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The influence of the chelate effect on supramolecular structure formation: synthesis and crystal structures of zinc thiourea and thiosemicarbazide complexes with terephthalate

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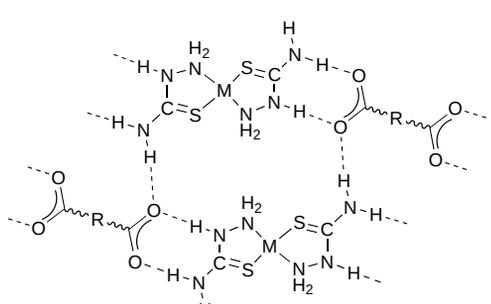
The lability of the ligand with a potential hydrogen bond donor–hydrogen bond donor arrangement was found to be the predominant factor in determining the structures of the adducts formed between zinc(II) complexes of thiourea [tu, $NH_2C(S)NH_2$] and thiosemicarbazide [tsc, $NH_2C(S)NHNH_2$] and the terephthalate anion [tere, $C_6H_4(CO_2^-)_2$-1,4]. Reaction of $[Zn(tsc)_2][NO_3]_2$, containing the bidentate thiosemicarbazide ligand, with sodium terephthalate led to a hydrogen-bonded structure, $[Zn(tsc)_2(OH_2)_2][tere]\cdot 2H_2O$, **1**, in which the cations and anions are linked into chains through charge-augmented double hydrogen bonds between two NH protons on the tsc ligands and two oxygen lone pairs on the carboxylate. This chain formation is similar to that previously observed for related nickel complexes, although there are major differences in the way in which these chains are linked together into sheets. In contrast to the thiosemicarbazide complex, the reaction of $[Zn(tu)_4][NO_3]_2$, containing unidentate thiourea ligands, with sodium terephthalate led to the formation of a co-ordinatively-bonded polymer, $[Zn_2(\mu\text{-}tu)(tu)_2(\mu\text{-}tere)_2]\cdot 4H_2O$, **2**, in which the terephthalate anions have displaced some of the thiourea ligands from each zinc co-ordination sphere. The zigzag tapes formed by the terephthalate ligands bridging zinc atoms are linked together into double strands *via* bridging thiourea ligands.

There is currently great interest in incorporating metal ions into supramolecular arrays[1,2] and one way in which this can be achieved is by exploiting multiple hydrogen bond interactions.[3] We have recently demonstrated that it is possible to form arrays of bis(thiosemicarbazide)nickel(2+) cations and dicarboxylate anions with the two components linked into chains by charge-augmented double hydrogen bonds.[4] Despite a change in the co-ordination geometry of the nickel atom from distorted square planar in $[Ni(tsc)_2][tere]$ **3** [tsc = $NH_2C(S)NHNH_2$, tere = $C_6H_4(CO_2^-)_2$-1,4] to octahedral in $[Ni(tsc)_2(OH_2)_2][fum]$ **4** (fum = fumarate, *trans*-$^-O_2CCH{=}CHCO_2^-$) and the presence of two aqua ligands in **4**, the in-plane hydrogen bonding arrays in both **3** and **4** are identical (as shown below).



3 M = Ni, R = C_6H_4
4 M = $Ni(OH_2)_2$, R = CH=CH

These observations pose two important questions. Firstly, how tolerant is this supramolecular array to changes in the metal ion and the dicarboxylate, and secondly, can the bidentate thiosemicarbazide ligand be replaced by the unidentate thiourea ligand? This latter change would lead to not only an increased number of hydrogen bond donor groups attached to the metal ion but also to a three-dimensional arrangement of these groups. We begin to address these questions by changing the metal ion to Zn^{2+} and comparing the structures formed by thiosemicarbazide and thiourea complexes with terephthalate anions.

Results and Discussion

Synthesis and crystal structure of $[Zn(tsc)_2(OH_2)_2][tere]\cdot 2H_2O$ 1

X-Ray quality single crystals of the complex $[Zn(tsc)_2(OH_2)_2][tere]\cdot 2H_2O$ **1** were prepared by mixing aqueous solutions of bis(thiosemicarbazide)zinc(II) nitrate and sodium terephthalate. The X-ray analysis of complex **1** reveals (Fig. 1) a hydrogen-bonded polymeric structure similar to that reported previously for the nickel analogue.[4] The zinc atom and the terephthalate ring are positioned on crystallographically independent symmetry centres (as in the nickel complex) resulting in a *trans* disposition of the two thiosemicarbazide ligands. Here, however, the metal is six-co-ordinate, having a distorted

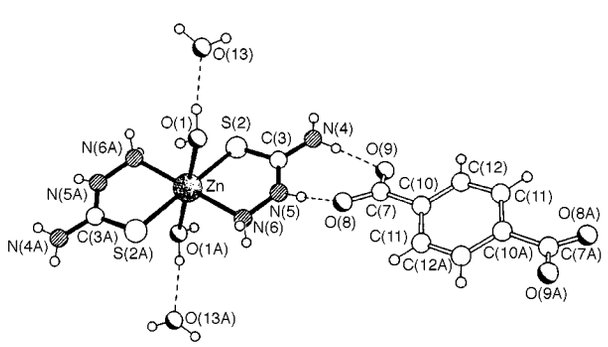


Fig. 1 The basic structural motif linking the cations and anions in complex **1**. The hydrogen bonding geometries X···O, H···O distances (Å), X–H···O angles (°) are N(5)···O(8) 2.76, 1.87, 169; N(4)···O(9) 2.84, 1.94, 177 and O(1)···O(13) 2.84, 1.95, 171. All N–H and/or O–H distances have been normalised to 0.90 Å

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Zn–O(1)	2.381(2)	Zn–S(2)	2.402(1)
Zn–N(6)	2.109(2)		
O(1)–Zn–S(2)	87.69(5)	O(1)–Zn–S(2A)	92.31(5)
N(6)–Zn–O(1)	84.97(8)	N(6)–Zn–O(1A)	95.03(8)
N(6)–Zn–S(2)	83.36(6)	N(6)–Zn–S(2A)	96.64(6)
O(1)–Zn–O(1A)	180.0	S(2)–Zn–S(2A)	180.0
N(6)–Zn–N(6A)	180.0		

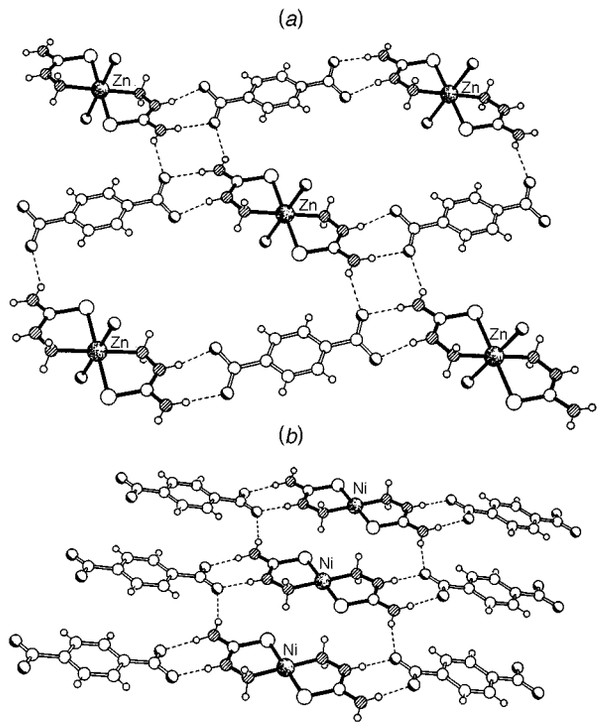


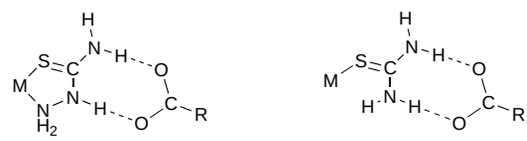
Fig. 2 Comparison of the cross-linking of chains in (*a*) the zinc complex **1** and (*b*) the nickel complex **3**.[4] The geometry of the cross-linking hydrogen bond in the zinc complex is N · · · O 2.82, H · · · O 2.11 Å and N–H · · · O 135°. The N–H distances have been normalised to 0.90 Å

octahedral geometry with the axial sites being occupied by weakly bound aqua ligands [2.381(2) Å, Table 1] (*cf.* a square planar geometry for the nickel compound). The presence of the aqua ligands results in a noticeable lengthening of the equatorial Zn–N and Zn–S bonds [2.109(2) and 2.402(1) Å respectively] from those observed in comparable four-co-ordinate complexes;[5] a similar effect is seen in the related nickel complexes.[4] The carboxylate oxygen atoms of the terephthalate hydrogen bond to the imido [N(5)] and one of the thioamido [N(4)] hydrogen atoms to form ribbon-like zigzag chains directly analogous to those observed in the nickel complex.[4] This hydrogen-bonding motif can be described in Etter's graph set notation[6,7] as $R_2^2(8)$.

The major difference between the zinc and nickel complexes is in the cross-linking of these chains. In both structures this occurs *via* N–H · · · O hydrogen bonds between the thioamido hydrogen atom not involved in chain formation and one of the carboxylate oxygen atoms. However, in the zinc complex adjacent chains are slipped laterally with respect to each other by a terephthalate unit to create large and small hydrogen-bonded ring systems, whereas in the nickel complex two similarly sized ring systems are formed (Fig. 2). The small eight-membered rings observed in the structure of **1** can be represented in graph set notation as $R_4^2(8)$, one of the most common motifs in hydrogen-bonded structures.[8,9] The difference in hydrogen-bonding motif between the zinc and nickel structures may be a consequence of the additional co-ordinated and included water molecules in the former which serve to link adjacent hydrogen-bonded sheets and occupy the apparent voids in the sheets created by the large hydrogen-bonded ring systems.†

Synthesis and crystal structure of $[Zn_2(\mu\text{-tu})(tu)_2(\mu\text{-tere})_2]\cdot 4H_2O$ **2**

Thiourea (tu) has the same potential hydrogen bond donor–hydrogen bond donor arrangement as tsc, although as a unidentate ligand more hydrogen bonding sets can be positioned around the metal atom. This can in principle lead to the formation of more extensive hydrogen-bonding networks and the development of three-dimensional structures as opposed to chains and sheets.



The addition of an aqueous solution containing 2 equivalents of sodium terephthalate to an aqueous solution of $[Zn(tu)_4][NO_3]_2$ gave, on standing for 24 h, colourless crystals which were shown by IR spectroscopy to contain both thiourea and terephthalate. The single-crystal X-ray analysis showed the structure not to be the anticipated hydrogen-bonded polymer, but instead the co-ordinatively-bonded polymer, $[Zn_2(\mu\text{-tu})(tu)_2(\mu\text{-tere})_2]\cdot 4H_2O$ **2**. Hence, two thiourea ligands have been displaced from each zinc co-ordination sphere by two terephthalates. This is in direct contrast to **1**, in which the terephthalate displaced neither the bidentate tsc ligands nor the aqua ligands, and is linked to the cation only through hydrogen bonds.

The asymmetric unit of polymer **2** (shown in Fig. 3) contains two crystallographically independent zinc centres, two terephthalate anions and three thiourea moieties. Each zinc atom is co-ordinated to two terephthalate oxygen atoms [Zn–O 1.928(4)–1.991(4) Å, Table 2] and two thiourea sulfur atoms in

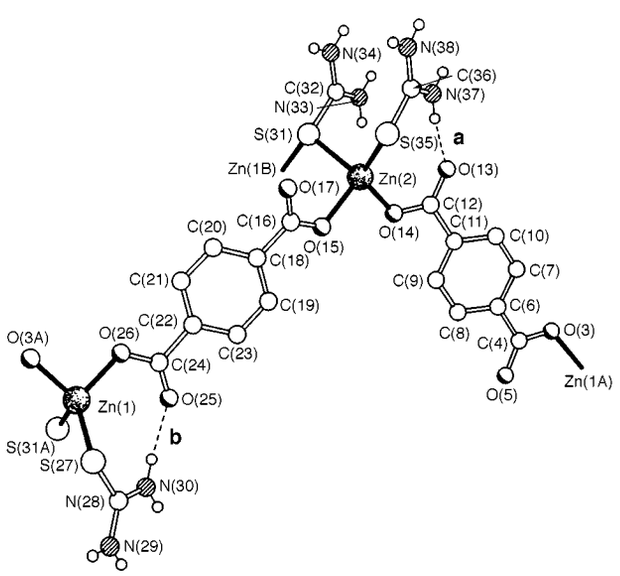


Fig. 3 The asymmetric unit in polymer **2** showing two of the three intramolecular hydrogen bonds

† The included water molecule acts as both a donor and acceptor of hydrogen bonds. The donor hydrogen bonds are to a carboxylate oxygen atom O(8) and to the aqua ligand O(1) with O · · · O, H · · · O and O–H · · · O geometries of 2.97, 2.10 Å and 163°, and 2.89, 2.01 Å and 166° respectively. The acceptor bonds are from N(6)–H and the aqua ligand, O(1)–H. The geometry of the former is 2.98, 2.09 Å and 168° whilst that of the latter is given in Fig. 1.

Table 2 Selected bond lengths (Å) and angles (°) for polymer **2**

Zn(1)–O(26)	1.938(4)	Zn(1)–O(3)	1.953(4)
Zn(1)–S(27)	2.296(2)	Zn(1)–S(31)	2.396(2)
Zn(2)–O(14)	1.928(4)	Zn(2)–O(15)	1.991(4)
Zn(2)–S(35)	2.309(2)	Zn(2)–S(31)	2.413(2)
O(26)–Zn(1)–O(3)	94.1(2)	O(26)–Zn(1)–S(27)	119.9(1)
O(3)–Zn(1)–S(27)	111.4(2)	O(26)–Zn(1)–S(31)	106.1(1)
O(3)–Zn(1)–S(31)	115.3(2)	S(27)–Zn(1)–S(31)	109.6(1)
O(14)–Zn(2)–O(15)	91.3(2)	O(14)–Zn(2)–S(35)	124.6(1)
O(15)–Zn(2)–S(35)	117.4(1)	O(14)–Zn(2)–S(31)	117.0(1)
O(15)–Zn(2)–S(31)	97.4(1)	S(35)–Zn(2)–S(31)	105.6(1)
Zn(1)–S(31)–Zn(2)	110.8(1)		

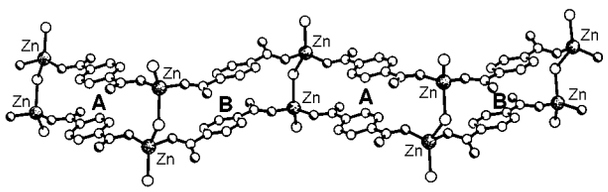


Fig. 4 Part of one of the polymeric tapes present in the structure of polymer **2**, the amido groups having been omitted for clarity. The interplanar and centroid · · · centroid separations (Å) associated with the π stacking between the terephthalate units are **A**, 3.33 and 3.85; **B**, 3.53 and 4.00. The shortest Zn · · · Zn contact is 3.96 Å

a distorted tetrahedral arrangement with angles ranging between 94.1(2) and 119.9(1)° at Zn(1) and 91.3(2) and 124.6(1)° at Zn(2). The terephthalate units serve to link independent zinc centres to create polymer chains that extend in the crystallographic $10\bar{1}$ direction. Two of the three thiourea ligands are unidentate, with Zn–S distances [2.296(2) and 2.309(2) Å] similar to those observed for other zinc bis(thiourea) dicarboxylates,[10–13] whereas the third is bridging zinc atoms of adjacent polymer chains [Zn–S 2.396(2) and 2.413(2) Å] to form the double stranded zigzag tape depicted in Fig. 4. This provides the first example of a structure in which thiourea is bonded to zinc in this manner.

The conformation of the zigzag tape is stabilised by a combination of intramolecular N–H · · · O hydrogen bonds between amido hydrogen atoms and non-co-ordinated terephthalate oxygen atoms (**a**, **b** and **c** in Figs. 3 and 5) and π–π stacking between pairs of centrosymmetrically related terephthalate rings (**A** and **B** in Fig. 4). Adjacent tapes are cross-linked *via* intermolecular N–H · · · O hydrogen bonds (**d**–**h** in Fig. 5) to form a series of linked hydrogen-bonded macro-rings, one of which is shown in Fig. 5. The macro-rings are approximately rectangular, and neighbouring rings, related by a glide operation, are rotated in the plane by *ca*. 90° about a corner and stacked so that the voids within one ring are overlaid by an edge of the next thereby preventing the formation of any continuous channels within the structure.

The four included water molecules, which are distributed over three full and three partial occupancy sites, do not appear to play any major role in determining the extended hydrogen-bonded structure. Indeed, only one of these molecules lies within hydrogen-bonding distance of amido H-atoms, linking a pair of hydrogen atoms not utilised in the extended network described above.

The structure of **2** displays certain features in common with the recently reported structure of an acridine-pendant zinc cyclen (cyclen = 1,4,7,10-tetraazacyclododecane) complex.[14] In this structure terephthalate dianions bridge two zinc centres, and these dizinc units are linked together into zigzag chains, reminiscent of those in **2**, by π–π interactions involving the acridine groups. These chains are cross-linked by further intermolecular interactions.

The facile displacement of thiourea from the zinc co-ordination sphere has been further demonstrated by the reaction of $[Zn(tu)_4][NO_3]_2$ with one equivalent of $Na_3[C_6H_3(CO_2)_3$-1,3,5]. In this case, the product isolated by crystallisation was the previously reported complex $Na_2[Zn_2\{C_6H_3(CO_2)_3$-$1,3,5\}_2]\cdot 11H_2O$, as confirmed by a comparison of the unit cell data with those reported previously.[15] In contrast to the reaction with terephthalate, all of the co-ordinated thiourea ligands have been replaced from the metal co-ordination sphere by carboxylate anions.

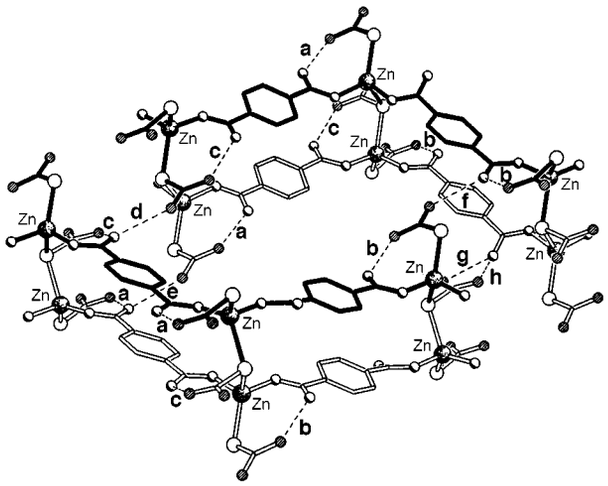


Fig. 5 One of the hydrogen-bonded macro-rings formed by the cross-linking between adjacent polymeric tapes in the structure of polymer **2**. Hydrogen bond geometries N · · · O, H · · · O distances (Å), N–H · · · O angles (°): **a**, 2.75, 1.88, 162; **b**, 2.81, 1.92, 168; **c**, 2.78, 1.88, 175; **d**, 2.92, 2.05, 164; **e**, 2.87, 2.02, 158; **f**, 2.89, 2.00, 170; **g**, 2.84, 2.03, 148 and **h**, 2.89, 2.12, 142. All N–H distances have been normalised to 0.90 Å

Conclusion

The work described in this paper suggests that in order to build up hydrogen-bonded polymers based on complexes of an ion such as Zn^{2+} it is important to take into account the strength and lability of the metal–ligand bond. The unidentate thiourea ligand, though superficially attractive due to the increased number of hydrogen-bonding sets present on the zinc complex cation and their three-dimensional orientation, proves sufficiently labile on Zn^{2+} to be replaced to some extent by the terephthalate, which acts as a ligand rather than as a hydrogen-bond acceptor. As a consequence of this, the reaction of $[Zn(tu)_4][NO_3]_2$ with sodium terephthalate leads to an unusual co-ordinatively-bonded polymer rather than the anticipated hydrogen-bonded polymer. The ligand lability may be reduced if it is bidentate, as illustrated by the structure of $[Zn(tsc)_2(OH_2)_2]$[tere]·$2H_2O$ **1** or by co-ordinating it to a more inert metal ion. Of course, the dissociation constant of the metal–ligand bond may also be influenced by the class **a** or **b** nature of the metal ion.

Experimental

Microanalyses (C, H and N) were carried out by the microanalytical services at Imperial College and the University of Bath. Infrared spectra were recorded on a Perkin-Elmer 1720 spectrometer as KBr pellets. The compounds $[Zn(tsc)_2][NO_3]_2$ and $[Zn(tu)_4][NO_3]_2$ were prepared following the procedures described in refs. 16 and 17 respectively.

Synthesis of $[Zn(tsc)_2(OH_2)_2][tere]\cdot 2H_2O$

An aqueous solution of Na_2tere (0.114 g, 0.54 mmol) was added to an aqueous solution of $[Zn(tsc)_2][NO_3]_2$ (0.200 g, 0.54 mmol). The solution was allowed to stand for 12 h after which time colourless crystals had grown. Yield 0.136 g (56%) (Found: C, 24.8; H, 4.5; N, 17.4. $C_{10}H_{22}N_6O_8S_2Zn$ requires C, 24.8; H,

4.6; N, 17.4%). ν_{max}/cm^{-1} 3341s and 3114s (NH); δ_{max}/cm^{-1} 1647vs (NH_2); ν_{max}/cm^{-1} 1588s and 1381vs (CO_2).

Synthesis of $[Zn_2(\mu\text{-tu})(tu)_2(\mu\text{-tere})_2]\cdot 4H_2O$

An aqueous solution of Na_2tere (0.086 g, 0.41 mmol) was added to an aqueous solution of $[Zn(tu)_4][NO_3]_2$ (0.100 g, 0.20 mmol). The solution was allowed to stand for 24 h after which time colourless crystals had grown. Yield 0.136 g (88%) (Found: C, 30.1; H, 3.5; N, 10.8. $C_{19}H_{28}N_6O_{12}S_3Zn_2$ requires C, 30.1; H, 3.7; N, 11.1%). ν_{max}/cm^{-1} 3396s, 3321s, 3189m and 3141m (NH); δ_{max}/cm^{-1} 1643m (NH_2); ν_{max}/cm^{-1} 1591s and 1364s (CO_2).

Reaction of $[Zn(tu)_4][NO_3]_2$ with $Na_3[C_6H_3(CO_2)_3\text{-}1,3,5]$. Synthesis of $Na_2[Zn_2\{C_6H_3(CO_2)_3\text{-}1,3,5\}_2]$

An aqueous solution of $Na_3[C_6H_3(CO_2)_3$-1,3,5] (0.028 g, 0.10 mmol) was added to an aqueous solution of $[Zn(tu)_4][NO_3]_2$ (0.050 g, 0.10 mmol). The solution was allowed to stand for 12 h after which time colourless crystals of $Na_2[Zn_2\{C_6H_3(CO_2)_3\text{-}1,3,5\}_2]\cdot 11H_2O$ had grown. The compound was identified by comparison of the unit cell dimensions to those previously reported.[15]

Crystal structure determinations

Crystal data for complex 1. $C_{10}H_{18}N_6O_6S_2Zn\cdot 2H_2O$, M = 483.8, triclinic, space group $P\bar{1}$, a = 6.163(2), b = 7.786(2), c = 10.316(3) Å, α = 93.42(2), β = 96.17(3), γ = 108.79(2)°, U = 463.6(2) Å^3, Z = 1 (the molecule has crystallographic C_i symmetry), D_c = 1.733 g cm^{-3}, μ(Cu-Kα) = 44.5 cm^{-1}, $F(000)$ = 250. A clear block of dimensions 0.33 × 0.27 × 0.23 mm was used.

Data collection and processing. Data were measured on a Siemens P4/PC diffractometer with Cu-Kα radiation (graphite monochromator) using ω scans. 1444 Independent reflections were measured ($2\theta \leqslant 124°$) of which 1389 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors, and a semiempirical absorption correction (based on ψ scans) was applied; the maximum and minimum transmission factors were 0.42 and 0.32 respectively.

Structure analysis and refinement. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from a ΔF map, and the N–H and O–H hydrogen atoms were refined isotropically subject to a distance constraint. The positions of the C–H hydrogen atoms were idealised, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares based on F^2 to give $R1 = 0.031$, $wR2 = 0.086$‡ for the observed data and 161 parameters. The maximum and minimum residual electron densities in the final ΔF map were 0.26 and −0.33 e Å^{-3} respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.000 and 0.001 respectively.

Crystal data for polymer 2. $C_{19}H_{20}N_6O_8S_3Zn_2\cdot 4H_2O$, M = 759.4, monoclinic, space group $P2_1/c$, a = 10.798(1), b = 22.821(1), c = 11.988(1) Å, β = 103.75(1)°, U = 2869.3(3) Å^3, Z = 4, D_c = 1.758 g cm^{-3}, μ(Cu-Kα) = 47.3 cm^{-1}, $F(000)$ = 1552. A clear plate of dimensions 0.25 × 0.18 × 0.15 mm was used.

Data collection and processing. Data were measured on a Siemens P4 rotating anode diffractometer with Cu-Kα radiation (graphite monochromator) using ω scans. 4223 Independent reflections were measured ($2\theta \leqslant 120°$) of which 3706 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors, but not for absorption.

Structure analysis and refinement. The structure was solved by direct methods. The major occupancy non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the polymer were located from a ΔF map, and the N–H hydrogen atoms were refined isotropically subject to a distance constraint. The positions of the C–H hydrogen atoms were idealised, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms (the hydrogen atoms of the water molecules were not located). Refinement was by full-matrix least squares based on F^2 to give $R1 = 0.065$, $wR2 = 0.174$‡ for the observed data and 436 parameters. The maximum and minimum residual electron densities in the final ΔF map were 0.87 and −0.94 e Å^{-3} respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.000 and −0.003 respectively.

For both structures, computations were carried out using the SHELXTL PC program system.[18]

CCDC reference number 186/696.

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‡ $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

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