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Zinc thiosemicarbazide dicarboxylates: the influence of the anion shape on supramolecular structure

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Abstract

The syntheses and crystal structures of the zinc thiosemicarbazide dicarboxylate compounds [Zn(tsc)$_2$(OH$_2$)$_2$][fumarate] **2**, [Zn(tsc)$_2$(citraconate)]$\cdot$H$_2$O **3**, [Zn(tsc)(μ-1,4-phenylenediacetate)] **4**, [Zn(Ettsc)$_2$(citraconate)]$\cdot$3H$_2$O **5**, [Zn(Ettsc)$_2$(Hphthalate)][Hphthalate]$\cdot$H$_2$O **6**, [Zn(Metsc)$_2$(Hphthalate)][Hphthalate]$\cdot$H$_2$O **7**, [Zn(Me$_2$tsc)$_2$(OH$_2$)][terephthalate]$\cdot$2H$_2$O **8** and [Zn(EtMe$_2$tsc)$_2$(OH$_2$)][terephthalate] **9** are reported. The supramolecular structures of the terephthalate and fumarate compounds **2**, **8** and **9** consist of chains of cations and anions, in which the ions are linked by hydrogen bonding. In contrast, compounds **3**, **5**, **6** and **7** contain carboxylate groups co-ordinated to the metal centre to give either neutral or monocationic species. These differences can be rationalised on the basis of the dicarboxylate structure, in particular the angle between the carboxylate vectors. Compound **4** forms co-ordination polymers in an analogous manner to thiourea derivatives.

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1. Introduction

Crystal engineering is the name often given to the branch of supramolecular chemistry concerned with the *planning and utilisation of crystal-orientated syntheses and the evaluation of the physical and chemical properties of the resultant crystalline materials* [1]. Although routine prediction of crystal structures remains a distant goal, progress in this field has arisen through the identification and use of '*supramolecular synthons*', [2]—small units that are anticipated to interact together strongly, and thus dictate the intermolecular interactions between molecules or ions. Many of these '*supramolecular synthons*' involve multiple hydrogen bonds, and rely on the strength and directionality of these interactions [3]. The geometric preferences of transition metal centres can be exploited to orient hydrogen bonding groups in pre-ordained directions [4].

We have previously shown that the interactions between bis(thiosemicarbazide)nickel [5,6] or–zinc [7] cations and dicarboxylate anions can lead to the formation of one-dimensional chains in which the cations and anions are linked by charge-augmented hydrogen bonds involving DD:AA motifs (D = hydrogen bond donor, A = hydrogen bond acceptor) in which the secondary interactions are all attractive. For example, the metathesis reaction between [Zn(tsc)$_2$](NO$_3$)$_2$ [tsc = thiosemicarbazide] and sodium terephthalate gives [Zn(tsc)$_2$(OH$_2$)$_2$][terephthalate]$\cdot$2H$_2$O **1**, part of the structure of which is shown in Fig. 1. In this paper, we investigate the effects of changing the thiosemicarbazide and the dicarboxylate on the products of this reaction. Substitution of those hydrogen atoms not involved in chain formation by alkyl groups has been shown to affect the presence of the DD:AA interaction in nickel complexes, and the manner in which the chains are linked when they are observed [6]. Variation of the dicarboxylate influences both the relative orientation of, and the distance between the two carboxylate groups. The thiosemicarbazide ligands and dicarboxylates used in this paper are shown in Fig. 2.

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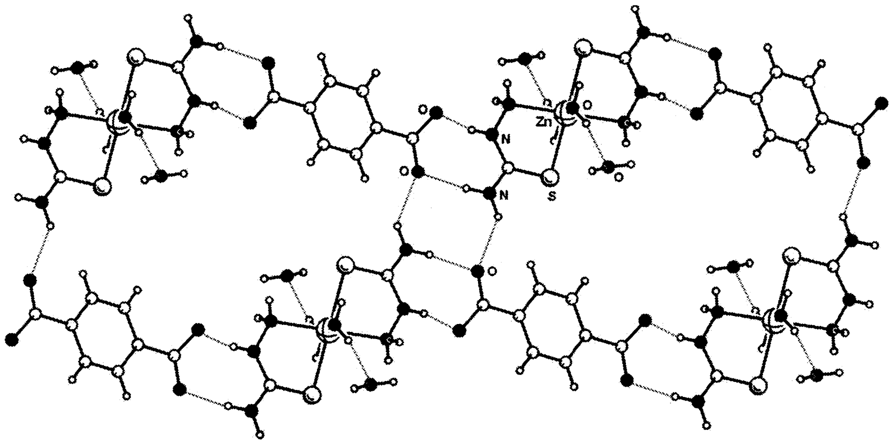

Fig. 1. The supramolecular structure of $[Zn(tsc)_2(OH_2)_2][terephthalate]\cdot 2H_2O$ **1**.

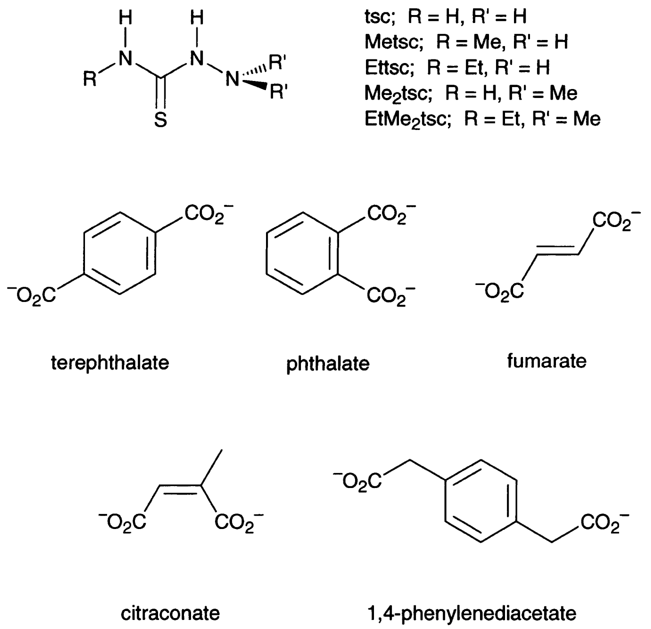

Fig. 2. Thiosemicarbazide and dicarboxylate structures.

2. Synthesis and characterisation of the zinc thiosemicarbazide dicarboxylate compounds 2–9

The compounds $[Zn(tsc)_2(OH_2)_2][fumarate]$ **2**, $[Zn(tsc)_2(citraconate)]\cdot H_2O$ **3** and [Zn(tsc)(μ-1,4-phenylenediacetate)] **4** were prepared by reaction of $[Zn(tsc)_2](NO_3)_2$ with the relevant sodium dicarboxylate in aqueous solution. The compounds $[Zn(Ettsc)_2(citraconate)]\cdot 3H_2O$ **5**, $[Zn(Ettsc)_2(Hphthalate)][Hphthalate]\cdot H_2O$ **6** and $[Zn(Metsc)_2(Hphthalate)][Hphthalate]\cdot H_2O$ **7** were prepared by reaction of $[Zn(Metsc)_2](NO_3)_2$ or $[Zn(Ettsc)_2](NO_3)_2$ with sodium citraconate or phthalate in aqueous solution. The compounds $[Zn(Me_2tsc)_2(OH_2)][terephthalate]\cdot 2H_2O$ **8** and $[Zn(EtMe_2tsc)_2(OH_2)][terephthalate]$ **9** were prepared from the reaction of either $[Zn(Me_2tsc)_2](NO_3)_2$ or $[Zn(EtMe_2tsc)_2](NO_3)_2$ with sodium terephthalate in aqueous solution. In all cases, slow evaporation of the water led to the formation of colourless crystals which were analysed by single-crystal X-ray crystallography. The compounds were isolated in 61–73% yield as the only observed metal-containing products, and a combination of microanalysis and unit cell determinations confirmed that the crystals chosen for the structural determinations were representative of the bulk materials. Poor solubility of the compounds prevented satisfactory ^1H NMR spectra from being obtained. Selected bond lengths and angles for compounds **2**–**9** are given in Table 1.

2.1. *$[Zn(tsc)_2(OH_2)_2][fumarate]$ (2)*

In the crystal structure of **2**, the asymmetric unit consists of half a $[Zn(tsc)_2(OH_2)_2]^{2+}$ cation and half a fumarate anion, with the remainder of the ions generated through inversion centres located on the half-occupancy zinc atom and at the centre of the fumarate. The cation has distorted octahedral geometry with two mutually *trans* tsc ligands and two axial aqua ligands. The cations and anions are linked via DD:AA interactions [graph set $R_2^2(8)$] [8] between the parallel N–H groups of the tsc ligands and the oxygen atoms of the carboxylate groups of the fumarate to form one-dimensional chains, in the same manner as was previously observed in the terephthalate compound **1** [7]. The hydrogen-bonded chains in **2** are linked into two-dimensional sheets via N–H···O hydrogen bonds between the thioamido N–H group [N(3)–H(3B)] and a carboxylate oxygen atom O(2), (Fig. 3(a)). These interactions result in the formation of $R_4^4(18)$ and $R_4^2(18)$ rings, all of approximately equal dimensions. This is in contrast to **1**, in which linking of the hydrogen bonded chains into sheets led to both small [$R_4^2(18)$] and large

Table 1
Selected bond lengths (Å) and angles (°) for compounds **2**–**9**

	2[a]	**3**[b]	**5**[b]	**6**[c]	**7**[d]	**8**[e]	**9**[a]		**4**
Zn(1)–S(1)	2.4494(6)	2.3640(8)	2.3681(9)	2.3961(7)	2.4129(7)	2.3137(8)	2.3102(14)	Zn(1)–S(1)	2.283(3)
Zn(1)–S(2)		2.4220(8)	2.4438(10)	2.3795(7)	2.3738(7)	2.3247(8)		Zn(1)–N(1)	2.135(8)
Zn(1)–N(a)	2.167(2)	2.159(2)	2.159(3)	2.122(2)	2.114(2)	2.271(2)	2.2776(19)	Zn(1)–O(1)	1.968(6)
Zn(1)–N(b)		2.150(2)	2.137(3)	2.177(2)	2.215(2)	2.260(2)		Zn(1)–O(3)’	1.937(7)
Zn(1)–O	2.142(2)	2.0185(17)	2.005(2)	2.082(2)	2.049(2)	2.004(1)	1.968(2)	Zn(2)–S(2)	2.298(3)
								Zn(2)–N(4)	2.143(8)
N(a)–Zn(1)–S(1)	81.26(5)	82.53(6)	82.83(7)	83.55(5)	83.09(5)	82.08(5)	82.30(6)	Zn(2)–O(5)	1.984(7)
N(b)–Zn(1)–S(2)		82.70(6)	81.24(8)	81.19(6)	80.88(5)	82.55(5)		Zn(2)–O(7)	1.939(6)
								N(1)–Zn(1)–S(1)	86.5(2)
								N(4)–Zn(2)–S(2)	85.9(2)

[a] N(a)=N(1), O=O(3).
[b] N(a)=N(3), N(b)=N(6), O=O(1).
[c] N(a)=N(3), N(b)=N(6), O=O(2).
[d] N(a)=N(3), N(b)=N(6), O=O(5).
[e] N(a)=N(3), N(b)=N(6), O=O(1W).

$R_4^4(32)$ rings. This difference in the structures of **1** and **2** is concurrent with a disparity in the manner in which the sheets are linked together to form the gross structure. In the fumarate compound **2** the sheets are linked into the three-dimensional structure via an N–H···O interaction and two O–H···O hydrogen bonds in which the aqua ligands provide the hydrogen bond donors (Fig. 3(b)) in addition to a weaker N–H···S interaction [N(1)···S(1) 3.520(2) Å]. This contrasts with the structure of **1**, in which an included water molecule acts as a ‘linker’ between the sheets. These water molecules project into neighbouring sheets, and serve to fill the large rings in **1**.

2.2. [Zn(tsc)$_2$(citraconate)]·H$_2$O (**3**)

In the crystal structure of compound **3**, the asymmetric unit consists of a discrete, neutral [Zn(tsc)$_2$(citraconate)] molecule, formed via κ^1-co-ordination of the dicarboxylate to the zinc centre, and an included water molecule. The zinc centres have distorted trigonal bipyramidal geometry, as evidenced by the structural index parameter τ [9] which is 0.67, with the axial positions occupied by a sulfur atom from one tsc ligand and a nitrogen atom from the other. An intramolecular hydrogen bond to an oxygen atom on the non-co-ordinated carboxylate group [N(3)–H(3B)···O(4)] serves to lock the citraconate conformation [graph set S(9)].

Co-ordination of the dicarboxylate to the [Zn(tsc)$_2$]$^{2+}$ centre prevents formation of cation···anion···cation chains in the same manner as observed in **1** and **2**. However, [Zn(tsc)$_2$(citraconate)] contains both DD and AA hydrogen bonding sites, the latter from the unco-ordinated carboxylate group, and a DD:AA interaction is observed between these groups to form zigzag hydrogen bonded chains (Fig. 4). Inclusion of the DD and AA sites on the same molecule ensures that these chains are directional. However, neighbouring chains are orientated in opposite directions, so overall the crystal is non-polar. The chains are linked together by a combination of N–H···O hydrogen bonds and additional hydrogen bonds in which the included water provides either donor or acceptor sites [N(1)···O(1W) 3.033(4), H(1A)···O(1W) 2.27 Å, N(1)–H(1A)···O(1W) 148°; N(3)···O(2) 2.872(3), H(3A)···O(2) 2.00 Å, N(3)–H(3A)···O(2) 174°; N(4)···O(1W) 2.970(4), H(4A)···O(1W) 2.13 Å, N(4)–H(4A)···O(1W) 162°; N(5)···O(3) 2.856(3), H(5)···O(3) 2.00 Å, N(5)–H(5)···O(3) 163°; N(6)···O(4) 3.214(3), H(6B)···O(4) 2.35 Å, N(6)–H(6B)···O(4) 174°; O(1W)···O(3) 2.811(3), H(1WA)···O(3) 1.96 Å, O(1W)–H(1WA)···O(3) 165°; and O(1W)···O(1) 3.107(3), H(1WB)···O(1) 2.28 Å, O(1W)–H(1WB)···O(1) 162°]. Surprisingly, one of the NH groups [N(4)–H(4B)] is not involved in a hydrogen bond, being directed into the cleft between citraconate and tsc ligands.

2.3. [Zn(tsc)(μ-1,4-phenylenediacetate)] (**4**)

The asymmetric unit of compound **4** consists of two fragments, one of which contains a Zn(tsc) moiety κ^1-co-ordinated to a 1,4-phenylenediacetate, the other a Zn(tsc) moiety κ^1-co-ordinated to two halves of 1,4-phenylenediacetate anions. The presence of crystallographic inversion centres ensure that independent co-ordination polymers are generated from each of the fragments, one of which is shown in Fig. 5(a). Although this represents the only observation of co-ordination polymerisation including a Zn(tsc)$^{2+}$ centre, co-ordination polymers of the type [Zn(tu)$_2$(μ-dicarboxylate)] (tu = thiourea) are the most common product from the reaction of [Zn(tu)$_4$]$^{2+}$ with dicarboxylates [10].

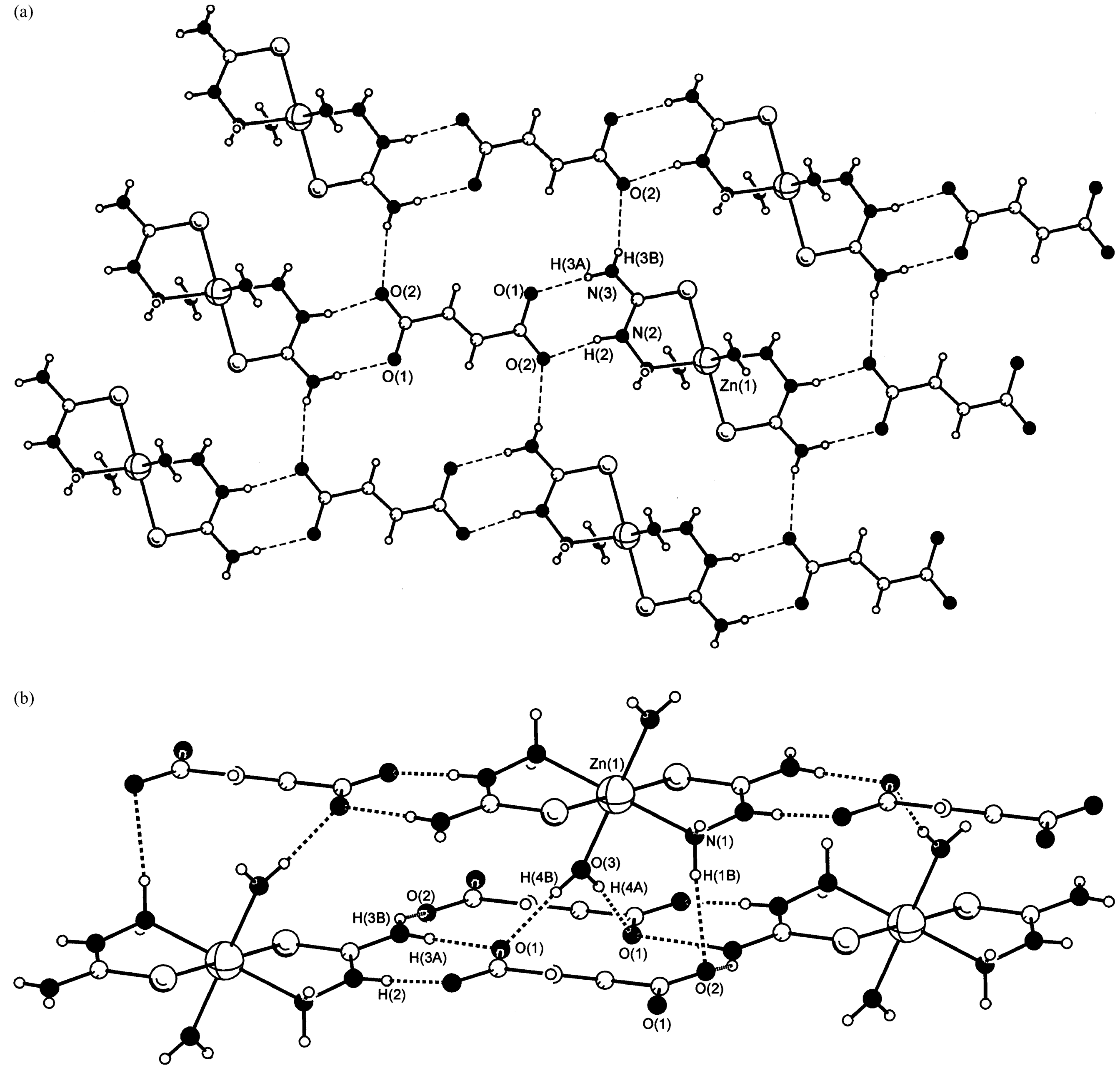

Fig. 3. Hydrogen bonding in compound **2**. (a) Formation of sheets. The hydrogen bond distances (Å) and angles (°) are N(2)···O(2) 2.788(3), H(2)···O(2) 1.95, N(2)–H(2)···O(2) 169; N(3)···O(1) 2.831(3), H(3A)···O(1) 2.00, N(3)–H(3A)···O(1) 175; and N(3)···O(2) 2.939(3), H(3B)···O(2) 2.22, N(3)–H(3B)···O(2) 149. (b) Linking of sheets. The hydrogen bond distances (Å) and angles (°) are N(1)···O(2) 3.236(3), H(1B)···O(2) 2.41, N(1)–H(1B)···O(2) 154; O(3)···O(1) 2.768(2), H(4A)···O(1) 1.95, O(3)–H(4A)···O(1) 172; and O(3)···O(1) 2.723(2), H(4B)···O(1) 1.90, O(3)–H(4B)···O(1) 173.

The co-ordination polymers based on Zn(1) and Zn(2) are linked by N–H···O hydrogen bonds, with the principal hydrogen bonding motif involving the parallel NH groups hydrogen bonding to a single non-co-ordinated carboxylate oxygen atom, with graph set $R_2^1(6)$ [N(2)···O(8) 2.85(1), H(2)···O(8) 2.07 Å, N(2)–H(2)···O(8) 150°; N(3)···O(8) 2.84(1), H(3A)···O(8) 2.06 Å, N(3)–H(3A)···O(8) 150°; N(5)···O(4) 2.77(1), H(5)···O(4) 2.00 Å, N(5)–H(5)···O(4) 149°; and N(6)···O(4) 2.93(1), H(6A)···O(4) 2.18 Å, N(6)–H(6A)···O(4) 144°]. Zn(1)- and Zn(2)-based polymers become proximate (Zn···Zn 4.4 Å) at intervals of 20.8 Å, and interact at these points through two pairs of N–H···O hydrogen bonds in which the co-ordinated carboxylate oxygen atoms act as hydrogen bond acceptors forming $R_2^2(6)$ motifs. (Fig. 5(b)).

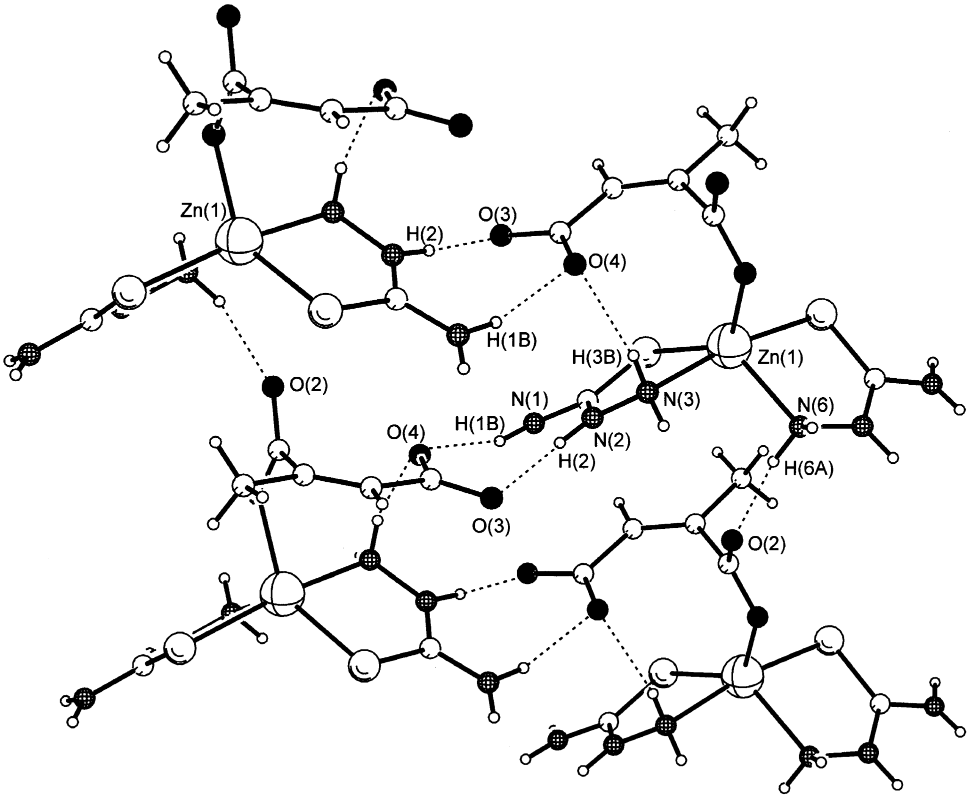

Fig. 4. Hydrogen bonding in compound **3**, linking the molecules into chains. The hydrogen bond distances (Å) and angles (°) are N(1)···O(4) 2.875(3), H(1B)···O(4) 2.02, N(1)–H(1B)···O(4) 162; N(2)···O(3) 2.782(3), H(2)···O(3) 1.91, N(2)–H(2)···O(3) 176; N(6)···O(2) 2.868(3), H(6A)···O(2) 2.01, N(6)–H(6A)···O(2) 164; and N(3)···O(4) 2.881(3), H(3B)···O(4) 2.06, N(3)–H(3B)···O(4) 154.

2.4. *[Zn(Ettsc)$_2$(citraconate)]·3H$_2$O (5)*

The crystal structure of compound **5** consists of molecules of [Zn(Ettsc)$_2$(citraconate)], with three independent molecules of water present per asymmetric unit. The co-ordination geometry around the zinc centre can be described as distorted square-pyramidal ($\tau = 0.41$), with two mutually *cis* thiosemicarbazide ligands occupying the basal positions and a carboxylate group κ^1-co-ordinated in the axial position. The conformation adopted by the citraconate differs from that in compound **3**: the C(8)–C(7)–O(1)–Zn(1) torsion angle in **5** is 146°, demonstrating co-ordination of a *syn* lone pair, whereas in contrast the equivalent torsion angle in **3** is 27°, demonstrating co-ordination of an *anti* lone pair. This change in co-ordination mode leads to a difference in the orientation of the non-co-ordinated carboxylate group, which in **5** lies essentially perpendicular to the two DD sets of N–H bonds. In contrast to **3**, there is no intramolecular hydrogen bonding in **5**.

DD:AA interactions between the Ettsc ligands and carboxylates are absent in this structure. The non-co-ordinated carboxylate does interact with two NH groups, but each is located on a different molecule. One of the sets of parallel NH groups [N(1)–H(1) and N(2)–H(2)] forms a $R_3^2(8)$ motif, in which one of the N–H groups is hydrogen-bonded to a carboxylate oxygen atom, while the other is hydrogen-bonded to a water molecule which is in turn hydrogen-bonded to the carboxylate oxygen. The second set of parallel NH groups [N(4)–H(4) and N(5)–H(5)] hydrogen bonds to two carboxylate oxygen atoms on different citraconates, which in turn are bridged by a water molecule giving a $R_4^2(10)$ motif (Fig. 6(a)). N–H···O interactions link the molecules into sheets, which are held together by hydrogen bonds involving the included water molecules in addition to an interaction between an Ettsc NH group and a carboxylate oxygen atom [N(3)···O(4) 2.892(4), H(3F)···O(4) 2.03 Å, N(3)–H(3F)···O(4) 158°] (Fig. 6(b)). Further hydrogen bonds involving the water molecules serve to assemble the sheets into bilayers, though there is no hydrogen bonding between these bilayers.

2.5. *[Zn(Rtsc)$_2$(Hphthalate)][Hphthalate]·H$_2$O (R = Et, 6; R = Me, 7)*

The structures of compounds **6** and **7** exhibit a number of common structural features, and therefore can be discussed together. Both asymmetric units consist of a [Zn(Rtsc)$_2$(Hphthalate)]$^+$ cation, a [Hphthalate]$^-$ anion and an included water molecule. In compound **6**

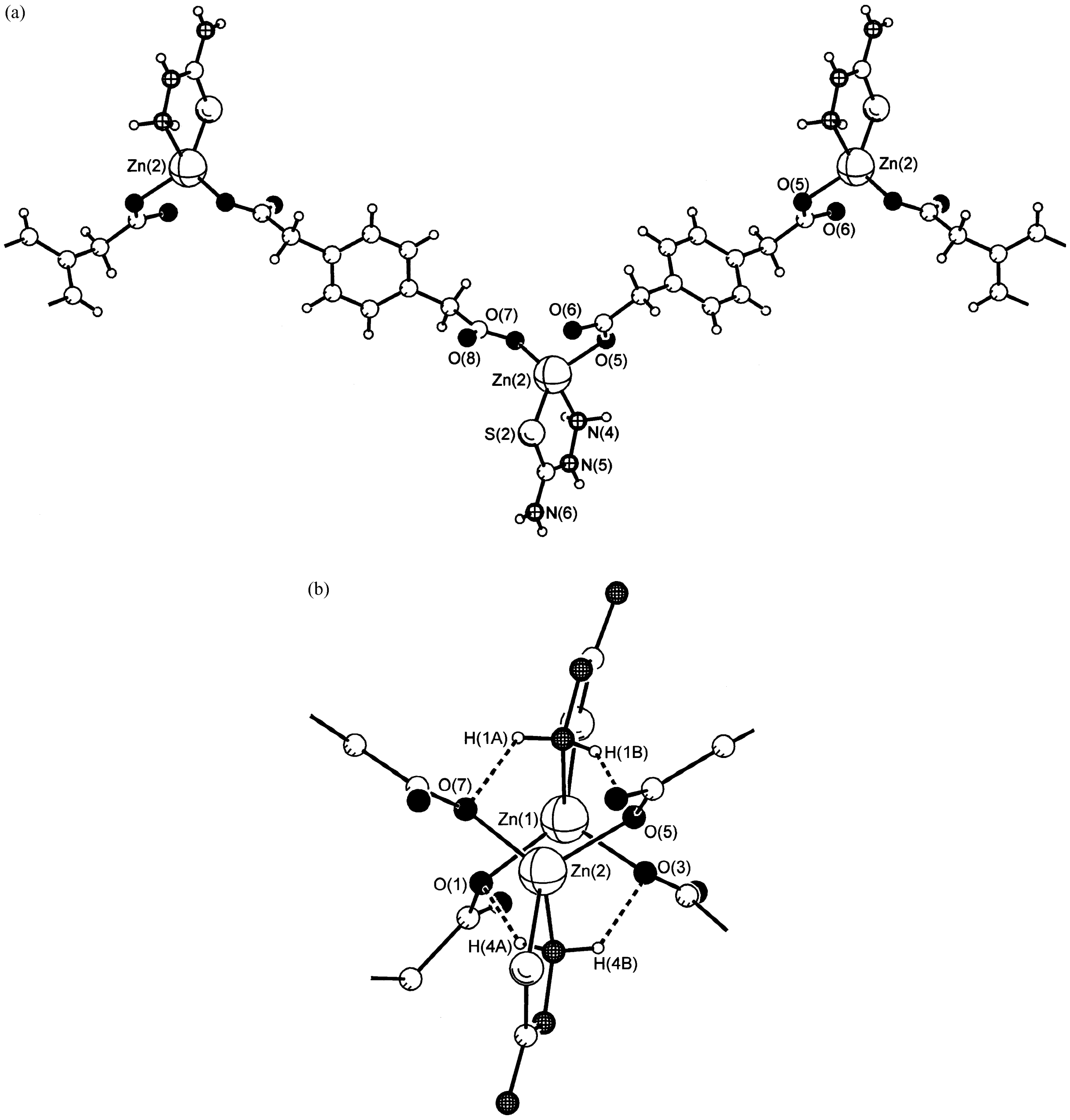

Fig. 5. (a) Part of one of the independent co-ordination polymers within the crystal structure of compound **4**. (b) Hydrogen bonding linking the co-ordination polymers in compound **4**. The hydrogen bond distances (Å) and angles (°) are N(1)···O(7) 3.02(1), H(1A)···O(7) 2.35, N(1)–H(1A)···O(7) 131; N(1)···O(5) 3.04(1), H(1B)···O(5) 2.20, N(1)–H(1B)···O(5) 154; N(4)···O(1) 2.96(1), H(4A)···O(1) 2.13, N(4)–H(4A)···O(1) 151; and N(4)···O(3) 3.08(1), H(4B)···O(3) 2.39, N(4)–H(4B)···O(3) 134.

the geometry around the zinc centre is distorted trigonal bipyramidal ($\tau = 0.73$) with a sulfur atom from one Rtsc ligand and a nitrogen atom from the other in the axial positions, and the remaining sulfur and nitrogen donors together with a κ^1-co-ordinated carboxylate in the equatorial positions. The geometry is similar in compound **7**, though the distortion towards a square pyramidal geometry is greater in this case ($\tau = 0.41$). Since in both **6** and **7**, in contrast to **3** and **5**, the non-co-ordinated carboxylate group is protonated, an additional hydrogen phthalate anion is included in order to balance the charges. The hydrogen bonding patterns in the two compounds are identical, and Fig. 7 depicts compound **6** only.

As in **3**, one of the NH groups from a co-ordinated amino group forms an intramolecular hydrogen bond [S(9)] to the non-co-ordinated carboxylic acid oxygen atom, effectively locking the conformation of the Hphthalate ligand [N(6)···O(4) 2.940(3), H(6B)···O(4) 2.21 Å, N(6)–H(6B)···O(4) 141°]. One of the sets of parallel NH groups [N(1)–H(1) and N(2)–H(2)] forms a DD:AA interaction with the co-ordinated Hphthalate

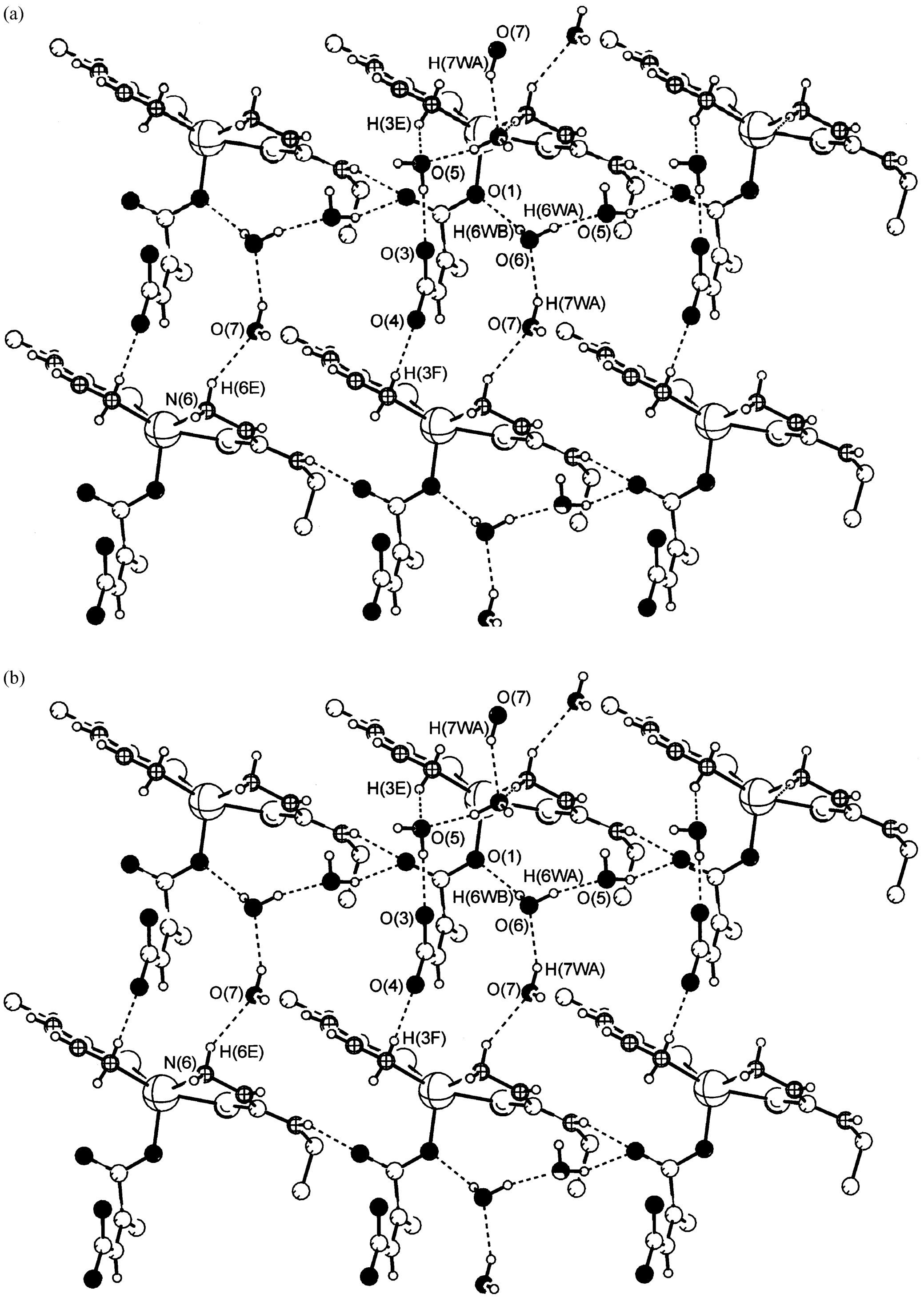

Fig. 6. Hydrogen bonding in compound **5**. (a) Hydrogen bonds involving the sets of parallel NH groups. The hydrogen bond distances (Å) and angles (°) are N(1)···O(7) 2.933(4), H(1)···O(7) 2.05, N(1)–H(1)···O(7) 178; N(2)···O(4) 2.849(4), H(2)···O(4) 2.05, N(2)–H(2)···O(4) 153; N(4)···O(2) 2.873(4), H(4)···O(2) 2.14, N(4)–H(4)···O(2) 139; N(5)···O(3) 2.812(4), H(5)···O(3) 1.97, N(5)–H(5)···O(3) 164; O(5)···O(3) 2.805(3), H(5WA)···O(3) 1.94, O(5)–H(5WA)···O(3) 162; O(5)···O(2) 2.811(3), H(5WB)···O(2) 1.96, O(5)–H(5WB)···O(2) 159; and O(7)···O(4) 2.713(4), H(7WB)···O(4) 1.85, O(7)–H(7WB)···O(4) 169. (b) Formation of sheets through hydrogen bonds involving the included water molecules.

ligand on a neighbouring cation (Fig. 7(a)), with the coordinated oxygen atom O(2) and carbonyl oxygen O(4) of the carboxylic acid acting as acceptors [$R_2^2(11)$]. This motif is similar to that observed between the coordination polymers in the structure of [Zn(tu)$_2$(μ-phthalate)] [10] and serves to link the molecules into chains. The other DD face [N(4)–H(4) and N(5)–H(5)] interacts with oxygen atoms from a carboxylate [O(6)]

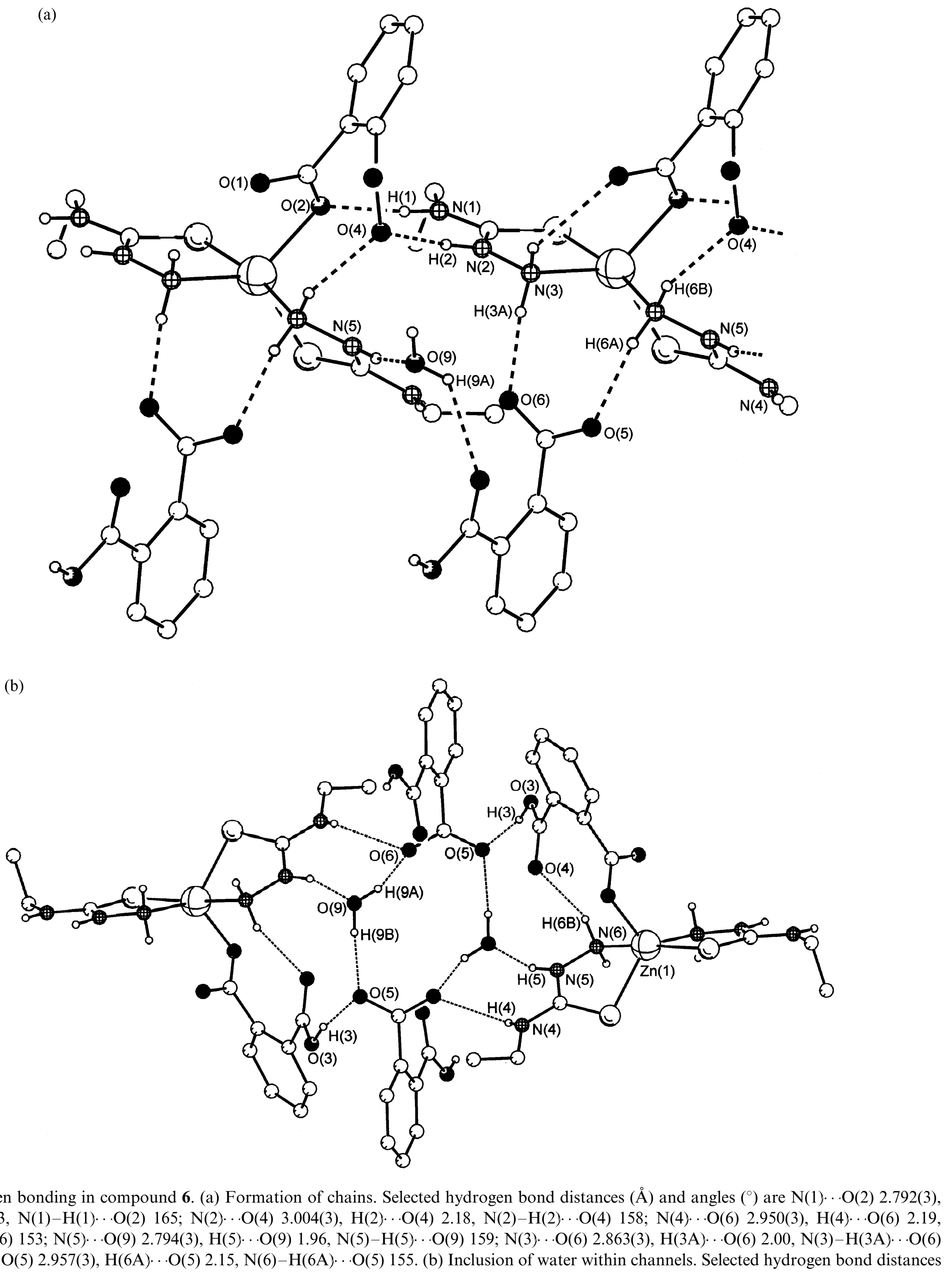

Fig. 7. Hydrogen bonding in compound **6**. (a) Formation of chains. Selected hydrogen bond distances (Å) and angles (°) are N(1)···O(2) 2.792(3), H(1)···O(2) 1.93, N(1)–H(1)···O(2) 165; N(2)···O(4) 3.004(3), H(2)···O(4) 2.18, N(2)–H(2)···O(4) 158; N(4)···O(6) 2.950(3), H(4)···O(6) 2.19, N(4)–H(4)···O(6) 153; N(5)···O(9) 2.794(3), H(5)···O(9) 1.96, N(5)–H(5)···O(9) 159; N(3)···O(6) 2.863(3), H(3A)···O(6) 2.00, N(3)–H(3A)···O(6) 163; and N(6)···O(5) 2.957(3), H(6A)···O(5) 2.15, N(6)–H(6A)···O(5) 155. (b) Inclusion of water within channels. Selected hydrogen bond distances (Å) and angles (°) are O(3)···O(5) 2.538(2), H(3)···O(5) 1.60, O(3)–H(3)···O(5) 168; O(9)···O(5) 2.936(3), H(9B)···O(5) 2.15, O(9)–H(9B)···O(5) 150; and O(9)···O(6) 2.902(3), H(9A)···O(6) 2.29, O(9)–H(9A)···O(6) 127.

and the included water molecule [O(9)]. The two coordinated NH_2 groups can together also be regarded as comprising two additional DD faces, with the faces made up from one NH group from each of the amino groups [11]. One of these 'new' faces [N(3)–H(3A) and N(6)–H(6A)] forms a DD:AA interaction with the carboxylate group of the non-co-ordinated [Hphthalate]$^-$ anion (Fig. 7(a)).

Further hydrogen bonding involves the included water molecules, which reside in channels within the structure (Fig. 7(b)). There is also π-stacking involving both co-ordinated and non-co-ordinated [Hphthalate]$^-$ anions.

2.6. *[Zn(Me$_2$tsc)$_2$(OH$_2$)][terephthalate]·2H$_2$O (**8**)*

In the crystal structure of **8**, the asymmetric unit consists of a [Zn(Me$_2$tsc)$_2$(OH$_2$)]$^{2+}$ cation, a terephthalate anion and two included water molecules. In the cation the metal geometry is distorted square pyramidal ($\tau = 0.20$) with the two Me$_2$tsc ligands orientated mutually *trans* and the aqua ligand co-ordinated in the axial position. The cations and anions are linked via DD:AA interactions between the two parallel N–H groups of the Me$_2$tsc ligands and the oxygen atoms of the carboxylate groups to form infinite chains (Fig. 8), similar to those in **1**. These chains are linked into pairs via N–H···O interactions to generate large [$R_4^4(32)$] and small [$R_4^2(8)$] rings, again in a similar manner to **1**. However, these pairs are not directly hydrogen-bonded to their neighbours, and sheet formation is mediated by hydrogen bonding involving the water molecules. Further O–H···O interactions [O(2W)···O(2) 2.942(3), H(2WA)···O(2) 2.06 Å, O(2W)–H(2WA)···O(2) 167°] serve to link these sheets into the three-dimensional structure.

The hydrogen bonding pattern observed in this structure is different from that observed in the nickel analogue [Ni(Me$_2$tsc)$_2$(OH$_2$)$_2$][terephthalate]·2H$_2$O [6]. In this compound the DD:AA interactions linking the cations and anions are surprisingly absent, though all potential hydrogen bond donors and acceptors are utilised in hydrogen bonding. However, the nickel complex has octahedral geometry, and the presence of the second co-ordinated water appears to be sufficient to change the hydrogen bonding pattern.

2.7. *[Zn(EtMe$_2$tsc)$_2$(OH$_2$)][terephthalate] (**9**)*

In the crystal structure of compound **9** the asymmetric unit consists of a discrete 5-co-ordinate [Zn(EtMe$_2$tsc)$_2$(OH$_2$)]$^{2+}$ cation and a terephthalate anion, and unlike **8** there is no included solvent. The co-ordination geometry of **9** is best described as distorted trigonal bipyramidal ($\tau = 0.65$) with sulfur and nitrogen atoms in the axial positions, and sulfur,

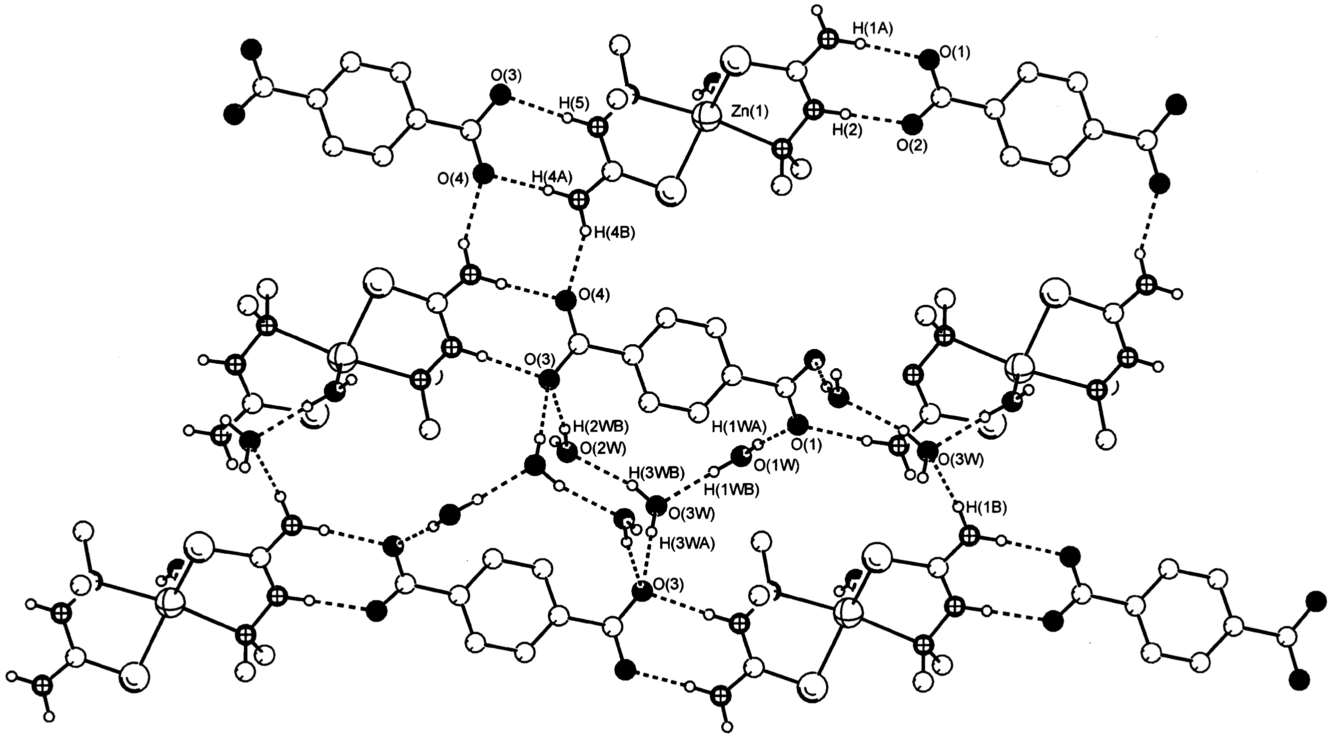

Fig. 8. Formation of hydrogen-bonded sheets in compound **8**. The hydrogen bond distances (Å) and angles (°) are N(1)···O(1) 2.838(2), H(1A)···O(1) 1.95, N(1)–H(1A)···O(1) 176; N(1)···O(3W) 3.106(3), H(1B)···O(3W) 2.27, N(1)–H(1B)···O(3W) 156; N(2)···O(2) 2.758(2), H(2)···O(2) 1.87, N(2)–H(2)···O(2) 176; N(4)···O(4) 2.804(2), H(4A)···O(4) 1.94, N(4)–H(4A)···O(4) 166; N(4)···O(4) 2.831(2), H(4B)···O(4) 2.02, N(4)–H(4B)···O(4) 152; N(5)···O(3) 2.816(2), H(5)···O(3) 1.94, N(5)–H(5)···O(3) 174; O(1W)···O(1) 2.652(2), H(1WA)···O(1) 1.77, O(1W)–H(1WA)···O(1) 172; O(1W)···O(3W) 2.729(2), H(1WB)···O(3W) 1.84, O(1W)–H(1WB)···O(3W) 173; O(2W)···O(3) 2.913(2), H(2WB)...O(3) 2.02, O(2W)–H(2WB)···O(3) 172; O(3W)···O(3) 2.864(2), H(3WA)···O(3) 1.98, O(3W)–H(3WA)···O(3) 179; and O(3W)···O(2W) 2.863(3), H(3WB)···O(2W) 2.01, O(3W)–H(3WB)···O(2W) 167.

nitrogen and co-ordinated water in the equatorial positions. The difference in co-ordination geometry between **8** and **9** does not affect the principal manner in which the cations and anions interact: they are linked into infinite chains via the same DD:AA motif observed in **1** and **8** involving the two N–H groups and the carboxylate oxygen atoms, (Fig. 9). These chains are in turn linked into the three-dimensional structure via O–H$\cdots$O interactions involving the co-ordinated water and a carboxylate oxygen atom.

3. Discussion

Compounds **1**–**9** were all isolated in good yield as the sole products from the seemingly straightforward reactions between a bis(thiosemicarbazide)zinc(II) nitrate and a sodium dicarboxylate. However, there is a remarkable structural diversity in the products. Compounds **1**, **2**, **8** and **9** form ionic compounds in which DD:AA interactions serve to link the cations and anions into hydrogen-bonded chains, compounds **3**, **5**, **6** and **7** form square pyramidal compounds in which a carboxylate is co-ordinated to the zinc along with the two thiosemicarbazide ligands, and compound **4** forms co-ordination polymers.

These differences in structure are not a consequence of differences in co-ordination geometry. The series of ionic compounds (**1**, **2**, **8** and **9**) includes 6-co-ordinate octahedral and 5-co-ordinate structures that range from square pyramidal to trigonal bipyramidal in the zinc geometry. Similarly, the 5-co-ordinate compounds containing co-ordinated dicarboxylate involve varying degrees of distortion. The energy surface between the two extremes of square pyramidal and trigonal bipyramidal is well established as being relatively flat [12], and although difficult to quantify it is likely that the metal geometry is sufficiently flexible to be able to facilitate the most effective hydrogen bonding network.

The differences in structure observed in this series of compounds are more readily rationalised on the basis of the shape of the dicarboxylate, specifically the relative orientation of the two carboxylate groups. Yaghi, O'Keeffe and co-workers have recently described the geometry of dicarboxylates in terms of three angles, θ, ψ and φ, and used these to help prepare porous metal-organic frameworks with predictable structures [13]. Starting from the planar terephthalate anion, θ represents bending in the centre of the anion with the two carboxylates remaining co-planar, ψ represents bending of the carboxylates towards each other, and φ represents the relative twisting of the planes of the carboxylate groups. These angles have been calculated from the

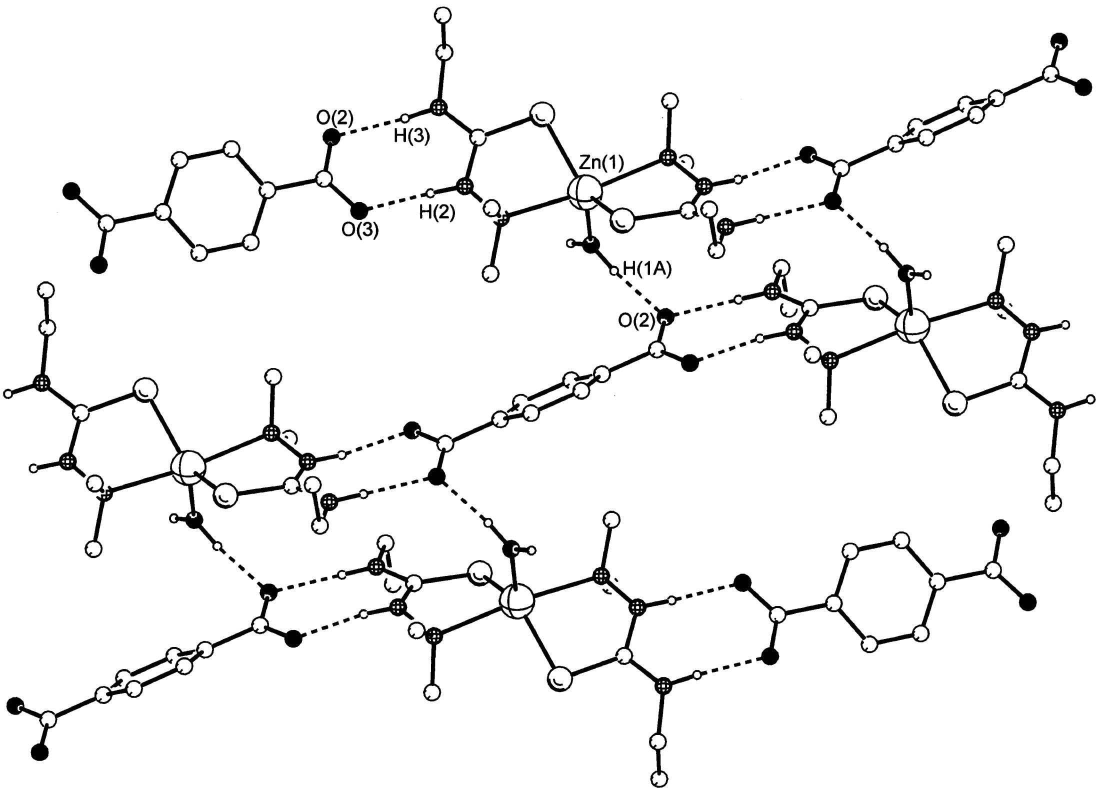

Fig. 9. Formation of the supramolecular structure in compound **9**. The hydrogen bond distances (Å) and angles (°) are N(2)$\cdots$O(3) 2.748(3), H(2)$\cdots$O(3) 1.88, N(2)–H(2)$\cdots$O(3) 172; N(3)$\cdots$O(2) 2.792(3), H(3)$\cdots$O(2) 1.90, N(3)–H(3)$\cdots$O(2) 176; and O(1)$\cdots$O(2) 2.635(2), H(1A)$\cdots$O(2) 1.77, O(1)–H(1A)$\cdots$(2) 169.

Table 2
Values for the angles θ, ψ and φ (°) for the dicarboxylates in the structures of compounds **1**–**9**

Dicarboxylate	Compound	θ	ψ	φ
Terephthalate	**1**	180	172	0
	8	180	180	30
	9	180	180	0
Fumarate	**2**	180	180	0
1,4-Phenylenediacetate	**4**[a]	180	180	0
	4[a]	171	177	39
Citraconate	**3**	69	180	89
	5	69	177	81
Phthalate	**6**[b]	59	164	56
	6[c]	63	177	84
	7[b]	63	163	52
	7[c]	64	178	89

[a] One of the two independent chains.
[b] Co-ordinated $[\text{Hphthalate}]^-$.
[c] Non-co-ordinated $[\text{Hphthalate}]^-$.

crystal structures of **1**–**9**, and are presented in Table 2. For terephthalate and fumarate, θ is 180° as the carboxylate groups are orientated in opposite directions; their compounds consist of ionic structures held together by DD:AA interactions despite the presence of various amounts of co-ordinated and non-co-ordinated water molecules. These chains are flexible to changes in ψ and φ, and for **8** the twist angle φ is 30°. For citraconate and phthalate $\theta < 90°$ and the compounds contain co-ordinated carboxylates. With such acute values of θ, one of the carboxylate groups needs to rotate in order to prevent steric repulsions between these groups, and this is reflected in the much higher values of φ observed in these compounds than for those of terephthalate or fumarate. Co-ordination of the dicarboxylate may be driven by basicity, since the first pK_a for phthalic acid (2.94) is slightly lower than that for terephthalic (3.54) or fumaric acid (3.02) [14]. However, it is more likely that this is a 'second choice' arrangement that is only observed when the more favourable ionic-type structure is precluded on geometric grounds. It is unclear why phthalate is protonated in the structures of **6** and **7** whereas citraconate is not in the structures of **3** and **5** as the second pK_a for citraconic acid is greater (6.17 vs. 5.43) [14,15]. It is noteworthy that in both **6** and **7** the co-ordinated hydrogen phthalate anion contains lower values of both ψ and φ than the non-co-ordinated hydrogen phthalate.

The 1,4-phenylenediacetate compound **4** is unusual, since the values for θ, ψ and φ for the dicarboxylate are similar to those for terephthalate, whereas the observed structure of **4** is very different to those of the terephthalate compounds **1**, **8** and **9**. The main structural difference between these dicarboxylates is the large lateral displacement of the C–C bond vectors to the carboxylates (5.3 Å). Although this would not preclude formation of hydrogen bonded chains in a compound $[\text{Zn(tsc)}_2]$[1,4-phenylenediacetate] based on DD:AA interactions, it is likely that the lateral displacement would hamper the interactions between these chains to form the three-dimensional structure. Although **4** represents the only observation of a co-ordination polymer in this series, these are the main products from the related reaction of $[\text{Zn(tu)}_4]^{2+}$ with dicarboxylates [10]. The major factor governing the difference in the product distributions from these reactions is the lower lability of the bidentate tsc ligand with respect to the monodentate thiourea ligand.

The DD:AA interaction between two parallel N–H groups from a co-ordinated thiosemicarbazide ligand and two oxygen atoms from a carboxylate [graph set $R_2^2(8)$] has been demonstrated to be a robust motif for use in crystal engineering. In the nine structures discussed in this paper, there are 18 carboxylate groups, of which 11 (61%) are involved in this type of hydrogen bonding. Of the seven which are not, six are prevented from doing so by co-ordination, and only one forms another hydrogen bonding motif. Hence 11 out of 12 non-co-ordinated carboxylate groups are involved in DD:AA interactions—a 'success rate' of 92%, which compares with the most robust hydrogen bonding motifs known [16]. Moreover, this occurs despite the presence of a competitive solvent, which is included in the lattice either free or co-ordinated. Indeed, with the rigid planar dicarboxylates terephthalate and fumarate, only one compound has been structurally characterised to date without cation···anion···cation chains with the ions linked through these interactions [6]. The structures in this paper support these observations, and show that when θ is acute these cation···anion···cation chains do not form. Instead carboxylate co-ordination is observed giving either neutral molecules or monocations, with the non-co-ordinated carboxylates in these species generally forming hydrogen bonds to parallel NH groups in tsc ligands.

4. Experimental

4.1. General experimental

Microanalyses (C, H and N) were carried out by Mr Alan Carver (University of Bath Microanalytical Service). Infrared spectra were recorded on a Nicolet Nexus FT-IR spectrometer as KBr pellets. 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. The compounds tsc, Metsc and Ettsc were purchased from commercial sources. Me_2tsc and EtMe$_2$tsc were synthesised using the literature method [17].

4.2. Synthesis of [Zn(tsc)$_2$](NO$_3$)$_2$, [Zn(Metsc)$_2$](NO$_3$)$_2$, [Zn(Ettsc)$_2$](NO$_3$)$_2$, [Zn(Me$_2$tsc)$_2$](NO$_3$)$_2$, and [Zn(EtMe$_2$tsc)$_2$](NO$_3$)$_2$

Thiosemicarbazide, (0.200 g, 2.20 mmol), dissolved in absolute ethanol (15 cm^3), was added dropwise to an absolute ethanolic solution of zinc(II) nitrate hexahydrate, (0.327 g, 1.1 mmol in 10 cm^3), whilst stirring. After approximately 10 min a white precipitate of [Zn(tsc)$_2$](NO$_3$)$_2$ was seen to form, and this was collected by filtration. Yield 0.35 g (81%).

[Zn(Metsc)$_2$](NO$_3$)$_2$, [Zn(Ettsc)$_2$](NO$_3$)$_2$, [Zn(Me$_2$tsc)$_2$](NO$_3$)$_2$, and [Zn(EtMe$_2$tsc)$_2$](NO$_3$)$_2$, were synthesised using analogous procedures, though a significant reduction in the solvent volume was required before the products crystallised in 70–85% yield.

*4.3. Synthesis of [Zn(tsc)$_2$(OH$_2$)$_2$][fumarate] (**2**)*

To an aqueous solution of [Zn(tsc)$_2$](NO$_3$)$_2$ (100 mg, 0.27 mmol) was added an aqueous solution of sodium fumarate, (43 mg, 0.27 mmol). After approximately 24 h a colourless crystalline material, [Zn(tsc)$_2$(OH$_2$)$_2$][fumarate], was seen to form, which was separated by filtration. Yield 73 mg (70%). Found C, 18.1; H, 3.98; N, 21.0. $C_6H_{16}N_6O_6S_2Zn$ requires C, 18.1; H, 4.05; N, 21.1%. IR (cm^{-1}): ν(NH)/(OH) 3514s, 3294s, 3000s (br); ν(CO$_2$)/δ(NH) 1638m, 1558s, 1438s.

Syntheses of compounds **3**–**9** were carried out using the appropriate bis(thiosemicarbazide)zinc nitrate (0.100 g) and one equivalent of the appropriate sodium dicarboxylate in an analogous manner to that of compound **2**.

*4.4. Synthesis of [Zn(tsc)$_2$(citraconate)]·H$_2$O (**3**)*

Yield 65 mg (61%). Found C, 21.3; H, 4.13; N, 21.3. $C_7H_{16}N_6O_5S_2Zn$ requires C, 21.4; H, 4.09; N, 21.3%. IR (cm^{-1}): ν(NH)/(OH) 3381s, 3215s; v(CO$_2$)/δ(NH) 1604m, 1531s, 1444m.

*4.5. Synthesis of [Zn(tsc)(μ–1,4-phenyldiacetate)] (**4**)*

Yield 67 mg (71%). Found C, 37.4; H, 3.84; N, 12.05. $C_{11}H_{13}N_3O_4SZn$ requires C, 37.9; H, 3.76; N, 12.0%. IR (cm^{-1}): ν(NH)/(OH) 3167w; ν(CO$_2$)/δ(NH) 1570m, 1458s.

*4.6. Synthesis of [Zn(Ettsc)$_2$(citraconate)]·3H$_2$O (**5**)*

Yield 85 mg (65%). Found C, 27.1; H, 5.75; N, 17.3. $C_{11}H_{28}N_6O_7S_2Zn$ requires C, 27.2; H, 5.77; N, 17.3%. IR (cm^{-1}): ν(NH)/(OH) 3461s, 3307s (br), 2975s; v(CO$_2$)/δ(NH) 1651s, 1557m.

*4.7. Synthesis of [Zn(Ettsc)$_2$(Hphthalate)][Hphthalate]·H$_2$O (**6**)*

Yield 52 mg (70%). Found C, 40.6; H, 4.86; N, 12.5. $C_{22}H_{32}N_6O_9S_2Zn$ requires C, 40.5; H, 4.64; N, 12.9%. IR (cm^{-1}): ν(NH)/(OH) 3396s, 3228s (br); ν(CO$_2$)/δ(NH) 1598s, 1457s (br).

4.8. Synthesis of [Zn(Metsc)$_2$(Hphthalate)][Hphthalate]·H$_2$O (7)

Yield 45 mg (63%). Found C, 39.0; H, 4.11; N, 13.2. $C_{20}H_{28}N_6O_9S_2Zn$ requires C, 38.5; H, 4.20; N, 13.5%. IR (cm^{-1}): ν(NH)/(OH) 3448s (br); ν(CO$_2$)/δ(NH) 1604s (br), 1425s.

*4.9. Synthesis of [Zn(Me$_2$tsc)$_2$(OH$_2$)][terephthalate]·2H$_2$O (**8**)*

Yield 83 mg (73%). Found C, 31.7; H, 5.35; N, 15.8. $C_{14}H_{28}N_6O_7S_2Zn$ requires C, 32.2; H, 5.37; N, 16.1%. IR (cm^{-1}): ν(NH)/(OH) 3275m; ν(CO$_2$)/δ(NH) 1613s, 1533s, 1447s.

*4.10. Synthesis of [Zn(EtMe$_2$tsc)$_2$(OH$_2$)][terephthalate] (**9**)*

Yield 89 mg (72%). Found C, 39.6; H, 5.91; N, 15.3. $C_{18}H_{32}N_6O_5S_2Zn$ requires C, 39.9; H, 5.91; N, 15.5%. IR (cm^{-1}): ν(NH)/(OH) 3255s; ν(CO$_2$)/δ(NH) 1604s, 1565s, 1358m.

5. Crystallography

Single-crystals of compounds **2**–**9** were prepared by the methods above and analysed on either an Enraf–Nonius CAD4 automatic four-circle diffractometer (**2**, **3**, **8** and **9**) or a Nonius Kappa CCD diffractometer (**4**, **5**, **6** and **7**) Table 3. The structures were solved using SHELXS-97 and refined using SHELXL-97 [18]. Hydrogen atoms were included at calculated positions on carbon centres. All hydrogens attached to nitrogen and oxygen atoms were located in the electron density maps and refined at fixed distances from their parent atom.

6. Supplementary material available

Crystallographic data for compounds **2**–**9** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 189017–189024. Copies of the data can be obtained free of

Table 3
Crystallographic parameters for compounds **2**–**9**

Complex	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Empirical formula	$C_6H_{16}N_6O_6S_2Zn$	$C_7H_{16}N_6O_5S_2Zn$	$C_{22}H_{26}N_6O_8S_2Zn_2$	$C_{11}H_{28}N_6O_7S_2Zn$	$C_{22}H_{30}N_6O_9S_2Zn$	$C_{20}H_{26}N_6O_9S_2Zn$	$C_{14}H_{28}N_6O_7S_2Zn$	$C_{18}H_{32}N_6O_5S_2Zn$
M	397.74	393.75	695.33	485.88	652.01	623.96	521.91	541.99
Crystal size/mm	0.20 × 0.20 × 0.20	0.25 × 0.20 × 0.20	0.13 × 0.13 × 0.05	0.15 × 0.15 × 0.10	0.30 × 0.10 × 0.10	0.25 × 0.25 × 0.25	0.25 × 0.20 × 0.15	0.35 × 0.30 × 0.30
T(K)	293(2)	293(2)	293(2)	296(2)	170(2)	150(2)	293(2)	293(2)
λ(Å)	0.71069	0.71069	0.71070	0.71070	0.71070	0.71069	0.71069	0.71069
θ Range	2.67–24.97	2.59–24.97	3.08–24.20	3.36–27.13	3.64–27.48	3.76–27.49	2.04–24.98	2.36–24.96
Crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$C2/c$
a Å	6.4053(7)	11.650(3)	12.6541(10)	8.9190(6)	7.9700(1)	7.923(1)	9.344(2)	22.490(12)
b Å	7.8436(8)	7.6400(10)	11.518(2)	9.3860(7)	14.7810(2)	14.370(2)	10.672(2)	9.118(2)
c Å	7.9661(9)	17.590(3)	18.705(3)	13.017(1)	24.2320(4)	23.393(3)	12.753(2)	15.819(8)
α °	76.182(8)			90.099(3)			74.64(2)	
β °	78.570(10)	106.130(2)	99.516(10)	88.662(3)	92.0270(9)	92.638(6)	76.87(2)	129.74(3)
γ °	78.530(10)			81.684(4)			73.21(2)	
U	376.07(7)	1504.0(5)	2688.8(7)	1077.9(2)	2852.85(7)	2660.6 (6)	1158.3(4)	2494.6(19)
Z	2	4	4	2	4	4	2	4
μ (Mo Kα) (mm^{-1})	1.945	1.940	1.998	1.375	1.066	1.140	1.286	1.192
Reflections collected	1493	2873	18774	9661	48821	46061	4056	2301
Independent reflections	1322	2628	4273	4654	6525	6101	3411	2195
R(int)	0.0081	0.0146	0.1539	0.0500	0.0513	0.0668	0.0121	0.0125
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0298, 0.0797	0.0263, 0.0683	0.0804, 0.1934	0.0456, 0.0997	0.0404, 0.0971	0.0355, 0.0878	0.0236, 0.0655	0.0225, 0.0591
R indices (all data)	0.0306, 0.0824	0.0433, 0.0741	0.1151, 0.2176	0.0731, 0.1118	0.0575, 0.1058	0.0550, 0.0992	0.0318, 0.0686	0.0313, 0.0618

charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

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