : AA motifs in which the two oxygen atoms of a carboxylate act as the acceptors are not possible due to the manner in which the carboxylates co-ordinate, which effectively involves one of the parallel hydrogen bond acceptors. This can be witnessed in the Zn–O–C–C torsion angles which range from 141 to 178° for compounds **3**–**8** but are 50° for **2**.

DD : AA motifs are observed in a number of other structures, though in these cases the hydrogen bond acceptors are oxygen atoms on different carboxylate groups. Thus both the sets of co-ordinated and unco-ordinated oxygens act as double hydrogen bond acceptors in compound **3** whereas the two unco-ordinated oxygen atoms within a dicarboxylate, or two oxygen atoms in separate dicarboxylates, act as double hydrogen bond acceptors in **5**, **6** and **9**. Such interactions are not possible in **1** or **4** due to the distance between the oxygen atoms on different carboxylates. The hydrogen bonding parameters suggest a decrease in energy of the DD : AA interactions with increasing ring size. The flexibility of the zinc–dicarboxylate backbone is also important in determining the relative orientation of the thiourea ligands. The spiral orientations of **5**, **6** and **9** direct the thioureas in four directions whereas in **3** and **4** two thioureas are directed inwards and two outwards relative to the axis of the chain.

The structures described in this paper illustrate clearly how the distance between carboxylate groups in dicarboxylates and their relative orientation affects the nature of intra- and inter-molecular hydrogen bonding. A comparison of the structures of compounds **5**, **6** and **9** shows how quite complex hydrogen bonding patterns can be mirrored in the supramolecular arrays despite differences in both the packing and the relative directions of the spirals. In contrast, a comparison of the structures of **7** and **9** illustrates how seemingly small changes like the addition of an included water molecule are associated with dramatic changes in the supramolecular structure.

Table 2 Crystal data for compounds **2**, **3**, **4**, **5**, **6**, **7** and **8**

	2	**3**	**4**	**5**	**6**	**7**	**8**
Empirical formula	$C_6H_{10}N_4O_4S_2Zn$	$C_5H_{10}N_4O_4S_2Zn$	$C_{10}H_{14}N_4O_5S_2Zn$	$C_7H_{12}N_4O_4S_2Zn$	$C_{10}H_{12}N_4O_4S_2Zn$	$C_6H_{12}N_4O_5S_2Zn$	$C_{11}H_{14}N_4O_4S_2Zn$
M	331.67	319.66	399.74	345.70	381.73	349.69	791.5
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbcn*	$P2_1/n$	*C*2/*c*	$P2_12_12_1$	$P2_12_12_1$	*C*2/*c*	$P2_1/n$
a/Å	14.831(1)	7.5617(9)	20.257(3)	8.360(0)	8.307(2)	12.758(3)	16.767(2)
b/Å	6.901(1)	8.164(1)	9.795(1)	10.981(2)	10.919(2)	8.8030(10)	11.3460(10)
c/Å	11.379(1)	18.340(2)	16.303(3)	14.717(3)	15.890(2)	23.355(4)	17.045(3)
β/°		91.40(2)	94.50(2)			98.07(2)	109.39(1)
U/Å^3	1164.6(2)	1131.9(2)	3224.8(8)	1351.0(4)	1441.3(5)	2597.0(8)	3058.7(7)
Z	4	4	8	4	4	8	8
μ(Mo-Kα)/mm^{-1}	2.476	2.543	1.808	2.138	2.013	2.231	1.901
Reflections collected	1078	2230	3093	1915	1488	2480	5722
Independent reflections	1021	1988	2835	1418	1467	2286	5375
R(int)	0.0065	0.0130	0.0202	0.0282	0.0104	0.0085	0.0105
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0201, 0.0719	0.0250, 0.0641	0.0309, 0.0964	0.0338, 0.0883[a]	0.0214, 0.0573[b]	0.0237, 0.0610	0.0316, 0.1072
(all data)	0.0248, 0.0819	0.0302, 0.0662	0.0422, 0.1033	0.0577, 0.0963	0.0237, 0.0591	0.0333, 0.0640	0.0543, 0.1193

[a] Flack parameter = 0.01(3). [b] Flack parameter = 0.022(13).

Experimental

[ZnCl$_2$(tu)$_4$] was prepared following the literature method.[22] Sodium dicarboxylates were either purchased from commercial sources and used directly (fumarate and maleate) or prepared from the appropriate dicarboxylic acid and either sodium hydroxide or sodium hydrogencarbonate.

Synthesis of [Zn(tu)$_2$(μ-fum)], 2

An aqueous solution of sodium fumarate (36 mg, 0.23 mmol) was added to an aqueous solution of [ZnCl$_2$(tu)$_4$] (100 mg, 0.23 mmol) with no discernible change. After several hours a colourless crystalline precipitate was observed which was separated by filtration. Yield 53 mg (71%) (Found: C, 21.7; H, 2.96; N, 16.4. $C_6H_{10}N_4O_4S_2Zn$ requires C, 21.7; H, 3.04; N, 16.9%). IR/cm^{-1}: ν(NH) 3429s, 3382s, 3309s and 3137s; ν(CO$_2$)/δ(NH$_2$) 1632s, 1571s, 1513m and 1363s. Single crystals suitable for X-ray analysis were obtained by carrying the reaction out on a smaller scale in a more dilute solution. These crystals grew over several days.

Syntheses of compounds **3**–**8** were carried out using [ZnCl$_2$(tu)$_4$] (100 mg) and one equivalent of the appropriate sodium dicarboxylate in an analogous manner to that of **2**. [Zn(tu)$_2$(μ-mal)], **3**: Yield 51 mg (70%) (Found: C, 18.7; H, 3.15; N, 17.3. $C_5H_{10}N_4O_4S_2Zn$ requires C, 18.8; H, 3.15; N, 17.5%); IR/cm^{-1} ν(NH) 3453m, 3365s, 3290s and 3134s; ν(CO$_2$)/δ(NH$_2$) 1678s, 1638s, 1617s and 1411s. [Zn(tu)$_2$(μ-ipht)]·H$_2$O, **4**: Yield 71 mg (78%) (Found: C, 30.2; H, 3.54; N, 14.0. $C_{10}H_{14}N_4O_5S_2Zn$ requires C, 30.0; H, 3.53; N, 14.0%); IR/cm^{-1} ν(NH)/ν(OH) 3408s, 3333s and 3129s (br); ν(CO$_2$)/δ(NH$_2$) 1628s, 1607s, 1578m, 1552s, 1480m and 1394s. [Zn(tu)$_2$(μ-citr)], **5**: Yield 45 mg (62%) (Found: C, 24.4; H, 3.52; N, 15.9. $C_7H_{12}N_4O_4S_2Zn$ requires C, 24.3; H, 3.50; N, 16.2%); IR/cm^{-1} ν(NH) 3435s, 3381s, 3311s, 3204s and 3155s; ν(CO$_2$)/δ(NH$_2$) 1661s, 1643s, 1606s, 1582s, 1516s, 1440s and 1394s. [Zn(tu)$_2$(μ-pht)], **6**: Yield 60 mg (69%) (Found: C, 31.5; H, 3.16; N, 14.6. $C_{10}H_{12}N_4O_4S_2Zn$ requires C, 31.5; H, 3.16; N, 14.7%); IR/cm^{-1} ν(NH) 3455m, 3425s, 3313s and 3205s; ν(CO$_2$)/δ(NH$_2$) 1659s, 1645m, 1598s, 1570s, 1507s, 1441s and 1360vs. [Zn(tu)$_2$(μ-male)]·H$_2$O, **7**: Yield 57 mg (72%) (Found: C, 20.6; H, 3.44; N, 16.3. $C_6H_{12}N_4O_5S_2Zn$ requires C, 20.6; H, 3.46; N, 16.0%); IR/cm^{-1} ν(NH)/ν(OH) 3413s, 3313s, 3193s and 3148s; ν(CO$_2$)/δ(NH$_2$) 1670m, 1642s, 1580s, 1514s and 1420s. [Zn(tu)$_2$(μ-hpht)]$_2$, **8**: Yield 75 mg (83%) (Found: C, 33.4; H, 3.62; N, 14.0. $C_{11}H_{14}N_4O_4S_2Zn$ requires C, 33.4; H, 3.57; N, 14.2%); IR/cm^{-1} ν(NH) 3494m, 3416m, 3316s and 3183s; ν(CO$_2$)/δ(NH$_2$) 1654s, 1628s, 1584s, 1554s, 1508m, 1446m and 1386s.

Crystallography

Table 2 provides a summary of the crystal data, data collection (Mo-Kα) and refinement parameters for compounds **2**–**8**. The hydrogen atoms were included in calculated positions where relevant on carbon atoms, whereas the NH and OH protons were located and refined at a fixed distance of 0.89 Å from the relevant parent atoms. In structures **3**, **5**, **6**, **7** and **8** the distance between hydrogen atoms in each NH$_2$ group was constrained to be 1.54 Å and the thermal parameters of the hydrogen atoms attached to nitrogen and oxygen were refined. In the case of **4** the disordered oxygen positions were refined by allowing the solvent fragments at the three located positions to vibrate isotropically while varying their relative site occupancies. The ratios for the relative occupancies of each fraction of the water oxygen thus defined were subsequently fixed and the fragments allowed to vibrate anisotropically. The positions of the hydrogen atoms in the water molecule could not be located due to disorder.

Calculations were performed using SHELXS 86[23] (structure solutions) and SHELXL 93/SHELXL 97[24] (refinements). Thermal ellipsoid plots were generated using ORTEX.[25] All full matrix least-squares refinements were based on F^2 data.

CCDC reference number 186/2017.

See http://www.rsc.org/suppdata/dt/b0/b003210g/ for crystallographic files in .cif format.

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