



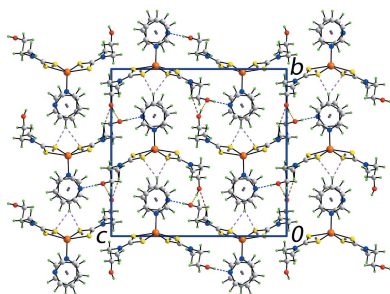
Crystal structure of bis[*N*-(2-hydroxyethyl)-*N*-methyldithiocarbamato- κ^2 *S,S'*](pyridine)zinc(II) pyridine monosolvate and its *N*-ethyl analogue

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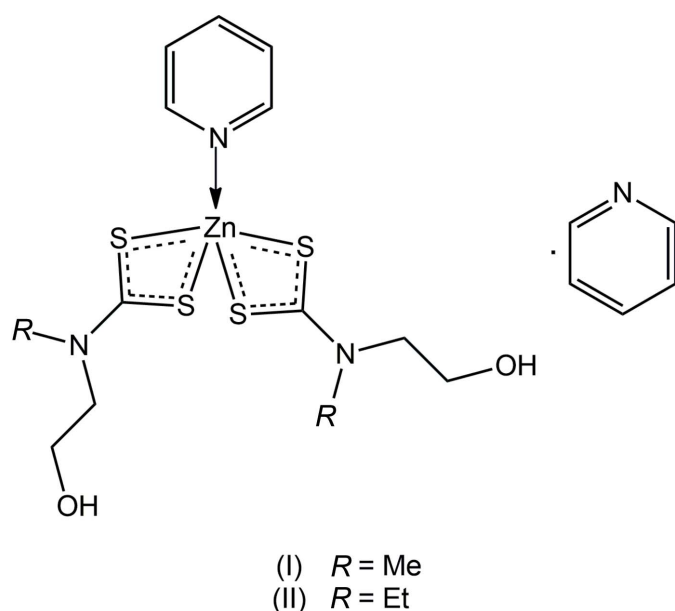
The common structural feature of the title compounds, [Zn(C₄H₈NOS₂)₂(C₅H₅N)]·C₅H₅N (I) and [Zn(C₅H₁₀NOS₂)₂(C₅H₅N)]·C₅H₅N (II), which differ by having dithiocarbamate N-bound methyl (I) and ethyl (II) groups, is the coordination of each Zn^{II} atom by two non-symmetrically chelating dithiocarbamate ligands and by a pyridine ligand; in each case, the non-coordinating pyridine molecule is connected to the Zn-containing molecule *via* a (hydroxy)O—H···N(pyridine) hydrogen bond. The resulting NS₄ coordination geometry is closer to a square-pyramid than a trigonal bipyramid in the case of (I), but almost intermediate between the two extremes in (II). The molecular packing features (hydroxy)O—H···O(hydroxy) hydrogen bonds, leading to supramolecular chains with a zigzag arrangement along [10 $\bar{1}$] (I) or a helical arrangement along [010] (II). In (I), π – π [inter-centroid distances = 3.4738 (10) and 3.4848 (10) Å] between coordinating and non-coordinating pyridine molecules lead to stacks comprising alternating rings along the *a* axis. In (II), weaker π – π contacts occur between centrosymmetrically related pairs of coordinating pyridine molecules [inter-centroid separation = 3.9815 (14) Å]. Further interactions, including C—H··· π (chelate) interactions in (I), lead to a three-dimensional architecture in each case.

1. Chemical context

Potentially multidentate ligands such as dithiocarbamate, [−]S₂CNRR', dithiocarbonate (xanthate), [−]S₂COR, and dithiophosphate, [−]S₂P(OR)(OR'), all belong to the 1,1-dithiolate class of ligands. While many similarities are apparent in their coordination propensities (Hogarth, 2005; Heard, 2005; Tiekink & Haiduc, 2005; Haiduc & Sowerby, 1996), stark differences sometimes occur. As a case in point are species formed with the potentially bidentate ligand *trans*-1,2-bis(4-pyridyl)ethylene (bpe). With Zn(S₂COEt)₂, a 1:1 compound can be prepared which crystallography shows to be a one-dimensional coordination polymer with a zigzag arrangement (Kang *et al.*, 2010). A similar structure is found for the *R* = *n*-Bu species, but in the case of a bulky cyclohexyl (Cy) group only the dimeric aggregate [Zn(S₂COCy)₂]₂(bpe) could be isolated (Kang *et al.*, 2010). Such steric control over supramolecular aggregation is well established in the structural chemistry of main group 1,1-dithiolate compounds (Tiekink, 2003, 2006). A similar situation to the above occurs for zinc(II) dithiophosphates, Zn[S₂P(OR)₂]₂, in that 1:1 one-dimensional coordination polymers can be formed with bpe when *R* = *i*-Pr (Welte & Tiekink, 2007), *R* = *i*-Bu (Welte & Tiekink, 2006) and *R* = Cy (Lai *et al.*, 2004). Interestingly, when *R* is small, a zigzag



chain is formed in the crystal but larger groups, *i.e.* $R = \text{Cy}$, lead to linear chains. The situation changes for zinc(II) dithiocarbamates of bpe, where only binuclear species, $[\text{Zn}(\text{S}_2\text{CNR}_2)_2](\text{bpe})$, have been isolated, *e.g.* $R = \text{Me}$ (Poplaukhin & Tiekink, 2009), $R = \text{Et}$ (Arman *et al.*, 2009*b*) and *i*-Pr (Arman *et al.*, 2009*a*). When an excess of bpe is introduced into the reaction with $R = \text{Et}$, the dimeric aggregate is again isolated and an additional molecule of bpe is incorporated into the crystal (Lai & Tiekink, 2003). This contrasting behaviour can be explained in terms of an effective chelating mode of the dithiocarbamate ligand owing to a 40% contribution of the ${}^2\text{-S}_2\text{C}=\text{N}^+\text{RR}'$ canonical form to the overall electronic structure. This reduces the Lewis acidity of the zinc cation and results in an inability to increase its coordination number beyond five in these systems.



In order to overcome the reluctance of zinc(II) dithiocarbamates to generate extended supramolecular architectures, the dithiocarbamate ligands can be functionalized with hydrogen-bonding potential, *i.e.* ${}^-\text{S}_2\text{CN}(R)\text{CH}_2\text{CH}_2\text{OH}$ (Howie *et al.*, 2008), and systematic studies conducted. This influence is nicely seen in the crystal of the binary species, $\text{Zn}[\text{S}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2]_2$, where the dimeric aggregate, mediated by Zn–S bridges, self-assembles into a three-dimensional architecture based on hydrogen bonding (Benson *et al.*, 2007). Studies have shown that binuclear aggregates with 4,4'-bipyridine (bipy) bridges can be formed with these functionalized dithiocarbamate ligands, consistent with the above, but extended arrays result, being stabilized *via* hydrogen bonding (Benson *et al.*, 2007), *e.g.* an open supramolecular layer in the case of $\{\text{Zn}[\text{S}_2\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{OH}]_2\}_2(\text{bipy})$, which allows for the construction of a doubly interpenetrated architecture. When the bridge is pyrazine, the three-dimensional architecture is sustained by (hydroxy)O–H...O(hydroxy) hydrogen bonding exclusively (Jotani *et al.*, 2017). When the bridge is significantly longer, *e.g.* (3-pyridyl) $\text{CH}_2\text{N}(\text{H})\text{C}(=\text{O})\text{C}(=\text{O})\text{N}(\text{H})\text{CH}_2(3\text{-pyridyl})$, *i.e.* LH_2 , the dimeric

Table 1
Geometric data (\AA , $^\circ$) for (I) and (II).

Parameter	(I); $n = 5$	(II); $n = 6$
Zn–S1	2.3618 (5)	2.3414 (6)
Zn–S2	2.5902 (5)	2.6140 (6)
Zn–S3	2.3678 (5)	2.3666 (6)
Zn–S4	2.5436 (5)	2.5627 (6)
Zn–N3	2.0504 (13)	2.0611 (16)
C1–S1, S2	1.7331 (15), 1.7176 (15)	1.7357 (18), 1.7168 (19)
C(n)–S3, S4	1.7309 (15), 1.7171 (15)	1.7388 (18), 1.7195 (19)
S1–Zn–S2	73.012 (16)	72.621 (17)
S3–Zn–S4	73.765 (16)	73.534 (16)
S1–Zn–S3	136.711 (17)	132.86 (2)
S1–Zn–S4	98.906 (17)	98.846 (19)
S2–Zn–S3	97.326 (17)	104.146 (17)
S2–Zn–S4	157.363 (16)	166.375 (19)
S1–Zn–N3	111.99 (3)	116.78 (5)
S2–Zn–N3	99.96 (4)	93.26 (5)
S3–Zn–N3	111.23 (3)	110.34 (5)
S4–Zn–N3	102.66 (4)	100.14 (5)
S1,S2,C1/S3,S4,C(n)	46.16 (2)	49.06 (5)
S1,S2,C1/pyridyl	83.78 (5)	78.21 (7)
S3,S4,C(n)/pyridyl	84.93 (4)	88.39 (5)

$\{\text{Zn}[\text{S}_2\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{OH}]_2\}_2(\text{LH}_2)$ aggregates are interwoven into supramolecular chains sustained by hydrogen bonding (Poplaukhin & Tiekink, 2010). In a continuation of these structural studies, herein the crystal and molecular structures of two pyridine adducts are described, namely $\{\text{Zn}[\text{S}_2\text{CN}(R)\text{CH}_2\text{CH}_2\text{OH}]_2(\text{pyridine})\cdot\text{pyridine}\}$ for $R = \text{Me}$ (I) and Et (II).

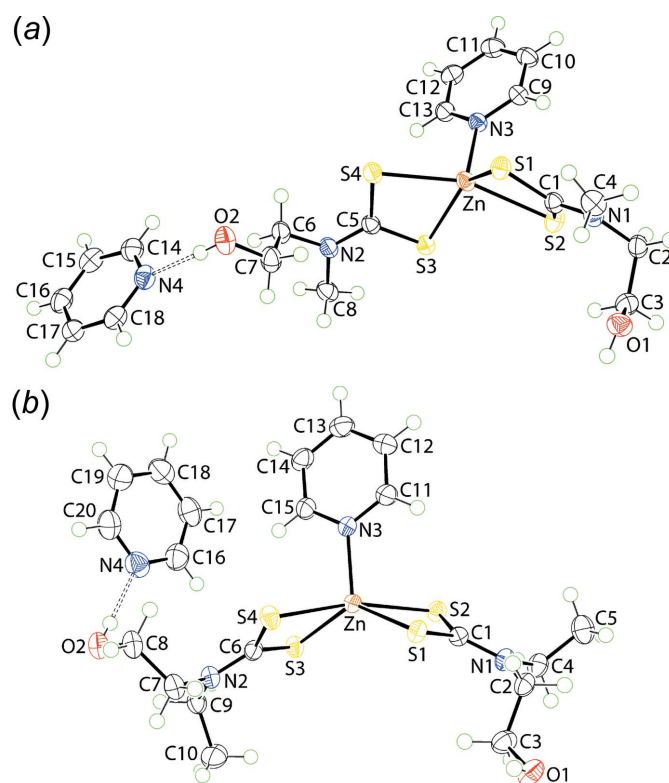


Figure 1
The molecular structures of (a) (I) and (b) (II), showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.

2. Structural commentary

The molecular structures of $\{\text{Zn}[\text{S}_2\text{CN}(R)\text{CH}_2\text{CH}_2\text{OH}]_2(\text{pyridine})\cdot\text{pyridine}\}$, for $R = \text{Me}$ (I) and Et (II), are shown in Fig. 1, and selected geometric parameters are given in Table 1. In (I), the dithiocarbamate ligands coordinate with non-symmetric Zn–S bond lengths which is conveniently quantified by $\Delta\text{Zn–S} = \text{Zn–S}_{\text{long}} - \text{Zn–S}_{\text{short}}$. For the S1-dithiocarbamate ligand, $\Delta\text{Zn–S} = 0.23 \text{ \AA}$, but this decreases to 0.17 \AA for the S3-ligand. From the data in Table 1, there is a tendency for the sulfur atoms forming the shorter Zn–S bonds to be involved in the longer C–S bonds. The pyridine-N atom occupies the fifth position in the five-coordinate zinc cation and forms N–Zn–S angles in the range $99.96(4)$ to $111.99(3)^\circ$. Further, the pyridine ring is almost orthogonal to the planes through each of the chelate rings, Table 1. The value of τ , which ranges from 0.0 to 1.0° for ideal square-pyramidal to trigonal-bipyramidal, respectively (Addison *et al.*, 1984), computes to 0.34 , suggesting a distortion towards a square-pyramidal geometry. If this was the case, the basal plane comprises the four sulfur atoms (r.m.s. deviation = 0.1841 \AA) and the zinc cation lies $0.6877(3) \text{ \AA}$ out of the plane in the direction of the pyridine-N3 atom. The asymmetric unit of (I) is completed by a second pyridine molecule that is connected to the (hydroxy)O2–H atom *via* a hydrogen bond, Table 2.

To a first approximation the structure of (II) resembles that of (I). The values of $\Delta\text{Zn–S}$, at 0.27 and 0.19 \AA for the S1- and S3-dithiocarbamate ligands, respectively, are slightly greater than the equivalent values in (I), and this is also seen in the greater disparity in the associated C–S bond lengths, Table 1. The range of N–Zn–S bond angles is also broader, at $93.26(5)$ – $116.78(5)^\circ$ and there is a disparity in the CS₂/pyridine dihedral angles of 10.2° , *cf.* 1.1° for (I). The value of τ is 0.56 , indicating a small tendency towards trigonal-bipyramidal, certainly when compared with the coordination geometry for (I). The widest angle subtended at the zinc cation is by the two less tightly held sulfur atoms, *i.e.* $166.375(19)^\circ$.

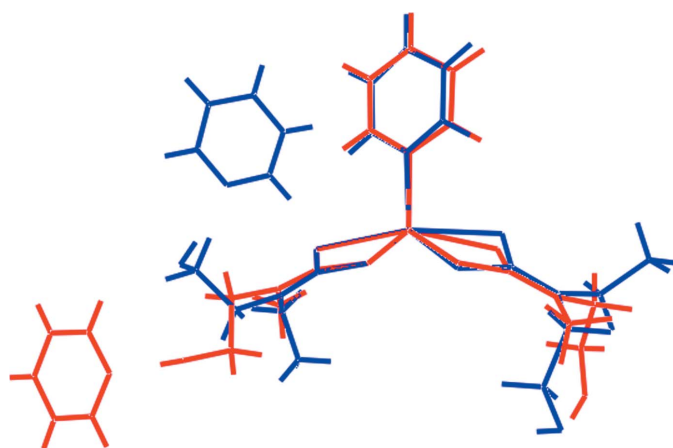


Figure 2
Overlay diagram of the asymmetric units of (I), red image, and (II). The molecules have been overlapped so the more symmetrically coordinating dithiocarbamate ligands are coincident.

Table 2
Hydrogen-bond geometry (\AA , $^\circ$) for (I).

Cg1 and Cg2 are the centroids of the Zn/S1/S2/C1 and Zn/S3/S4/C5 rings, respectively.

D–H...A	D–H	H...A	D...A	D–H...A
O1–H1O...O2 ⁱ	0.84 (2)	1.88 (2)	2.7008 (18)	164 (2)
O2–H2O...N4	0.85 (2)	1.87 (2)	2.713 (2)	178 (2)
C8–H8C...O1 ⁱⁱ	0.98	2.56	3.418 (2)	146
C11–H11...Cg1 ⁱⁱⁱ	0.95	2.87	3.7324 (18)	151
C11–H11...Cg2 ⁱⁱⁱ	0.95	2.98	3.7772 (18)	142

Symmetry codes: (i) $x - \frac{3}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x - \frac{3}{2}, -y + \frac{1}{2}, z - \frac{3}{2}$; (iii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

Table 3
Hydrogen-bond geometry (\AA , $^\circ$) for (II).

D–H...A	D–H	H...A	D...A	D–H...A
O1–H1O...O2 ⁱ	0.84 (2)	1.99 (2)	2.817 (2)	167 (3)
O2–H2O...N4	0.84 (3)	1.93 (3)	2.753 (3)	167 (3)
C2–H2B...S3 ⁱⁱ	0.99	2.84	3.773 (2)	157
C14–H14...S2 ⁱⁱⁱ	0.95	2.69	3.443 (2)	137

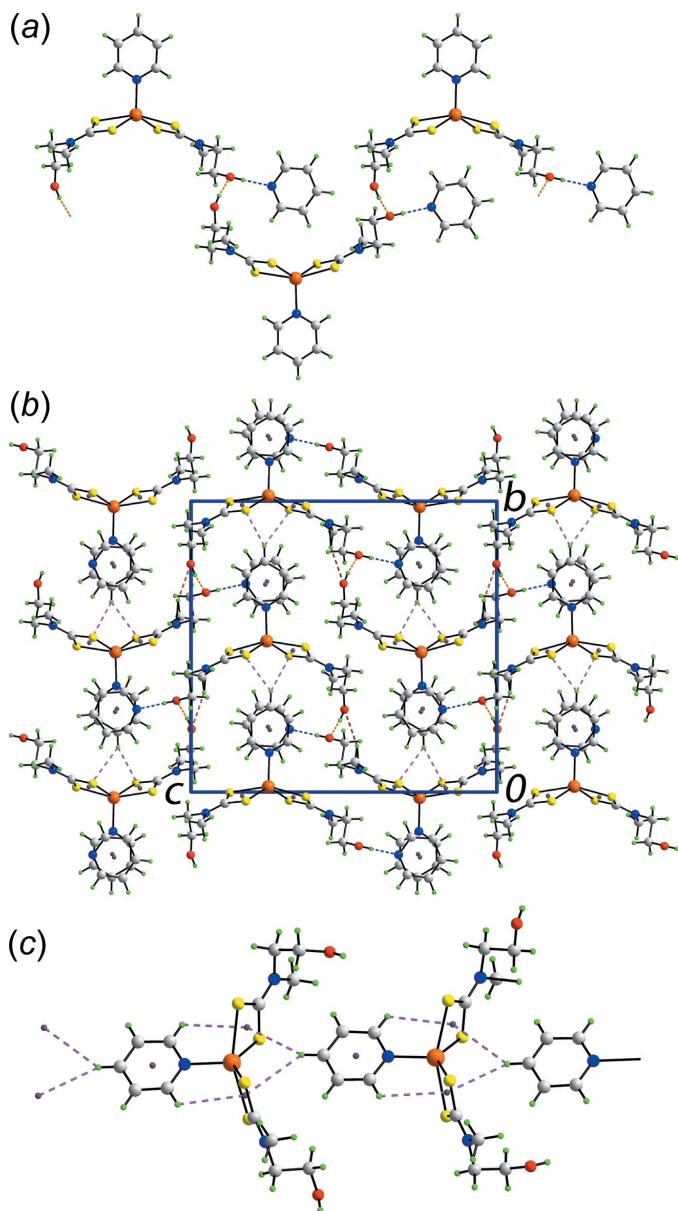
Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + 1, -y + 1, -z + 1$.

As for (I), distortions in the coordination geometry can be traced to the tight chelate angles, disparity in donor sets, bond lengths, *etc.* The solvent molecule in (II) is also associated with the O2-hydroxy group *via* a hydrogen bond.

Despite the relatively close agreement between the coordination geometries of the $\text{Zn}[\text{S}_2\text{CN}(R)\text{CH}_2\text{CH}_2\text{OH}]_2$ molecules in (I) and (II), the overlay diagram shown in Fig. 2 emphasizes the differences in the relative orientations of the less symmetrically coordinating dithiocarbamate ligands and the coordinating pyridine molecules. More striking are the opposite orientations adopted by the hydroxy groups of the more symmetrically coordinating dithiocarbamate ligands and therefore, the pyridine molecules to which they are connected. This impacts significantly upon the molecular packing as described in the next Section.

3. Supramolecular features

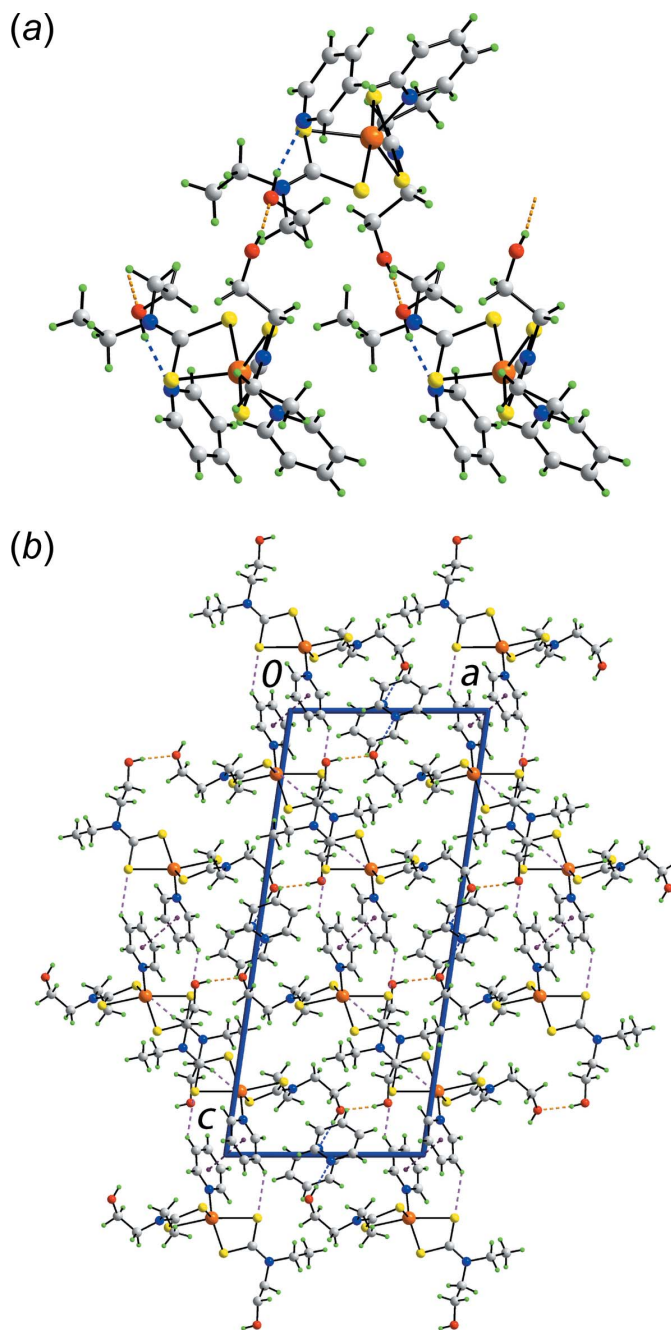
The key geometric parameters characterizing the intermolecular interactions operating in the crystals of (I) and (II) are collated in Tables 2 and 3, respectively. In the molecular packing of (I), (hydroxy)O–H...O(hydroxy) hydrogen bonding between the two independent hydroxy groups leads to a supramolecular zigzag chain aligned along $[10\bar{1}]$ with the solvent pyridine molecules associated with the chain *via* (hydroxy)O–H...N(pyridine) hydrogen bonding, Fig. 3a. While the hydroxy-O2 atom is involved in two conventional hydrogen bonds, the hydroxy-O1 atom is not. Rather, it participates in a (methyl)C–H...O(hydroxy) interaction, Table 2. Globally, molecules stack along the *a* axis with solvent pyridine molecules interspersed between coordinating pyridine molecules to form columns connected by $\pi(\text{coordinating pyridine})-\pi(\text{solvent pyridine})$ interactions so that each ring


Figure 3

Molecular packing in (I): (a) supramolecular zigzag chain aligned along $[10\bar{1}]$ and sustained by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding, with the solvent pyridine molecules attached *via* $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonding, (b) a view of the unit-cell contents in projection down the a axis and (c) supramolecular chain along the b axis sustained by (pyridine) $\text{C}-\text{H}\cdots\pi$ (chelate ring) interactions. The $\text{O}-\text{H}\cdots\text{O}$, $\text{O}-\text{H}\cdots\text{N}$, $\text{C}-\text{H}\cdots\text{O}$, $\pi-\pi$ and $\text{C}-\text{H}\cdots\pi$ (chelate ring) interactions are shown as orange, blue, brown, purple and pink dashed lines, respectively.

forms two contacts. The separations between the ring centroids are 3.4738 (10) and 3.4848 (10) Å for an angle of inclination = 0.28 (7)°; symmetry operations: $2-x, 1-y, -z$ and $1-x, 1-y, -z$. Further connections between the constituent molecules are of the type (solvent pyridine) $\text{C}-\text{H}\cdots\pi$ (chelate ring). As seen from Fig. 3a, the solvent pyridine molecules are located in a position proximate to the chelate rings enabling such interactions to form. A view of the unit-cell contents is shown in Fig. 3b.

The result of the aforementioned (solvent pyridine) $\text{C}-\text{H}\cdots\pi$ (chelate ring) interactions is a supramolecular chain aligned along the b axis as shown in Fig. 3c. Such interactions are well known in the supramolecular chemistry of metal 1,1-dithiolates in general and dithiocarbamates in particular owing to significant delocalization of π -electron density over the chelate rings relative to other 1,1-dithiolate ligands such as


Figure 4

Molecular packing in (II): (a) supramolecular helical chain aligned along $[010]$ and sustained by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding, with the solvent pyridine molecules attached *via* $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonding, and (b) a view of the unit-cell contents in projection down the a axis. The $\text{O}-\text{H}\cdots\text{S}$, $\text{O}-\text{H}\cdots\text{N}$, $\text{C}-\text{H}\cdots\text{S}$ and $\pi-\pi$ interactions are shown as orange, blue, pink and purple dashed lines, respectively.

Table 4
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	[Zn(C ₄ H ₈ NOS ₂) ₂ (C ₅ H ₅ N)]·C ₅ H ₅ N	[Zn(C ₅ H ₁₀ NOS ₂) ₂ (C ₅ H ₅ N)]·C ₅ H ₅ N
<i>M_r</i>	524.06	552.09
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>
Temperature (K)	98	98
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.9457 (9), 17.638 (2), 18.552 (3)	11.2961 (16), 8.6514 (12), 25.716 (4)
β (°)	91.619 (2)	98.265 (3)
<i>V</i> (Å ³)	2271.9 (5)	2487.0 (6)
<i>Z</i>	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	1.47	1.35
Crystal size (mm)	0.40 × 0.30 × 0.25	0.30 × 0.15 × 0.10
Data collection		
Diffractometer	AFC12K/SATURN724	AFC12K/SATURN724
Absorption correction	Multi-scan (<i>ABSCOR</i> ; Higashi, 1995)	Multi-scan (<i>ABSCOR</i> ; Higashi, 1995)
<i>T</i> _{min} , <i>T</i> _{max}	0.766, 1.000	0.823, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	25102, 13197, 11207	38694, 15181, 12445
<i>R</i> _{int}	0.031	0.044
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.918	0.920
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.056, 0.140, 1.09	0.067, 0.167, 1.12
No. of reflections	13197	15181
No. of parameters	270	288
No. of restraints	2	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.70, -1.48	0.92, -1.61

Computer programs: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2005), *SHELXS* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *QMol* (Gans & Shalloway, 2001), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

those cited above (Tiekink & Zukerman-Schpector, 2011; Tiekink, 2017). The unusual feature in the present case is that the (pyridine)C–H hydrogen bond forming the interaction is bifurcated (Tan *et al.*, 2016), Table 3. Finally, for completeness, it is noted that analogous but intramolecular (coordinating pyridine)C–H··· π (chelate ring) interactions also occur, Fig. 3c, with (pyridine)C–H···ring centroid separations of 2 × 2.90 Å and C–H···ring centroid angles of 113°. These interactions might account for the symmetric disposition of the coordinating pyridine molecule with respect to the ZnS₄ arrangement.

In the crystal of (II), (hydroxy)O–H···O(hydroxy) hydrogen bonds between the two independent hydroxy groups are also formed but, in this case, leading to a supramolecular helical chain aligned along [010] and again with the solvent pyridine molecules associated *via* (hydroxy)O–H···N(pyridine) hydrogen bonding, Fig. 4a. Connections between the chains are of the type (coordinating pyridine)- and (methylene)C–H···S interactions as well as weak π – π contacts between centrosymmetrically related coordinating pyridine molecules [inter-centroid separation = 3.9815 (14) Å for symmetry operation 1 – *x*, 1 – *y*, 1 – *z*]. A view of the unit-cell contents is shown in Fig. 4b. As for (I), it is noted that intramolecular coordinating (pyridine)C–H··· π (chelate ring) interactions occur [(pyridine)C–H···ring centroid separations are 2.93 and 2.90 Å, and C–H···ring centroid angles are 110 and 112°].

4. Database survey

As a result of encouraging biological activities, *e.g.* as anti-cancer agents (Cvek *et al.*, 2008; Tan *et al.*, 2015) and for applications in tropical diseases (Manar *et al.*, 2017), as well as their utility as single-source precursors for the deposition of ZnS nanomaterials (Hrubaru *et al.*, 2016; Manar *et al.*, 2017), zinc dithiocarbamates continue to be well studied. The compounds are generally binuclear as there are equal numbers of chelating and tridentate, μ_2 -bridging ligands, leading to distorted square-pyramidal coordination spheres (Tiekink, 2003). The structures of the precursor molecules are readily disrupted by the addition of small donor molecules such as in the present report with pyridine. Indeed, one of the first pyridine adducts of a zinc dithiocarbamate to be described was that of Zn(S₂CNET₂)₂(pyridine), which was motivated by the desire to destroy the binuclear structure observed for the binary dithiocarbamate compound to form a lighter (*i.e.* lower molecular weight) species to facilitate chemical vapour deposition studies (Malik *et al.*, 1999). A search of the Cambridge Structural Database (Groom *et al.*, 2016) reveals over 25 ‘hits’ for related Zn(S₂CNRR′)₂(pyridine) species. More sophisticated monodentate nitrogen-donor adducts are also known, such as substituted pyridines, *e.g.* 3-hydroxypyridine (Jotani *et al.*, 2016), and non-aromatic donors such as piperidine (Zaeva *et al.*, 2011) and urotropine (hexamethylenetetramine; Câmpian *et al.*, 2016). All of the

adducts reveal similar mononuclear structures with NS_4 coordination geometries, similar to those described above for (I) and (II). Finally, it is interesting to note that the aforementioned $Zn(S_2CNEt_2)_2$ (pyridine) adduct has also been characterized as a mono-pyridine solvate (Ivanov *et al.*, 1998), indicating that hydrogen bonding of the type observed in (I) and (II) is not a prerequisite for incorporation of solvent pyridine in the crystal.

5. Synthesis and crystallization

The $Zn[S_2CN(R)CH_2CH_2OH]_2$, $R = Me$ and Et , precursors were prepared as per established procedures (Benson *et al.*, 2007). Crystals were of (I) were prepared in the following manner. In a typical experiment, $Zn[S_2CN(R)CH_2CH_2OH]_2$, $R = Me$ and Et (50 mg), was dissolved in pyridine (10 ml) and carefully layered with hexanes (10 ml). Crystals were harvested directly from solution and mounted immediately onto the diffractometer to avoid loss of pyridine.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. For each of (I) and (II), carbon-bound H atoms were placed in calculated positions ($C-H = 0.95-0.99 \text{ \AA}$) and were included in the riding model approximation, with $U_{iso}(H)$ set to $1.2-1.5U_{eq}(C)$. The O-bound H atoms were located in difference-Fourier maps but were refined with a distance restraint of $O-H = 0.84 \pm 0.01 \text{ \AA}$, and with $U_{iso}(H)$ set to $1.5U_{eq}(O)$. For (I), the maximum and minimum residual electron density peaks of 0.70 and 1.48 e \AA^{-3} , respectively, were located 1.03 and 1.02 \AA from the Zn atom. For (II), the maximum and minimum residual electron density peaks of 0.92 and 1.61 e \AA^{-3} , respectively, were located 1.02 and 0.61 \AA from the Zn atom.

Acknowledgements

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supporting information

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Crystal structure of bis[*N*-(2-hydroxyethyl)-*N*-methyldithiocarbamato- κ^2 S,S'](pyridine)zinc(II) pyridine monosolvate and its *N*-ethyl analogue

Pavel Poplaukhin and Edward R. T. Tiekink

Computing details

For both structures, data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2005); cell refinement: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2005); data reduction: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2005); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *QMol* (Gans & Shalloway, 2001) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Bis[*N*-(2-hydroxyethyl)-*N*-methyldithiocarbamato- κ^2 S,S'](pyridine)zinc(II) pyridine monosolvate (I)

Crystal data

[Zn(C₄H₈NOS₂)₂(C₅H₅N)]·C₅H₅N

$M_r = 524.06$

Monoclinic, $P2_1/n$

$a = 6.9457$ (9) Å

$b = 17.638$ (2) Å

$c = 18.552$ (3) Å

$\beta = 91.619$ (2)°

$V = 2271.9$ (5) Å³

$Z = 4$

$F(000) = 1088$

$D_x = 1.532$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å

Cell parameters from 14301 reflections

$\theta = 2.3$ – 40.7°

$\mu = 1.47$ mm⁻¹

$T = 98$ K

Prism, colourless

$0.40 \times 0.30 \times 0.25$ mm

Data collection

AFC12K/SATURN724

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan

(ABSCOR; Higashi, 1995)

$T_{\min} = 0.766$, $T_{\max} = 1.000$

25102 measured reflections

13197 independent reflections

11207 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 40.7^\circ$, $\theta_{\min} = 2.3^\circ$

$h = -12 \rightarrow 6$

$k = -32 \rightarrow 24$

$l = -24 \rightarrow 33$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.140$

$S = 1.09$

13197 reflections

270 parameters

2 restraints

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 1.0614P]$

where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.70 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.48 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn	0.76451 (3)	0.48081 (2)	0.24723 (2)	0.01870 (5)
S1	1.01537 (5)	0.53140 (2)	0.32115 (2)	0.02020 (7)
S2	0.62546 (6)	0.50167 (2)	0.37379 (2)	0.02190 (7)
S3	0.49806 (5)	0.52874 (2)	0.17907 (2)	0.01974 (7)
S4	0.89209 (6)	0.51679 (2)	0.12469 (2)	0.02174 (7)
O1	0.74031 (18)	0.71648 (7)	0.50152 (7)	0.0249 (2)
H1O	0.673 (3)	0.7534 (10)	0.4870 (14)	0.037*
O2	0.96838 (19)	0.68555 (7)	−0.04784 (7)	0.0271 (2)
H2O	0.912 (3)	0.6949 (15)	−0.0879 (8)	0.041*
N1	0.59677 (19)	0.57633 (7)	0.04818 (7)	0.0197 (2)
N2	0.90043 (19)	0.57235 (7)	0.45207 (7)	0.0195 (2)
N3	0.77129 (17)	0.36463 (7)	0.24459 (6)	0.01762 (19)
N4	0.7983 (2)	0.71567 (9)	−0.17816 (8)	0.0242 (2)
C1	0.8516 (2)	0.53850 (8)	0.38962 (7)	0.0178 (2)
C2	0.7607 (2)	0.58086 (8)	0.50946 (8)	0.0212 (2)
H2A	0.8312	0.5863	0.5563	0.025*
H2B	0.6813	0.5344	0.5117	0.025*
C3	0.6293 (2)	0.64871 (9)	0.49820 (9)	0.0235 (3)
H3A	0.5617	0.6449	0.4506	0.028*
H3B	0.5313	0.6496	0.5359	0.028*
C4	1.0894 (2)	0.60795 (9)	0.46490 (9)	0.0240 (3)
H4A	1.1826	0.5859	0.4322	0.036*
H4B	1.1326	0.5991	0.5149	0.036*
H4C	1.0792	0.6626	0.4561	0.036*
C5	0.6568 (2)	0.54396 (8)	0.11027 (7)	0.0177 (2)
C6	0.7319 (2)	0.59353 (8)	−0.00895 (8)	0.0208 (2)
H6A	0.6629	0.5923	−0.0564	0.025*
H6B	0.8343	0.5545	−0.0092	0.025*
C7	0.8224 (3)	0.67163 (9)	0.00288 (9)	0.0262 (3)
H7A	0.7215	0.7111	−0.0021	0.031*
H7B	0.8790	0.6747	0.0524	0.031*
C8	0.3984 (2)	0.60330 (9)	0.03608 (9)	0.0239 (3)
H8A	0.3140	0.5788	0.0705	0.036*
H8B	0.3547	0.5907	−0.0132	0.036*
H8C	0.3941	0.6584	0.0428	0.036*
C9	0.8304 (2)	0.32452 (8)	0.30251 (8)	0.0195 (2)

H9	0.8710	0.3509	0.3449	0.023*
C10	0.8342 (2)	0.24592 (9)	0.30270 (9)	0.0230 (3)
H10	0.8770	0.2189	0.3445	0.028*
C11	0.7742 (2)	0.20738 (9)	0.24053 (10)	0.0244 (3)
H11	0.7753	0.1535	0.2392	0.029*
C12	0.7130 (2)	0.24853 (9)	0.18064 (9)	0.0227 (3)
H12	0.6708	0.2235	0.1377	0.027*
C13	0.7145 (2)	0.32700 (8)	0.18455 (8)	0.0200 (2)
H13	0.6739	0.3553	0.1433	0.024*
C14	0.7583 (2)	0.65504 (10)	-0.21958 (10)	0.0254 (3)
H14	0.7787	0.6060	-0.1997	0.030*
C15	0.6883 (2)	0.66082 (10)	-0.29017 (10)	0.0266 (3)
H15	0.6625	0.6167	-0.3181	0.032*
C16	0.6568 (2)	0.73237 (11)	-0.31896 (9)	0.0266 (3)
H16	0.6091	0.7381	-0.3672	0.032*
C17	0.6958 (2)	0.79563 (10)	-0.27655 (9)	0.0251 (3)
H17	0.6742	0.8453	-0.2949	0.030*
C18	0.7671 (2)	0.78459 (10)	-0.20678 (9)	0.0242 (3)
H18	0.7952	0.8279	-0.1779	0.029*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn	0.02335 (9)	0.01525 (7)	0.01732 (8)	0.00012 (5)	-0.00244 (6)	0.00023 (5)
S1	0.02114 (15)	0.02096 (14)	0.01852 (14)	-0.00256 (11)	0.00097 (12)	-0.00106 (11)
S2	0.02227 (16)	0.02518 (16)	0.01831 (14)	-0.00572 (12)	0.00155 (12)	-0.00305 (12)
S3	0.02062 (15)	0.02014 (14)	0.01851 (14)	0.00136 (11)	0.00147 (12)	0.00278 (11)
S4	0.02038 (15)	0.02581 (16)	0.01907 (15)	0.00265 (12)	0.00130 (12)	0.00458 (11)
O1	0.0293 (6)	0.0186 (4)	0.0266 (5)	-0.0002 (4)	-0.0016 (4)	-0.0008 (4)
O2	0.0313 (6)	0.0283 (5)	0.0217 (5)	-0.0070 (4)	0.0008 (4)	0.0036 (4)
N1	0.0234 (5)	0.0184 (5)	0.0173 (5)	0.0002 (4)	-0.0007 (4)	0.0023 (4)
N2	0.0236 (5)	0.0177 (4)	0.0170 (5)	-0.0017 (4)	-0.0012 (4)	-0.0007 (4)
N3	0.0192 (5)	0.0162 (4)	0.0174 (5)	-0.0002 (3)	-0.0005 (4)	0.0006 (3)
N4	0.0208 (5)	0.0307 (6)	0.0210 (5)	-0.0014 (5)	0.0015 (4)	0.0012 (5)
C1	0.0218 (6)	0.0152 (5)	0.0163 (5)	-0.0018 (4)	-0.0009 (4)	0.0008 (4)
C2	0.0281 (7)	0.0193 (5)	0.0162 (5)	-0.0008 (5)	0.0003 (5)	-0.0002 (4)
C3	0.0271 (7)	0.0205 (6)	0.0228 (6)	0.0002 (5)	0.0011 (5)	-0.0023 (5)
C4	0.0257 (7)	0.0206 (6)	0.0255 (7)	-0.0040 (5)	-0.0050 (6)	-0.0011 (5)
C5	0.0211 (5)	0.0153 (5)	0.0168 (5)	0.0000 (4)	-0.0011 (4)	0.0000 (4)
C6	0.0269 (6)	0.0195 (5)	0.0159 (5)	-0.0015 (5)	0.0003 (5)	0.0008 (4)
C7	0.0373 (8)	0.0205 (6)	0.0211 (6)	-0.0052 (5)	0.0038 (6)	0.0005 (5)
C8	0.0245 (6)	0.0243 (6)	0.0226 (6)	0.0025 (5)	-0.0044 (5)	0.0023 (5)
C9	0.0205 (6)	0.0186 (5)	0.0193 (5)	0.0001 (4)	-0.0010 (4)	0.0027 (4)
C10	0.0222 (6)	0.0195 (5)	0.0273 (7)	0.0013 (5)	0.0020 (5)	0.0065 (5)
C11	0.0232 (6)	0.0166 (5)	0.0336 (8)	-0.0009 (4)	0.0036 (6)	0.0008 (5)
C12	0.0226 (6)	0.0197 (6)	0.0258 (7)	-0.0018 (5)	0.0012 (5)	-0.0048 (5)
C13	0.0215 (6)	0.0192 (5)	0.0192 (5)	-0.0004 (4)	-0.0005 (5)	-0.0009 (4)
C14	0.0217 (6)	0.0255 (7)	0.0292 (7)	-0.0020 (5)	0.0053 (5)	0.0015 (5)

C15	0.0222 (6)	0.0298 (7)	0.0280 (7)	-0.0044 (5)	0.0031 (6)	-0.0072 (6)
C16	0.0215 (6)	0.0376 (8)	0.0205 (6)	0.0012 (6)	0.0002 (5)	-0.0023 (6)
C17	0.0236 (6)	0.0277 (7)	0.0240 (6)	0.0036 (5)	0.0031 (5)	0.0020 (5)
C18	0.0213 (6)	0.0274 (7)	0.0241 (6)	-0.0008 (5)	0.0024 (5)	-0.0029 (5)

Geometric parameters (Å, °)

Zn—N3	2.0504 (13)	C4—H4B	0.9800
Zn—S1	2.3618 (5)	C4—H4C	0.9800
Zn—S3	2.3678 (5)	C6—C7	1.528 (2)
Zn—S4	2.5436 (5)	C6—H6A	0.9900
Zn—S2	2.5902 (5)	C6—H6B	0.9900
S1—C1	1.7331 (15)	C7—H7A	0.9900
S2—C1	1.7176 (15)	C7—H7B	0.9900
S3—C5	1.7309 (15)	C8—H8A	0.9800
S4—C5	1.7171 (15)	C8—H8B	0.9800
O1—C3	1.423 (2)	C8—H8C	0.9800
O1—H1O	0.840 (9)	C9—C10	1.387 (2)
O2—C7	1.424 (2)	C9—H9	0.9500
O2—H2O	0.847 (9)	C10—C11	1.392 (2)
N1—C5	1.3412 (19)	C10—H10	0.9500
N1—C6	1.467 (2)	C11—C12	1.384 (2)
N1—C8	1.469 (2)	C11—H11	0.9500
N2—C1	1.3385 (18)	C12—C13	1.386 (2)
N2—C2	1.469 (2)	C12—H12	0.9500
N2—C4	1.469 (2)	C13—H13	0.9500
N3—C9	1.3410 (18)	C14—C15	1.388 (3)
N3—C13	1.3462 (19)	C14—H14	0.9500
N4—C14	1.341 (2)	C15—C16	1.385 (3)
N4—C18	1.342 (2)	C15—H15	0.9500
C2—C3	1.516 (2)	C16—C17	1.388 (2)
C2—H2A	0.9900	C16—H16	0.9500
C2—H2B	0.9900	C17—C18	1.386 (3)
C3—H3A	0.9900	C17—H17	0.9500
C3—H3B	0.9900	C18—H18	0.9500
C4—H4A	0.9800		
N3—Zn—S1	111.99 (3)	S4—C5—S3	117.71 (8)
N3—Zn—S3	111.23 (3)	N1—C6—C7	110.61 (12)
S1—Zn—S3	136.711 (17)	N1—C6—H6A	109.5
N3—Zn—S4	102.66 (4)	C7—C6—H6A	109.5
S1—Zn—S4	98.906 (17)	N1—C6—H6B	109.5
S3—Zn—S4	73.765 (16)	C7—C6—H6B	109.5
N3—Zn—S2	99.96 (4)	H6A—C6—H6B	108.1
S1—Zn—S2	73.012 (16)	O2—C7—C6	111.01 (13)
S3—Zn—S2	97.326 (17)	O2—C7—H7A	109.4
S4—Zn—S2	157.363 (16)	C6—C7—H7A	109.4
C1—S1—Zn	87.95 (5)	O2—C7—H7B	109.4

C1—S2—Zn	81.14 (5)	C6—C7—H7B	109.4
C5—S3—Zn	86.84 (5)	H7A—C7—H7B	108.0
C5—S4—Zn	81.65 (5)	N1—C8—H8A	109.5
C3—O1—H1O	110.0 (18)	N1—C8—H8B	109.5
C7—O2—H2O	107.1 (19)	H8A—C8—H8B	109.5
C5—N1—C6	121.26 (13)	N1—C8—H8C	109.5
C5—N1—C8	122.44 (13)	H8A—C8—H8C	109.5
C6—N1—C8	116.04 (12)	H8B—C8—H8C	109.5
C1—N2—C2	121.13 (13)	N3—C9—C10	122.33 (14)
C1—N2—C4	122.30 (13)	N3—C9—H9	118.8
C2—N2—C4	116.41 (12)	C10—C9—H9	118.8
C9—N3—C13	118.61 (13)	C9—C10—C11	118.73 (14)
C9—N3—Zn	120.98 (10)	C9—C10—H10	120.6
C13—N3—Zn	120.40 (10)	C11—C10—H10	120.6
C14—N4—C18	117.84 (15)	C12—C11—C10	119.15 (15)
N2—C1—S2	121.64 (11)	C12—C11—H11	120.4
N2—C1—S1	120.75 (11)	C10—C11—H11	120.4
S2—C1—S1	117.60 (8)	C11—C12—C13	118.69 (15)
N2—C2—C3	112.86 (12)	C11—C12—H12	120.7
N2—C2—H2A	109.0	C13—C12—H12	120.7
C3—C2—H2A	109.0	N3—C13—C12	122.49 (14)
N2—C2—H2B	109.0	N3—C13—H13	118.8
C3—C2—H2B	109.0	C12—C13—H13	118.8
H2A—C2—H2B	107.8	N4—C14—C15	122.92 (16)
O1—C3—C2	109.50 (13)	N4—C14—H14	118.5
O1—C3—H3A	109.8	C15—C14—H14	118.5
C2—C3—H3A	109.8	C16—C15—C14	118.56 (15)
O1—C3—H3B	109.8	C16—C15—H15	120.7
C2—C3—H3B	109.8	C14—C15—H15	120.7
H3A—C3—H3B	108.2	C15—C16—C17	119.20 (16)
N2—C4—H4A	109.5	C15—C16—H16	120.4
N2—C4—H4B	109.5	C17—C16—H16	120.4
H4A—C4—H4B	109.5	C18—C17—C16	118.38 (15)
N2—C4—H4C	109.5	C18—C17—H17	120.8
H4A—C4—H4C	109.5	C16—C17—H17	120.8
H4B—C4—H4C	109.5	N4—C18—C17	123.10 (15)
N1—C5—S4	121.59 (11)	N4—C18—H18	118.5
N1—C5—S3	120.70 (11)	C17—C18—H18	118.5
C2—N2—C1—S2	-1.26 (19)	Zn—S3—C5—S4	1.93 (7)
C4—N2—C1—S2	-176.42 (11)	C5—N1—C6—C7	-87.22 (17)
C2—N2—C1—S1	177.95 (10)	C8—N1—C6—C7	87.01 (16)
C4—N2—C1—S1	2.79 (19)	N1—C6—C7—O2	173.90 (13)
Zn—S2—C1—N2	174.33 (12)	C13—N3—C9—C10	-0.2 (2)
Zn—S2—C1—S1	-4.90 (7)	Zn—N3—C9—C10	179.15 (11)
Zn—S1—C1—N2	-173.92 (12)	N3—C9—C10—C11	-0.1 (2)
Zn—S1—C1—S2	5.32 (8)	C9—C10—C11—C12	0.1 (2)
C1—N2—C2—C3	-82.38 (17)	C10—C11—C12—C13	0.3 (2)

C4—N2—C2—C3	93.05 (16)	C9—N3—C13—C12	0.7 (2)
N2—C2—C3—O1	-64.00 (16)	Zn—N3—C13—C12	-178.73 (12)
C6—N1—C5—S4	-3.14 (19)	C11—C12—C13—N3	-0.7 (2)
C8—N1—C5—S4	-177.00 (11)	C18—N4—C14—C15	0.6 (2)
C6—N1—C5—S3	176.46 (10)	N4—C14—C15—C16	-0.6 (3)
C8—N1—C5—S3	2.6 (2)	C14—C15—C16—C17	-0.1 (2)
Zn—S4—C5—N1	177.80 (12)	C15—C16—C17—C18	0.7 (2)
Zn—S4—C5—S3	-1.81 (7)	C14—N4—C18—C17	0.1 (2)
Zn—S3—C5—N1	-177.69 (12)	C16—C17—C18—N4	-0.7 (3)

Hydrogen-bond geometry (\AA , $^\circ$)

Cg1 and Cg2 are the centroids of the Zn/S1/S2/C1 and Zn/S3/S4/C5 rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O \cdots O2 ⁱ	0.84 (2)	1.88 (2)	2.7008 (18)	164 (2)
O2—H2O \cdots N4	0.85 (2)	1.87 (2)	2.713 (2)	178 (2)
C8—H8C \cdots O1 ⁱⁱ	0.98	2.56	3.418 (2)	146
C11—H11 \cdots Cg1 ⁱⁱⁱ	0.95	2.87	3.7324 (18)	151
C11—H11 \cdots Cg2 ⁱⁱⁱ	0.95	2.98	3.7772 (18)	142

Symmetry codes: (i) $x-3/2, -y+1/2, z-1/2$; (ii) $x-3/2, -y+1/2, z-3/2$; (iii) $-x+3/2, y-1/2, -z+1/2$.

Bis[*N*-ethyl-*N*-(2-hydroxyethyl)dithiocarbamato- κ^2 S,S'](pyridine)zinc(II) pyridine monosolvate (II)

Crystal data

$[\text{Zn}(\text{C}_5\text{H}_{10}\text{NOS}_2)_2(\text{C}_5\text{H}_5\text{N})]\cdot\text{C}_5\text{H}_5\text{N}$

$M_r = 552.09$

Monoclinic, $P2_1/n$

$a = 11.2961$ (16) \AA

$b = 8.6514$ (12) \AA

$c = 25.716$ (4) \AA

$\beta = 98.265$ (3) $^\circ$

$V = 2487.0$ (6) \AA^3

$Z = 4$

$F(000) = 1152$

$D_x = 1.474$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71069$ \AA

Cell parameters from 12656 reflections

$\theta = 2.4\text{--}40.8^\circ$

$\mu = 1.35$ mm^{-1}

$T = 98$ K

Prism, colourless

$0.30 \times 0.15 \times 0.10$ mm

Data collection

AFC12K/SATURN724

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan

(ABSCOR; Higashi, 1995)

$T_{\min} = 0.823$, $T_{\max} = 1.000$

38694 measured reflections

15181 independent reflections

12445 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.044$

$\theta_{\max} = 40.8^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -20 \rightarrow 20$

$k = -14 \rightarrow 15$

$l = -44 \rightarrow 34$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.067$

$wR(F^2) = 0.167$

$S = 1.12$

15181 reflections

288 parameters

2 restraints

Hydrogen site location: inferred from

neighbouring sites

H atoms treated by a mixture of independent

and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 2.0316P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.003$

$$\Delta\rho_{\max} = 0.92 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.61 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn	0.47427 (2)	0.44028 (3)	0.64271 (2)	0.01851 (5)
S1	0.55997 (4)	0.55454 (6)	0.72177 (2)	0.01876 (8)
S2	0.70555 (4)	0.44837 (5)	0.64257 (2)	0.01879 (8)
S3	0.42049 (4)	0.18271 (5)	0.61898 (2)	0.01930 (8)
S4	0.26154 (4)	0.40105 (6)	0.66400 (2)	0.02107 (9)
O1	0.78229 (14)	0.4876 (2)	0.88352 (6)	0.0266 (3)
H1O	0.7169 (18)	0.521 (4)	0.8910 (14)	0.040*
O2	-0.04706 (14)	0.05941 (19)	0.60039 (7)	0.0250 (3)
H2O	-0.019 (3)	0.082 (4)	0.5728 (9)	0.038*
N1	0.79784 (14)	0.52998 (19)	0.74066 (7)	0.0192 (3)
N2	0.21137 (14)	0.10140 (19)	0.64833 (7)	0.0191 (3)
N3	0.43968 (14)	0.58368 (19)	0.57831 (6)	0.0187 (2)
N4	0.03600 (19)	0.1826 (3)	0.51379 (8)	0.0305 (4)
C1	0.70026 (15)	0.5128 (2)	0.70533 (7)	0.0174 (3)
C2	0.79109 (17)	0.5804 (2)	0.79481 (7)	0.0205 (3)
H2A	0.7252	0.6560	0.7946	0.025*
H2B	0.8667	0.6323	0.8094	0.025*
C3	0.7695 (2)	0.4432 (2)	0.82968 (8)	0.0254 (4)
H3A	0.6879	0.4021	0.8188	0.030*
H3B	0.8274	0.3600	0.8252	0.030*
C4	0.91884 (16)	0.4924 (2)	0.72956 (8)	0.0221 (3)
H4A	0.9121	0.4266	0.6978	0.027*
H4B	0.9610	0.4319	0.7593	0.027*
C5	0.9930 (2)	0.6340 (3)	0.72107 (10)	0.0293 (4)
H5A	0.9530	0.6931	0.6911	0.044*
H5B	1.0723	0.6016	0.7140	0.044*
H5C	1.0015	0.6989	0.7526	0.044*
C6	0.28789 (15)	0.2160 (2)	0.64413 (7)	0.0177 (3)
C7	0.10530 (17)	0.1225 (2)	0.67473 (8)	0.0225 (3)
H7A	0.1238	0.2000	0.7031	0.027*
H7B	0.0869	0.0236	0.6912	0.027*
C8	-0.00393 (18)	0.1750 (2)	0.63788 (9)	0.0245 (3)
H8A	-0.0681	0.2023	0.6587	0.029*
H8B	0.0163	0.2691	0.6191	0.029*
C9	0.23077 (18)	-0.0579 (2)	0.63059 (8)	0.0218 (3)
H9A	0.2790	-0.0544	0.6014	0.026*

H9B	0.1525	-0.1050	0.6171	0.026*
C10	0.2944 (2)	-0.1585 (3)	0.67444 (11)	0.0345 (5)
H10A	0.3766	-0.1216	0.6842	0.052*
H10B	0.2957	-0.2658	0.6623	0.052*
H10C	0.2519	-0.1529	0.7050	0.052*
C11	0.4984 (2)	0.7171 (2)	0.57605 (8)	0.0261 (4)
H11	0.5525	0.7493	0.6058	0.031*
C12	0.4829 (2)	0.8101 (3)	0.53160 (10)	0.0308 (4)
H12	0.5255	0.9046	0.5311	0.037*
C13	0.4043 (2)	0.7634 (3)	0.48801 (9)	0.0264 (4)
H13	0.3918	0.8253	0.4572	0.032*
C14	0.34453 (19)	0.6245 (3)	0.49038 (8)	0.0247 (3)
H14	0.2910	0.5887	0.4610	0.030*
C15	0.36386 (18)	0.5381 (2)	0.53632 (8)	0.0223 (3)
H15	0.3219	0.4435	0.5380	0.027*
C16	0.1423 (2)	0.1930 (3)	0.49671 (11)	0.0329 (5)
H16	0.2075	0.1355	0.5144	0.039*
C17	0.1613 (2)	0.2840 (3)	0.45431 (11)	0.0331 (5)
H17	0.2376	0.2875	0.4430	0.040*
C18	0.0669 (3)	0.3698 (3)	0.42880 (10)	0.0333 (5)
H18	0.0776	0.4342	0.3999	0.040*
C19	-0.0426 (3)	0.3600 (3)	0.44606 (11)	0.0363 (5)
H19	-0.1091	0.4175	0.4294	0.044*
C20	-0.0536 (2)	0.2647 (3)	0.48810 (11)	0.0345 (5)
H20	-0.1298	0.2571	0.4994	0.041*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn	0.01866 (9)	0.01800 (9)	0.01757 (10)	-0.00288 (6)	-0.00185 (7)	0.00161 (6)
S1	0.01561 (16)	0.02345 (19)	0.01692 (18)	-0.00013 (13)	0.00130 (13)	-0.00153 (14)
S2	0.01858 (17)	0.02160 (19)	0.01603 (18)	-0.00044 (13)	0.00187 (13)	-0.00093 (13)
S3	0.01541 (16)	0.01877 (17)	0.0240 (2)	-0.00086 (13)	0.00388 (14)	-0.00173 (14)
S4	0.01822 (17)	0.01765 (18)	0.0277 (2)	-0.00105 (13)	0.00452 (15)	-0.00333 (15)
O1	0.0226 (6)	0.0376 (8)	0.0186 (6)	0.0032 (6)	-0.0002 (5)	0.0005 (6)
O2	0.0206 (6)	0.0278 (7)	0.0269 (7)	-0.0051 (5)	0.0040 (5)	-0.0044 (5)
N1	0.0155 (5)	0.0211 (6)	0.0201 (7)	0.0018 (5)	-0.0001 (5)	-0.0021 (5)
N2	0.0168 (6)	0.0185 (6)	0.0223 (7)	-0.0018 (4)	0.0039 (5)	-0.0020 (5)
N3	0.0173 (6)	0.0200 (6)	0.0179 (6)	-0.0015 (5)	-0.0009 (5)	0.0008 (5)
N4	0.0324 (9)	0.0331 (10)	0.0265 (9)	-0.0055 (7)	0.0055 (7)	-0.0009 (7)
C1	0.0170 (6)	0.0171 (6)	0.0179 (7)	0.0001 (5)	0.0021 (5)	0.0005 (5)
C2	0.0203 (7)	0.0219 (7)	0.0182 (7)	-0.0001 (5)	-0.0016 (5)	-0.0037 (6)
C3	0.0305 (9)	0.0247 (9)	0.0195 (8)	0.0015 (7)	-0.0011 (7)	-0.0007 (6)
C4	0.0173 (7)	0.0228 (8)	0.0257 (8)	0.0030 (6)	0.0010 (6)	-0.0034 (6)
C5	0.0244 (9)	0.0304 (10)	0.0343 (11)	-0.0031 (7)	0.0081 (8)	-0.0063 (8)
C6	0.0152 (6)	0.0183 (6)	0.0191 (7)	0.0004 (5)	0.0006 (5)	-0.0004 (5)
C7	0.0209 (7)	0.0244 (8)	0.0230 (8)	-0.0042 (6)	0.0059 (6)	-0.0039 (6)
C8	0.0184 (7)	0.0237 (8)	0.0320 (10)	-0.0030 (6)	0.0058 (7)	-0.0053 (7)

C9	0.0209 (7)	0.0183 (7)	0.0259 (9)	-0.0030 (5)	0.0028 (6)	-0.0027 (6)
C10	0.0365 (12)	0.0214 (9)	0.0426 (13)	0.0023 (8)	-0.0043 (10)	0.0032 (8)
C11	0.0302 (9)	0.0223 (8)	0.0231 (9)	-0.0048 (7)	-0.0050 (7)	0.0024 (6)
C12	0.0340 (11)	0.0256 (9)	0.0310 (11)	-0.0052 (8)	-0.0019 (8)	0.0084 (8)
C13	0.0276 (9)	0.0293 (9)	0.0222 (9)	0.0031 (7)	0.0034 (7)	0.0060 (7)
C14	0.0252 (8)	0.0312 (9)	0.0165 (7)	-0.0003 (7)	-0.0006 (6)	0.0002 (6)
C15	0.0216 (7)	0.0252 (8)	0.0191 (8)	-0.0037 (6)	-0.0001 (6)	0.0002 (6)
C16	0.0294 (10)	0.0324 (11)	0.0360 (12)	-0.0016 (8)	0.0013 (9)	-0.0034 (9)
C17	0.0310 (10)	0.0351 (11)	0.0354 (12)	-0.0064 (9)	0.0124 (9)	-0.0079 (9)
C18	0.0419 (13)	0.0323 (11)	0.0257 (10)	-0.0095 (9)	0.0050 (9)	-0.0009 (8)
C19	0.0340 (12)	0.0349 (12)	0.0383 (13)	-0.0018 (9)	-0.0006 (10)	0.0013 (10)
C20	0.0258 (10)	0.0403 (13)	0.0384 (13)	-0.0036 (9)	0.0079 (9)	-0.0017 (10)

Geometric parameters (Å, °)

Zn—N3	2.0611 (16)	C5—H5B	0.9800
Zn—S1	2.3414 (6)	C5—H5C	0.9800
Zn—S3	2.3666 (6)	C7—C8	1.513 (3)
Zn—S4	2.5627 (6)	C7—H7A	0.9900
Zn—S2	2.6140 (6)	C7—H7B	0.9900
S1—C1	1.7357 (18)	C8—H8A	0.9900
S2—C1	1.7168 (19)	C8—H8B	0.9900
S3—C6	1.7388 (18)	C9—C10	1.521 (3)
S4—C6	1.7195 (19)	C9—H9A	0.9900
O1—C3	1.424 (3)	C9—H9B	0.9900
O1—H1O	0.841 (10)	C10—H10A	0.9800
O2—C8	1.425 (3)	C10—H10B	0.9800
O2—H2O	0.839 (10)	C10—H10C	0.9800
N1—C1	1.332 (2)	C11—C12	1.388 (3)
N1—C2	1.472 (2)	C11—H11	0.9500
N1—C4	1.472 (2)	C12—C13	1.386 (3)
N2—C6	1.330 (2)	C12—H12	0.9500
N2—C7	1.471 (2)	C13—C14	1.384 (3)
N2—C9	1.478 (2)	C13—H13	0.9500
N3—C11	1.337 (3)	C14—C15	1.388 (3)
N3—C15	1.338 (2)	C14—H14	0.9500
N4—C20	1.331 (4)	C15—H15	0.9500
N4—C16	1.339 (3)	C16—C17	1.387 (4)
C2—C3	1.528 (3)	C16—H16	0.9500
C2—H2A	0.9900	C17—C18	1.384 (4)
C2—H2B	0.9900	C17—H17	0.9500
C3—H3A	0.9900	C18—C19	1.376 (4)
C3—H3B	0.9900	C18—H18	0.9500
C4—C5	1.518 (3)	C19—C20	1.379 (4)
C4—H4A	0.9900	C19—H19	0.9500
C4—H4B	0.9900	C20—H20	0.9500
C5—H5A	0.9800		

N3—Zn—S1	116.78 (5)	S4—C6—S3	117.38 (10)
N3—Zn—S3	110.34 (5)	N2—C7—C8	113.14 (17)
S1—Zn—S3	132.86 (2)	N2—C7—H7A	109.0
N3—Zn—S4	100.14 (5)	C8—C7—H7A	109.0
S1—Zn—S4	98.846 (19)	N2—C7—H7B	109.0
S3—Zn—S4	73.534 (16)	C8—C7—H7B	109.0
N3—Zn—S2	93.26 (5)	H7A—C7—H7B	107.8
S1—Zn—S2	72.621 (17)	O2—C8—C7	112.46 (17)
S3—Zn—S2	104.146 (17)	O2—C8—H8A	109.1
S4—Zn—S2	166.375 (19)	C7—C8—H8A	109.1
C1—S1—Zn	88.79 (6)	O2—C8—H8B	109.1
C1—S2—Zn	80.65 (6)	C7—C8—H8B	109.1
C6—S3—Zn	87.20 (6)	H8A—C8—H8B	107.8
C6—S4—Zn	81.50 (6)	N2—C9—C10	112.35 (18)
C3—O1—H1O	110 (2)	N2—C9—H9A	109.1
C8—O2—H2O	106 (3)	C10—C9—H9A	109.1
C1—N1—C2	121.87 (16)	N2—C9—H9B	109.1
C1—N1—C4	122.92 (16)	C10—C9—H9B	109.1
C2—N1—C4	115.14 (15)	H9A—C9—H9B	107.9
C6—N2—C7	121.79 (16)	C9—C10—H10A	109.5
C6—N2—C9	122.90 (15)	C9—C10—H10B	109.5
C7—N2—C9	115.16 (15)	H10A—C10—H10B	109.5
C11—N3—C15	118.92 (17)	C9—C10—H10C	109.5
C11—N3—Zn	121.12 (13)	H10A—C10—H10C	109.5
C15—N3—Zn	119.77 (13)	H10B—C10—H10C	109.5
C20—N4—C16	117.0 (2)	N3—C11—C12	122.10 (19)
N1—C1—S2	122.69 (14)	N3—C11—H11	119.0
N1—C1—S1	120.38 (14)	C12—C11—H11	119.0
S2—C1—S1	116.93 (10)	C13—C12—C11	119.2 (2)
N1—C2—C3	111.04 (16)	C13—C12—H12	120.4
N1—C2—H2A	109.4	C11—C12—H12	120.4
C3—C2—H2A	109.4	C12—C13—C14	118.50 (19)
N1—C2—H2B	109.4	C12—C13—H13	120.8
C3—C2—H2B	109.4	C14—C13—H13	120.8
H2A—C2—H2B	108.0	C13—C14—C15	119.14 (19)
O1—C3—C2	111.00 (17)	C13—C14—H14	120.4
O1—C3—H3A	109.4	C15—C14—H14	120.4
C2—C3—H3A	109.4	N3—C15—C14	122.16 (19)
O1—C3—H3B	109.4	N3—C15—H15	118.9
C2—C3—H3B	109.4	C14—C15—H15	118.9
H3A—C3—H3B	108.0	N4—C16—C17	122.9 (2)
N1—C4—C5	113.35 (17)	N4—C16—H16	118.5
N1—C4—H4A	108.9	C17—C16—H16	118.5
C5—C4—H4A	108.9	C18—C17—C16	118.8 (2)
N1—C4—H4B	108.9	C18—C17—H17	120.6
C5—C4—H4B	108.9	C16—C17—H17	120.6
H4A—C4—H4B	107.7	C19—C18—C17	118.8 (2)
C4—C5—H5A	109.5	C19—C18—H18	120.6

C4—C5—H5B	109.5	C17—C18—H18	120.6
H5A—C5—H5B	109.5	C18—C19—C20	118.4 (3)
C4—C5—H5C	109.5	C18—C19—H19	120.8
H5A—C5—H5C	109.5	C20—C19—H19	120.8
H5B—C5—H5C	109.5	N4—C20—C19	124.1 (2)
N2—C6—S4	121.85 (14)	N4—C20—H20	117.9
N2—C6—S3	120.76 (14)	C19—C20—H20	117.9
C2—N1—C1—S2	-177.90 (14)	Zn—S3—C6—S4	6.11 (10)
C4—N1—C1—S2	-1.3 (3)	C6—N2—C7—C8	90.0 (2)
C2—N1—C1—S1	1.6 (2)	C9—N2—C7—C8	-94.3 (2)
C4—N1—C1—S1	178.23 (14)	N2—C7—C8—O2	67.3 (2)
Zn—S2—C1—N1	170.49 (16)	C6—N2—C9—C10	92.7 (2)
Zn—S2—C1—S1	-9.02 (9)	C7—N2—C9—C10	-82.9 (2)
Zn—S1—C1—N1	-169.57 (15)	C15—N3—C11—C12	0.3 (3)
Zn—S1—C1—S2	9.94 (10)	Zn—N3—C11—C12	175.27 (19)
C1—N1—C2—C3	85.5 (2)	N3—C11—C12—C13	-0.2 (4)
C4—N1—C2—C3	-91.4 (2)	C11—C12—C13—C14	-0.4 (4)
N1—C2—C3—O1	170.55 (16)	C12—C13—C14—C15	0.9 (3)
C1—N1—C4—C5	104.7 (2)	C11—N3—C15—C14	0.3 (3)
C2—N1—C4—C5	-78.4 (2)	Zn—N3—C15—C14	-174.80 (16)
C7—N2—C6—S4	-5.9 (3)	C13—C14—C15—N3	-0.8 (3)
C9—N2—C6—S4	178.76 (15)	C20—N4—C16—C17	0.0 (4)
C7—N2—C6—S3	173.16 (15)	N4—C16—C17—C18	0.9 (4)
C9—N2—C6—S3	-2.2 (3)	C16—C17—C18—C19	-0.8 (4)
Zn—S4—C6—N2	173.37 (16)	C17—C18—C19—C20	-0.1 (4)
Zn—S4—C6—S3	-5.69 (9)	C16—N4—C20—C19	-1.0 (4)
Zn—S3—C6—N2	-172.97 (15)	C18—C19—C20—N4	1.0 (4)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O \cdots O2 ⁱ	0.84 (2)	1.99 (2)	2.817 (2)	167 (3)
O2—H2O \cdots N4	0.84 (3)	1.93 (3)	2.753 (3)	167 (3)
C2—H2B \cdots S3 ⁱⁱ	0.99	2.84	3.773 (2)	157
C14—H14 \cdots S2 ⁱⁱⁱ	0.95	2.69	3.443 (2)	137

Symmetry codes: (i) $-x+1/2, y+1/2, -z+3/2$; (ii) $-x+3/2, y+1/2, -z+3/2$; (iii) $-x+1, -y+1, -z+1$.