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Divalent complexes of 3-hydroxy-4-methyl-2(3*H*)-thiazolethione with Co–Zn: synthesis, X-ray crystal structures and the structure-directing influence of C–H···S interactions†

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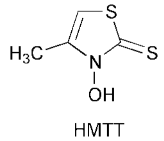
Divalent complexes of the cyclic thiohydroxamic acid 3-hydroxy-4-methyl- 2(3*H*)-thiazolethione with first-row d-block elements Co–Zn have been synthesised and the crystal structures of the Zn and Ni complexes have been determined by single-crystal X-ray diffraction. Single crystals suitable for X-ray analysis could not be obtained for the Cu or Co complexes, but their structures have been elucidated from laboratory powder X-ray diffraction data using a molecular-modelling approach. Directional intermolecular interactions in the complexes are weak in nature, comprising C–H···O and C–H···π contacts. Close C–H···S contacts also exist, but a general CSD survey shows that these interactions do not display any structure-directing properties which might facilitate their use in crystal engineering strategies.

Introduction

The influence of crystal structure and intermolecular interactions on the bulk physicochemical properties of molecular materials is of increasing general interest. Interactions between molecules in the solid state affect properties as diverse as solubility, molecular magnetism and conductivity, for example.[1,2] Development of solid-state structure–property relationships is, therefore, of vital importance. As knowledge of the relationship between solid-state structure and bulk properties develops for a particular class of molecular material, there arises the possibility of tailoring structures for applications where specific properties are necessary. To this end, there is considerable current interest in elucidating the nature of intermolecular interactions with the prospect of identifying those which may be useful for control of solid-state structure.[3,4]

Accompanying this, there is a growing trend in the literature towards reporting a wide variety of intermolecular contacts observed in crystal structures as "structure-directing" and hence to speculate on their application for crystal design.[5] For proper consideration of the structure-directing nature of intermolecular interactions, it is necessary to consider an extensive sample—observation of a certain contact in a single structure is no indication of its general utility. Thus, it is widely accepted that database studies represent the most satisfactory methods for establishing the consistent directional properties of intermolecular interactions in the solid state. Information extracted from numerous crystal structures in the Cambridge Structural Database (CSD), for example, established conclusively the directional hydrogen-bond characteristics of C–H···O interactions.[6,7]

We have recently been pursuing a solid-state approach to the study of cyclic thiohydroxamic acids,[8,9] and examine here the divalent complexes of 3-hydroxy-4-methyl-2(3*H*)-thiazolethione (HMTT) with the d-block elements Co–Zn. The crystal structures of the Zn and Ni complexes have been determined by single-crystal X-ray diffraction, and those of the Cu and Co complexes have been elucidated from laboratory powder X-ray diffraction data using a molecular-modelling approach. In an effort to rationalise the crystal structures of these materials, we have been concerned with the analysis of weak intermolecular interactions, particularly those involving sulfur. Two comprehensive database studies have been reported recently concerning the ability of sulfur to act as an acceptor for "strong" hydrogen-bond donors, namely O–H and N–H groups.[10,11] It has been shown that sulfur as part of an $R^1R^2C{=}S$ unit is a good hydrogen-bond acceptor only when R^1 and R^2 form an extended delocalised system with C=S, since delocalisation enhances the δ-negativity of the sulfur atom. C–H donors were not considered in the study, although it has been suggested that it is unlikely that these will form hydrogen bonds of any significant strength with C=S.[12] Divalent sulfur, particularly as part of a C–S–C unit has been shown to be an extremely poor hydrogen-bond acceptor as a result of it bearing a partial positive charge.[11] In this work, we analyse the structure-directing influence of C–H···S interactions in the complexes $M(MTT)_2$, and also for sulfur as part of a general M–S–C unit. Coordination to a divalent metal cation imparts a partial negative charge to the sulfur atom in a manner similar to that in a delocalised $R^1R^2C{=}S$ unit such that the hydrogen-bond acceptor characteristics of the two groups would be expected to be comparable. The results presented have considerable implications for the proposed use of C–H···S interactions in general crystal engineering strategies.


HMTT

Results and discussion

Crystal structure of $Zn(MTT)_2$ 1

The zinc complex **1** exhibits pseudo-C_2 point symmetry and is therefore chiral (Fig. 1). The complex crystallises in the

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† Electronic supplementary information (ESI) available: lists of CSD refcodes retrieved from the database analyses and high-temperature PXRD profiles elucidating the solid-state structures of **3** and **4** following dehydration. See http://www.rsc.org/suppdata/dt/b1/b104203n/

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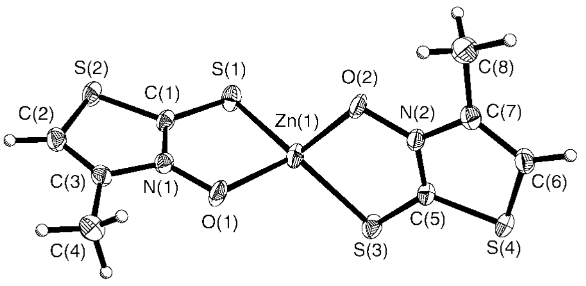

Fig. 1 Molecular unit in **1** with displacement ellipsoids shown at 50% probability.

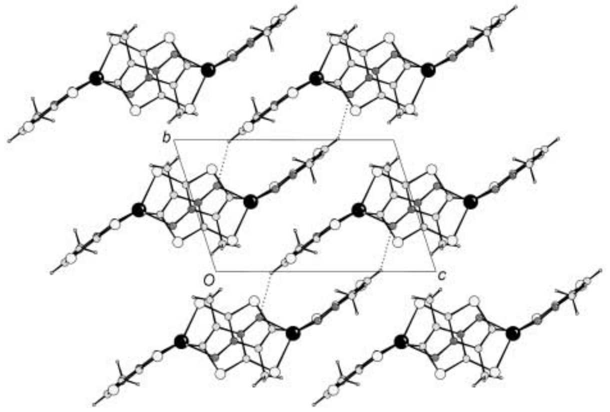

Fig. 2 Projection onto (100) of **1** showing stacking in two approximately perpendicular directions. C–H · · · O interactions are indicated by dotted lines.

centrosymmetric space group $P\bar{1}$ such that both enantiomers are present in the crystal. Within the molecule, the planes defined by the thiazole rings in the MTT ligands form an interplane angle of 88.9°, and the molecules pack such that they stack in two essentially perpendicular directions (Fig. 2). Such an arrangement leads to efficient packing of the planar MTT ligands, maximising cohesive dispersion interactions in the crystal. In one direction (approximately along $[01\bar{1}]$), adjacent MTT ligands adopt alternate interplane separations of 3.46 and 3.52 Å. In the other direction (approximately along $[2\bar{1}\bar{1}]$), adjacent rings are coplanar with alternate interplane separations of 3.41 and 3.76 Å. C–H · · · O interactions exist between the vinylic protons and the oxygens of the N–O groups (H(6) · · · O(1) = 2.42 Å, C(6)–H(6) · · · O(1) = 135.0°; H(2) · · · O(2) = 2.41 Å, C(2)–H(2) · · · O(2) = 137.8°; Fig. 2). In each stacking direction, the closer of the two interplane distances corresponds to pairs of molecules linked *via* these C–H · · · O interactions. The directional nature of C–H · · · O interactions is, of course, well established, and their influence in the crystal structure of **1** is particularly clear; MTT ligands adjacent in stacks of molecules are drawn closer together compared with ligands in those molecules between which C–H · · · O interactions are not present. Such an arrangement cannot result simply from optimisation of isotropic dispersion interactions.

Table 1 Details of Rietveld refinement for **2**

Space group	$P2_1/n$
a/Å	4.0859(2)
b/Å	12.7571(8)
c/Å	11.9876(7)
β/°	97.010(7)
V/Å^3	620.18(7)
$2\theta_{\min}$, $2\theta_{\max}$/°	8, 65
No. profile points	5699
No. parameters	22
Peak shape function	Thompson *et al.* (pseudo-Voigt, ref. 15)
Asymmetry model	Finger *et al.* (ref. 16)
Background	Linear interpolation (10 terms)
R_{exp}	0.021
R_{p}	0.044
R_{wp}	0.057
χ^2	2.7

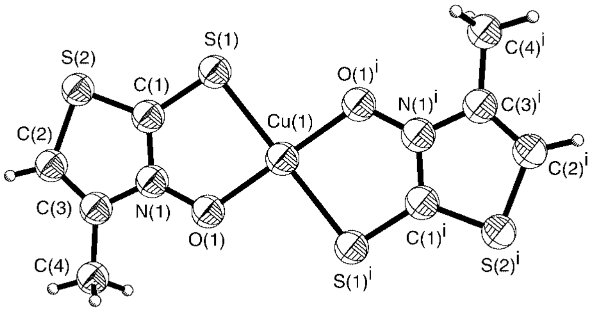

Fig. 3 Molecular unit in **2** with ellipsoids shown at arbitrary size. Atoms related by a centre of symmetry are denoted by the superscript i.

Determination of the crystal structure of Cu(MTT)$_2$ 2

Complex **2** displays extremely poor solubility in most common solvents, prohibiting growth from solution of single crystals suitable for X-ray analysis. PXRD data were collected therefore from the bulk polycrystalline material, and were indexed on the basis of a monoclinic lattice with refined unit-cell parameters a = 4.082(4), b = 12.752(15), c = 11.982(9) Å, β = 96.95(8)° (F(21) = 26.1 (0.016, 50)).[13] The unit-cell volume is comparable with that of **1**, suggesting the presence of two Cu(MTT)$_2$ molecules in the unit cell. For the most likely monoclinic space group, $P2_1/c$, (selected on the basis of well known space group statistics) the copper atom must occupy a centre of symmetry and the molecule must, therefore, be centrosymmetric, *i.e.* *trans*-square planar. A *trans*-Cu(MTT)$_2$ molecule (Fig. 3) was modelled with Cu–O and Cu–S bond distances derived from the analogous pyrithione complex Cu(PT)$_2$ (1.943 and 2.309 Å, respectively),[14] and utilising MTT ligands with geometry taken from the crystal structure of **1**. The crystal structure was constructed in $P2_1/n$ by placing the copper atoms at the origin and at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. To remove any unreasonable intermolecular contacts, the structure was energy-minimised with fixed unit-cell parameters and the Cu(MTT)$_2$ units allowed to rotate about the copper centres.‡ The PXRD profile simulated from the minimised model showed excellent agreement with the measured profile, and the model was progressed therefore to Rietveld refinement. Lattice parameters, background coefficients and peak-profile coefficients were refined initially with fixed atomic positions. A single isotropic displacement parameter common to all atoms was also refined. This step converged with R_p = 0.153 and R_{wp} = 0.213. In subsequent refinement steps, the molecules were allowed to rotate as rigid bodies about the positions of the copper atoms. This step converged with R_p = 0.044 and R_{wp} = 0.057 (χ^2 = 2.7). Details of the Rietveld refinement are given in Table 1 and the final profile fit is shown in Fig. 4. Attempts to refine the structure with bond-distance restraints in place of rigid-body constraints led to unreasonable deviations in the molecular geometry with no appreciable improvement to the profile fit. This may be attributed to the relatively low resolution of the PXRD data.

In the solid-state, **2** forms stacks running along the a direction, with additional contacts between the copper centres and

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‡ Energy minimisation was performed using the Dreiding force field, which does not contain default parameters for copper. It was found that parameterisation of the force field was not necessary for successful minimisation—it was sufficient simply to model the copper atom as zinc, for which default parameters are available. Full details of the general methodology will be presented in a forthcoming publication.

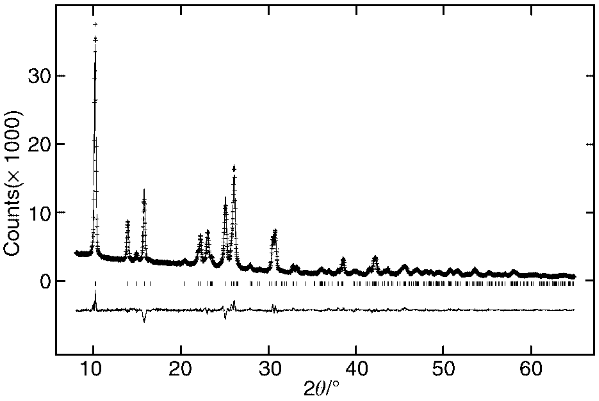


Fig. 4 Calculated (solid line), observed (crosses) and difference PXRD profiles for the Rietveld refinement of **2**. Reflection positions are indicated by tick marks. No significant intensity was observed for $2\theta > 65°$ (equivalent to 1.34 Å resolution).

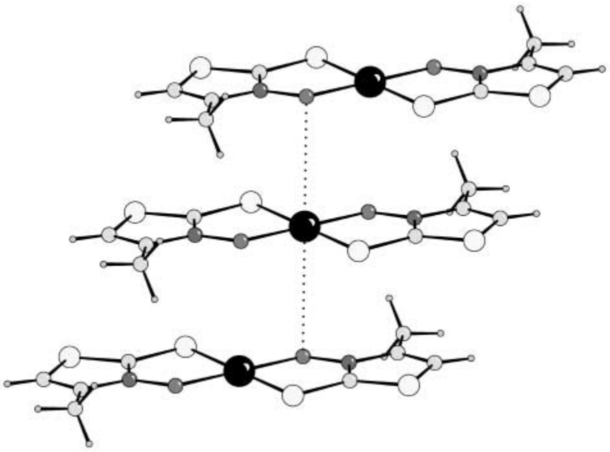


Fig. 5 Octahedral coordination geometry about Cu^{2+} in **2** showing the axial Jahn–Teller distortion.

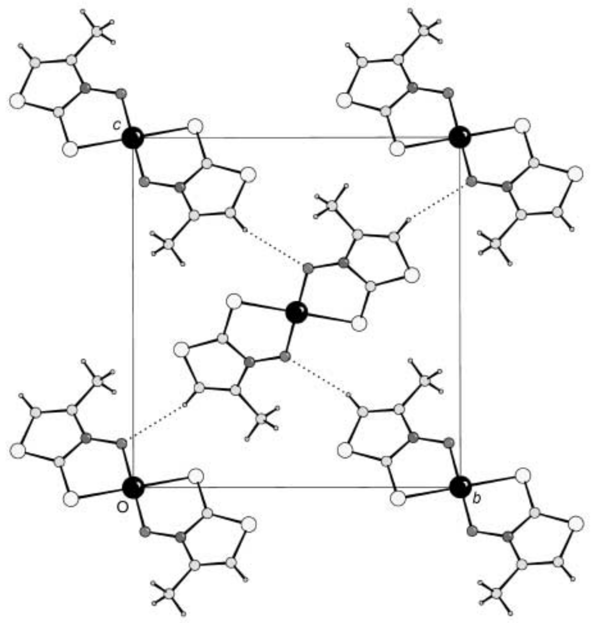


Fig. 6 Projection onto (100) showing stacks of **2** packed in a herringbone manner. C–H · · · O contacts are indicated by dotted lines.

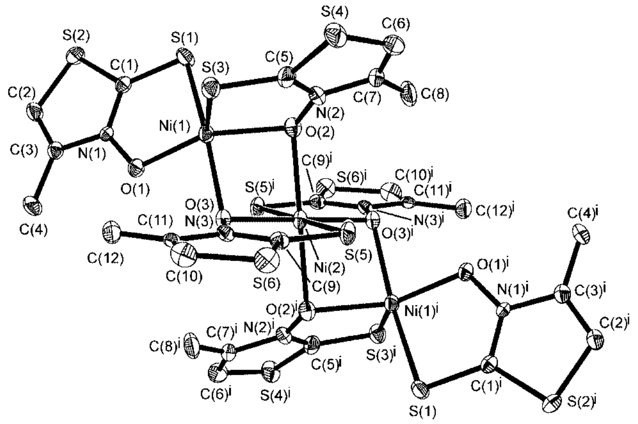


Fig. 7 $[Ni(MTT)_2]_3$ trimer in the crystal structure of **5**. Symmetry-related atoms are indicated by the superscript i and hydrogen atoms are omitted for clarity (symmetry code (i): $1 - x, 1 - y, 1 - z$).

oxygen atoms of adjacent molecules (Cu(1)–O(1′) = 3.492(1) Å). The copper atom may be considered, therefore, to adopt a tetragonally-distorted octahedral geometry with oxygen atoms in the axial positions (Fig. 5), indicative of a Jahn–Teller distortion about Cu^{2+} (d^9). Within the stacks, MTT ligands are coplanar with interplane separations of 3.40 Å, an arrangement that maximises cohesive dispersion interactions. The stacks are packed in a herringbone manner (Fig. 6), and C–H · · · O contacts exist between the vinylic protons and oxygens of $Cu(MTT)_2$ molecules in adjacent stacks (H(2) · · · O(1) = 2.80 Å, C(2)–H(2) · · · O(1) = 123.6°).

Crystal structure of $Ni(MTT)_2$ 5

In the solid state, **5** forms centrosymmetric trimers, containing Ni^{2+} in both 6- and 5-coordination (Fig. 7). Analysis of the coordination preferences of Ni^{2+} for similar compounds in the CSD indicate that this is the first example of nickel in a 5-coordinate environment with O/S donor ligands. The central 6-coordinate nickel atom occupies a centre of symmetry and adopts distorted octahedral coordination *via* two bidentate MTT ligands and two additional axial Ni–O bonds to neighbouring $Ni(MTT)_2$ units. The 5-coordinate nickel atom adopts a geometry intermediate between trigonal bipyramidal (with S(1) and O(3) in the axial positions) and square pyramidal (with S(3) in the axial position). The planes defined by the thiazole rings in the MTT ligands in the outer $Ni(MTT)_2$ units form an interplane angle of 87.1°, comparable with that in **1**. The trimers pack such that the MTT ligands in the outer $Ni(MTT)_2$ units are coplanar with an interplane separation of 3.72 Å, an arrangement similar to that in **1**.

Comparison with **1** and **2** suggests that the vinylic hydrogens in **5**, H(2), H(6) and H(10), are likely to be sufficiently acidic to participate in intermolecular hydrogen-bond interactions. C–H · · · O interactions are not observed in **5**, however; the C(10)–H(10) vector is directed towards the centroid (G) of an MTT ligand in an adjacent trimer (Fig. 8; H(10) · · · G = 3.35 Å, C(10)–H(10) · · · G = 163.9°), indicative of a C–H · · · π interaction. The directional nature of these interactions has been demonstrated previously by CSD analysis.[7,17] The closest approach to H(2) in the outer $Ni(MTT)_2$ unit is made by the sulfur atom of the central $Ni(MTT)_2$ unit in an adjacent trimer (H(2) · · · S(5) = 2.79 Å; C(2)–H(2) · · · S(5) = 155.4°). H(6) also approaches a sulfur atom of an adjacent trimer, but with a somewhat greater separation (H(6) · · · S(1) = 2.91 Å; C(6)–H(6) · · · S(1) = 151.4°). The geometries of these interactions appear comparable to those generally accepted for directional C–H · · · O interactions, and it may be postulated, therefore, that a second type of directional interaction, namely C–H · · · S, exists in **5**. Of course, observation of close C–H · · · S contacts in this isolated crystal structure is no indication of the general directional properties of such interactions, and a more general CSD study was therefore undertaken in order to establish

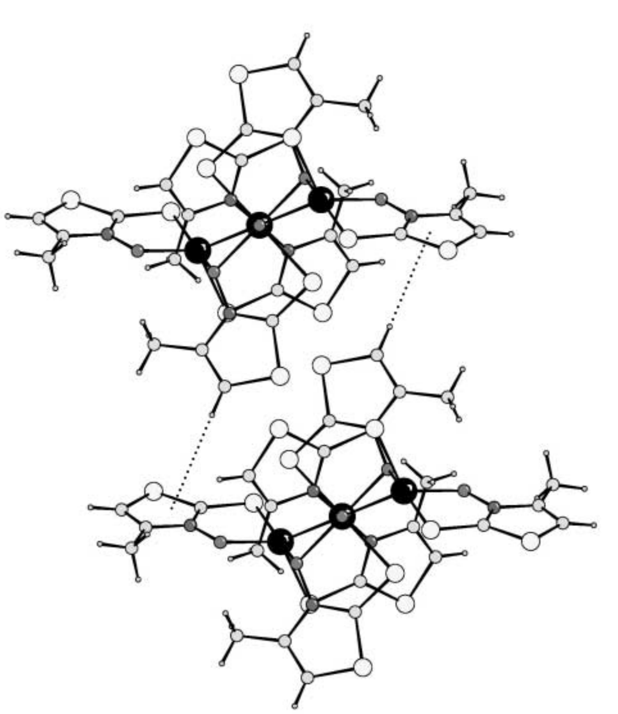
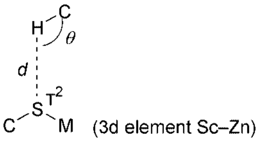


Fig. 8 C–H···π interactions between vinylic hydrogens in **5** and MTT ligands in adjacent $[Ni(MTT)_2]_3$ trimers.

the structure-directing properties of C–H···S interactions involving sulfur in a general M–S–C group.

C–H···S interactions: a CSD study

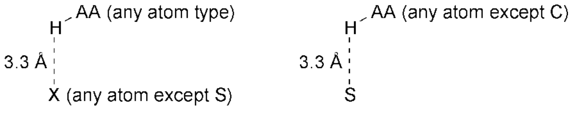
A survey of the CSD (April 2000 release)[18] was performed using the search fragment illustrated in Scheme 1. The non-bonded H···S contact was specified as intermolecular only, in order to eliminate fragments in which the H···S distance was constrained by intramolecular geometry. Practical considerations necessitate the application of some arbitrary distance cut-off for the intermolecular H···S distance, although it has been noted previously that a distance cut-off is not a satisfactory criterion for assessing hydrogen-bond characteristics—directionality is the significant property.[19] The cut-off was specified as 3.3 Å, *ca.* 0.4 Å greater than the sum of the van der Waals radii for H and S. The total (intramolecular) coordination number of the sulfur atom was specified as two. To avoid any possible ambiguities in the bond orders of the C–S–M linkage, the C–S and S–M bonds were specified as "any" type. Structures were retained only where they had a crystallographic *R*-factor less than 0.10, error-free coordinates (according to CSD checking criteria) and no disorder or polymerisation. All hydrogen-atom positions determined from X-ray data were normalised to the standard neutron-derived bond distance (1.08 Å) along the bond vector derived from the X-ray results.[20] For comparison, an analogous search was performed using an O–H donor group.



Scheme 1 Search fragment used for CSD survey of C–H···S interactions. T^2 denotes a total intramolecular coordination number of 2.

For the C–H···S interactions, the initial search located a total of 8340 unique fragments in 1451 structures, all of which were determined from X-ray data. The cone-corrected distribution[21] of C–H···S angles suggests a slight tendency towards linearity, but a scatterplot of H···S distance, *d*(SH), *versus* C–H···S angle (θ) shows that there is no significant correlation between these parameters (Fig. 9(a)); the correlation coefficient is −0.407. For O–H···S interactions, the search located 74 unique fragments in 51 structures. In this case, the cone-corrected distribution of O–H···S angles shows a marked tendency towards linearity, and a scatterplot of H···S distance *versus* O–H···S angle shows a distinct correlation, with the shortest contacts being the most linear (Fig. 9(b)); the correlation coefficient in this case is −0.905. The CSD survey indicates, therefore, that sulfur in a C–S–M linkage may act as a hydrogen-bond acceptor for O–H donors, but not for C–H donors. This result is in agreement with that suggested by Allen *et al.* and suggests that sulfur in a C–S–M linkage displays hydrogen-bond acceptor characteristics similar to sulfur in a C=S group.[10]

It is noteworthy that even at the conservative 3.3 Å distance cut-off, only 74 O–H···S contacts were located, compared with 8430 for C–H···S. This reflects to some extent the relative proportions of C–H and O–H donor groups in a typical organic molecule, but also suggests that even though O–H···S interactions display directional hydrogen-bond characteristics, O–H groups generally form hydrogen bonds with atoms other than sulfur. It is clear, therefore, that the frequency of hydrogen-bond formation derived in this manner provides little information on the inherent hydrogen-bond characteristics of a given interaction—although O–H···S interactions are relatively rare, their directional characteristics confirm that they are hydrogen bonds. The fact that they are rare indicates only that they are weak, and interactions such as O–H···O will be formed in preference. C–H···S interactions will be even weaker than O–H···S, and in the presence of other stronger interactions, they will readily be distorted. It is questionable, therefore, that a general CSD survey can reveal the inherent directional characteristics of the C–H···S interaction, since in all cases they are likely to be distorted by other interactions within the crystal. A more meaningful analysis may perhaps be derived from structures where C–H···S interactions are the only prospective directional intermolecular forces. The question is then whether C–H···S interactions can be structure-directing in the absence of other stronger structure-directing interactions. To investigate this hypothesis, the database subset from the previous search for C–H···S interactions was re-examined with the fragments illustrated in Scheme 2 specified as absent. Thus, the retrieved structures contain C–H···S interactions with H···S contacts less than 3.3 Å and no other H···X contacts within the same distance cut-off. This search located 215 fragments in 27 structures. The directional dependence of the C–H···S interactions in this subset is illustrated in Fig. 10. Equivalent filters applied to the subset of O–H···S interactions resulted in only 2 structures remaining and no meaningful analysis could be performed for this subset.



Scheme 2 Search fragments specified as absent in the CSD search designed to locate structures containing C–H···S interactions as the only directional intermolecular contacts.

It is clear that the angular dependence of the unconstrained C–H···S contacts still does not approach linearity, and the scatterplot (Fig. 10) confirms that there is no significant correlation between the H···S distance and the C–H···S angle; the correlation coefficient is −0.381. It may be concluded, therefore, that C–H···S interactions to sulfur in a C–S–M linkage do not display directional hydrogen-bond character-

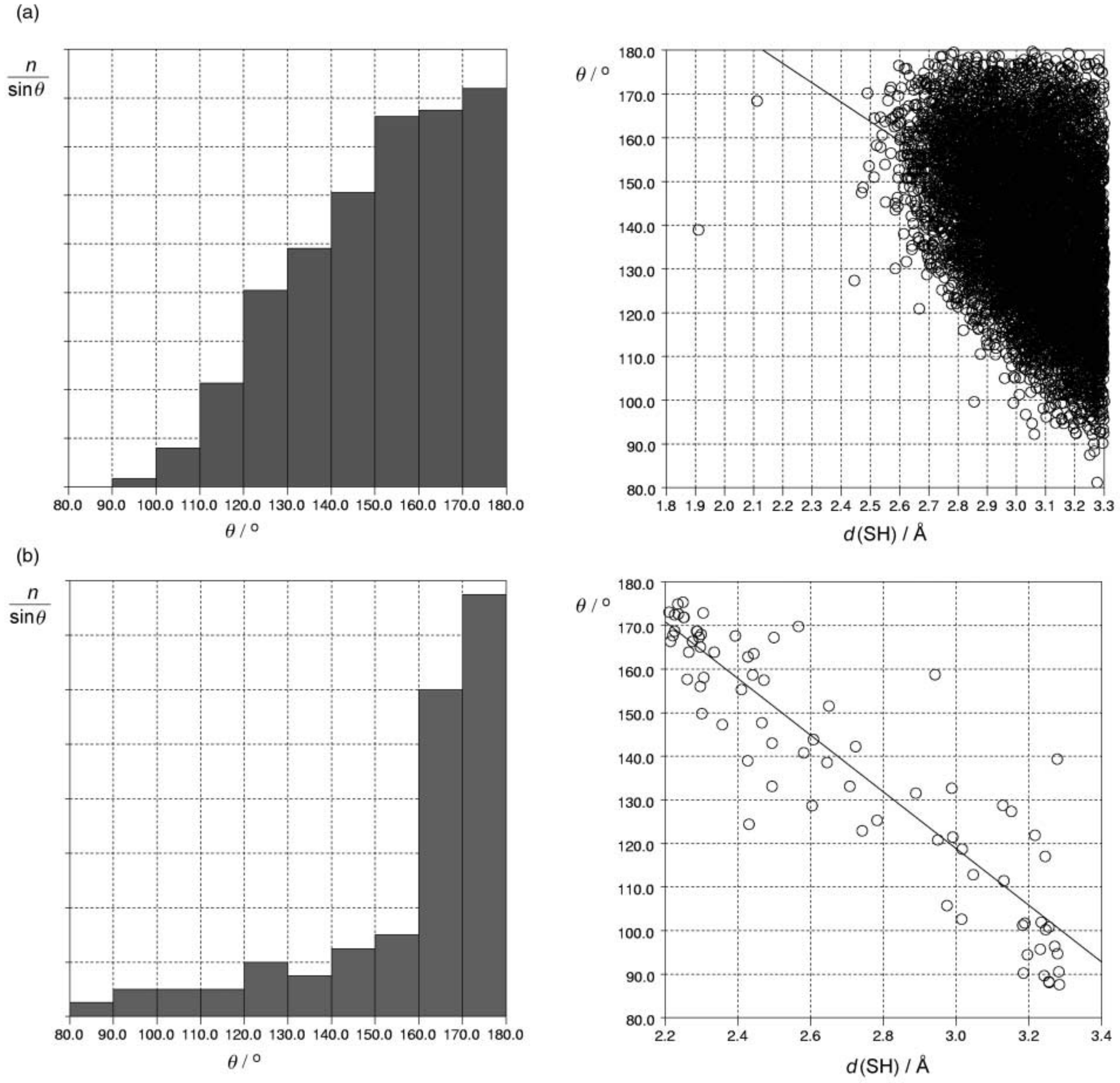


Fig. 9 Cone-corrected angular distributions and distance-angle scatterplots for (a) intermolecular C–H · · · S contacts and (b) intermolecular O–H · · · S contacts. The least-squares best-fit line through the data points is indicated in the scatterplots.

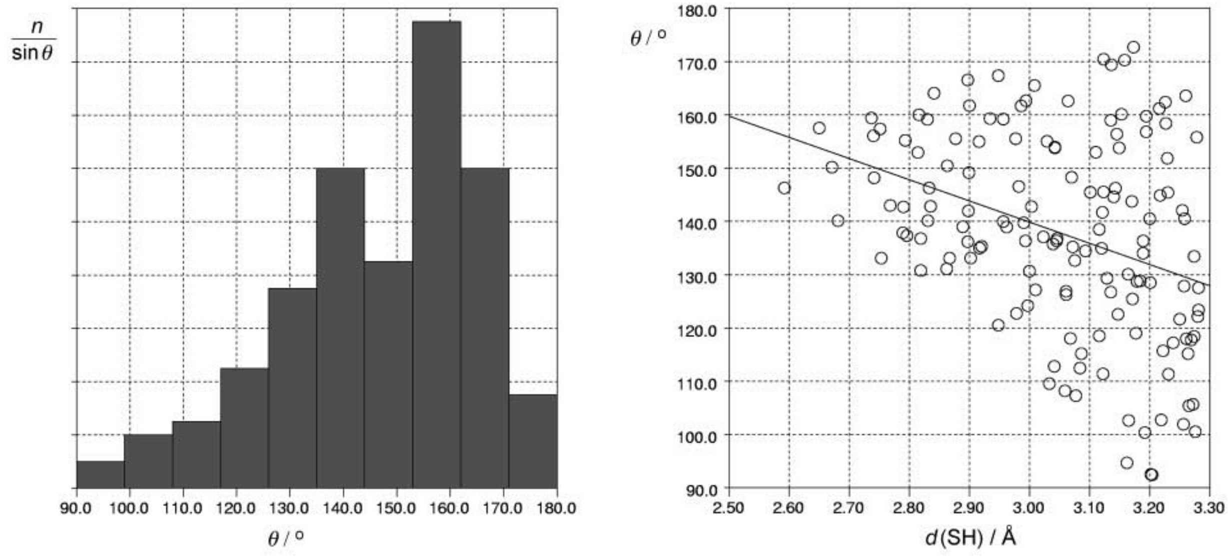


Fig. 10 Cone-corrected angular dependence and distance-angle scatterplot for unconstrained intermolecular C–H · · · S contacts. The least-squares best-fit line through the data points is indicated in the scatterplot.

Table 2 Physical characteristics of the complexes **1**–**4**

		Colour	mp/ °C	C[a] (%)	H[a] (%)	N[a] (%)	μ_{eff}/μ_B	Mass loss 25–200 °C (%)
1	$Zn(C_4H_4NOS_2)_2$	White	262–263	26.6 (26.9)	2.1 (2.3)	7.7 (7.9)	—	None
2	$Cu(C_4H_4NOS_2)_2$	Green	258–260	26.9 (26.9)	2.2 (2.3)	7.7 (7.9)	1.75 (1.73)	None
3	$Ni(C_4H_4NOS_2)_2(H_2O)$	Yellow	268–270	25.6 (26.0)	2.8 (2.7)	7.2 (7.6)	3.14 (2.83)	5.0 (4.9)
4	$Co(C_4H_4NOS_2)_2(H_2O)$	Pink	235–236	25.6 (26.0)	2.7 (2.7)	7.3 (7.6)	4.38 (3.88)	4.8 (4.9)

[a] Figures in parentheses denote values calculated from proposed formulae.

istics in metallo-organic solids, *i.e.* C–H · · · S interactions may not be considered to be structure-directing.

Does this result suggest then that a C–H · · · S interaction to sulfur in a C–S–M unit is not inherently directional? Considering the C–H bond as a dipole and the sulfur atom as a region of negative charge, the interaction between them cannot be inherently isotropic with respect to the angle θ. C–H · · · S interactions fall quite clearly within the range of the modern definition of hydrogen bonding: "any cohesive interaction X–H · · · A where H carries a positive and A a negative (partial or full) charge and the charge on X is more negative than on H".[22] Indeed, evidence from NMR studies for intramolecular C–H · · · S interactions in metallo-organic complexes has been reported on several occasions.[23,24] It is also clear, however, that these interactions are very weak, and variation of the interaction energy with the angle θ is minimal such that C–H · · · S interactions are readily distorted by the influence of other interactions in a crystal. The key feature to note regarding CSD studies of weak directional interactions is that it is never possible to exclude the influence of isotropic dispersion interactions in the manner in which other *directional* forces may be excluded by omitting certain sub-fragments. The influence of dispersion interactions may be minimised perhaps by considering only very small molecules, but any distinction of this sort would be arbitrary and would not lead to any useful general conclusions. In this case, the CSD study shows that C–H · · · S interactions are so weak, and so close to being isotropic, that they do not exert any structure-directing influence over and above that of isotropic dispersion interactions. It is clear, therefore, that C–H · · · S interactions do not display any true structure-directing influence and their utility in crystal design strategies will be negligible.

Experimental

Synthesis

3-Hydroxy-4-methyl-2(3*H*)-thiazolethione (HMTT) was obtained from the Aldrich Chemical Company and recrystallised from CH_2Cl_2. The sodium salt hydrate Na(MTT)·xH$_2$O was prepared by addition of 1 mol equiv. of NaOH to a suspension of HMTT in water, followed by evaporation of the solvent. The metal complexes were prepared subsequently by combination of aqueous solutions of MCl_2 (M = Zn, Cu, Ni, Co) and Na(MTT) in a 1 : 2 molar ratio at room temperature. The resulting precipitates were removed by filtration under gravity and dried in air at room temperature. Complexes with Zn^{2+} and Cu^{2+} were precipitated as the anhydrous divalent complexes $Zn(MTT)_2$ **1** and $Cu(MTT)_2$ **2**, respectively. Single crystals of **1** were prepared by slow evaporation of a solution in dmso. Complexes with Ni^{2+} and Co^{2+} were precipitated as the monohydrates $Ni(MTT)_2(H_2O)$ **3** and $Co(MTT)_2(H_2O)$ **4**, respectively. The proposed formulae were confirmed by elemental analyses (Table 2), and for **3** and **4**, the water content was confirmed by thermogravimetric analyses. Attempts to prepare single crystals of **3** and **4** suitable for X-ray diffraction have been unsuccessful to date. Recrystallisation from dmso produces the solvates $Ni(MTT)_2(dmso)_2$ and $Co(MTT)_2(dmso)_2$.[25] From methanol, **4** yields $Co(MTT)_2(MeOH)_2$.[26] Single crystals of anhydrous $Ni(MTT)_2$ **5** were produced by recrystallisation of **3** from dmf. Powder X-ray diffraction (PXRD) analyses of the bulk samples of **3** and **4** have been performed, but it has not been possible to index unambiguously the profiles, and no further progress has been made with elucidating these solid-state structures.

To examine the solid-state structures of **3** and **4** following dehydration, PXRD analyses were also performed for both samples at 100 °C. For **3**, comparison of the resulting PXRD profile with that simulated from the single-crystal structure of **5** shows that the hydrate **3** transforms to the anhydrous **5** at elevated temperature. On dehydration of **4**, $Co(MTT)_2$ (**6**) is formed, which adopts a structure identical to that of the zinc complex **1**. For both **5** and **6**, rehydration was not observed on returning to room temperature in air.

Characterisation

The C, H and N elemental analyses were obtained using a CE-440 Exeter Analytical elemental analyser. Thermogravimetric analyses were performed using a Polymer Laboratories TGA 1500 apparatus; samples were heated from room temperature to 200 °C at a heating rate of 10 °C min^{-1}, in a flow of N_2 gas (*ca.* 25 ml min^{-1}). Melting points were determined using an optical microscope equipped with a hot-stage attachment. Magnetic-susceptibility measurements were performed at room temperature with a digital susceptibility balance, using $HgCo(SCN)_4$ as a calibrant ($\chi = 16.44 \times 10^{-6}$).[27] Diamagnetic corrections were applied using a combination of the diamagnetic susceptibility measured for HMTT and Pascal's constants for the metal ions.[28]

Single-crystal X-ray diffraction

Single-crystal X-ray diffraction analyses were performed using a Nonius Kappa CCD system for **1** and a Rigaku AFC7R diffractometer equipped with a rotating-anode source for **5**. In both cases, the crystals were mounted in inert oil and cooled to 180(1) K in a stream of cold N_2 gas. Data were corrected for absorption using the multi-scan procedure of Blessing for **1**,[29] and using φ-scans for **5**.[30] Crystallographic data are summarised in Table 3. Full-matrix least-squares refinement was performed against F^2 data using SHELXL-97.[31] Hydrogen atoms were placed geometrically and allowed to ride during subsequent refinement with an isotropic displacement parameter fixed at 1.2 times the carbon to which they are attached. For the discussion of intermolecular distances and angles, the positions of the hydrogen atoms were normalised to the standard neutron-derived bond distance (1.08 Å) along the bond vector derived from the X-ray results.[20]

CCDC reference numbers 168626 and 168628.

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) analyses were performed on a Stoe STADI-P high-resolution diffractometer, with Ge(111)-monochromated Cu-Kα radiation (λ = 1.5406 Å) and a position-sensitive detector covering *ca.* 6° in 2θ. Patterns were measured in transmission mode using an ω–2θ scan technique over the range $3 \le 2\theta \le 65°$ with a step size of 0.5° and a count

Table 3 Crystallographic data for **1** and **5**

	1	**5**
Empirical formula	$C_8H_8N_2O_2S_4Zn$	$C_8H_8N_2O_2S_4Ni$
M	357.77	351.11
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	7.6216(4)	10.067(5)
b/Å	7.6954(4)	10.167(8)
c/Å	11.7788(6)	11.184(4)
α/°	105.147(3)	92.71(6)
β/°	96.210(3)	114.00(4)
γ/°	106.593(3)	111.2(5)
V/Å^3	626.47(6)	933.9(9)
T/K	180(1)	180(1)
Z	2	3
μ (Mo-Kα)/mm^{-1}	2.61	2.22
Total data	3892	4505
Unique data	2798	4266
Observed data $[F^2 > 2\sigma(F^2)]$	2352	2796
R_{int}	0.027	0.056
$R1\ [F^2 > 2\sigma(F^2)]$	0.031	0.057
$wR2\ [F^2 > 2\sigma(F^2)]$	0.071	0.113
Goodness of fit on F^2,S	1.045	1.009

time of 360 s per step (total data collection time *ca.* 12 hours). High-temperature measurements were performed on the same instrument equipped with a furnace attachment. Samples were mounted in 0.3 mm quartz capillaries and data were collected in Debye–Scherrer geometry with rotation about the capillary axis. The sample was heated at a rate of 10 °C min^{-1} and maintained at the temperature of interest for 3 h prior to data collection to ensure thermal equilibration of the sample. The capillary remained open to the atmosphere throughout the measurement.

CCDC reference number 168627.

See http://www.rsc.org/suppdata/dt/b1/b104203n/ for crystallographic data in CIF or other electronic format.

Molecular modelling and Rietveld refinement

All molecular-modelling procedures were performed using the Cerius^2 software package.[32] Energy-minimisation of the postulated structure of **2** was performed using the Dreiding force field[33] with partial atomic charges derived from the electrostatic potential calculated using semi-empirical molecular orbital methods (MOPAC-AM1);[34,35] such charges have been shown to be superior for treatment of organic molecules.[36] Since neither the Dreiding force field nor the AM1 model are parameterised for Cu^{2+}, this atom was modelled as Zn^{2+} (for which default parameters are available). It was found that such an approach was sufficient to treat this complex, *i.e.* extensive parameterisation was not necessary. Details of the general applicability of this approach will be presented in a forthcoming publication. Rietveld refinement was performed for **2** using the GSAS suite of programs.[37]

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References

1 W. Jones, in *Organic Molecular Solids: Properties and Applications*, ed. W. Jones, CRC Press, New York, 1997.
2 H. G. Brittain, in *Polymorphism in Pharmaceutical Solids*, ed. H. G. Brittain, Dekker, New York, 1999.
3 D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375.
4 G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989.
5 A pertinent example is given by: E. A. Marseglia, F. Grepioni, D. Braga and E. Tedesco, *Mol. Cryst. Liq. Cryst.*, 2000, **348**, 137.
6 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063.
7 G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, New York, 1999.
8 A. D. Bond and W. Jones, *J. Phys. Org. Chem.*, 2000, **13**, 395.
9 A. D. Bond, N. Feeder, S. J. Teat and W. Jones, *Tetrahedron*, 2000, **56**, 6617.
10 F. H. Allen, C. M. Bird, R. S. Rowland and P. R. Raithby, *Acta Crystallogr., Sect. B*, 1997, **53**, 680.
11 F. H. Allen, C. M. Bird, R. S. Rowland and P. R. Raithby, *Acta Crystallogr., Sect. B*, 1997, **53**, 696.
12 F. H. Allen, *personal communication*, 2000.
13 G. S. Smith and R. L. Snyder, *J. Appl. Crystallogr*, 1979, **12**, 60.
14 A. D. Bond, N. Feeder, S. J. Teat and W. Jones, *Acta Crystallogr., Sect. C*, 2001, **57**, in press.
15 P. Thompson, D. E. Cox and J. B. Hastings, *J. Appl. Crystallogr.*, 1987, **20**, 79.
16 L. W. Finger, D. E. Cox and A. P. Jephcoat, *J. Appl. Crystallogr.*, 1994, **27**, 892.
17 Y. Umezawa, S. Tsuboyama, K. Honda, J. Uzawa and M. Nishio, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1207.
18 F. H. Allen, O. Kennard and R. Taylor, *Acc. Chem. Res.*, 1983, **16**, 146.
19 T. Steiner and G. R. Desiraju, *Chem. Commun.*, 1998, 891.
20 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
21 J. Kroon and J. A. Kanters, *Nature*, 1974, **248**, 667.
22 T. Steiner and W. Saenger, *J. Am. Chem. Soc.*, 1993, **115**, 4540.
23 T. Ueno, M. Inohara, N. Ueyama and A. Nakamura, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1077.
24 W.-Y. Sun, X.-F. Shi, L. Zhang, J. Hu and J.-H. Wei, *J. Inorg. Biochem.*, 1999, **76**, 259.
25 A. D. Bond and W. Jones *Transition Met. Chem.*, 2001, in press.
26 A. D. Bond and W. Jones, *Acta Crystallogr., Sect. E*, 2001, **57**, m140.
27 B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1958, 4190.
28 B. N. Figgis and J. Lewis, in *Modern Coordination Chemistry: Principles and Methods* ed. J. Lewis and R. G. Wilkins, Wiley Interscience, New York, 1960.
29 R. H. Blessing., *Acta Crystallogr., Sect. A.*, 1995, **51**, 33.
30 A. C. T. North, D. C. Phillips and F. S. Matthews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
31 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
32 Molecular Simulations, Inc., Cerius^2, Version 4.0, San Diego, USA, 1999.
33 S. L. Mayo, B. D. Olafson and W. A. Goddard III, *J. Phys. Chem.*, 1990, **94**, 8897.
34 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
35 J. J. P. Stewart, *J. Comput. Aided Mol. Des.*, 1990, **4**, 1.
36 H. R. Karfunkel and R. J. Gdanitz, *J. Comput. Chem.*, 1992, **13**, 1171.
37 A. C. Larson and R. B. Von Dreele, GSAS, Program for Rietveld Refinement, University of California, USA, 1997.