

The Influence of Functional Group Orientation on the Structure of Zinc 1,1,4-Trimethylthiosemicarbazide Dicarboxylates: Probing the Limits of Crystal Engineering Strategies

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The reaction of $[\text{Zn}(\text{tmtsc})_2](\text{NO}_3)_2$ [tmtsc = 1,1,4-trimethylthiosemicarbazide, $\text{MeNHC}(\text{S})\text{NHNMe}_2$] with a range of sodium dicarboxylates has been shown to lie on the borderline between commonly used crystal engineering strategies. The products exhibit a wide range of structural diversity with the main driving force being the relative orientation of the carboxylate groups. Thus, fumarate leads to the hydrogen-bonded aggregate $[\text{Zn}(\text{tmtsc})_2(\text{OH}_2)]\text{[fumarate]}$ (**2**) in which cations and anions are linked by hydrogen bond donor-donor acceptor-acceptor (DD:AA) interactions, whereas isophthalate and (+)-camphorate lead to coordination polymers $[\text{Zn}(\text{tmtsc})(\mu\text{-isophthalate})]$ (**3a**) and $[\text{Zn}(\text{tmtsc})(\mu\text{-camphorate})]$ (**4**) with the metal centres linked by bridging dicarboxylate ligands. In the case of isophthalate, a hydrated product $[\text{Zn}(\text{tmtsc})(\mu\text{-isophthalate})]\cdot\text{H}_2\text{O}$ (**3b**) was also characterised, although microanalysis and powder X-ray diffraction revealed this to be a minor product. Incorporation of water was shown to lead to a change in carboxylate coordination

mode from η^1 in **3a** to η^2 in **3b**. Use of terephthalate leads to the compound $[\{\text{Zn}(\text{tmtsc})(\text{OH}_2)\}_2(\mu\text{-terephthalate})]\text{[terephthalate]}\cdot 2\text{H}_2\text{O}$ (**5**), in which half of the terephthalates bridge metal centres, to form dimers, and the remainder link the dimeric cations through DD:AA hydrogen bond interactions. Homophthalate leads to discrete dimers $[\text{Zn}(\text{tmtsc})(\mu\text{-homophthalate})]_2$ (**6**), whereas acetylenedicarboxylate yields the unexpected compound $[\text{Zn}(\text{tmtsc})_2(\text{OH}_2)]\text{[O}_2\text{CCH=CC(O)N(Me)C(=NNMe}_2\text{)S]}_2\cdot\text{H}_2\text{O}$ (**7**) in which the dicarboxylate has reacted with tmtsc to give a 2-hydrazono-4-oxo-1,3-thiazolidineacetate, which is subsequently trapped in the solid state by DD:AA hydrogen bonding interactions with $[\text{Zn}(\text{tmtsc})_2(\text{OH}_2)]^{2+}$. All products were characterised by single crystal X-ray crystallography, and the representational nature of these crystal structures to the bulk materials was confirmed by microanalysis and powder diffraction. © Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

Progress in the field of crystal engineering has largely arisen as a result of the identification and use of *supramolecular synthons*^[1] – small units within molecules that are anticipated to interact with each other in a predictable manner. There are currently two main strategies adopted in crystal engineering, in which these supramolecular synthons are based either on metal-ligand interactions^[2] or, alternatively, on intermolecular interactions such as hydrogen bonds,^[3] and recently there have been reports using both of these approaches together.^[4] We are particularly interested in the competitive interplay between the two strategies, and as a consequence have focussed our attention on systems in which both types of aggregation are possible.

As part of this study, we have shown that $[\text{Zn}(\text{thiourea})_4]^{2+}$ cations react with dicarboxylates by dis-

placing thiourea ligands to give polymers or dimers in which the zinc centres are linked by bridging dicarboxylates.^[5,6] In contrast, under similar conditions $[\text{M}(\text{tsc})_2]^{2+}$ ($\text{M} = \text{Zn, Ni}$; tsc = thiosemicarbazide) cations give ionic structures of the type $[\text{M}(\text{tsc})_2]\text{[dicarboxylate]}$ in which the cations and anions are linked together into tapes by hydrogen bonds.^[5,7] Hence, changing the ligands on the metal centre from uni- to bidentate has been shown to alter the mode of supramolecular assembly and consequently the type of structure formed.

In this paper we report on the reactions of $[\text{Zn}(\text{tmtsc})_2]^{2+}$ [tmtsc = 1,1,4-trimethylthiosemicarbazide, $\text{MeNHC}(\text{S})\text{NHNMe}_2$] with a range of dicarboxylates. The presence of the tertiary amine group in the tmtsc ligand was expected to increase its lability relative to tsc,^[8] and therefore enhance the possibility of ligand displacement from the metal coordination sphere. This has been borne out and, in contrast to the reactions with $[\text{Zn}(\text{thiourea})_4]^{2+}$ or $[\text{M}(\text{tsc})_2]^{2+}$, reactions with $[\text{Zn}(\text{tmtsc})_2]^{2+}$ give a wide variety of structural types, with that observed from a particular reaction depending on the relative orientation of the carboxylate groups within the anion.

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Results and Discussion

Synthesis

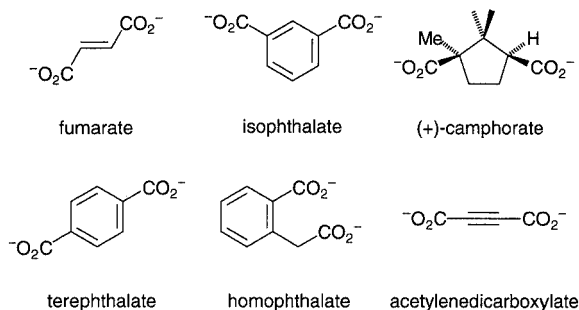
The complex $[\text{Zn}(\text{tmtsc})_2](\text{NO}_3)_2$ was prepared from the reaction of zinc(II) nitrate with tmtsc in ethanol. Recrystallisation of the product from water gave single crystals of $[\text{Zn}(\text{tmtsc})_2(\text{OH}_2)_2](\text{NO}_3)_2$ (**1**), the identity of which was confirmed crystallographically. Selected bond lengths and angles for **1** are given in Table 1.

Table 1. Selected bond lengths (Å) and angles (°) for compounds **1**, **3a**, **3b** and **6**

[a]	1	3a	3b	6
Zn(1)–S	2.4186(5)	2.327(2)	2.3267(9)	2.3814(7)
Zn(1)–N(1)	2.2513(15)	2.098(5)	2.195(2)	2.162(2)
Zn(1)–O(1)	2.1224(14)	1.933(4)	2.078(2)	2.0165(16)
Zn(1)–O(2)			2.334(2)	2.540(2)
Zn(1)–O(3)'		1.930(4)	2.343(2)	2.2823(19)
Zn(1)–O(4)'			2.056(2)	2.054(2)
N(1)–Zn(1)–S	81.76(4)	86.66(14)	84.09(6)	84.15(6)
O(1)–Zn(1)–O' [b]		116.13(17)	103.61(8)	137.90(8)

[a] Primed atoms generated by symmetry transformations $-x + 3/2, y - 1/2, z + 1/2$ (**3a**), $-x + 1, y - 1/2, -z + 1/2$ (**3b**) and $-x + 1, -y + 1, -z$ (**6**). [b] O' = O(3)' for **3a**; O' = O(4)' for **3b** and **6**.

Reaction of $[\text{Zn}(\text{tmtsc})_2](\text{NO}_3)_2$, in aqueous solution, with sodium salts of fumaric, (+)-camphoric, terephthalic, homophthalic and acetylenedicarboxylic acids gave compounds $[\text{Zn}(\text{tmtsc})_2(\text{OH}_2)]$ [fumarate] (**2**), $[\text{Zn}(\text{tmtsc})-(\mu-(+)\text{camphorate})]$ (**4**), $[\{\text{Zn}(\text{tmtsc})(\text{OH}_2)\}_2(\mu\text{-terephthalate})][\text{terephthalate}] \cdot 2\text{H}_2\text{O}$ (**5**), $[\text{Zn}(\text{tmtsc})(\mu\text{-homophthalate})_2]$ (**6**) and $[\text{Zn}(\text{tmtsc})_2(\text{OH}_2)]$ [O₂CCH=CC(O)N(Me)C(=NNMe₂)S] $\cdot\text{H}_2\text{O}$ (**7**), as the only isolated compounds in good yield. The analogous reaction with isophthalate gave two compounds, $[\text{Zn}(\text{tmtsc})(\mu\text{-isophthalate})]$ (**3a**) and $[\text{Zn}(\text{tmtsc})(\mu\text{-isophthalate})] \cdot \text{H}_2\text{O}$ (**3b**), with the anhydrous complex **3a** the major product. The empirical formulae of compounds **2**, **3a**, **4**, **5**, **6** and **7** were confirmed by microanalyses, and the structures of all the compounds were determined by single crystal X-ray analyses. A comparison of the experimental powder diffraction data with that simulated from the single-crystal data confirmed that the crystal structures are representative of the bulk materials, with the experimental data for isophthalate consistent with **3a**. The dicarboxylates used are illustrated in Scheme 1.



Scheme 1. Structures of the dicarboxylates used

Supramolecular Structures of **2–7**

The crystal structure of compound **2** consists of $[\text{Zn}(\text{tmtsc})_2(\text{OH}_2)]^{2+}$ cations and fumarate anions. The coordination geometry around the zinc centre is distorted square pyramidal ($\tau = 0.39$),^[9] with mutually *trans* tmtsc ligands. Selected bond lengths and angles are given in Table 2, and hydrogen bonding parameters are given in Table 3. Two hydrogen bonds between the parallel NH

Table 2. Selected bond lengths (Å) and angles (°) for compounds **2** and **7**

	2	7
Zn(1)–S(1)	2.3127(8)	2.3425(8)
Zn(1)–S(2)	2.3073(8)	2.3319(8)
Zn(1)–N(1)	2.306(2)	2.240(2)
Zn(1)–N(4)	2.280(2)	2.239(2)
Zn(1)–O(w) ^[a]	1.986(2)	1.993(2)
S(1)–Zn(1)–S(2)	141.34(3)	143.74(3)
N(1)–Zn(1)–N(4)	164.60(7)	168.84(7)
N(1)–Zn(1)–S(1)	82.25(5)	82.38(5)
N(4)–Zn(1)–S(2)	82.68(5)	81.99(5)
O(w)–Zn(1)–N(1)	97.15(7)	95.40(7)
O(w)–Zn(1)–N(4)	98.23(7)	95.75(7)
O(w)–Zn(1)–S(1)	108.10(6)	102.55(5)
O(w)–Zn(1)–S(2)	110.56(6)	113.69(6)

[a] O(w) = O(5) for **2**, O(w) = O(7) for **7**.

Table 3. Hydrogen bond lengths (Å) and angles (°) for compounds **2–7**

		$d(\text{D}\cdots\text{A})/\text{\AA}$	$d(\text{H}\cdots\text{A})/\text{\AA}$	$\angle(\text{DH}\cdots\text{A})^\circ$
2	N(2)–H(2) $\cdots$ O(1)	2.803(2)	1.94(2)	173(2)
	N(3)–H(3) $\cdots$ O(2)	2.730(2)	1.86(2)	172(2)
	N(5)–H(5) $\cdots$ O(3)	2.831(3)	1.95(2)	177(3)
	N(6)–H(6) $\cdots$ O(4)	2.731(3)	1.87(2)	176(3)
	O(5)–H(5A) $\cdots$ O(4)	2.649(2)	1.82(2)	170(2)
3a	O(5)–H(5B) $\cdots$ O(2)	2.588(2)	1.71(2)	172(4)
	N(2)–H(2) $\cdots$ O(2)	2.765(6)	2.01(6)	142(5)
	N(3)–H(3) $\cdots$ O(2)	2.909(7)	2.19(6)	138(5)
3b	N(3)–H(3) $\cdots$ O(3)	2.793(3)	2.10(3)	146(3)
	N(2)–H(2) $\cdots$ O(5)	2.869(3)	2.08(3)	171(3)
	O(5)–H(5A) $\cdots$ O(2)	2.890(4)	2.15(4)	163(4)
	O(5)–H(5B) $\cdots$ O(1)	2.877(3)	2.13(4)	163(4)
4	N(2)–H(2) $\cdots$ O(2)	2.758(4)	1.91(2)	167(3)
	N(3)–H(3) $\cdots$ O(8)	2.907(4)	2.16(2)	141(3)
	N(5)–H(5) $\cdots$ O(4)	2.747(4)	1.89(3)	164(4)
	N(6)–H(6) $\cdots$ O(5)	2.892(4)	2.13(3)	144(4)
5	N(2)–H(2) $\cdots$ O(1)	2.871(2)	2.00(2)	170(2)
	N(3)–H(3) $\cdots$ O(2)	2.779(2)	1.91(2)	179(2)
	O(5)–H(5A) $\cdots$ O(6)	2.654(3)	1.80(3)	173(3)
	O(5)–H(5B) $\cdots$ O(3)	2.665(3)	1.79(2)	173(4)
	O(6)–H(6A) $\cdots$ O(1)	2.854(3)	2.01(2)	166(3)
6	O(6)–H(6B) $\cdots$ O(4)	2.812(3)	2.07(3)	145(4)
	N(2)–H(2) $\cdots$ O(2)	2.790(3)	1.94(2)	159(3)
	N(3)–H(3) $\cdots$ O(2)	2.982(3)	2.19(2)	151(3)
7	N(2)–H(2) $\cdots$ O(2)	2.676(2)	1.79(2)	173(2)
	N(3)–H(3) $\cdots$ O(1)	2.901(2)	2.03(2)	179(2)
	N(5)–H(5) $\cdots$ O(4)	2.651(2)	1.77(2)	177(2)
	N(6)–H(6) $\cdots$ O(5)	2.831(2)	1.95(2)	171(2)
	O(7)–H(7A) $\cdots$ O(1)	2.640(2)	1.78(2)	170(3)
	O(7)–H(7B) $\cdots$ O(8)	2.640(2)	1.81(2)	165(2)
	O(8)–H(8A) $\cdots$ O(5)	2.697(3)	1.83(2)	169(3)
	O(8)–H(8B) $\cdots$ N(12)	3.034(3)	2.20(3)	159(5)

groups on the tmtsc ligands and the two oxygen atoms of the carboxylate groups serve to link the cations and anions together into tapes (Figure 1). These hydrogen bond donor-donor acceptor-acceptor (DD:AA) interactions are similar to those observed in $[\text{Zn}(\text{tsc})_2(\text{OH}_2)_2][\text{terephthalate}] \cdot 2\text{H}_2\text{O}$ ^[5] and in nickel thiosemicarbazide dicarboxylates^[7] [graph set^[10] $R_2^2(8)$]. The cation...anion tapes in **2** are linked into sheets by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds from the aqua ligands in a neighbouring plane to carboxylate oxygen atoms. Since the aqua ligands within each tape are all orientated in the same direction, these $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds ensure that the sheets exist as bilayers, with weaker $\text{C}-\text{H}\cdots\text{O}$ interactions linking these bilayers into the gross structure. Similar DD:AA interactions were observed between the tmtsc ligands and the nitrate anions in the structure of **1**. However, a mismatch in both the charge and shape of the ions guarantees that the DD:AA interactions do not lead to tape formation in the nitrate – instead, discrete $[\text{Zn}(\text{tmtsc})_2(\text{OH}_2)_2](\text{NO}_3)_2$ units are linked only by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds.

The crystal structures of compounds **3a** and **3b** reveal that, in contrast to **2**, both compounds are coordination polymers with isophthalates bridging between metal centres (Figure 2). In both structures each zinc(II) centre is coordinated to a tmtsc ligand and two isophthalate ligands; in **3b** included water molecules are also present in the lattice. Selected bond lengths and angles for both **3a** and **3b** are given

in Table 1 and hydrogen bonding parameters are given in Table 3.

The coordination geometry around the zinc centre in compound **3a** is distorted tetrahedral with the carboxylates η^1 -coordinated (Figure 2, top), as observed in $[\text{Zn}(\text{thiourea})_2(\mu\text{-dicarboxylate})]$ polymers.^[6] Coordination of the carboxylates prevents the formation of DD:AA interactions, although hydrogen bonding is still present, linking the chains through two $\text{N}-\text{H}\cdots\text{O}$ interactions from the NH groups to a single carboxylate oxygen atom [graph set $R_1^1(6)$].

The presence of the lattice water molecule in compound **3b** leads to differences in the manner in which the chains are linked together (Figure 2, bottom). One of the NH groups hydrogen bonds to a carboxylate oxygen atom, whereas the other forms an $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond to the included water molecule. Two $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds from the water to carboxylate oxygen atoms complete the hydrogen bonding, with one of these leading to the formation of $R_3^3(10)$ rings. Significant $\pi-\pi$ interactions are also present, with the shortest $\text{C}\cdots\text{C}$ distance between isophthalate rings being 3.45 Å. In order to accommodate the hydrogen bonding in **3b** there is a change in the metal coordination geometry relative to that in **3a**, with both carboxylate groups unsymmetrically η^2 -coordinated, thus affording distorted octahedral geometry at the metal centre. Consequently the longer Zn–O distances have been reduced from 2.838(5)

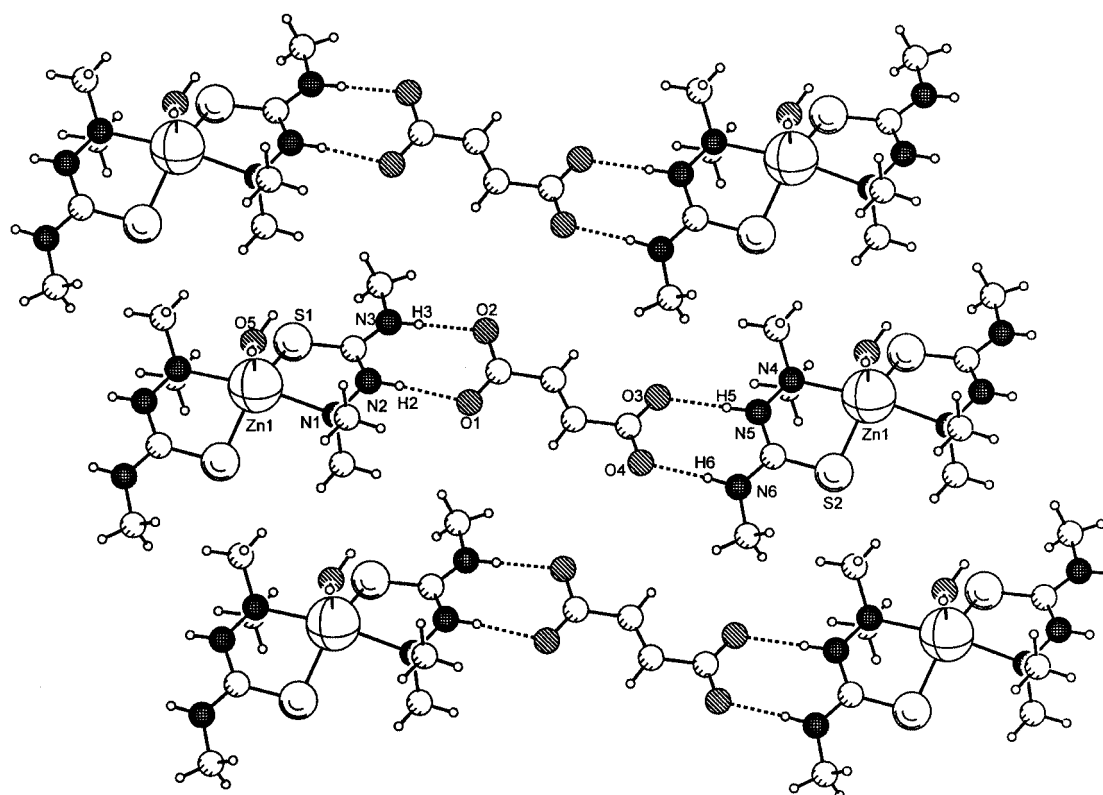


Figure 1. The solid state structure of $[\text{Zn}(\text{tmtsc})_2(\text{OH}_2)][\text{fumarate}]$ (**2**)

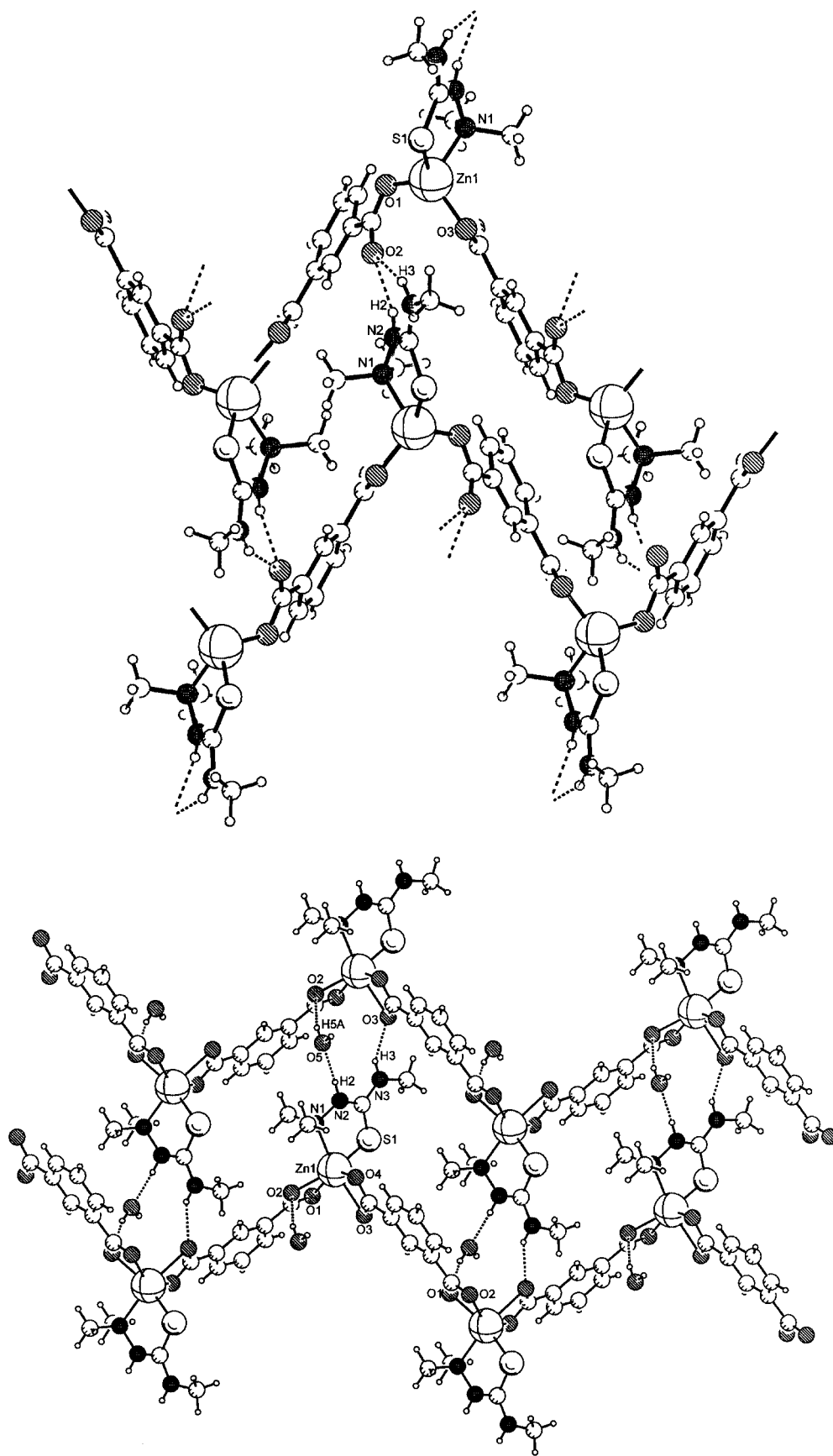


Figure 2. The solid state structures of (top) $[\text{Zn}(\text{tmtsc})(\mu\text{-isophthalate})]$ (**3a**) and (bottom) $[\text{Zn}(\text{tmtsc})(\mu\text{-isophthalate})]\cdot\text{H}_2\text{O}$ (**3b**)

and 3.071(4) Å in **3a** to 2.334(2) and 2.343(2) Å in **3b** on incorporation of the water. The increase in coordination number has little effect on the Zn–S distance, but leads to a significant increase in the Zn–N bond length and a reduction of the tmtsc bite angle (Table 1).

Compound **4**, incorporating the (+)-camphorate dianion, also exists as a coordination polymer, with the (+)-camphorates linking the zinc centres. The asymmetric unit of this compound contains two independent Zn(tmtsc) groups and two independent (+)-camphorates. Both zinc centres are five-coordinate, with one carboxylate group bound η^1 and the other η^2 . Selected bond lengths and angles are given in Table 4 and hydrogen bonding parameters are given in Table 3. The two independent (+)-camphorate dianions differ in that one contains two η^1 -carboxylates whereas the other contains two η^2 -carboxylates.

The structure of **4** differs from those for **3a** and **3b** by virtue of the manner in which the coordination polymers interact with each other. In **4** this is through two N–H...O hydrogen bonds from each of the tmtsc ligands, with the acceptors being oxygen atoms on separate carboxylate groups (Figure 3). One of these oxygen atoms is non-coordinated [O(2) or O(4)] whereas the other forms the longer Zn–O bond of an η^2 -carboxylate [O(5) or O(8)]. This hydrogen bonding pattern is facilitated by a change in conformation of the tmtsc ligand. A rotation of 180° around the C–N(amino) bond means that the two NH groups within each ligand are no longer orientated in the same direction. Such a conformational change has been observed

Table 4. Selected bond lengths (Å) and angles (°) for compound **4**

Zn(1)–S(1)	2.3564(8)
Zn(1)–N(1)	2.169(2)
Zn(1)–O(1)	1.968(2)
Zn(1)–O(8)' [a]	2.081(2)
Zn(1)–O(7)'	2.254(2)
Zn(2)–S(2)	2.3494(9)
Zn(2)–N(4)	2.163(3)
Zn(2)–O(5)	2.124(3)
Zn(2)–O(6)	2.251(2)
Zn(2)–O(3)	1.978(2)
N(1)–Zn(1)–S(1)	83.48(7)
O(1)–Zn(1)–O(8)'	128.68(9)
N(4)–Zn(2)–S(2)	83.93(7)
O(3)–Zn(2)–O(5)	130.73(10)

[a] Primed atoms generated by symmetry transformation $x, y, z - 1$.

previously in the structure of *cis*-[Ni(4-Et-tsc)₂][terephthalate]^[11] although in the nickel complex the *cis* orientation of the ligands results in the formation of a new DD face which is involved in hydrogen bonding. This does not happen for **4** however, and the loss of potential secondary interactions is compensated by the formation of four strong hydrogen bonds.

The crystal structure of compound **5** consists of [$\{Zn(tmtsc)(OH_2)\}_2(\mu\text{-terephthalate})\}^{2+}$ cations, terephthalate anions and included water molecules. The geometry around the zinc centres in **5** is distorted square pyramidal ($\tau = 0.36^{[9]}$), with the carboxylate unsymmetrically coordin-

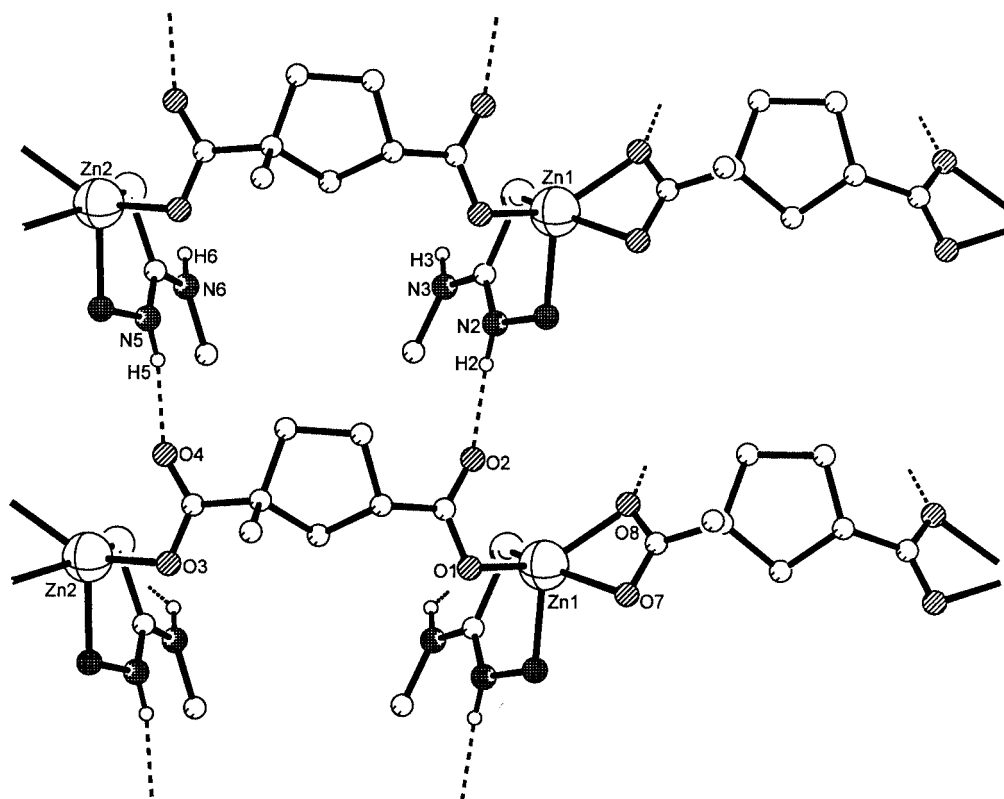


Figure 3. The solid state structure of [Zn(tmtsc)(μ-(+)-camphorate)] (**4**), with all carbon-bound hydrogen atoms omitted for clarity

ated. Selected bond lengths and angles are given in Table 5 and hydrogen bonding parameters are given in Table 3. The cation in **5** can be regarded in hydrogen bonding terms as an “expanded” $[\text{Zn}(\text{tmtsc})_2]^{2+}$ cation, since both contain the same number and relative orientation of NH groups. The cations and anions in **5** interact through two hydrogen bonds in a similar DD:AA manner to that observed in **2**, which overall serves to link the ions into tapes (Figure 4). These tapes are connected into sheets by hydrogen bonding to water molecules, although, in contrast to **2**, these involve both water included within the lattice and coordinated water ligands from tapes above and below the sheets. Since each cation contains two axial coordinated water molecules, pointing in opposite directions, the sheets are all linked in the same manner, which contrasts with the bilayers observed in **2**. The structure of **5** can be regarded as intermediate between those of **2** and **3**, as half the dicarboxylates link the metal centres together through coordinative bonds while the remaining half link the metal centres through hydrogen bonds to the coordinated tmtsc ligands. Despite the

importance of dicarboxylates in crystal engineering this is, to the best of our knowledge, the first occasion a structure has been observed in which the anion fulfils both discrete coordination and hydrogen bonding roles.

The crystal structure of compound **6** consists of discrete $[\text{Zn}(\text{tmtsc})(\mu\text{-homophthalate})]_2$ molecules (Figure 5), in which the two zinc centres are crystallographically equivalent, related through an inversion centre. Selected bond lengths and angles are given in Table 2, and hydrogen bonding parameters are given in Table 3. Each carboxylate group is unsymmetrically η^2 -coordinated, though the $\text{Zn}(1)-\text{O}(2)$ distance is long $[2.540(2) \text{ \AA}]$. This oxygen atom is involved in $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonding (see below). The distorted octahedral coordination geometry around the metal centres is similar to that observed in **3b**. The dimeric structure of **6**

Table 5. Selected bond lengths (Å) and angles (°) for compound **5**

$\text{Zn}(1)-\text{S}(1)$	2.3036(7)
$\text{Zn}(1)-\text{N}(1)$	2.119(2)
$\text{Zn}(1)-\text{O}(3)$	2.289(2)
$\text{Zn}(1)-\text{O}(4)$	2.005(2)
$\text{Zn}(1)-\text{O}(5)$	1.993(2)
$\text{N}(1)-\text{Zn}(1)-\text{S}(1)$	86.55(5)
$\text{O}(3)-\text{Zn}(1)-\text{O}(4)$	60.62(8)
$\text{N}(1)-\text{Zn}(1)-\text{O}(4)$	137.87(9)
$\text{S}(1)-\text{Zn}(1)-\text{O}(3)$	159.58(7)
$\text{O}(5)-\text{Zn}(1)-\text{O}(4)$	106.94(9)
$\text{O}(5)-\text{Zn}(1)-\text{O}(3)$	90.68(8)
$\text{O}(5)-\text{Zn}(1)-\text{N}(1)$	103.89(8)
$\text{O}(5)-\text{Zn}(1)-\text{S}(1)$	109.56(6)

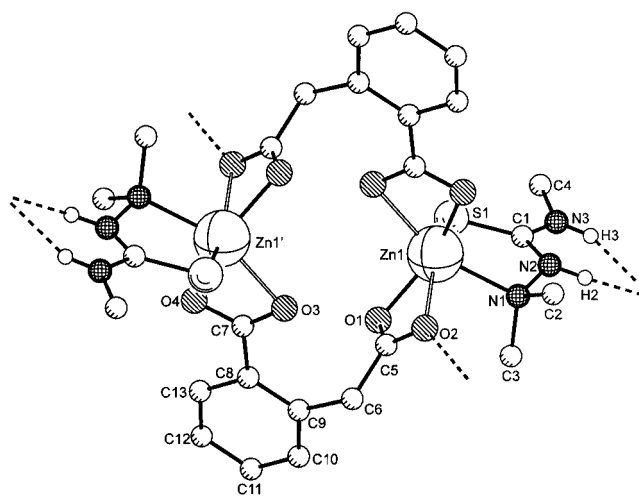


Figure 5. The molecular structure of $[\text{Zn}(\text{tmtsc})(\mu\text{-homophthalate})]_2$ (**6**), with all carbon-bound hydrogen atoms omitted for clarity

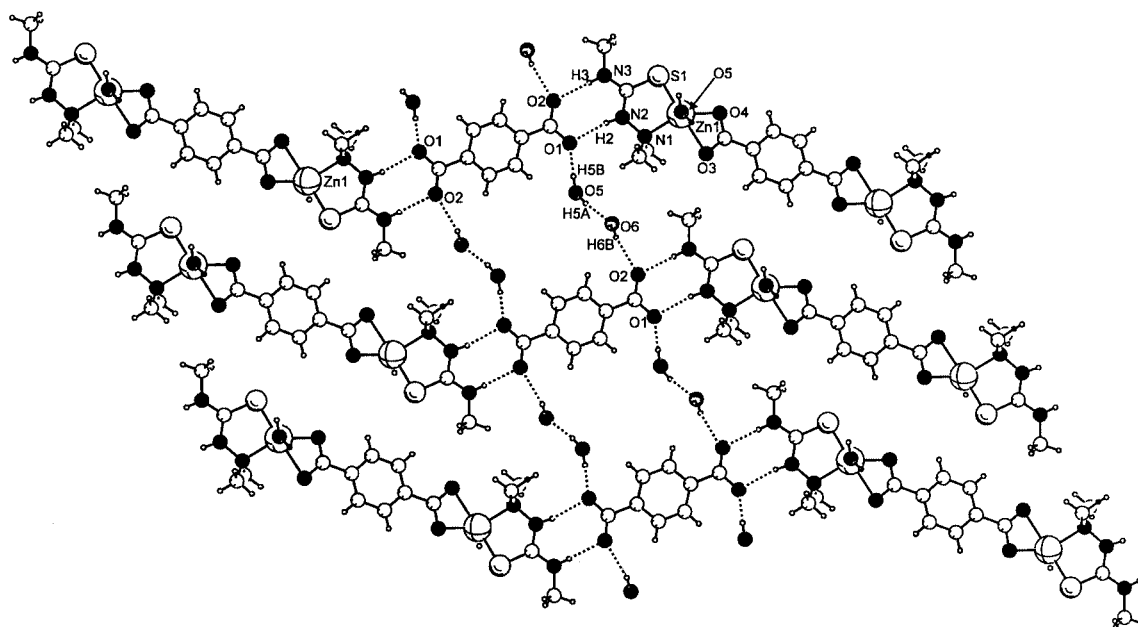


Figure 4. The solid state structure of $[\{\text{Zn}(\text{tmtsc})(\text{OH}_2)\}_2(\mu\text{-terephthalate})][\text{terephthalate}] \cdot 2\text{H}_2\text{O}$ (**5**)

is similar to that previously observed in $[\text{Zn}\{\text{SC}(\text{NH}_2)_2\}_2(\mu\text{-homophthalate})]_2$ [6] strongly suggesting that dimer formation is driven by the relative orientation of the carboxylate groups in the homophthalate dianion. In contrast to **6**, $[\text{Zn}\{\text{SC}(\text{NH}_2)_2\}_2(\mu\text{-homophthalate})]_2$ contains η^1 -coordinated carboxylate groups, with non-bonded Zn–O distances of 2.86(3) and 3.05(3) Å. The distances across the ring in **6**, as represented by the $\text{O}(2)\cdots\text{O}(2)'$ and $\text{O}(3)\cdots\text{O}(3)'$ separations, are 5.9 and 3.9 Å respectively, hence the dimers are somewhat flattened relative to those present in $[\text{Zn}\{\text{SC}(\text{NH}_2)_2\}_2(\mu\text{-homophthalate})]_2$ ($\text{O}\cdots\text{O}$ 5.3 and 4.9 Å).

Molecules of **6** are linked in the solid state through two $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds to a single carboxylate oxygen

atom O(2), in an analogous manner to **3a** [graph set $\text{R}_2^1(6)$]. Each molecule provides hydrogen bond donors in one dimension and hydrogen bond acceptors in a second, as shown schematically in Figure 6 (top). These interactions therefore serve to link the molecules into sheets (Figure 6, bottom). Despite the presence of carboxylate oxygen atoms which are not involved in hydrogen bonding, there are no hydrogen bond interactions linking the sheets together.

The reaction between $[\text{Zn}(\text{tmtsc})_2](\text{NO}_3)_2$ and acetylenedicarboxylate does not give a compound in which the dicarboxylate is incorporated, either as a ligand or as a hydrogen bonded anion. Instead, a reaction (Scheme 2) between acetylenedicarboxylate and a tmtsc molecule occurs to give a

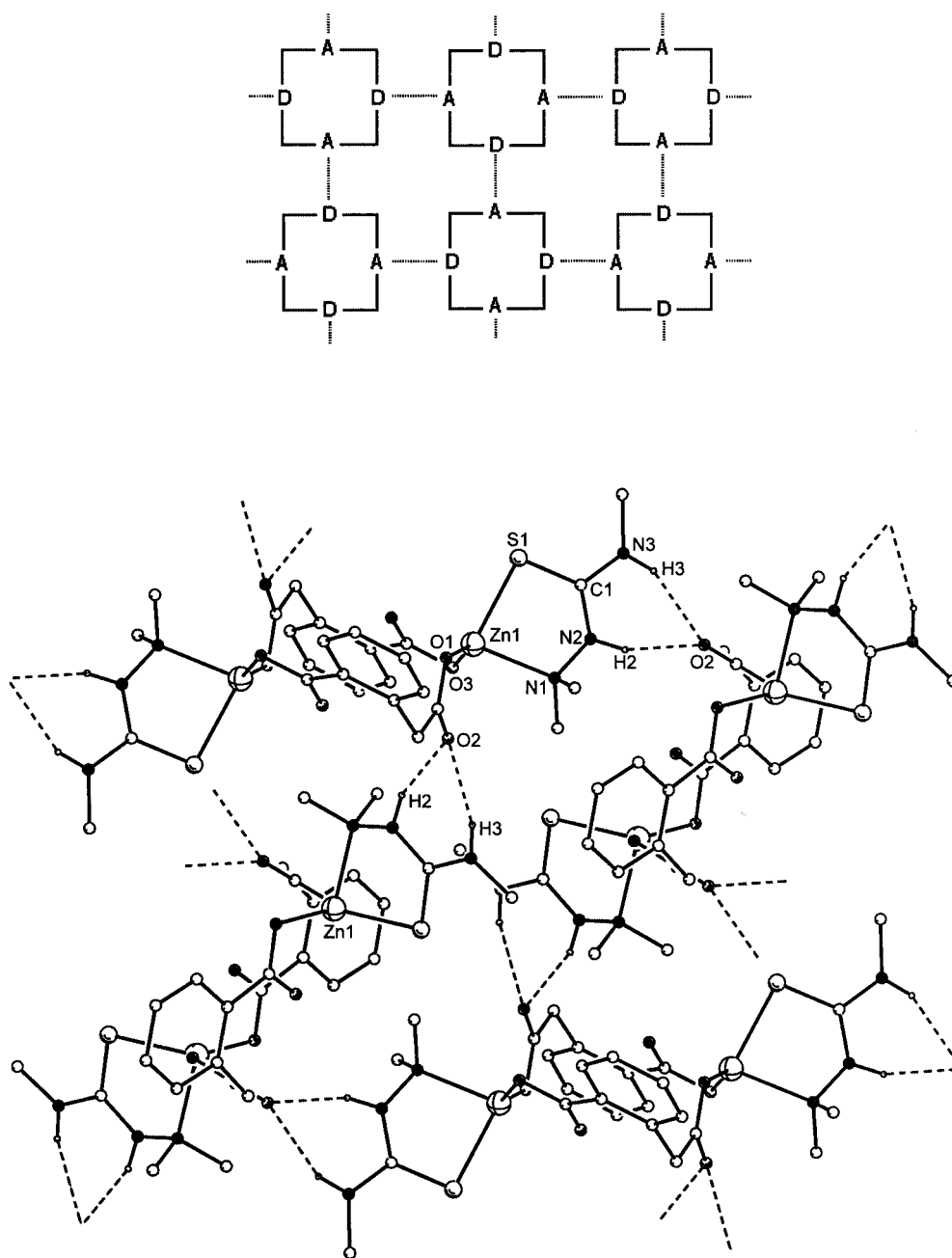
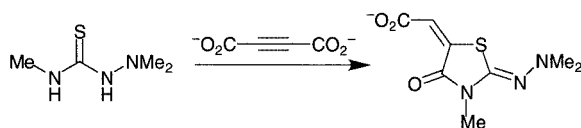


Figure 6. Intermolecular interactions present in $[\text{Zn}(\text{tmtsc})(\mu\text{-homophthalate})]_2$ (**6**); (top) schematic representation of hydrogen bonded sheets; (bottom) part of the extended structure, with all carbon-bound hydrogen atoms omitted for clarity



Scheme 2. Conversion of 1,1,4-trimethylthiosemicarbazide into the anion observed in compound 7

2-hydrazono-4-oxo-1,3-thiazolidineacetate, which is itself incorporated into the structure as the anion. Thus the identity of **7**, as determined by the crystal structure, is $[\text{Zn}(\text{tmtsc})_2(\text{OH}_2)] [\text{O}_2\text{CCH}=\text{CC}(\text{O})\text{N}(\text{Me})\text{C}(\text{=NNMe}_2)\text{S}]_2 \cdot \text{H}_2\text{O}$ (Figure 7). The $[\text{Zn}(\text{tmtsc})_2(\text{OH}_2)]^{2+}$ cation has a distorted square pyramidal geometry ($\tau = 0.41^{[9]}$) with the tmtsc ligands mutually *trans* as in **2** and **5**. Selected bond lengths and angles are given in Table 2, with hydrogen bond parameters given in Table 3. Reactions between thiosemicarbazides and acetylenedicarboxylic acid giving similar products have been reported previously,^[12] and the observation of such a reaction here provides evidence of the lability of the tmtsc ligand on zinc, as is also evident from the structures of **3–6**.

The heterocyclic anion contains a carboxylate group, and these oxygen atoms are involved in DD:AA hydrogen bonds with the parallel NH groups of the tmtsc ligands. Thus the principal hydrogen bonding motif in **7** is the same as that in both **2** and **5**. However, the presence of only one carboxylate group per anion means that extended cation...anion tapes cannot be formed, and instead the available interactions afford only $[\text{cation}][\text{anion}]_2$ units as observed for **1**. These units are linked together into the gross structure of **7** *via* hydrogen bonds involving the coordinated and included water molecules, where the former acts as a hydrogen bond donor to both a carboxylate oxygen atom and the included water, and the latter acts as a hydrogen bond donor to a carboxylate oxygen atom and a nitrogen atom.

Discussion

Compounds **2–7** were all isolated in good yield as the sole products from the reactions between $[\text{Zn}(\text{tmtsc})_2](\text{NO}_3)_2$ and a dicarboxylate under identical conditions. There is a wide structural diversity in the prod-

ucts ranging from coordination polymers (**3a**, **3b**, **4**) to hydrogen-bonded ionic aggregates (**2**) via an intermediate structure (**5**) in which half the anions are coordinated. This diversity confirms the initial premise concerning the lability of tmtsc lying between those of tsc and thiourea. The metal coordination number varies from 4 to 6, and is not a major factor in determining the supramolecular structure – this is witnessed by the zinc centres in the coordination polymers **3a**, **3b** and **4** having coordination numbers of 4, 6 and 5 respectively. The products observed are also not affected by changes in the stoichiometry of $[\text{Zn}(\text{tmtsc})_2](\text{NO}_3)_2$ and dicarboxylate used in the reaction, nor do differences appear to be related to the basicity of the dicarboxylates or the pH of the reaction mixture. However, it is possible to rationalise the structural differences on the basis of the dicarboxylate shape, 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 angular parameters to help in the design and preparation of 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 coplanar, ψ represents bending of the carboxylates towards each other, and ϕ represents the relative twisting of the planes of the carboxylate groups. For terephthalate and fumarate in the structures of **5** and **2**, θ and ψ are 180° and ϕ is close to zero, as the carboxylate groups are almost coplanar and orientated in opposite directions. These compounds consist of ionic structures based on cation...anion tapes, held together by DD:AA hydrogen bond interactions. This is consistent with previous structures containing these anions,^[5,7] though the formation of **5**, in which half of the terephthalates are coordinated giving “extended” $[\{\text{Zn}(\text{tmtsc})(\text{OH}_2)\}_2(\mu\text{-terephthalate})]^{2+}$ cations is somewhat unexpected, as the nickel compound $[\text{Ni}(\text{tmtsc})_2(\text{OH}_2)_2][\text{terephthalate}]$ readily forms in a comparative reaction. The presence of the extended cation in **5** does prevent unfavourable interactions between the methyl groups on neighbouring tapes that would occur if simple $[\text{Zn}(\text{tmtsc})_2]^{2+}$ cations were incorporated in the orientation

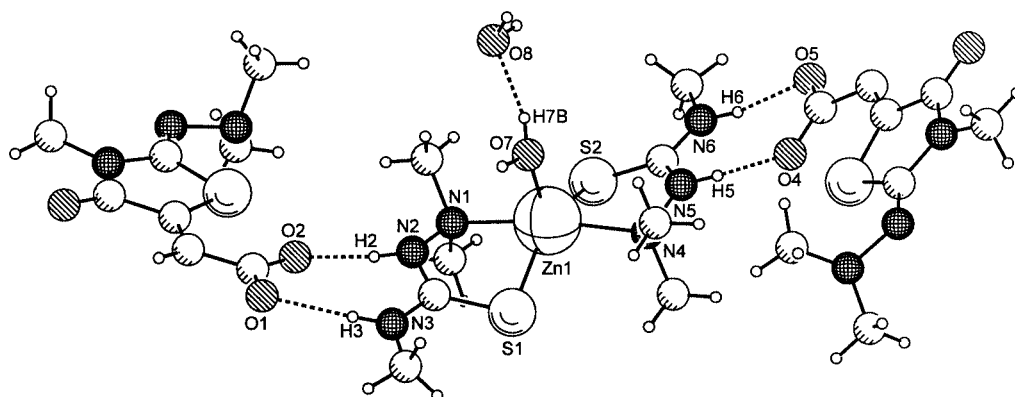


Figure 7. Part of the solid state structure of $[\text{Zn}(\text{tmtsc})_2(\text{OH}_2)] [\text{O}_2\text{CCH}=\text{CC}(\text{O})\text{N}(\text{Me})\text{C}(\text{=NNMe}_2)\text{S}]_2 \cdot \text{H}_2\text{O}$ (**7**)

adopted. Despite possessing the same angular parameters, terephthalate and fumarate differ in the distance between the carboxylate groups and the fact that for fumarate these are not co-linear, there being a lateral displacement of 1.07 Å.

While isophthalate and camphorate are structurally very different, it is noteworthy that each possesses one of the angular parameters – θ for isophthalate and ϕ for camphorate – that has been reduced from the 180° value for terephthalate to 120°, and both of these dicarboxylates form coordination polymers with Zn(tmtsc) centres. While the carboxylate orientations in **3a**, **3b** and **4** do not preclude hydrogen bonded structures, they may reduce their likelihood since there are more limited ways in which the resultant zig-zag tapes would be able to pack.

The structures of **6** and $[\text{Zn}\{\text{SC}(\text{NH}_2)_2\}_2(\mu\text{-homophthalate})_2]$ reflect a clear propensity for homophthalate to form dimers, despite the dicarboxylates in these complexes adopting different coordination modes. In the $[\text{Zn}\{\text{SC}(\text{NH}_2)_2\}_2]^{2+}$ system this tendency is particularly marked since homophthalate is the only dicarboxylate out of 13 structurally characterised compounds not to form a coordination polymer. A search of the CSD^[14] reveals no examples of homophthalate coordination polymers, and it is noticeable that dimerisation of Mo_2 units has also been observed with this dicarboxylate.^[15]

The reaction between $[\text{Zn}(\text{tmtsc})_2](\text{NO}_3)_2$ and acetylenedicarboxylate gave an unexpected product in **7**. The coupling reaction between tmtsc and acetylenedicarboxylate has generated a 2-hydrazono-4-oxo-1,3-thiazolidineacetate anion, and the structure of **7** illustrates the potential for trapping reaction products in hydrogen bonded networks through the use of species containing complementary hydrogen bonding groups.

Four of the seven carboxylate-containing structures reported in this paper contain water, either as a ligand (**2**), included in the lattice (**3b**), or both (**5** and **7**). The tmtsc ligand has only two hydrogen bond donors whereas a carboxylate group can accept four or even more hydrogen bonds. Therefore use of tmtsc as a ligand in these systems leads to a relative deficiency of hydrogen bond donors in the gross structure which can be overcome by inclusion of water. This solvent inclusion also affords greater flexibility in the relative orientations of hydrogen bonding groups.

Conclusions

In this paper we have demonstrated that a deceptively simple series of compounds – those resulting from the reaction between $[\text{Zn}(\text{tmtsc})_2]^{2+}$ and a dicarboxylate – have widely differing structures, with the relative orientation of the carboxylate groups a major factor in determining the type of structure formed. The variety of structural types obtained from this reaction series contrasts with the products observed from analogous reactions using thiourea or thiosemicarbazide complexes. Thiourea is invariably dis-

placed from $[\text{Zn}\{\text{SC}(\text{NH}_2)_2\}_4]^{2+}$ leading to coordination polymers or cyclic oligomers, all containing tetrahedral zinc centres, whereas thiosemicarbazide is generally retained on the metal leading to structures in which the ions are only associated through hydrogen bonds. The tmtsc ligand lies between these two extremes confirming our initial premise concerning its lability, and this places $[\text{Zn}(\text{tmtsc})_2]^{2+}$ on the borderline between the two main strategies currently employed in crystal engineering. These observations are important in helping to define the limits of the different crystal engineering strategies.

Experimental Section

Microanalyses were carried out by Mr. Alan Carver (University of Bath Microanalytical Service). 1,1,4-Trimethylthiosemicarbazide (tmtsc) was prepared from the reaction of *N,N*-dimethylhydrazine with methyl isothiocyanate in diethyl ether.^[16] Sodium dicarboxylates were either purchased from commercial sources and used directly (fumarate and terephthalate) or prepared from the appropriate dicarboxylic acid and either sodium hydroxide or sodium hydrogen carbonate.

Synthesis of $[\text{Zn}(\text{tmtsc})_2](\text{NO}_3)_2$: 1,1,4-Trimethylthiosemicarbazide (0.448 g, 3.36 mmol) in ethanol (10 cm³) was added to zinc nitrate hexahydrate (0.500 g, 1.68 mmol) in ethanol (10 cm³) and the solution stirred for 1 h. The volume of the solution was reduced to 5 cm³ in vacuo, and the colourless crystals that precipitated overnight were separated by filtration. Yield 0.75 g (98%). On recrystallisation from water, crystals of $[\text{Zn}(\text{tmtsc})_2(\text{OH}_2)_2](\text{NO}_3)_2$ (**1**) were obtained.

Synthesis of **2:** Aqueous solutions of sodium fumarate (35 mg, 0.22 mmol) and $[\text{Zn}(\text{tmtsc})_2](\text{NO}_3)_2$ (100 mg, 0.22 mmol) were mixed. After approximately 24 hours colourless crystals formed, and these were isolated by filtration. Yield 80 mg (79%). $\text{C}_{12}\text{H}_{26}\text{N}_6\text{O}_5\text{S}_2\text{Zn}$ (463.9): calcd. C 31.1, N 18.1, H 5.65; found C 31.3, N 18.1, H 5.71.

Synthesis of **3a and **3b**:** As for **2** using sodium isophthalate (53 mg, 0.25 mmol) and $[\text{Zn}(\text{tmtsc})_2](\text{NO}_3)_2$ (115 mg, 0.25 mmol). Yield 81 mg (88%). $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_4\text{SZn}$ (362.7): calcd. C 39.7, N 11.6, H 4.17; found C 39.6, N 11.5, H 4.22.

Synthesis of **4:** As for **2** using sodium (1*R*,3*S*)-(+)-camphorate (54 mg, 0.22 mmol) and $[\text{Zn}(\text{tmtsc})_2](\text{NO}_3)_2$ (100 mg, 0.22 mmol). Yield 56 mg (64%). $\text{C}_{14}\text{H}_{25}\text{N}_3\text{O}_4\text{SZn}$ (396.8) calcd. C 42.4, N 10.6, H 6.35; found C 42.1, N 10.6, H 6.28.

Synthesis of **5:** As for **2** using sodium terephthalate (46 mg, 0.22 mmol) and $[\text{Zn}(\text{tmtsc})_2](\text{NO}_3)_2$ (100 mg, 0.22 mmol). Yield 63 mg (72%). $\text{C}_{24}\text{H}_{38}\text{N}_6\text{O}_{12}\text{S}_2\text{Zn}_2$ (797.5): calcd. C 36.2, N 10.5, H 4.80; found C 36.5, N 10.4, H 4.79.

Synthesis of **6:** As for **2** using sodium homophthalate (49 mg, 0.22 mmol) and $[\text{Zn}(\text{tmtsc})_2](\text{NO}_3)_2$ (100 mg, 0.22 mmol). Yield 59 mg (71%). $\text{C}_{26}\text{H}_{34}\text{N}_6\text{O}_8\text{S}_2\text{Zn}_2$ (753.5): calcd. C 41.5, N 11.2, H 4.55; found C 41.2, N 10.9, H 4.48.

Synthesis of **7:** As for **2** using sodium acetylenedicarboxylate (35 mg, 0.22 mmol) and $[\text{Zn}(\text{tmtsc})_2](\text{NO}_3)_2$ (100 mg, 0.22 mmol). Yellow crystals. Yield 74 mg (82% based on tmtsc).

Table 6. Crystallographic data for complexes **1**, **2**, **3a**, **3b**, **4**, **5**, **6** and **7**

	1	2	3a	3b	4	5	6	7
Formula	C ₈ H ₂₆ N ₈ O ₈ S ₂ Zn	C ₁₂ H ₂₆ N ₆ O ₅ S ₂ Zn	C ₁₂ H ₁₅ N ₃ O ₄ SZn	C ₁₂ H ₁₇ N ₃ O ₅ SZn	C ₁₄ H ₂₅ N ₃ O ₄ SZn	C ₁₂ H ₁₉ N ₃ O ₆ SZn	C ₁₃ H ₁₇ N ₃ O ₄ SZn	C ₂₄ H ₄₆ N ₁₂ O ₈ S ₄ Zn
<i>M_r</i>	491.86	463.88	362.70	380.72	396.80	398.73	376.73	824.34
<i>T</i> / K	170(2)	293(2)	150(2)	293(2)	100(2)	293(2)	150(2)	293(2)
Crystal size/mm	0.25 × 0.15 × 0.15	0.30 × 0.20 × 0.20	0.05 × 0.04 × 0.02	0.17 × 0.15 × 0.15	0.30 × 0.13 × 0.10	0.20 × 0.20 × 0.20	0.30 × 0.13 × 0.10	0.23 × 0.20 × 0.20
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> na2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> / Å	9.6360(3)	8.122(1)	15.716(2)	8.488(1)	26.6250(4)	7.397(1)	9.6890(2)	9.623(2)
<i>b</i> / Å	12.4200(4)	8.364(1)	11.792(2)	14.444(2)	7.5350(1)	9.384(1)	12.2920(3)	11.844(2)
<i>c</i> / Å	9.8170(3)	16.247(6)	7.603(1)	13.675(2)	18.6840(4)	12.085(2)	13.2240(3)	17.848(5)
<i>α</i> / °	90	97.11(2)	90	90	90	98.90(1)	90	102.56(1)
<i>β</i> / °	118.4370(16)	101.98(1)	90	104.92(1)	103.7490(7)	90.80(2)	94.835(1)	102.69(1)
<i>γ</i> / °	90	103.200(9)	90	90	90	99.40(1)	90	92.467(10)
<i>U</i> / Å ³	1033.13(6)	1034.0(4)	1409.0(3)	1620.0(4)	3640.97(11)	817.0(2)	1569.34(6)	1928.2(7)
<i>Z</i>	2	2	4	4	8	2	4	2
<i>d</i> _{calc} / g cm ^{−3}	1.555	1.490	1.710	1.561	1.448	1.621	1.594	1.420
<i>μ</i> / mm ^{−1}	1.442	1.423	1.910	1.670	1.485	1.664	1.718	0.912
<i>θ</i> _{min} , <i>θ</i> _{max}	2.91, 27.49	2.54, 24.97	2.10, 29.33	2.09, 24.98	3.59, 27.49	2.23, 24.98	3.59, 27.48	2.18, 24.97
Reflections collected	12570	4023	13734	3201	27784	3229	37834	7485
Independent reflections	2369	3618	3894	2840	8071	2857	3580	6764
<i>R</i> _{int}	0.0385	0.0117	0.1073	0.0167	0.0430	0.0119	0.0959	0.0095
No. parameters, restraints	144, 5	257, 6	189, 3	219, 0	447, 5	235, 6	210, 2	486, 8
Final <i>R</i> ₁ , <i>wR</i> ₂	0.0287, 0.0955	0.0280, 0.0736	0.0667, 0.1473	0.0298, 0.0747	0.0375, 0.0842	0.0272, 0.0841	0.0332, 0.0893	0.0312, 0.0850
[<i>I</i> > 2σ(<i>I</i>)]								
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0368, 0.1056	0.0346, 0.0764	0.0852, 0.1530	0.0423, 0.0781	0.0468, 0.0884	0.0363, 0.0899	0.0476, 0.1018	0.0409, 0.0894

C₂₄H₄₆N₁₂O₈S₄Zn (824.3): calcd. C 35.0, N 20.4, H 5.62; found C 34.7, N 20.1, H 5.59.

The syntheses of **2–7** were repeated on a smaller scale in more dilute solutions in order to obtain crystals of suitable quality for the single-crystal X-ray analyses.

For compounds **2**, **3b**, **5** and **7**, data were collected on an Enraf–Nonius CAD4 automatic four-circle diffractometer and for compounds **1**, **4** and **6** data were collected on a Nonius Kappa CCD diffractometer, in all cases using Mo-*K*_α radiation (graphite monochromated) with $\lambda = 0.71069$ Å for **2**, **3b**, **5** and **7** and 0.71070 Å for **1**, **4** and **6**. Due to small crystal size, data for compound **3a** were collected at Station 9.8 at the SRS, Daresbury using synchrotron radiation (silicon 111 monochromated) with $\lambda = 0.68980$ Å. Crystallographic data are presented in Table 6. Lorentz and polarisation corrections were applied in all analyses and extinction coefficients were applied for compounds **2**, **3a**, **3b** and **4**. Absorption corrections (SORTAV^[17]) were applied to the data for **1**, **4** and **6**. The structures were solved by direct methods (SHELXS-86^[18] or SHELXS-97) with full-matrix least-squares (SHELXL-97^[19]) refinement based on *F*². Non-hydrogen atoms were treated anisotropically. Hydrogen atoms were refined in calculated positions where relevant on carbon atoms, whereas the NH and OH hydrogen atoms were located and refined at a fixed distance of 0.89 Å from the parent atom throughout. CCDC 191738–191745 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44–1223/336–033; Email: deposit@ccdc.cam.ac.uk].

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