Crystal structures of (2,2′-bipyridyl-κ²*N*,*N*′)bis[*N*,*N*-bis(2-hydroxyethyl)dithiocarbamato-κ²*S*,*S*′]zinc dihydrate and (2,2′-bipyridyl-κ²*N*,*N*′)bis[*N*-(2-hydroxyethyl)-*N*-isopropyldithiocarbamato-κ²*S*,*S*′]-zinc

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The common feature of the title compounds, $[Zn(C_5H_{10}NO_2S_2)_2(C_{10}H_8N_2)]\cdot 2H_2O$, (I), and $[Zn(C_6H_{12}NOS_2)_2(C_{10}H_8N_2)]$, (II), is the location of the Zn^{II} atoms on a twofold rotation axis. Further, each Zn^{II} atom is chelated by two symmetry-equivalent and symmetrically coordinating dithiocarbamate ligands and a 2,2′-bipyridine ligand. The resulting N_2S_4 coordination geometry is based on a highly distorted octahedron in each case. In the molecular packing of (I), supramolecular ladders mediated by O—H···O hydrogen bonding are found whereby the uprights are defined by $\{\cdots HO(water)\cdots HO(hydroxy)\cdots\}_n$ chains parallel to the a axis and with the rungs defined by 'Zn[S₂CN(CH₂CH₂)₂]₂'. The water molecules connect the ladders into a supramolecular layer parallel to the ab plane *via* water-O—H···S and pyridyl-C—H···O(water) interactions, with the connections between layers being of the type pyridyl-C—H···S. In (II), supramolecular layers parallel to the ab plane are sustained by hydroxy-O—H···S hydrogen bonds with connections between layers being of the type pyridyl-C—H···S.

1. Chemical context

The dithiocarbamate ligand $^-S_2CNRR'$, is well known as an effective chelator of transition metals, main group elements and lanthanides (Hogarth, 2005; Heard, 2005). The resulting four-membered MS_2C chelate ring has metalloaromatic character (Masui, 2001) and may act as an acceptor for C—H···π(chelate) interactions (Tiekink & Zukerman-Schpector, 2011) much in the same way as the now widely accepted C—H···π(arene) interactions. While other 1,1-dithiolate species may also form analogous interactions – these were probably first discussed in cadmium xanthate (^-S_2COR) structures (Chen *et al.*, 2003) – dithiocarbamate compounds have a greater propensity to form C—H···π(chelate) interactions, an observation related to the relatively greater contribution of the canonical structure $^{2-}S_2C=N^+RR'$ to the overall electronic structure that enhances the electron density in the chelate ring (Tiekink & Zukerman-Schpector, 2011). This factor explains the strong chelation ability of the dithiocarbamate ligand and at the same time accounts for the reduced Lewis acidity of the metal cation in metal dithiocarbamates which reduces the ability of these species to form extended architectures in their interactions with Lewis bases. One way of overcoming the relative inability of the metal cation to engage in supramolecular association is to functionalize the dithiocarbamate ligand with, relevant to the
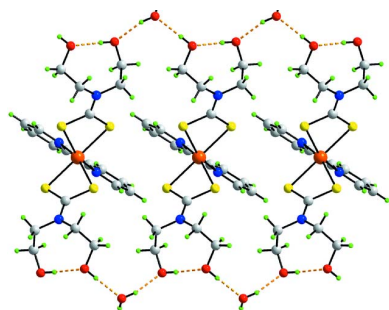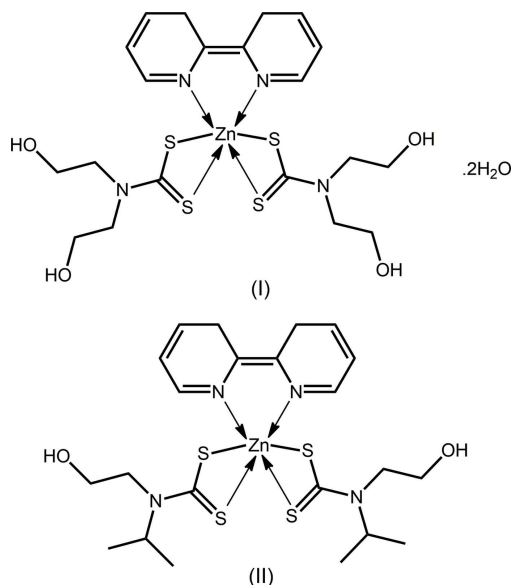
Table 1
Geometric data (Å, °) for (I), unsolvated (I) and for (II).

Parameter	(I)[a]	unsolvated (I)	(II)[b]
Zn—S1	2.5361 (5)	2.4632 (12)	2.5068 (5)
Zn—S2	2.5163 (5)	2.5968 (13)	2.5247 (5)
Zn—S3	2.5361 (5)	2.5030 (12)	2.5068 (5)
Zn—S4	2.5163 (5)	2.6045 (13)	2.5247 (5)
Zn—N2	2.1682 (15)	2.157 (4)	2.1695 (15)
Zn—N3	2.1682 (15)	2.154 (3)	2.1695 (15)
C—S	1.7198 (18)–1.7253 (18)	1.696 (4)–1.726 (5)	1.7221 (19)–1.7301 (18)
S1—Zn—S2	71.376 (15)	70.46 (4)	71.289 (16)
S3—Zn—S4	71.376 (15)	70.15 (4)	71.289 (16)
N2—Zn—N2	75.71 (8)	74.72 (12)	75.08 (8)

Notes: (a) S3, S4 and N3 are S1^i, S2^i and N2^i for (i) $\frac{3}{2} - x, \frac{1}{2} - y, z$; (b) S3, S4 and N3 are S1^i, S2^i and N2^i for (i) $1 - x, y, \frac{3}{2} - z$.

present report, hydrogen-bonding functionality. In this context and as a continuation of earlier studies of the zinc-triad elements with dithiocarbamate ligands featuring hydroxyethyl groups capable of forming hydrogen-bonding interactions (Benson *et al.*, 2007; Broker & Tiekink, 2011; Zhong *et al.*, 2004; Tan *et al.*, 2013, 2016; Safbri *et al.*, 2016; Howie *et al.*, 2009), herein, the crystal and molecular structures of two new zinc dithiocarbamates, Zn[S$_2$CN(CH$_2$CH$_2$OH)$_2$]$_2$-(bipy)·2H$_2$O, (I), and Zn[S$_2$CN(*i*Pr)CH$_2$CH$_2$OH]$_2$(bipy), (II) where bipy = 2,2′-bipyridine are described.

(I)

(II)

2. Structural commentary

The molecular structure of the zinc compound in (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. The zinc cation is located on a twofold rotation axis and is chelated by two symmetry-equivalent dithiocarbamate ligands and the 2,2′-bipyridine ligand, which is bisected by the twofold rotation axis. The dithiocarbamate ligand chelates in a symmetric mode with the difference between the Zn—S$_{long}$ and Zn—S$_{short}$ bond lengths being 0.02 Å. The shorter Zn—S bond is approximately *trans* to a pyridyl-N atom. The N$_2$S$_4$ coordination geometry is based on an octahedron. In this

description, one triangular face is defined by the S1, S2^i and N2^i atoms, and the other by the symmetry equivalent atoms [symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} - y, z$]. The dihedral angle between the two faces is 3.07 (4)° and the twist angle between them is approximately 35°, *cf.* 0 and 60° for ideal trigonal–prismatic and octahedral angles, respectively. The twist toward a trigonal prism is related in part to the acute bite angles subtended by the chelating ligands (Table 1).

Compound (I) was characterized herein as a dihydrate and may be compared with an unsolvated literature precedent (Deng *et al.*, 2007) for which selected geometric data are also collected in Table 1. First and foremost, the molecular symmetry observed in unsolvated (I) is lacking. Also, the range of Zn—S bond lengths is significantly broader at 0.14 Å, but the trend that the shorter Zn—S bonds are approximately *trans* to the pyridyl-N atoms persists. The dihedral angle between the trigonal faces is 5.33 (6)° and the twist between them is 31°, indicating an intermediate coordination geometry.

The molecule of compound (II) (Fig. 2) is also located about a twofold rotation axis and presents geometric features closely resembling those of (I), Table 1. The angle between the triangular faces is 1.50 (5)° and the twist angle is approxi-
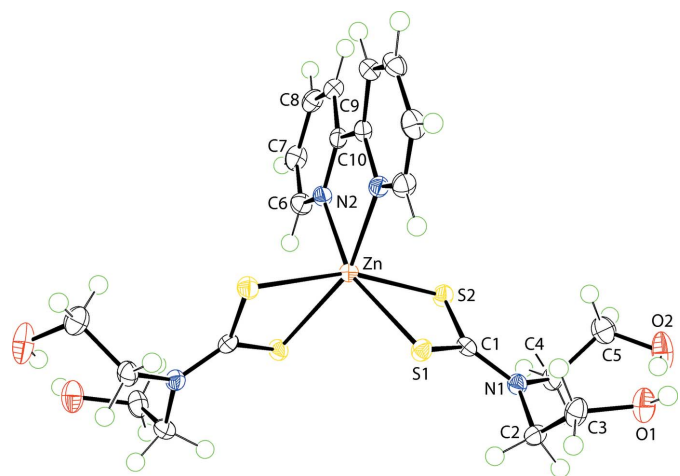

Figure 1
The molecular structure of the zinc compound in (I), showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level; the water molecules of crystallization have been omitted. The unlabelled atoms are related by the symmetry operation $\frac{3}{2} - x, \frac{1}{2} - y, z$.
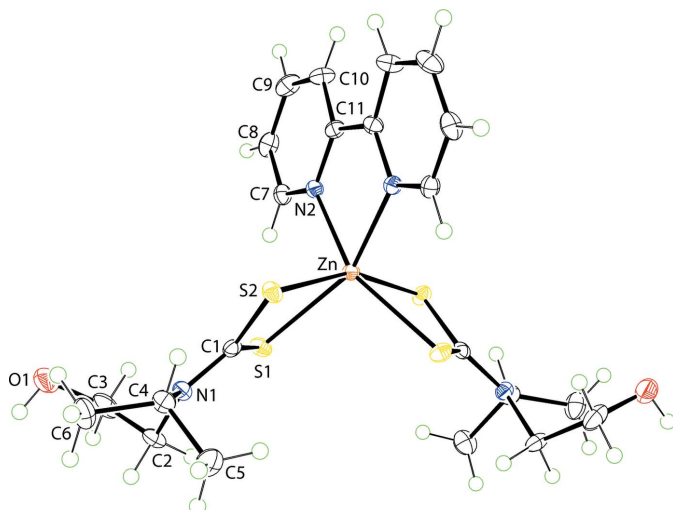
chains parallel to the *a* axis that serve as the uprights in the supramolecular ladders whereby the rungs are defined by 'Zn(S$_2$CN(CH$_2$CH$_2$)$_2$' (Fig. 3*a*). The water molecules are pivotal in connecting the ladders into a supramolecular layer parallel to the *ab* plane by forming water-O—H$\cdots$S and

Figure 2
The molecular structure of (II), showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level. The unlabelled atoms are related by the symmetry operation $1 - x, y, \frac{3}{2} - z$.

mately 30°, again indicating a highly distorted coordination geometry.

3. Supramolecular features

Geometric parameters characterizing the intermolecular interactions operating in the crystal structures of (I) and (II) are collected in Tables 2 and 3, respectively.

In the molecular packing of (I), supramolecular ladders mediated by O—H$\cdots$O hydrogen bonding are found. There is an intramolecular hydroxy-O—H$\cdots$O(hydroxy) hydrogen bond as well as intermolecular hydroxy-O—H$\cdots$O(water) and water-O—H$\cdots$O(hydroxy) hydrogen bonds. This mode of association results in supramolecular $\{\cdots \text{HO(water)} \cdots \text{HO(hydroxy)} \cdots \text{HO(hydroxy)} \cdots\}_n$ jagged

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$O\cdots$O1	0.83 (2)	1.87 (2)	2.696 (2)	177 (3)
O1—H1$O\cdots$O1W	0.83 (2)	1.88 (2)	2.7115 (19)	177 (2)
O1W—H1$W\cdots$O2^i	0.83 (2)	1.91 (2)	2.7216 (19)	166 (2)
O1W—H2$W\cdots$S2^{ii}	0.83 (2)	2.45 (2)	3.2733 (15)	170 (2)
C7—H7$\cdots$O1W^{iii}	0.95	2.58	3.517 (2)	171
C6—H6$\cdots$S2^{iv}	0.95	2.81	3.490 (2)	129
C9—H9$\cdots$S1^v	0.95	2.84	3.6857 (18)	149

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

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$O\cdots$S2^i	0.84 (2)	2.45 (2)	3.2437 (16)	160 (2)
C5—H5$B\cdots$O1^i	0.98	2.54	3.512 (2)	175
C9—H9$\cdots$S2^{ii}	0.95	2.86	3.550 (2)	130

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

Figure 3
Molecular packing in (I), showing (*a*) the supramolecular ladders aligned along the *a* axis and sustained by O—H$\cdots$O hydrogen bonding, (*b*) the supramolecular layers parallel to the *ab* plane whereby the ladders in (*a*) are connected by O—H$\cdots$S and C—H$\cdots$O interactions, and (*c*) a view of the unit-cell contents in projection down the *a* axis, showing C—H$\cdots$S interactions along the *c* axis connecting the layers in (*b*). The O—H$\cdots$O, O—H$\cdots$S, C—H$\cdots$O and C—H$\cdots$S interactions are shown as orange, blue, pink and green dashed lines, respectively.

(a)

(b)

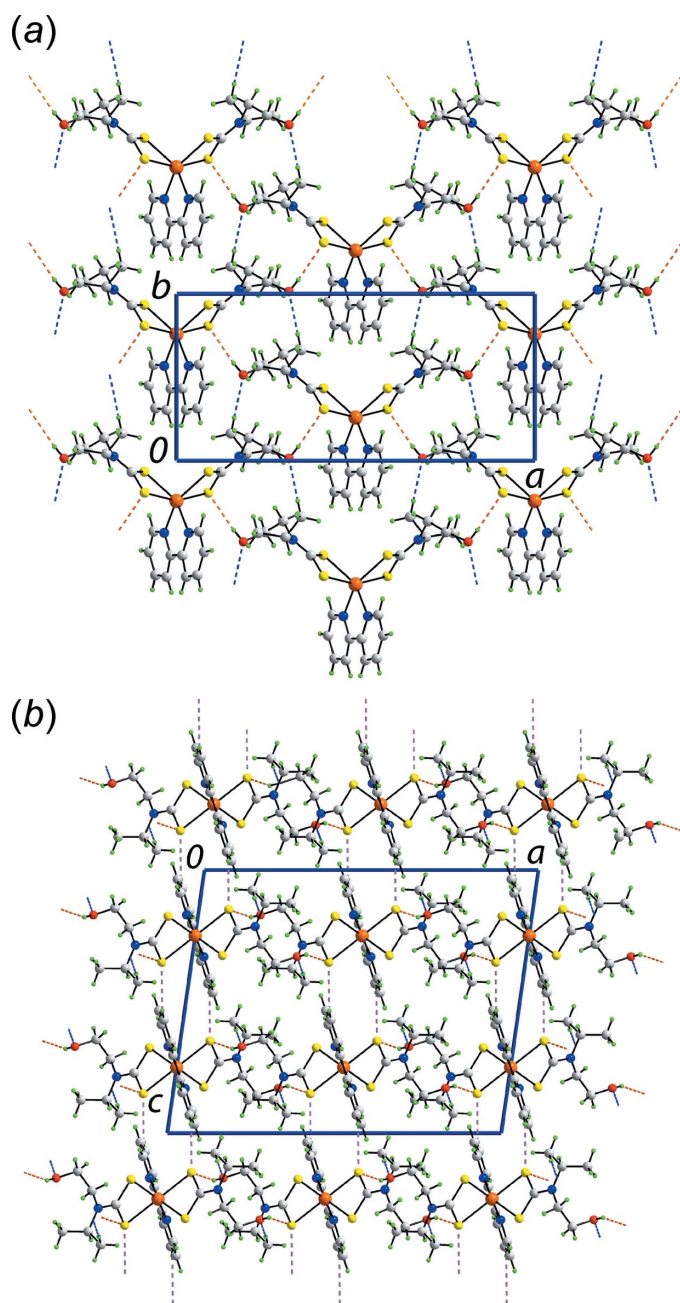**Figure 4**
Molecular packing in (II), showing (*a*) the supramolecular layers parallel to the *ab* plane sustained by O—H···S and C—H···O interactions, and (*b*) a view of the unit-cell contents in projection down the *b* axis, showing C—H···S interactions along the *c* axis connecting the layers in (*b*). The O—H···S, C—H···O and C—H···S interactions are shown as orange, blue and pink dashed lines, respectively.

pyridyl-C—H···O(water) interactions (Fig. 3*b*). The connections between layers to consolidate the three-dimensional architecture are of the type pyridyl-C—H···S (Fig. 3*c*).

Naturally, the molecular packing in the unsolvated form of (I) is distinct (Deng *et al.*, 2007). However, a detailed analysis of the packing is restricted as one of the hydroxy groups is disordered over two sites. Further, there are large voids in the crystal structure, amounting to approximately 570 Å^3 or

19.2% of the available volume (Spek, 2009). This is reflected in the crystal packing index of 59.2% which compares to 71.3% in (I). Globally, the crystal structure comprises alternating layers of hydrophilic and hydrophobic regions with the former arranged as supramolecular rods, indicating significant hydrogen bonding in this region of the crystal structure.

In the molecular packing of (II), hydroxy-O—H···S hydrogen bonds lead to supramolecular layers parallel to the *ab* plane (Fig. 4*a*). Additional stabilization to this arrangement is provided by methyl-C—H···O(hydroxy) interactions. Connections between layers to consolidate the three-dimensional packing are of the type pyridyl-C—H···S (Fig. 4*b*).

4. Database survey

Binary zinc dithiocarbamates are generally binuclear as a result of the presence of chelating and tridentate, μ_2-bridging ligands, leading to penta-coordinate geometries (Tiekink, 2003). The exceptional structures arise when the steric bulk of at least one of the terminal substituents is too great to allow for supramolecular association, *e.g.* R = cyclohexyl (Cox & Tiekink, 2009) and R = benzyl (Decken *et al.*, 2004). However, there is a subtle energetic balance between the two forms as seen in the crystal structure of Zn[S$_2$CN(i-Bu)$_2$]$_2$ which comprises equal numbers of mono- and bi-nuclear molecules (Ivanov *et al.*, 2005). As the R groups are generally aliphatic, there is limited scope for controlled supramolecular aggregation between the molecules. This changes in the case of the present study as at least one R group has an hydroxyethyl substituent. Indeed, a rich tapestry of structures have been observed for zinc compounds with this family of dithiocarbamate ligands.

The common feature of the molecular structures of the known binary species, Zn[S$_2$NC(R)CH$_2$CH$_2$OH]$_2$, is the adoption of a binuclear motif (Benson *et al.*, 2007; Tan *et al.*, 2015). In the molecular packing of these species, when R = CH$_2$CH$_2$OH, a three-dimensional architecture is constructed based on hydrogen bonding (Benson *et al.*, 2007). When the hydrogen-bonding potential is reduced, as in the case when R = Et, linear supramolecular chains are formed (Benson *et al.*, 2007). When R = Me, and in the 2:1 adduct with the bridging ligand (3-pyridyl)CH$_2$N(H)C(=O)C(=O)-N(H)CH$_2$(3-pyridyl), interwoven supramolecular chains are formed based on hydrogen bonding (Poplaukhin & Tiekink, 2010). Extensive hydrogen bonding is also noted in co-crystals, *e.g.* for R = Me in the 2:1 adduct with (3-pyridyl)CH$_2$N(H)-C(=S)C(=S)N(H)CH$_2$(3-pyridyl), a 2:1 co-crystal with S$_8$ has been characterized in which a two-dimensional array sustained by O—H···O hydrogen bonding is found (Poplaukhin *et al.*, 2012). From the foregoing, it is clear that a rich structural chemistry exists for these compounds, well worthy of further investigation. Complementing these interests are the observations that zinc compounds with these ligands (Tan *et al.*, 2015), along with gold (Jamaludin *et al.*, 2013) and bismuth (Ishak *et al.*, 2014) exhibit exciting anti-cancer potential.

Table 4
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$[Zn(C_5H_{10}NO_2S_2)_2(C_{10}H_8N_2)]\cdot 2H_2O$	$[Zn(C_6H_{12}NOS_2)_2(C_{10}H_8N_2)]$
M_r	618.10	578.12
Crystal system, space group	Orthorhombic, $Pccn$	Monoclinic, $C2/c$
Temperature (K)	100	100
a, b, c (Å)	6.7730 (3), 23.1063 (11), 16.9483 (8)	19.4997 (11), 9.0027 (5), 15.5352 (8)
α, β, γ (°)	90, 90, 90	90, 98.031 (5), 90
V (Å^3)	2652.4 (2)	2700.5 (3)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.28	1.25
Crystal size (mm)	$0.40 \times 0.30 \times 0.20$	$0.25 \times 0.25 \times 0.15$
Data collection		
Diffractometer	Agilent SuperNova Dual diffractometer with an Atlas detector	Agilent SuperNova Dual diffractometer with an Atlas detector
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2012)	Multi-scan (*CrysAlis PRO*; Agilent, 2012)
T_{min}, T_{max}	0.778, 1.000	0.737, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21039, 3047, 2607	11190, 3095, 2657
R_{int}	0.049	0.048
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650	0.650
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.066, 1.02	0.030, 0.073, 1.03
No. of reflections	3047	3095
No. of parameters	171	155
No. of restraints	4	1
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.39, −0.34	0.38, −0.35

Computer programs: *CrysAlis PRO* (Agilent, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

5. Synthesis and crystallization

The potassium salts of the dithiocarbamate anions (Howie *et al.*, 2008; Tan *et al.*, 2013) and zinc compounds (Benson *et al.*, 2007) were prepared in accord with the literature methods. The 1:1 adducts with 2,2′-bipyridine were prepared in the following manner. $Zn[S_2CN(CH_2CH_2OH)_2]_2$ (0.20 g, 0.47 mmol) and 2,2′-bipyridine (Sigma Aldrich; 0.07 g, 0.47 mmol) were dissolved in acetone (30 ml) and ethanol (10 ml), respectively. The solution of 2,2′-bipyridine was added dropwise into the other solution with stirring for about 30 mins, resulting in a change from a colourless to a light-yellow solution. The mixture was left to stand to allow for crystallization and crystals of (I) for X-ray analysis were harvested directly. Compound (II) was prepared and harvested similarly from the reaction of $Zn[S_2CN(iPr)CH_2CH_2OH]_2$ (0.20 g, 0.47 mmol) in chloroform (30 ml) and 2,2′-bipyridine (0.07 g, 0.47 mmol) in acetone (10 ml).

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 = 0.95–1.00 Å) and were included in the refinement 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 a difference Fourier map but were refined with a distance restraint of O—H = 0.84±0.01 Å, and with U_{iso}(H) set to 1.5U_{eq}(O).

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supporting information

Crystal structures of (2,2′-bipyridyl-*κ²N,N′*)bis[*N,N*-bis(2-hydroxyethyl)dithiocarbamato-*κ²S,S′*]zinc dihydrate and (2,2′-bipyridyl-*κ²N,N′*)bis[*N*-(2-hydroxyethyl)-*N*-isopropyldithiocarbamato-*κ²S,S′*]zinc

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Computing details

For both compounds, data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis PRO* (Agilent, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(I) (2,2′-Bipyridyl-*κ²N,N′*)bis[*N,N*-bis(2-hydroxyethyl)dithiocarbamato-*κ²S,S′*]zinc dihydrate

Crystal data

[Zn(C$_5$H$_{10}$NO$_2$S$_2$)$_2$(C$_{10}$H$_8$N$_2$)]·2H$_2$O	D_x = 1.548 Mg m^{-3}
M_r = 618.10	Mo $K\alpha$ radiation, λ = 0.71073 Å
Orthorhombic, *Pccn*	Cell parameters from 5870 reflections
a = 6.7730 (3) Å	θ = 2.6–27.5°
b = 23.1063 (11) Å	μ = 1.28 mm^{-1}
c = 16.9483 (8) Å	T = 100 K
V = 2652.4 (2) Å^3	Prism, light-yellow
Z = 4	0.40 × 0.30 × 0.20 mm
$F(000)$ = 1288	

Data collection

Agilent SuperNova Dual diffractometer with an Atlas detector	T_{min} = 0.778, T_{max} = 1.000
	21039 measured reflections
Radiation source: SuperNova (Mo) X-ray Source	3047 independent reflections
	2607 reflections with $I > 2\sigma(I)$
Mirror monochromator	R_{int} = 0.049
Detector resolution: 10.4041 pixels mm^{-1}	θ_{max} = 27.5°, θ_{min} = 2.6°
ω scan	$h = -8 \rightarrow 8$
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2012)	$k = -30 \rightarrow 29$
	$l = -22 \rightarrow 21$

Refinement

Refinement on F^2	4 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.027	$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 1.8882P]$
$wR(F^2)$ = 0.066	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.02	$(\Delta/\sigma)_{max}$ = 0.001
3047 reflections	$\Delta\rho_{max}$ = 0.39 e Å^{-3}
171 parameters	$\Delta\rho_{min}$ = −0.34 e Å^{-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 ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
Zn	0.7500	0.2500	0.25218 (2)	0.01179 (9)
S1	0.88162 (6)	0.32477 (2)	0.15608 (3)	0.01323 (11)
S2	0.48554 (6)	0.32443 (2)	0.22814 (3)	0.01403 (11)
N1	0.5960 (2)	0.39933 (6)	0.11619 (8)	0.0123 (3)
N2	0.5960 (2)	0.21427 (6)	0.35319 (8)	0.0122 (3)
O1	0.8068 (2)	0.51852 (6)	0.09325 (9)	0.0221 (3)
H1O	0.899 (3)	0.5406 (9)	0.1051 (14)	0.033*
O2	0.4459 (2)	0.52831 (6)	0.15907 (9)	0.0273 (3)
H2O	0.559 (2)	0.5263 (11)	0.1401 (14)	0.041*
O1W	1.1132 (2)	0.58995 (6)	0.12670 (8)	0.0202 (3)
H1W	1.225 (2)	0.5761 (10)	0.1348 (14)	0.030*
H2W	1.096 (3)	0.6133 (8)	0.1634 (10)	0.030*
C1	0.6497 (3)	0.35475 (8)	0.16217 (10)	0.0123 (4)
C2	0.7307 (3)	0.42078 (8)	0.05455 (10)	0.0151 (4)
H2A	0.6521	0.4409	0.0137	0.018*
H2B	0.7958	0.3872	0.0291	0.018*
C3	0.8882 (3)	0.46162 (8)	0.08437 (11)	0.0178 (4)
H3A	0.9390	0.4478	0.1358	0.021*
H3B	0.9996	0.4627	0.0466	0.021*
C4	0.3983 (3)	0.42555 (8)	0.12367 (11)	0.0151 (4)
H4A	0.3018	0.3948	0.1369	0.018*
H4B	0.3597	0.4422	0.0721	0.018*
C5	0.3875 (3)	0.47266 (8)	0.18629 (12)	0.0200 (4)
H5A	0.2503	0.4750	0.2061	0.024*
H5B	0.4731	0.4615	0.2311	0.024*
C6	0.4312 (3)	0.18264 (8)	0.34890 (11)	0.0161 (4)
H6	0.3897	0.1689	0.2988	0.019*
C7	0.3183 (3)	0.16904 (8)	0.41461 (11)	0.0170 (4)
H7	0.2017	0.1465	0.4096	0.020*
C8	0.3791 (3)	0.18905 (8)	0.48773 (11)	0.0154 (4)
H8	0.3034	0.1810	0.5336	0.019*
C9	0.5519 (3)	0.22098 (8)	0.49310 (10)	0.0140 (4)
H9	0.5975	0.2346	0.5428	0.017*
C10	0.6574 (2)	0.23279 (7)	0.42442 (10)	0.0115 (3)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn	0.01403 (15)	0.01109 (16)	0.01025 (15)	0.00054 (11)	0.000	0.000

S1	0.0126 (2)	0.0131 (2)	0.0140 (2)	0.00237 (17)	0.00144 (16)	0.00154 (16)
S2	0.0142 (2)	0.0131 (2)	0.0149 (2)	0.00035 (17)	0.00304 (17)	0.00135 (16)
N1	0.0122 (7)	0.0119 (7)	0.0127 (7)	0.0013 (6)	−0.0001 (6)	−0.0003 (6)
N2	0.0126 (7)	0.0115 (7)	0.0124 (7)	0.0007 (6)	−0.0003 (6)	−0.0006 (6)
O1	0.0191 (7)	0.0139 (7)	0.0332 (8)	−0.0013 (6)	0.0019 (6)	0.0008 (6)
O2	0.0186 (7)	0.0141 (7)	0.0491 (10)	0.0024 (6)	0.0051 (7)	−0.0030 (6)
O1W	0.0197 (7)	0.0191 (8)	0.0219 (7)	0.0019 (6)	0.0003 (6)	−0.0048 (6)
C1	0.0142 (9)	0.0118 (9)	0.0110 (8)	−0.0004 (7)	−0.0005 (7)	−0.0028 (6)
C2	0.0182 (9)	0.0148 (9)	0.0123 (9)	0.0008 (7)	0.0018 (7)	0.0027 (7)
C3	0.0151 (9)	0.0147 (10)	0.0236 (10)	0.0024 (7)	0.0032 (7)	0.0034 (8)
C4	0.0130 (9)	0.0145 (9)	0.0176 (9)	0.0033 (7)	−0.0019 (7)	0.0004 (7)
C5	0.0168 (9)	0.0196 (10)	0.0235 (10)	0.0026 (8)	0.0020 (8)	−0.0027 (8)
C6	0.0169 (9)	0.0149 (9)	0.0164 (9)	−0.0014 (7)	−0.0036 (7)	−0.0019 (7)
C7	0.0131 (9)	0.0150 (10)	0.0228 (10)	−0.0033 (7)	−0.0017 (7)	0.0023 (8)
C8	0.0137 (9)	0.0157 (9)	0.0169 (9)	0.0007 (7)	0.0027 (7)	0.0047 (7)
C9	0.0159 (9)	0.0131 (9)	0.0129 (9)	0.0007 (7)	−0.0003 (7)	0.0017 (7)
C10	0.0115 (8)	0.0093 (8)	0.0136 (9)	0.0004 (7)	−0.0017 (7)	0.0001 (7)

Geometric parameters (Å, º)

Zn—N2^i	2.1682 (15)	C2—C3	1.511 (3)
Zn—N2	2.1682 (14)	C2—H2A	0.9900
Zn—S2^i	2.5163 (5)	C2—H2B	0.9900
Zn—S2	2.5163 (5)	C3—H3A	0.9900
Zn—S1^i	2.5361 (5)	C3—H3B	0.9900
Zn—S1	2.5361 (5)	C4—C5	1.522 (3)
S1—C1	1.7198 (18)	C4—H4A	0.9900
S2—C1	1.7253 (18)	C4—H4B	0.9900
N1—C1	1.342 (2)	C5—H5A	0.9900
N1—C2	1.473 (2)	C5—H5B	0.9900
N1—C4	1.475 (2)	C6—C7	1.387 (3)
N2—C6	1.336 (2)	C6—H6	0.9500
N2—C10	1.347 (2)	C7—C8	1.385 (3)
O1—C3	1.434 (2)	C7—H7	0.9500
O1—H1O	0.832 (10)	C8—C9	1.386 (3)
O2—C5	1.422 (2)	C8—H8	0.9500
O2—H2O	0.830 (10)	C9—C10	1.393 (2)
O1W—H1W	0.835 (10)	C9—H9	0.9500
O1W—H2W	0.832 (9)	C10—C10^i	1.485 (3)
N2^i—Zn—N2	75.71 (8)	H2A—C2—H2B	107.6
N2^i—Zn—S2^i	92.61 (4)	O1—C3—C2	109.67 (15)
N2—Zn—S2^i	102.13 (4)	O1—C3—H3A	109.7
N2^i—Zn—S2	102.13 (4)	C2—C3—H3A	109.7
N2—Zn—S2	92.61 (4)	O1—C3—H3B	109.7
S2^i—Zn—S2	161.36 (2)	C2—C3—H3B	109.7
N2^i—Zn—S1^i	159.33 (4)	H3A—C3—H3B	108.2
N2—Zn—S1^i	94.50 (4)	N1—C4—C5	113.40 (15)

S2^i—Zn—S1^i	71.377 (15)	N1—C4—H4A	108.9
S2—Zn—S1^i	96.394 (15)	C5—C4—H4A	108.9
N2^i—Zn—S1	94.50 (4)	N1—C4—H4B	108.9
N2—Zn—S1	159.33 (4)	C5—C4—H4B	108.9
S2^i—Zn—S1	96.394 (15)	H4A—C4—H4B	107.7
S2—Zn—S1	71.376 (15)	O2—C5—C4	114.03 (16)
S1^i—Zn—S1	100.09 (2)	O2—C5—H5A	108.7
C1—S1—Zn	85.11 (6)	C4—C5—H5A	108.7
C1—S2—Zn	85.62 (6)	O2—C5—H5B	108.7
C1—N1—C2	120.14 (14)	C4—C5—H5B	108.7
C1—N1—C4	120.76 (15)	H5A—C5—H5B	107.6
C2—N1—C4	119.02 (14)	N2—C6—C7	122.73 (17)
C6—N2—C10	118.74 (15)	N2—C6—H6	118.6
C6—N2—Zn	124.56 (12)	C7—C6—H6	118.6
C10—N2—Zn	115.97 (11)	C8—C7—C6	118.61 (17)
C3—O1—H1O	107.5 (17)	C8—C7—H7	120.7
C5—O2—H2O	109.3 (18)	C6—C7—H7	120.7
H1W—O1W—H2W	105 (2)	C7—C8—C9	119.16 (17)
N1—C1—S1	121.46 (13)	C7—C8—H8	120.4
N1—C1—S2	120.88 (13)	C9—C8—H8	120.4
S1—C1—S2	117.64 (10)	C8—C9—C10	118.85 (16)
N1—C2—C3	114.22 (15)	C8—C9—H9	120.6
N1—C2—H2A	108.7	C10—C9—H9	120.6
C3—C2—H2A	108.7	N2—C10—C9	121.89 (16)
N1—C2—H2B	108.7	N2—C10—C10^i	115.54 (10)
C3—C2—H2B	108.7	C9—C10—C10^i	122.56 (11)
C2—N1—C1—S1	4.9 (2)	N1—C4—C5—O2	85.17 (19)
C4—N1—C1—S1	−178.34 (12)	C10—N2—C6—C7	1.4 (3)
C2—N1—C1—S2	−173.68 (12)	Zn—N2—C6—C7	−168.48 (14)
C4—N1—C1—S2	3.1 (2)	N2—C6—C7—C8	−0.1 (3)
Zn—S1—C1—N1	−173.88 (14)	C6—C7—C8—C9	−1.1 (3)
Zn—S1—C1—S2	4.70 (9)	C7—C8—C9—C10	1.1 (3)
Zn—S2—C1—N1	173.85 (14)	C6—N2—C10—C9	−1.4 (3)
Zn—S2—C1—S1	−4.73 (9)	Zn—N2—C10—C9	169.27 (13)
C1—N1—C2—C3	−81.8 (2)	C6—N2—C10—C10^i	179.44 (18)
C4—N1—C2—C3	101.31 (18)	Zn—N2—C10—C10^i	−9.8 (2)
N1—C2—C3—O1	−80.47 (19)	C8—C9—C10—N2	0.2 (3)
C1—N1—C4—C5	86.7 (2)	C8—C9—C10—C10^i	179.3 (2)
C2—N1—C4—C5	−96.50 (19)		

Symmetry code: (i) −*x*+3/2, −*y*+1/2, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O1	0.83 (2)	1.87 (2)	2.696 (2)	177 (3)
O1—H1*O*···O1*W*	0.83 (2)	1.88 (2)	2.7115 (19)	177 (2)

O1W—H1W···O2^{ii}	0.83 (2)	1.91 (2)	2.7216 (19)	166 (2)
O1W—H2W···S2^{iii}	0.83 (2)	2.45 (2)	3.2733 (15)	170 (2)
C7—H7···O1W^{iv}	0.95	2.58	3.517 (2)	171
C6—H6···S2^{v}	0.95	2.81	3.490 (2)	129
C9—H9···S1^{vi}	0.95	2.84	3.6857 (18)	149

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

(II) (2,2′-Bipyridyl-$\kappa^2 N,N'$)bis[N-(2-hydroxyethyl)-N-isopropyldithiocarbamato-$\kappa^2 S,S'$]zinc

Crystal data

[Zn(C$_6$H$_{12}$NOS$_2$)$_2$(C$_{10}$H$_8$N$_2$)]	$F(000) = 1208$
$M_r = 578.12$	$D_x = 1.422$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 19.4997$ (11) Å	Cell parameters from 3771 reflections
$b = 9.0027$ (5) Å	$\theta = 2.3$–27.5°
$c = 15.5352$ (8) Å	$\mu = 1.25$ mm^{-1}
$\beta = 98.031$ (5)°	$T = 100$ K
$V = 2700.5$ (3) Å^3	Prism, light-yellow
$Z = 4$	0.25 × 0.25 × 0.15 mm

Data collection

Agilent SuperNova Dual diffractometer with Atlas detector	$T_{min} = 0.737, T_{max} = 1.000$
	11190 measured reflections
Radiation source: SuperNova (Mo) X-ray Source	3095 independent reflections
	2657 reflections with $I > 2\sigma(I)$
Mirror monochromator	$R_{int} = 0.048$
Detector resolution: 10.4041 pixels mm^{-1}	$\theta_{max} = 27.5°, \theta_{min} = 2.5°$
ω scan	$h = -21 \rightarrow 25$
Absorption correction: multi-scan	$k = -11 \rightarrow 10$
(*CrysAlis PRO*; Agilent, 2012)	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	1 restraint
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.030$	$w = 1/[\sigma^2(F_o^2) + (0.0309P)^2 + 1.2812P]$
$wR(F^2) = 0.073$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
3095 reflections	$\Delta\rho_{max} = 0.38$ e Å^{-3}
155 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Zn	0.5000	0.74113 (3)	0.7500	0.01278 (9)
S1	0.58946 (2)	0.56650 (5)	0.82428 (3)	0.01649 (12)
S2	0.58906 (2)	0.69208 (5)	0.65006 (3)	0.01671 (12)
O1	0.81368 (8)	0.48579 (17)	0.82921 (10)	0.0311 (4)

H1O	0.8403 (11)	0.416 (2)	0.8210 (17)	0.047*
N1	0.67544 (8)	0.47424 (17)	0.71467 (10)	0.0146 (3)
N2	0.46566 (8)	0.93220 (16)	0.67036 (10)	0.0138 (3)
C1	0.62467 (10)	0.56746 (19)	0.72861 (12)	0.0141 (4)
C2	0.70163 (10)	0.3630 (2)	0.78132 (12)	0.0193 (4)
H2A	0.7249	0.2822	0.7533	0.023*
H2B	0.6619	0.3191	0.8056	0.023*
C3	0.75234 (11)	0.4277 (2)	0.85548 (13)	0.0270 (5)
H3A	0.7288	0.5078	0.8837	0.032*
H3B	0.7651	0.3491	0.8994	0.032*
C4	0.69560 (10)	0.4583 (2)	0.62598 (12)	0.0182 (4)
H4	0.6837	0.5539	0.5946	0.022*
C5	0.65197 (11)	0.3372 (2)	0.57632 (13)	0.0256 (5)
H5A	0.6028	0.3617	0.5737	0.038*
H5B	0.6613	0.2419	0.6061	0.038*
H5C	0.6638	0.3301	0.5172	0.038*
C6	0.77272 (11)	0.4326 (3)	0.62649 (14)	0.0273 (5)
H6A	0.7989	0.5095	0.6617	0.041*
H6B	0.7836	0.4371	0.5668	0.041*
H6C	0.7854	0.3347	0.6513	0.041*
C7	0.43644 (10)	0.9239 (2)	0.58712 (12)	0.0169 (4)
H7	0.4245	0.8288	0.5631	0.020*
C8	0.42296 (10)	1.0474 (2)	0.53475 (12)	0.0208 (4)
H8	0.4014	1.0375	0.4763	0.025*
C9	0.44151 (11)	1.1856 (2)	0.56917 (13)	0.0242 (5)
H9	0.4330	1.2725	0.5346	0.029*
C10	0.47270 (11)	1.1956 (2)	0.65477 (13)	0.0212 (4)
H10	0.4863	1.2894	0.6795	0.025*
C11	0.48384 (10)	1.0669 (2)	0.70400 (11)	0.0151 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn	0.01357 (17)	0.01108 (16)	0.01328 (16)	0.000	0.00045 (12)	0.000
S1	0.0208 (3)	0.0152 (2)	0.0139 (2)	0.00390 (18)	0.00368 (19)	0.00164 (17)
S2	0.0166 (3)	0.0176 (3)	0.0158 (2)	0.00287 (19)	0.00185 (18)	0.00486 (18)
O1	0.0267 (9)	0.0260 (9)	0.0369 (9)	0.0060 (7)	−0.0081 (7)	−0.0051 (7)
N1	0.0148 (8)	0.0147 (8)	0.0139 (8)	0.0021 (6)	0.0006 (6)	−0.0012 (6)
N2	0.0136 (8)	0.0141 (8)	0.0135 (8)	−0.0003 (6)	0.0015 (6)	−0.0003 (6)
C1	0.0145 (10)	0.0128 (9)	0.0142 (9)	−0.0027 (7)	−0.0008 (7)	−0.0016 (7)
C2	0.0231 (11)	0.0150 (10)	0.0191 (10)	0.0072 (8)	0.0004 (8)	0.0017 (8)
C3	0.0301 (13)	0.0275 (12)	0.0208 (11)	0.0131 (9)	−0.0054 (9)	−0.0023 (9)
C4	0.0202 (10)	0.0195 (10)	0.0157 (10)	0.0018 (8)	0.0053 (8)	−0.0018 (7)
C5	0.0280 (12)	0.0292 (12)	0.0191 (10)	−0.0040 (9)	0.0020 (9)	−0.0073 (9)
C6	0.0200 (11)	0.0360 (13)	0.0266 (12)	0.0052 (9)	0.0051 (9)	−0.0051 (9)
C7	0.0150 (10)	0.0201 (10)	0.0152 (9)	−0.0009 (7)	0.0006 (7)	−0.0020 (7)
C8	0.0199 (11)	0.0300 (12)	0.0119 (9)	0.0049 (8)	0.0002 (8)	0.0041 (8)
C9	0.0296 (12)	0.0224 (11)	0.0211 (11)	0.0079 (9)	0.0058 (9)	0.0099 (8)

C10	0.0304 (12)	0.0127 (10)	0.0205 (10)	0.0032 (8)	0.0042 (9)	0.0015 (8)
C11	0.0166 (10)	0.0144 (9)	0.0149 (10)	0.0022 (7)	0.0041 (8)	−0.0007 (7)

Geometric parameters (Å, °)

Zn—N2^i	2.1695 (15)	C3—H3B	0.9900
Zn—N2	2.1695 (15)	C4—C6	1.521 (3)
Zn—S1	2.5068 (5)	C4—C5	1.525 (3)
Zn—S1^i	2.5068 (5)	C4—H4	1.0000
Zn—S2^i	2.5247 (5)	C5—H5A	0.9800
Zn—S2	2.5247 (5)	C5—H5B	0.9800
S1—C1	1.7221 (19)	C5—H5C	0.9800
S2—C1	1.7301 (18)	C6—H6A	0.9800
O1—C3	1.417 (3)	C6—H6B	0.9800
O1—H1O	0.833 (10)	C6—H6C	0.9800
N1—C1	1.338 (2)	C7—C8	1.381 (3)
N1—C2	1.479 (2)	C7—H7	0.9500
N1—C4	1.492 (2)	C8—C9	1.382 (3)
N2—C7	1.340 (2)	C8—H8	0.9500
N2—C11	1.348 (2)	C9—C10	1.386 (3)
C2—C3	1.525 (3)	C9—H9	0.9500
C2—H2A	0.9900	C10—C11	1.388 (3)
C2—H2B	0.9900	C10—H10	0.9500
C3—H3A	0.9900	C11—C11^i	1.479 (4)
N2^i—Zn—N2	75.08 (8)	O1—C3—H3B	108.7
N2^i—Zn—S1	95.47 (4)	C2—C3—H3B	108.7
N2—Zn—S1	154.06 (4)	H3A—C3—H3B	107.6
N2^i—Zn—S1^i	154.07 (4)	N1—C4—C6	113.45 (16)
N2—Zn—S1^i	95.47 (4)	N1—C4—C5	109.62 (16)
S1—Zn—S1^i	102.32 (2)	C6—C4—C5	112.05 (17)
N2^i—Zn—S2^i	88.40 (4)	N1—C4—H4	107.1
N2—Zn—S2^i	107.78 (4)	C6—C4—H4	107.1
S1—Zn—S2^i	95.822 (17)	C5—C4—H4	107.1
S1^i—Zn—S2^i	71.289 (16)	C4—C5—H5A	109.5
N2^i—Zn—S2	107.78 (4)	C4—C5—H5B	109.5
N2—Zn—S2	88.39 (4)	H5A—C5—H5B	109.5
S1—Zn—S2	71.288 (16)	C4—C5—H5C	109.5
S1^i—Zn—S2	95.822 (17)	H5A—C5—H5C	109.5
S2^i—Zn—S2	159.86 (3)	H5B—C5—H5C	109.5
C1—S1—Zn	86.29 (6)	C4—C6—H6A	109.5
C1—S2—Zn	85.55 (6)	C4—C6—H6B	109.5
C3—O1—H1O	109.6 (19)	H6A—C6—H6B	109.5
C1—N1—C2	120.14 (15)	C4—C6—H6C	109.5
C1—N1—C4	120.40 (15)	H6A—C6—H6C	109.5
C2—N1—C4	118.15 (14)	H6B—C6—H6C	109.5
C7—N2—C11	118.51 (16)	N2—C7—C8	122.95 (17)
C7—N2—Zn	124.18 (12)	N2—C7—H7	118.5

C11—N2—Zn	116.66 (12)	C8—C7—H7	118.5
N1—C1—S1	121.98 (14)	C7—C8—C9	118.59 (18)
N1—C1—S2	121.71 (14)	C7—C8—H8	120.7
S1—C1—S2	116.28 (11)	C9—C8—H8	120.7
N1—C2—C3	113.23 (16)	C8—C9—C10	119.06 (18)
N1—C2—H2A	108.9	C8—C9—H9	120.5
C3—C2—H2A	108.9	C10—C9—H9	120.5
N1—C2—H2B	108.9	C9—C10—C11	119.24 (18)
C3—C2—H2B	108.9	C9—C10—H10	120.4
H2A—C2—H2B	107.7	C11—C10—H10	120.4
O1—C3—C2	114.06 (17)	N2—C11—C10	121.63 (17)
O1—C3—H3A	108.7	N2—C11—C11ⁱ	115.33 (10)
C2—C3—H3A	108.7	C10—C11—C11ⁱ	123.03 (11)
C2—N1—C1—S1	1.8 (2)	C1—N1—C4—C5	−89.1 (2)
C4—N1—C1—S1	168.55 (13)	C2—N1—C4—C5	77.9 (2)
C2—N1—C1—S2	−176.25 (13)	C11—N2—C7—C8	−1.2 (3)
C4—N1—C1—S2	−9.5 (2)	Zn—N2—C7—C8	−171.67 (14)
Zn—S1—C1—N1	−170.98 (15)	N2—C7—C8—C9	1.2 (3)
Zn—S1—C1—S2	7.21 (9)	C7—C8—C9—C10	−0.2 (3)
Zn—S2—C1—N1	171.03 (15)	C8—C9—C10—C11	−0.7 (3)
Zn—S2—C1—S1	−7.16 (9)	C7—N2—C11—C10	0.3 (3)
C1—N1—C2—C3	−79.6 (2)	Zn—N2—C11—C10	171.46 (14)
C4—N1—C2—C3	113.39 (18)	C7—N2—C11—C11ⁱ	−179.62 (19)
N1—C2—C3—O1	−62.3 (2)	Zn—N2—C11—C11ⁱ	−8.5 (3)
C1—N1—C4—C6	144.80 (18)	C9—C10—C11—N2	0.7 (3)
C2—N1—C4—C6	−48.2 (2)	C9—C10—C11—C11ⁱ	−179.4 (2)

Symmetry code: (i) −x+1, y, −z+3/2.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···S2ⁱⁱ	0.84 (2)	2.45 (2)	3.2437 (16)	160 (2)
C5—H5B···O1ⁱⁱ	0.98	2.54	3.512 (2)	175
C9—H9···S2ⁱⁱⁱ	0.95	2.86	3.550 (2)	130

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