Bis(N'-{(E)-[(2E)-1,3-diphenylprop-2-en-1-ylidene]amino}-N-ethylcarbamimidothioato-κ²N',S)zinc(II): crystal structure and Hirshfeld surface analysis

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The title Zn^{II} complex, $[Zn(C_{18}H_{18}N_3S)_2]$, (I), features two independent but chemically equivalent molecules in the asymmetric unit. In each, the thiosemicarbazonate monoanion coordinates the Zn^{II} atom *via* the thiolate-S and imine-N atoms, with the resulting N_2S_2 donor set defining a distorted tetrahedral geometry. The five-membered $ZnSCN_2$ chelate rings adopt distinct conformations in each independent molecule, *i.e.* one ring is almost planar while the other is twisted about the Zn—S bond. In the crystal, the two molecules comprising the asymmetric unit are linked by amine-N—H⋯N(imine) and amine-N—H⋯S(thiolate) hydrogen bonds *via* an eight-membered heterosynthon, {⋯HNCN⋯HNCS}. The dimeric aggregates are further consolidated by benzene-C—H⋯S(thiolate) interactions and are linked into a zigzag supramolecular chain along the *c* axis *via* amine-N—H⋯S(thiolate) hydrogen bonds. The chains are connected into a three-dimensional architecture *via* phenyl-C—H⋯π(phenyl) and π–π interactions, the latter occurring between chelate and phenyl rings [inter-centroid separation = 3.6873 (11) Å]. The analysis of the Hirshfeld surfaces calculated for (I) emphasizes the different interactions formed by the independent molecules in the crystal and the impact of the π–π interactions between chelate and phenyl rings.

1. Chemical context

Thiosemicarbazone molecules, derived from thiosemicarbazide, $H_2N—NH—C(=S)—NH_2$, constitute an important class of mixed hard–soft, nitrogen–sulfur donor ligands which have been extensively investigated in their coordination chemistry towards both transition metals (Lobana *et al.*, 2009) and main group elements (Casas *et al.*, 2000). Complexes of thiosemicarbazones, including Zn^{II} complexes (Da Silva *et al.*, 2013), have been evaluated variously as potential anti-cancer (Afrasiabi *et al.*, 2003), anti-viral (Garoufis *et al.*, 2009) and anti-bacterial (Quiroga & Ranninger, 2004) therapeutics for over 50 years (Dilworth & Hueting, 2012). The interesting properties of their metal complexes, such as structural diversity, accessible redox activities, the ability to fine-tune ligand substitution, access to radical species, catalytic properties, distinct spectroscopic properties, *etc.* afford them many potential advantages over organic-based drugs (van Rijt &
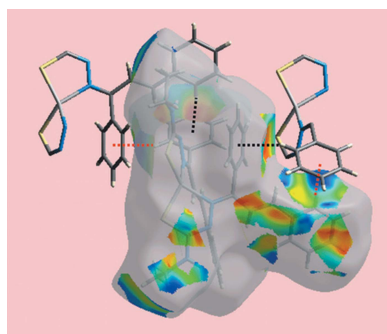
Sadler, 2009; Meggers, 2009). Recent studies have focused upon their suitability as single-source precursors for ZnS nanomaterials (Pawar *et al.*, 2017). Thiosemicarbazones can exist as thione–thiol tautomers and can bind to a metal centre in neutral or anionic forms as monodentate, bidentate or bridging ligands (Viñuelas-Zahínos *et al.*, 2011). The presence of additional, suitably positioned donor atoms can increase their coordination ability/denticity, giving rise to different coordination geometries, such as tetrahedral, octahedral and pentagonal-bipyramidal. (Umamatheswari *et al.*, 2011). As part of a programme investigating thiosemicarbazones and their metal complexes (Tan *et al.*, 2015), the crystal and molecular structures of the title compound (I) are described, complemented by an analysis of the Hirshfeld surface.
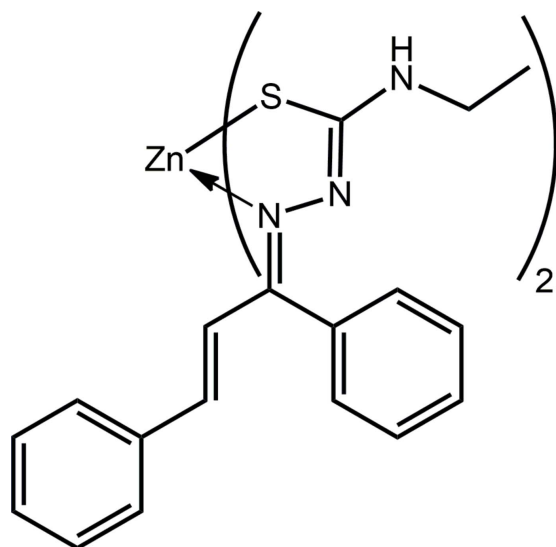

2. Structural commentary

Two independent molecules comprise the asymmetric unit of (I), and these are illustrated in Fig. 1. The mono-anion derived from the thiosemicarbazone ligand is chelating, coordinating the Zn^{II} atom *via* the thiolate-S and imine-N atoms. Referring to Table 1, the Zn—S bond lengths in the molecules span a narrow range of just over 0.01 Å, *i.e.* 2.2688 (5) Å for Zn1—S2, to 2.2827 (6) Å for Zn1—S1, whereas the Zn—N bonds show more variability, spanning a range of over 0.02 Å, *i.e.* 2.0496 (15) Å for Zn2—N12, to 2.0727 (16) Å for Zn2—N9. The similarity in bond lengths extends to the angles subtended at the Zn^{II} atoms which, for the Zn1-containing molecule range from 87.00 (5)° for S2—Zn1—N6, to 134.00 (5)° for S2—Zn1—N3, *i.e.* a range of 47°; the acute angle is associated with the chelate angle. A slightly narrower range is noted for the Zn2-containing molecule, *i.e.* 85.99 (5)° for S3—Zn2—N9, to 131.29 (5)° for S3—Zn2—N12, *i.e.* about 45°. The assignment of four-coordinate geometries can be quantified by the values of τ_4, which range from 1.00 for an ideal tetrahedron to 0.00 for perfect square-planar geometry (Yang *et al.*, 2007). The values of τ_4 in (I) compute to 0.70 and 0.74 for the Zn1- and Zn2-containing molecules, respectively, indicating significant distortions from the ideal tetrahedral angles. The

Table 1
Selected geometric parameters (Å, °).

Zn1—N6	2.0522 (16)	Zn2—N12	2.0496 (15)
Zn1—N3	2.0528 (16)	Zn2—N9	2.0727 (16)
Zn1—S2	2.2688 (5)	Zn2—S3	2.2707 (6)
Zn1—S1	2.2827 (6)	Zn2—S4	2.2823 (5)
N2—C1	1.323 (2)	N8—C37	1.311 (3)
N3—C4	1.315 (2)	N9—C40	1.307 (3)
N5—C19	1.321 (2)	N11—C55	1.309 (2)
N6—C22	1.311 (2)	N12—C58	1.308 (2)
C5—C6	1.342 (3)	C41—C42	1.339 (3)
C23—C24	1.336 (3)	C59—C60	1.344 (3)
S1—Zn1—S2	118.67 (2)	S3—Zn2—S4	124.97 (2)
S1—Zn1—N3	87.25 (5)	S3—Zn2—N9	85.99 (5)
S1—Zn1—N6	126.78 (5)	S3—Zn2—N12	131.29 (5)
S2—Zn1—N3	134.00 (5)	S4—Zn2—N9	124.42 (5)
S2—Zn1—N6	87.00 (5)	S4—Zn2—N12	87.23 (5)
N3—Zn1—N6	107.95 (6)	N9—Zn2—N12	105.85 (6)

conformation about each of the imine C=N bonds is *E*, as are the conformations about the ethylene bonds, Table 1.

The thiosemicarbazone ligands chelate the Zn^{II} atoms to form five-membered ZnSCN$_2$ rings. The chelate rings adopt different conformations in each independent molecule. For the Zn1-containing molecule, the Zn1/S1/C1/N2/N3 ring is almost planar (r.m.s. deviation = 0.005 Å) but the Zn1/S2/C19/
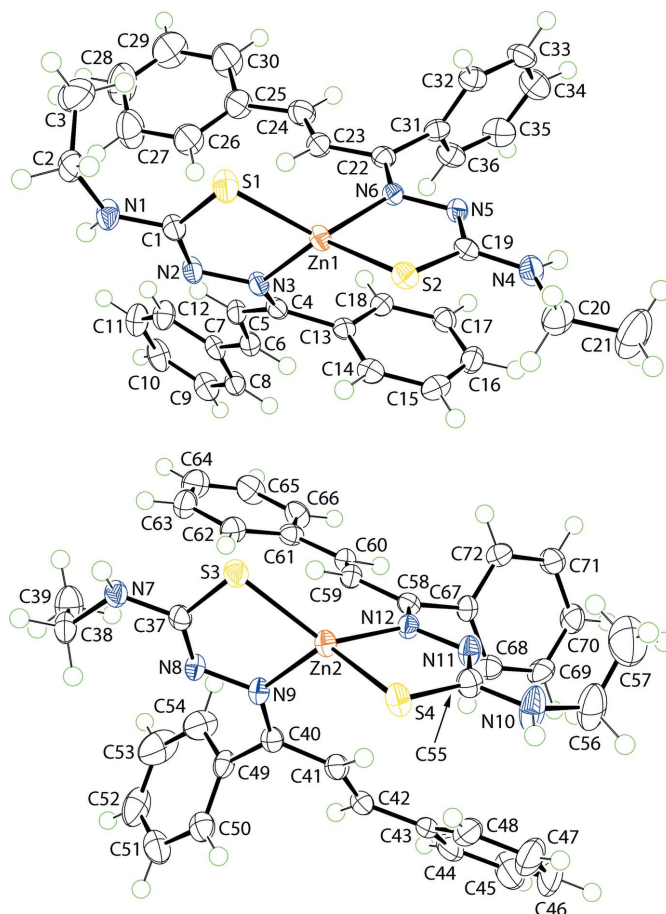
Figure 1
The molecular structures of the two molecules comprising the asymmetric unit of (I) showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.

Table 2
Selected dihedral angles (°) for (I).

Dihedral angle	Zn1,S1-ring	Zn1,S2-ring	Zn2,S3-ring	Zn2,S4-ring
Zn,S,C,N_2/central phenyl	74.54 (8)	71.88 (8)	64.79 (9)	64.53 (8)
Zn,S,C,N_2/terminal phenyl	28.13 (8)	20.17 (10)	33.66 (11)	7.89 (9)
Central phenyl/terminal phenyl	62.67 (10)	82.41 (11)	84.36 (13)	66.04 (10)

Table 3
A comparison of some physical properties of the independent molecules comprising the asymmetric unit of (I).

Molecule	volume, V (Å^3)	area, A (Å^2)	$A{:}V$	globularity, G	asphericity, Ω
Zn1-molecule	847.78	646.01	0.762	0.671	0.062
Zn2-molecule	853.45	615.74	0.722	0.707	0.065

N5/N6 ring is twisted about the Zn1—S2 bond. A similar situation pertains to the Zn2-containing molecule where there is a small twist about the Zn2—S3 bond in the Zn2/S3/C37/N8/N9 ring and the Zn2/S4/C55/N11/N12 ring is planar to within an r.m.s. deviation of 0.008 Å. To a first approximation, for each thiosemicarbazone ligand, all atoms but the terminal ethyl and central phenyl rings lie in a plane. This is quantified in the dihedral angle between each five-membered chelate ring and the central and terminal rings of the prop-2-en-1-ylidene substituent, as summarized in Table 2. The different conformations of the peripheral groups are highlighted in the overlay diagram, Fig. 2.

Some physical properties for the two independent molecules in (I), calculated in *Crystal Explorer* (Wolff *et al.*, 2012) and *PLATON* (Spek, 2009), are included in Table 3. These data indicate small but significant differences between the independent molecules, most notably, the Zn1-containing molecule is less spherical than the Zn2-containing molecule.
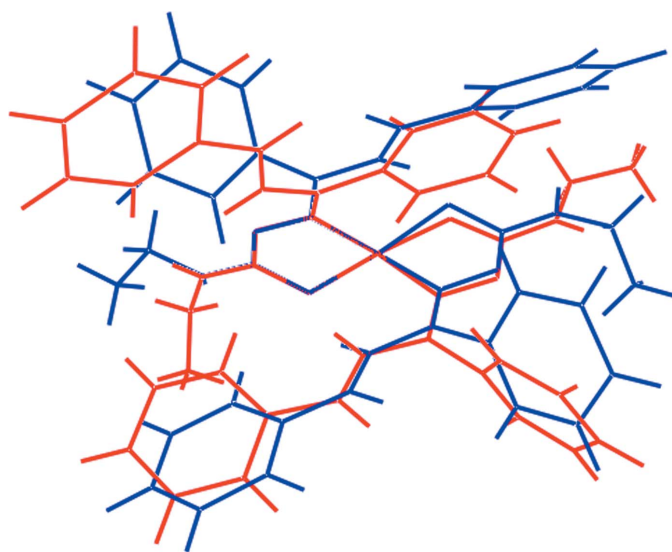
Figure 2
Structural overlay diagram of the two independent molecules of (I): Zn1-containing molecule (red image) and Zn2-containing molecule (blue). The molecules have been overlapped so that the two planar chelate rings are coincident.

3. Supramolecular features

The most prominent feature of the molecular packing is the formation of an eight-membered heterosynthon, {···HNCN···HNCS}, mediated by amine-N—H···N(imine)
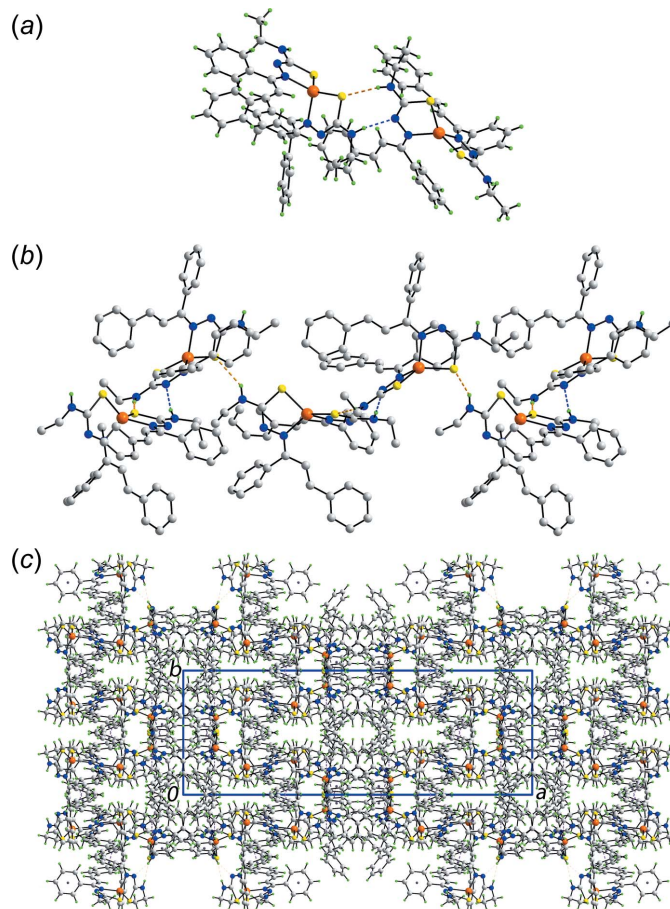
Figure 3
The molecular packing in (I): (*a*) a view of the supramolecular dimer sustained by amine-N—H···N(imine) and amine-N—H···S(thiolate) hydrogen bonds between the independent molecules, shown as blue and orange dashed lines, respectively, (*b*) a view of the supramolecular chain whereby the dimers in (*a*) are connected *via* amine-N—H···S(thiolate) hydrogen bonds and (*c*) a view of the unit-cell contents shown in projection down the *c* axis. The π–π and C—H···π interactions are shown as purple and pink dashed lines, respectively.
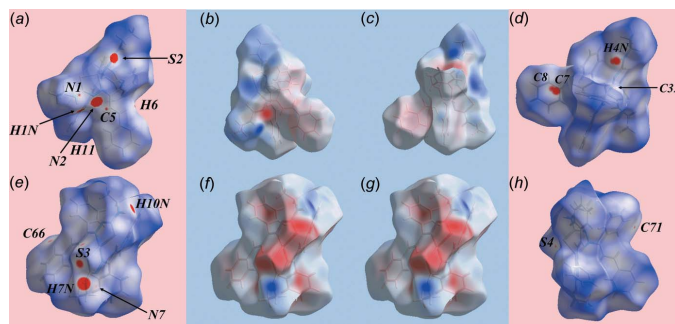
Figure 4
Hirshfeld surface plots for the (a)–(d) Zn1-containing molecule and (e)–(h) Zn2-containing molecule, plotted over d_{norm} in the ranges (a) −0.210 to +1.800 au, (d) −0.055 to +1.800 au, (e) −0.112 to +1.800 au and (h) −0.210 to +1.800 au and plotted over the electrostatic potential in the ranges (b) and (c) −0.118 to +0.058 au and (f) and (g) −0.046 to +0.088 au. In (b), (c), (f) and (g), the donors and acceptors are represented with blue and red regions, respectively.

Table 4
Hydrogen-bond geometry (Å, °).

$Cg1$ and $Cg2$ are the centroids of the C31–C36 and C13−C18 rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N···S3	0.87 (2)	2.65 (2)	3.5077 (19)	170 (2)
N7—H7N···N2	0.87 (2)	2.10 (2)	2.941 (2)	164 (2)
N10—H10N···S2^i	0.87 (1)	2.59 (2)	3.318 (2)	142 (2)
C11—H11···S4	0.95	2.86	3.715 (2)	151
C8—H8···$Cg1^{ii}$	0.95	2.73	3.608 (2)	154
C32—H32···$Cg2^{iii}$	0.95	2.64	3.532 (2)	157

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

and amine-N—H···S(thiolate) hydrogen-bonds which occur between the two molecules comprising the asymmetric unit, Fig. 3a and Table 4. Additional benzene-C—H···S(thiolate) interactions stabilize the dimeric aggregate, Table 4. The dimeric aggregates thus formed are connected into a zigzag supramolecular chain along the c axis via additional amine-N—H···S(thiolate) hydrogen-bonds, Fig. 3b. Chains are connected via π–π interactions occurring between Zn2-containing molecules, involving chelate rings, comprising the Zn2/S4/C55/N11/N12 atoms and phenyl (C61–C66) rings. Precedents for chelate/arene ring interactions have been established in the literature (Tomić et al., 2006; Tiekink, 2017). In the present case, the inter-centroid separation between rings is 3.6873 (11) Å and the angle between rings is 7.89 (9)°; symmetry operation: −x, 1 − y, 1 − z. Additional interactions between chains are of the type phenyl-C—H···π(phenyl) involving residues of the Zn1-containing molecule exclusively, Table 4. The result of the identified intermolecular interactions is the formation of a three-dimensional architecture, Fig. 3c.

4. Analysis of the Hirshfeld surfaces

The Hirshfeld surface calculations of (I), and for each of the Zn1- and Zn2-molecules, were performed according to a recent publication on related dithiocarbamate ligands (Jotani et al., 2016). From the views of the Hirshfeld surfaces mapped over d_{norm} in Fig. 4a and e, the bright-red spots near the amine-H1N, H7N, H10N, imime-N2 and thiolate-S2 and S3 atoms indicate their participation in N—H···N and N—H···S bonds between the two independent molecules. In the views of the Hirshfeld surfaces mapped over electrostatic potential for the Zn1-molecule in Fig. 4b and c, and for the Zn2-molecule in Fig. 4f and g, the hydrogen-bond donors and acceptors are represented by blue and red regions, respectively. Greater insight into intermolecular interactions in the crystal can be obtained by modifying the mapping range for d_{norm}, as shown in Fig. 4d and h, which reveals additional characteristic spots on the surface. A pair of red spots near amine-HN4 and near phenyl-C7 and C8 in Fig. 4d indicate the presence of short inter-atomic C···H/H···C contacts in the crystal, see Table 5 for data. The tiny, faint-red spots present near the amine-N1 and N7, phenyl-C32, C66 and C77, thiolate-S3, ethene-C5 and H6 atoms reflect the short inter-atomic C···N, C···S and C···H contacts, Table 5. The comparatively weak C—H···S interaction influential between the atoms of the independent molecules is represented by faint-red spots near atoms H11 and S3 in Fig. 4a and e, respectively. The immediate environments about the Zn1- and Zn2-molecules within shape-index-mapped Hirshfeld surfaces highlighting hydrogen-bonding and C—H···π interactions are illustrated in Fig. 5. The N—H···S and N—H···N hydrogen bonds linking the independent molecules are shown in Fig. 5a and 5b while the C—H···π and their reciprocal, i.e. π···H—C, contacts involving phenyl-C8 and C32 atoms as donors and phenyl (C31–C36 and C13–C18) rings as acceptors are shown in Fig. 5c.
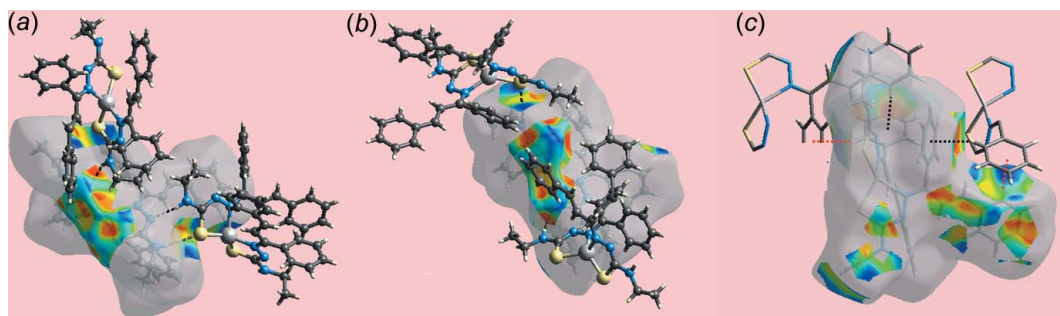
Figure 5
Views of Hirshfeld surface mapped over the shape-index property about a reference (a) Zn1-molecule and (b) Zn2-molecule, showing hydrogen bonds as black dashed lines and (c) Zn2-molecule showing C—H···π and its reciprocal π···H—C interactions as red and black dotted lines, respectively.
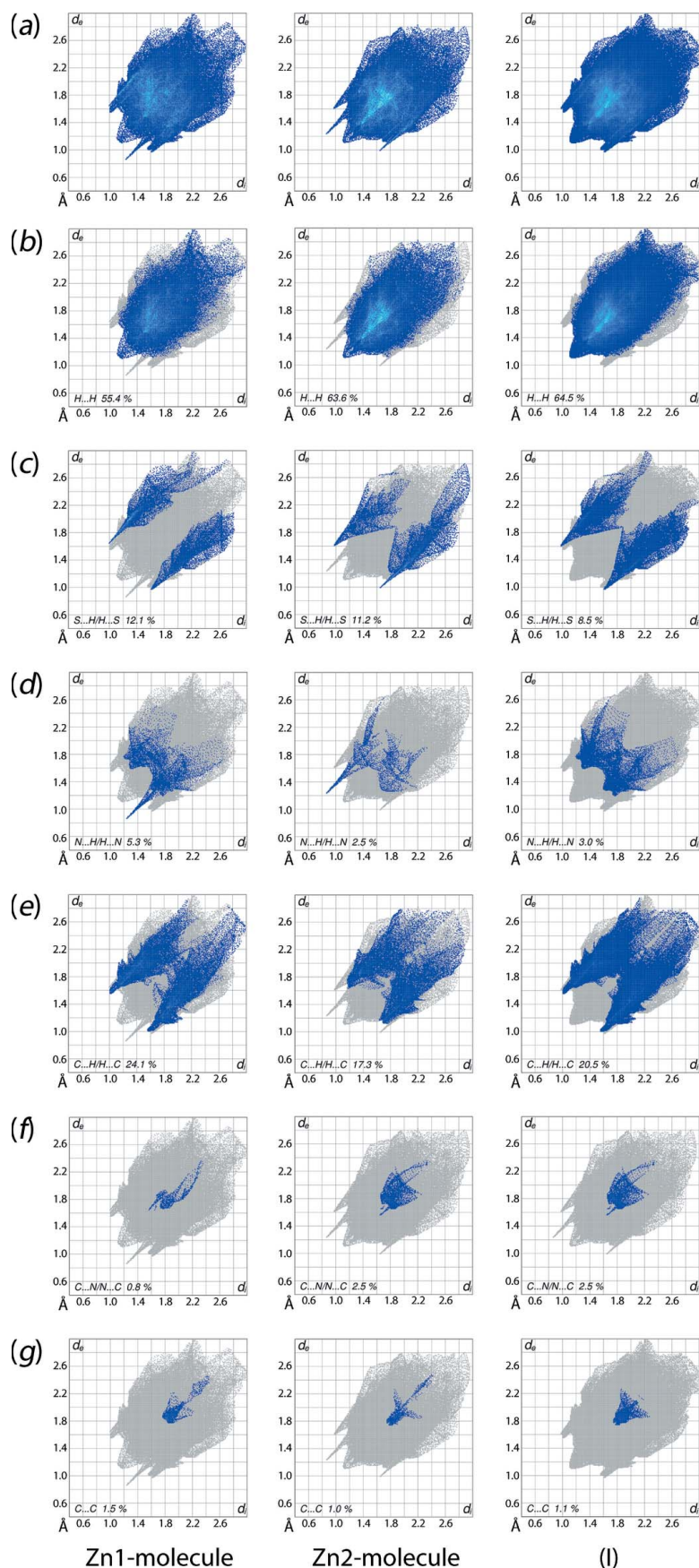
Figure 6
(*a*) The full two-dimensional fingerprint plots and fingerprint plots delineated into (*b*) H⋯H, (*c*) S⋯H/H⋯S, (*d*) N⋯H/H⋯H, (*e*) C⋯H/H⋯C, (*f*) C⋯N/N⋯C and (*g*) C⋯C contacts for the Zn1-and Zn2-molecules and for (I).

Table 5
Summary of short inter-atomic contacts (Å) in (I).

Contact	distance	symmetry operation
Zn1···H17	3.44	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
Zn2···H12	3.41	x, y, z
Zn2···C11	3.942 (2)	x, y, z
Zn2···C12	3.906 (2)	x, y, z
Zn2···C65	3.735 (2)	$-x, 1 - y, 1 - z$
Zn2···C66	3.938 (2)	$-x, 1 - y, 1 - z$
H3A···H30	2.27	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
H53···H53	2.23	$-x, y, \frac{1}{2} - z$
H45···H54	2.37	$-x, 2 - y, 1 - z$
C5···N7	3.214 (2)	x, y, z
C71···N1	3.223 (3)	$-x, 1 - y, 1 - z$
C66···S3	3.415 (2)	$x, 1 - y, 1 - z$
C3···H30	2.87	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
C6···H4N	2.816 (15)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
C7···H4N	2.570 (12)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
C8···H4N	2.652 (15)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
C19···H18	2.85	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
C32···H6	2.74	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
C33···H6	2.87	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
C43···H3B	2.85	$x, 1 + y, z$
C44···H2B	2.87	$x, 1 + y, z$
C48···H3B	2.82	$x, 1 + y, z$
C51···H70	2.80	$-x, 2 - y, 1 - z$
C60···H45	2.87	$-x, 2 - y, 1 - z$

Table 6
Percentage contributions of inter-atomic contacts to the Hirshfeld surfaces for the Zn1-molecule, Zn2-molecule and (I).

Contact	distance	symmetry operation	
	Zn1-molecule	Zn2-molecule	(I)
H···H	55.4	63.6	64.5
S···H/H···S	12.1	11.2	8.5
N···H/H···N	5.3	2.5	3.0
C···H/H···C	24.1	17.3	20.5
C···N/N···C	0.8	2.5	1.2
C···C	1.5	1.0	1.1
C···S/S···C	0.0	0.6	0.3
Zn···H/H···Zn	0.8	0.6	0.5
Zn···C/C···Zn	0.0	0.7	0.4

The overall two-dimensional fingerprint plots for each of the Zn1- and Zn2-molecules, and for the overall system, *i.e.* (I), are shown in Fig. 6a. In addition, the fingerprint plots delineated into H···H, S···H/H···S, N···H/H···N, C···H/H···C, C···N/N···C and C···C contacts (McKinnon *et al.*, 2007) are illustrated in Fig. 6b–g, respectively; their relative contributions are summarized quantitatively in Table 6. Owing
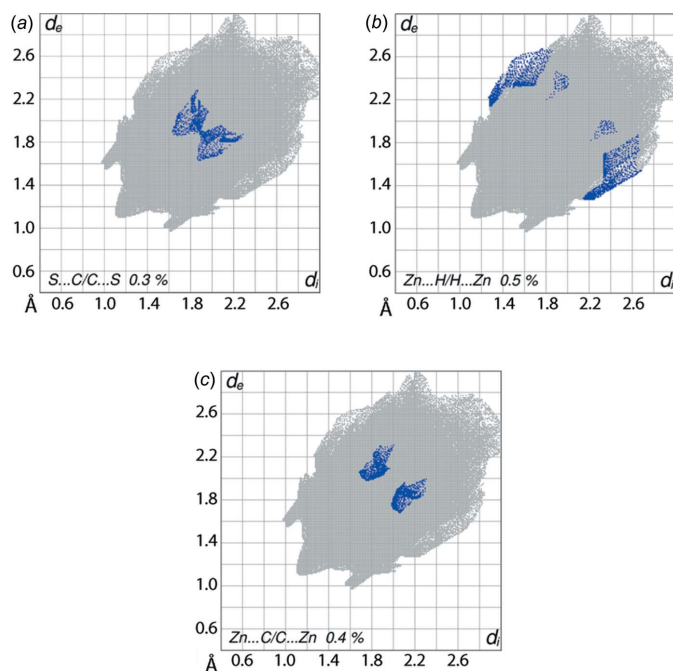

Figure 7
Fingerprint plots for (I) delineated into (a) S···C/C···2, (b) Zn···H/H···Zn and (c) Zn···C/C···Zn contacts.

to their significance upon the molecular packing, the fingerprint plots delineated into C···S/S···C, Zn···C/C···Zn and Zn···H/H···Zn contacts for (I) are also illustrated in Fig. 7.

The short inter-atomic H···H contacts for Zn1- and Zn2-molecules, Table 5, results in the peak at $d_e + d_i \sim 2.2$ Å, appearing broader for the former and narrower for the latter molecule in Fig. 6b. In the fingerprint plot delineated into S···H/H···S contacts, Fig. 6c, the distinct distribution of the points such as the well separated donor–acceptor regions for the Zn1-molecule and the adjoining regions for the Zn2-molecule are entirely consistent with the different patterns of contacts formed by these. A pair of thin spikes at $d_e + d_i \sim 2.7$ Å in the respective fingerprint plots in the donor and acceptor regions for the Zn1- and Zn2-molecules represents the N—H···S hydrogen bond linking the two independent molecules. This pair of spikes disappears in the plot for the overall system. Another N—H···S hydrogen bond is recognized in the plots as differently shaped donor–acceptor regions of the Zn1- and Zn2-molecules with their tips at $d_e + d_i \sim 2.6$ Å. As the contribution from S···H/H···S contacts to the Hirshfeld surfaces of the Zn1- and Zn2-molecules involves N—H···S hydrogen bonds and comparatively weak C—H···S interactions, the percentage contribution from these contacts to the Hirshfeld surface of the overall system is reduced to 8.5% due to disappearance of points corresponding to inter-linking N—H···S hydrogen bond. In Fig. 6d, a pair of spikes at $d_e + d_i \sim 2.1$ Å in the acceptor and donor regions of the Zn1- and Zn2-molecules, respectively, results from the linking N—H···N hydrogen bond between the independent molecules; the spikes disappear in the plot for the overall system.

The greater contribution, *i.e.* 24.1%, from C···H/H···C contacts to the Hirshfeld surface for the Zn1-molecule *cf.* 17.3% for the Zn2-molecule is due to the greater involvement of atoms of the Zn1-molecule in C—H···π interactions and short inter-atomic C···H/H···C contacts, Table 5. In the fingerprint plot delineated into C···H/H···C contacts for the Zn1 molecule, Fig. 6e, a pair of forceps-like tips at $d_e + d_i \sim 2.6$ Å represent a short inter-atomic C···H contact formed between the phenyl-C7 and amino-H7N atoms, Table 5. The other short inter-atomic C···H contacts involving the Zn1-molecule are merged within the plot. Similarly, a pair of forceps-like tips in the respective plot for Zn2-molecule at

$d_e + d_i \sim 2.8$ Å reflect the short inter-atomic C···H contact between the phenyl-C51 and -H70 atoms, with the other short contacts merged within the plot. In Fig. 6f, the short inter-atomic C···N contacts between atoms of the Zn1- and Zn2-molecules, Table 5, appear as a pair of short spikes with their tips at $d_e + d_i \sim 3.2$ Å. The small contributions from C···C contacts for the Zn1- and Zn2-molecules and for the overall system, Fig. 6g, suggests little impact on the molecular packing.

The presence of a short inter-atomic C···S contact between the thiolate-S3 and phenyl-C66 atoms is evident from the typical H-shaped plot in Fig. 7a and makes a contribution of 0.6% to the Hirshfeld surface of the Zn2-molecule. In the fingerprint plot delineated into Zn···H/H···Zn contacts, Fig. 7b, the tips at $d_e + d_i < 3.45$ Å with the shape of a folded sheet with a low density of points indicate the short contacts between these atoms. The presence of π–π stacking between chelate ring Zn2/S4/C55/N11/N12 and phenyl (C61–C66) rings of Zn2-molecules is evident from the presence of short inter-atomic Zn···C/C···Zn contacts, Table 5. In the fingerprint plot delineated into Zn···C/C···Zn contacts, Fig. 7c, these contacts are reflected by a pair of points with an S-shaped distribution at around $d_e + d_i \sim 1.9$ to 2.1 Å. This π–π stacking is also apparent from the small but effective contributions from Zn···C/C···Zn and C···N/N···C contacts to the Hirshfeld surface of the Zn2-molecule, Table 6.

5. Database survey

An analysis of the Cambridge Crystallographic Database (Groom et al., 2016) indicates there are nine literature precedents for the structure of (I), i.e. of general formula Zn[SC(NHR)=NN=CR'R'']₂ reflecting the interest in this class of compound. All of the structures resemble the molecular geometry described above for (I). The substituents at the hydrazone-C atom can be equivalent and alkyl, i.e. $R' = R'' = $ Me for the $R = $ Ph compound (Tan et al., 2009), or aryl, i.e. $R' = R'' = $ Ph for the $R = $ 3-FPh compound (Ferraz et al., 2012) or mixed alkyl/aryl, i.e. $R' = $ Me and $R'' = $ Ph for the $R = $ Ph compound (Wang et al., 2009); the latter structure has two molecules in the asymmetric unit. The R' and R'' groups can be part of a ring, e.g. cyclohexyl in the structure with $R = $ Me (Vikneswaran et al., 2016). In most examples, the N-bound group is aryl with the exceptions being the aforementioned structure and the cyclopentyl analogue (Vikneswaran et al., 2016). Clearly, there is immense scope for derivatization of these species which may assist in the optimization of their biological properties.

6. Synthesis and crystallization

Analytical grade reagents were used as procured without further purification. Equimolar quantities of 4-ethyl-3-thiosemicarbazide (1.1919 g, 0.01 mol) and 1,3-diphenylprop-2-en-1-one (2.0826 g, 0.01 mol) were dissolved in heated absolute ethanol (30 ml) separately and the mixtures were mixed with stirring. About five drops of concentrated hydrochloric acid

Table 7
Experimental details.

Crystal data	
Chemical formula	[Zn(C₃₆H₃₆N₆S₂)]
M_r	682.20
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	100
a, b, c (Å)	38.3604 (9), 13.6382 (3), 26.3548 (6)
β (°)	91.069 (2)
V (Å³)	13785.6 (5)
Z	16
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	0.87
Crystal size (mm)	0.30 × 0.30 × 0.30
Data collection	
Diffractometer	Agilent Technologies SuperNova Dual diffractometer with Atlas detector
Absorption correction	Gaussian (CrysAlis PRO; Agilent, 2012)
T_{min}, T_{max}	0.782, 0.830
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	37452, 15816, 12855
R_{int}	0.030
$(\sin \theta/\lambda)_{max}$ (Å⁻¹)	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.084, 1.04
No. of reflections	15816
No. of parameters	827
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³)	1.24, −0.48

Computer programs: CrysAlis PRO (Agilent, 2012), SHELXS97 (Sheldrick, 2008), SHELXL2014/7 (Sheldrick, 2015), ORTEP-3 for Windows (Farrugia, 2012), QMol (Gans & Shalloway, 2001) and DIAMOND (Brandenburg, 2006), publCIF (Westrip, 2010).

were added to the mixture to catalyse the reaction. The reaction mixture was kept under heating and stirring for about 10 mins, followed by stirring for 1 h at room temperature. The resulting yellow precipitate was filtered off, washed with chilled absolute ethanol and dried in vacuo. The resulting precipitate, N-ethyl-N-(1,3-diphenyl-2-propen-1-one)thiosemicarbazide (0.3090, 0.01 mol), was used without further purification and was dissolved in heated absolute ethanol (50 ml). Zn(CH₃COO)₂·2H₂O (0.1098 g, 0.50 mmol) was dissolved separately in heated absolute ethanol (30 ml) and then added into an ethanolic N-ethyl-N-(1,3-diphenyl-2-propen-1-one)thiosemicarbazide solution. The mixture was heated and stirred for about 10 mins, followed by stirring for 1 h at room temperature. The obtained yellow precipitate was filtered, washed with cold ethanol and dried in vacuo. Single crystals were grown at room temperature from the slow evaporation of a solution of dimethylformamide and acetonitrile (1:1 v/v 20 ml).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 7. The carbon-bound H atoms were placed in calculated positions (C—H = 0.95–0.99 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 nitrogen-bound H atoms were located in a difference-Fourier map but were refined with a distance restraint of N—H = 0.88±0.01 Å, and with U_{iso}(H) set to 1.2U_{eq}(N).

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supporting information

Bis(*N*′-{(*E*)-[(2*E*)-1,3-diphenylprop-2-en-1-ylidene]amino}-*N*-ethylcarbamimido-thioato-*κ*²*N*′,*S*)zinc(II): crystal structure and Hirshfeld surface analysis

Ming Yueh Tan, Karen A. Crouse, Thahira B. S. A. Ravoof, Mukesh M. Jotani and Edward R. T. Tiekink

Computing details

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: *SHELXL2014/7* (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*′-{(*E*)-[(2*E*)-1,3-diphenylprop-2-en-1-ylidene]amino}-*N*-ethylcarbamimidothioato-*κ*²*N*′,*S*)zinc(II)

Crystal data

[Zn(C$_{36}$H$_{36}$N$_6$S$_2$)]	$F(000) = 5696$
$M_r = 682.20$	$D_x = 1.315$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 38.3604\ (9)$ Å	Cell parameters from 15819 reflections
$b = 13.6382\ (3)$ Å	$\theta = 3.1–27.5°$
$c = 26.3548\ (6)$ Å	$\mu = 0.87$ mm^{-1}
$\beta = 91.069\ (2)°$	$T = 100$ K
$V = 13785.6\ (5)$ Å^3	Cube, yellow
$Z = 16$	$0.30 \times 0.30 \times 0.30$ mm

Data collection

Agilent Technologies SuperNova Dual diffractometer with Atlas detector	$T_{min} = 0.782$, $T_{max} = 0.830$
Radiation source: SuperNova (Mo) X-ray Source	37452 measured reflections
	15816 independent reflections
Mirror monochromator	12855 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4041 pixels mm^{-1}	$R_{int} = 0.030$
ω scan	$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
Absorption correction: gaussian (CrysAlis PRO; Agilent, 2012)	$h = -49\rightarrow48$
	$k = -17\rightarrow14$
	$l = -34\rightarrow22$

Refinement

Refinement on F^2	827 parameters
Least-squares matrix: full	4 restraints
$R[F^2 > 2\sigma(F^2)] = 0.037$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.084$	
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0268P)^2 + 19.4617P]$
15816 reflections	where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$　　　　　　　　　　　　　　　　$\Delta\rho_{min} = -0.48$ e Å^{-3}

$\Delta\rho_{max} = 1.24$ 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}
Zn1	0.18173 (2)	0.22341 (2)	0.28606 (2)	0.01520 (6)
S1	0.15381 (2)	0.14511 (4)	0.35017 (2)	0.02303 (12)
S2	0.18175 (2)	0.15280 (4)	0.20811 (2)	0.01718 (10)
N1	0.11691 (5)	0.24993 (13)	0.41537 (7)	0.0209 (4)
H1N	0.1105 (6)	0.3059 (10)	0.4281 (8)	0.025*
N2	0.14118 (4)	0.34387 (12)	0.35625 (6)	0.0167 (3)
N3	0.16200 (4)	0.35198 (12)	0.31407 (6)	0.0151 (3)
N4	0.23674 (4)	0.17761 (14)	0.15053 (6)	0.0215 (4)
H4N	0.2574 (3)	0.2004 (17)	0.1460 (9)	0.026*
N5	0.24781 (4)	0.22317 (12)	0.23164 (6)	0.0153 (3)
N6	0.23457 (4)	0.24038 (12)	0.27890 (6)	0.0138 (3)
C1	0.13684 (5)	0.25411 (15)	0.37405 (7)	0.0168 (4)
C2	0.10863 (6)	0.16246 (16)	0.44418 (8)	0.0240 (5)
H2A	0.1050	0.1069	0.4205	0.029*
H2B	0.0866	0.1732	0.4624	0.029*
C3	0.13712 (6)	0.1363 (2)	0.48203 (10)	0.0404 (6)
H3A	0.1590	0.1260	0.4642	0.061*
H3B	0.1308	0.0761	0.4999	0.061*
H3C	0.1401	0.1898	0.5065	0.061*
C4	0.17428 (5)	0.44016 (14)	0.30504 (7)	0.0151 (4)
C5	0.17094 (5)	0.52141 (15)	0.34000 (7)	0.0163 (4)
H5	0.1634	0.5076	0.3734	0.020*
C6	0.17784 (5)	0.61502 (15)	0.32811 (7)	0.0170 (4)
H6	0.1847	0.6271	0.2942	0.020*
C7	0.17592 (5)	0.70083 (15)	0.36164 (8)	0.0169 (4)
C8	0.18236 (5)	0.79338 (15)	0.34113 (8)	0.0194 (4)
H8	0.1871	0.7992	0.3060	0.023*
C9	0.18193 (5)	0.87665 (16)	0.37105 (9)	0.0239 (5)
H9	0.1861	0.9391	0.3564	0.029*
C10	0.17540 (6)	0.86904 (16)	0.42231 (9)	0.0263 (5)
H10	0.1753	0.9260	0.4430	0.032*
C11	0.16894 (6)	0.77787 (17)	0.44327 (8)	0.0274 (5)
H11	0.1644	0.7727	0.4785	0.033*
C12	0.16906 (5)	0.69427 (16)	0.41363 (8)	0.0221 (5)
H12	0.1645	0.6322	0.4285	0.026*
C13	0.19356 (5)	0.45041 (14)	0.25683 (7)	0.0141 (4)
C14	0.17819 (5)	0.41984 (15)	0.21118 (7)	0.0177 (4)

H14	0.1549	0.3964	0.2106	0.021*
C15	0.19675 (6)	0.42343 (15)	0.16651 (8)	0.0210 (4)
H15	0.1861	0.4036	0.1354	0.025*
C16	0.23107 (5)	0.45622 (15)	0.16752 (8)	0.0205 (4)
H16	0.2441	0.4569	0.1372	0.025*
C17	0.24639 (5)	0.48789 (15)	0.21253 (8)	0.0188 (4)
H17	0.2698	0.5109	0.2129	0.023*
C18	0.22768 (5)	0.48614 (14)	0.25713 (7)	0.0156 (4)
H18	0.2381	0.5092	0.2879	0.019*
C19	0.22494 (5)	0.18887 (14)	0.19800 (7)	0.0158 (4)
C20	0.21685 (6)	0.1434 (2)	0.10634 (8)	0.0307 (5)
H20A	0.1958	0.1847	0.1016	0.037*
H20B	0.2091	0.0751	0.1121	0.037*
C21	0.23816 (8)	0.1477 (3)	0.05985 (9)	0.0517 (8)
H21A	0.2450	0.2157	0.0534	0.078*
H21B	0.2245	0.1227	0.0309	0.078*
H21C	0.2591	0.1073	0.0647	0.078*
C22	0.25651 (5)	0.27184 (14)	0.31400 (7)	0.0159 (4)
C23	0.24220 (5)	0.29792 (15)	0.36244 (7)	0.0188 (4)
H23	0.2179	0.2878	0.3665	0.023*
C24	0.25988 (6)	0.33495 (17)	0.40216 (8)	0.0239 (5)
H24	0.2843	0.3432	0.3990	0.029*
C25	0.24426 (6)	0.36381 (17)	0.45037 (8)	0.0261 (5)
C26	0.20847 (6)	0.37796 (18)	0.45568 (8)	0.0300 (5)
H26	0.1933	0.3694	0.4271	0.036*
C27	0.19487 (7)	0.4042 (2)	0.50186 (9)	0.0386 (6)
H27	0.1705	0.4139	0.5048	0.046*
C28	0.21669 (7)	0.4165 (2)	0.54402 (9)	0.0422 (7)
H28	0.2073	0.4339	0.5759	0.051*
C29	0.25221 (7)	0.4033 (2)	0.53937 (9)	0.0420 (7)
H29	0.2672	0.4112	0.5681	0.050*
C30	0.26593 (7)	0.3784 (2)	0.49281 (9)	0.0354 (6)
H30	0.2904	0.3713	0.4897	0.043*
C31	0.29471 (5)	0.28225 (15)	0.30474 (7)	0.0174 (4)
C32	0.31570 (5)	0.19919 (16)	0.30292 (7)	0.0201 (4)
H32	0.3059	0.1363	0.3086	0.024*
C33	0.35100 (6)	0.20793 (17)	0.29278 (8)	0.0251 (5)
H33	0.3652	0.1510	0.2919	0.030*
C34	0.36554 (6)	0.29898 (18)	0.28396 (9)	0.0297 (5)
H34	0.3895	0.3045	0.2759	0.036*
C35	0.34490 (6)	0.38236 (18)	0.28701 (9)	0.0281 (5)
H35	0.3549	0.4452	0.2818	0.034*
C36	0.30974 (5)	0.37415 (16)	0.29771 (8)	0.0218 (4)
H36	0.2958	0.4315	0.3003	0.026*
Zn2	0.09256 (2)	0.62509 (2)	0.50259 (2)	0.01479 (6)
S3	0.09646 (2)	0.48949 (4)	0.45303 (2)	0.01870 (11)
S4	0.13339 (2)	0.67287 (4)	0.56165 (2)	0.01954 (11)
N7	0.08819 (4)	0.49976 (13)	0.35350 (6)	0.0174 (4)

H7N	0.1005 (5)	0.4464 (11)	0.3560 (8)	0.021*
N8	0.07995 (4)	0.64722 (12)	0.39142 (6)	0.0158 (3)
N9	0.08139 (4)	0.70030 (12)	0.43591 (6)	0.0154 (3)
N10	0.11345 (5)	0.74709 (17)	0.64894 (7)	0.0315 (5)
H10N	0.1359 (3)	0.7553 (19)	0.6528 (9)	0.038*
N11	0.06752 (4)	0.70684 (13)	0.59836 (6)	0.0185 (4)
N12	0.05551 (4)	0.66810 (12)	0.55301 (6)	0.0150 (3)
C37	0.08771 (5)	0.55407 (15)	0.39636 (7)	0.0151 (4)
C38	0.08438 (6)	0.54449 (17)	0.30322 (7)	0.0220 (5)
H38A	0.0963	0.5030	0.2781	0.026*
H38B	0.0959	0.6095	0.3035	0.026*
C39	0.04633 (6)	0.5567 (2)	0.28717 (8)	0.0317 (5)
H39A	0.0351	0.4922	0.2855	0.048*
H39B	0.0449	0.5878	0.2537	0.048*
H39C	0.0344	0.5978	0.3119	0.048*
C40	0.07469 (5)	0.79387 (15)	0.43138 (7)	0.0157 (4)
C41	0.07700 (5)	0.85264 (15)	0.47690 (7)	0.0181 (4)
H41	0.0890	0.8251	0.5053	0.022*
C42	0.06363 (5)	0.94259 (15)	0.48250 (7)	0.0191 (4)
H42	0.0524	0.9716	0.4538	0.023*
C43	0.06507 (6)	0.99939 (16)	0.52936 (8)	0.0234 (5)
C44	0.04271 (7)	1.07947 (17)	0.53472 (9)	0.0335 (6)
H44	0.0270	1.0961	0.5078	0.040*
C45	0.04319 (10)	1.1348 (2)	0.57862 (11)	0.0568 (9)
H45	0.0276	1.1884	0.5819	0.068*
C46	0.06614 (12)	1.1125 (2)	0.61746 (11)	0.0708 (12)
H46	0.0666	1.1511	0.6474	0.085*
C47	0.08860 (10)	1.0336 (2)	0.61298 (10)	0.0592 (10)
H47	0.1044	1.0182	0.6400	0.071*
C48	0.08810 (7)	0.97724 (18)	0.56942 (8)	0.0348 (6)
H48	0.1035	0.9231	0.5667	0.042*
C49	0.06507 (5)	0.83867 (15)	0.38153 (7)	0.0178 (4)
C50	0.08664 (6)	0.90851 (16)	0.36002 (8)	0.0221 (5)
H50	0.1071	0.9298	0.3777	0.027*
C51	0.07828 (7)	0.94734 (17)	0.31242 (8)	0.0307 (5)
H51	0.0934	0.9938	0.2973	0.037*
C52	0.04817 (8)	0.91847 (19)	0.28721 (9)	0.0383 (6)
H52	0.0423	0.9456	0.2550	0.046*
C53	0.02658 (8)	0.8502 (2)	0.30887 (10)	0.0424 (7)
H53	0.0057	0.8311	0.2917	0.051*
C54	0.03516 (6)	0.80927 (18)	0.35533 (9)	0.0299 (5)
H54	0.0205	0.7607	0.3695	0.036*
C55	0.10145 (5)	0.70964 (16)	0.60429 (7)	0.0189 (4)
C56	0.09005 (6)	0.7936 (2)	0.68573 (9)	0.0394 (7)
H56A	0.1035	0.8408	0.7069	0.047*
H56B	0.0716	0.8304	0.6672	0.047*
C57	0.07404 (9)	0.7204 (2)	0.71847 (11)	0.0536 (8)
H57A	0.0610	0.6731	0.6975	0.080*

H57B	0.0581	0.7530	0.7418	0.080*
H57C	0.0923	0.6861	0.7380	0.080*
C58	0.02184 (5)	0.67592 (15)	0.54521 (7)	0.0150 (4)
C59	0.00695 (5)	0.63366 (15)	0.49947 (7)	0.0163 (4)
H59	0.0216	0.5953	0.4787	0.020*
C60	−0.02650 (5)	0.64535 (15)	0.48458 (7)	0.0163 (4)
H60	−0.0408	0.6829	0.5063	0.020*
C61	−0.04328 (5)	0.60656 (15)	0.43862 (7)	0.0173 (4)
C62	−0.02457 (5)	0.56030 (15)	0.40025 (7)	0.0202 (4)
H62	0.0001	0.5554	0.4031	0.024*
C63	−0.04178 (6)	0.52170 (17)	0.35816 (8)	0.0253 (5)
H63	−0.0289	0.4901	0.3324	0.030*
C64	−0.07776 (6)	0.52884 (18)	0.35333 (8)	0.0283 (5)
H64	−0.0895	0.5013	0.3246	0.034*
C65	−0.09651 (6)	0.57606 (18)	0.39027 (8)	0.0266 (5)
H65	−0.1211	0.5818	0.3868	0.032*
C66	−0.07939 (5)	0.61493 (16)	0.43230 (8)	0.0221 (5)
H66	−0.0924	0.6480	0.4574	0.027*
C67	−0.00047 (5)	0.72828 (15)	0.58235 (7)	0.0152 (4)
C68	0.00366 (5)	0.82902 (16)	0.58950 (8)	0.0201 (4)
H68	0.0202	0.8639	0.5701	0.024*
C69	−0.01618 (6)	0.87864 (16)	0.62458 (8)	0.0227 (5)
H69	−0.0136	0.9475	0.6288	0.027*
C70	−0.03976 (6)	0.82737 (16)	0.65346 (8)	0.0236 (5)
H70	−0.0530	0.8609	0.6781	0.028*
C71	−0.04412 (5)	0.72761 (16)	0.64660 (8)	0.0222 (5)
H71	−0.0604	0.6928	0.6665	0.027*
C72	−0.02476 (5)	0.67807 (15)	0.61072 (8)	0.0192 (4)
H72	−0.0281	0.6098	0.6056	0.023*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01408 (11)	0.01313 (12)	0.01848 (11)	0.00079 (9)	0.00292 (9)	−0.00149 (9)
S1	0.0274 (3)	0.0121 (2)	0.0300 (3)	0.0016 (2)	0.0121 (2)	0.0022 (2)
S2	0.0148 (2)	0.0176 (2)	0.0192 (2)	−0.00086 (19)	−0.00143 (19)	−0.0026 (2)
N1	0.0240 (9)	0.0138 (9)	0.0253 (9)	0.0008 (7)	0.0110 (7)	0.0027 (8)
N2	0.0158 (8)	0.0139 (8)	0.0206 (8)	0.0012 (7)	0.0073 (7)	0.0008 (7)
N3	0.0136 (8)	0.0138 (8)	0.0179 (8)	0.0017 (6)	0.0039 (6)	0.0006 (7)
N4	0.0153 (9)	0.0314 (11)	0.0178 (8)	0.0006 (8)	0.0004 (7)	−0.0059 (8)
N5	0.0161 (8)	0.0167 (9)	0.0130 (8)	0.0024 (7)	0.0014 (6)	−0.0020 (7)
N6	0.0145 (8)	0.0132 (8)	0.0137 (8)	0.0014 (6)	0.0011 (6)	−0.0005 (7)
C1	0.0154 (9)	0.0146 (10)	0.0204 (10)	0.0002 (8)	0.0034 (8)	0.0002 (8)
C2	0.0221 (11)	0.0212 (11)	0.0289 (11)	−0.0018 (9)	0.0092 (9)	0.0069 (10)
C3	0.0305 (13)	0.0499 (17)	0.0407 (14)	−0.0037 (12)	0.0011 (11)	0.0204 (13)
C4	0.0116 (9)	0.0147 (10)	0.0189 (10)	0.0018 (7)	0.0014 (7)	0.0015 (8)
C5	0.0145 (9)	0.0181 (10)	0.0165 (9)	−0.0001 (8)	0.0040 (7)	−0.0001 (8)
C6	0.0153 (9)	0.0190 (10)	0.0166 (9)	0.0001 (8)	0.0021 (8)	−0.0019 (8)

C7	0.0126 (9)	0.0155 (10)	0.0228 (10)	0.0000 (8)	0.0040 (8)	−0.0014 (8)
C8	0.0184 (10)	0.0184 (11)	0.0214 (10)	0.0020 (8)	0.0042 (8)	−0.0001 (9)
C9	0.0225 (11)	0.0145 (10)	0.0350 (12)	−0.0024 (9)	0.0058 (9)	0.0005 (10)
C10	0.0243 (11)	0.0201 (11)	0.0347 (12)	−0.0018 (9)	0.0078 (9)	−0.0123 (10)
C11	0.0276 (12)	0.0312 (13)	0.0236 (11)	−0.0059 (10)	0.0070 (9)	−0.0064 (10)
C12	0.0239 (11)	0.0191 (11)	0.0235 (11)	−0.0058 (9)	0.0065 (9)	−0.0008 (9)
C13	0.0163 (9)	0.0087 (9)	0.0174 (9)	0.0012 (7)	0.0014 (7)	0.0013 (8)
C14	0.0169 (10)	0.0138 (10)	0.0225 (10)	−0.0016 (8)	−0.0004 (8)	0.0017 (8)
C15	0.0273 (11)	0.0178 (11)	0.0177 (10)	−0.0005 (9)	−0.0030 (8)	0.0011 (9)
C16	0.0254 (11)	0.0192 (11)	0.0170 (10)	0.0019 (9)	0.0055 (8)	0.0014 (9)
C17	0.0165 (10)	0.0176 (10)	0.0222 (10)	0.0002 (8)	0.0033 (8)	0.0023 (9)
C18	0.0187 (10)	0.0130 (10)	0.0150 (9)	−0.0005 (8)	0.0004 (8)	−0.0004 (8)
C19	0.0152 (9)	0.0133 (10)	0.0188 (10)	0.0034 (8)	−0.0001 (8)	−0.0003 (8)
C20	0.0284 (12)	0.0446 (15)	0.0190 (10)	−0.0011 (11)	−0.0034 (9)	−0.0063 (11)
C21	0.0464 (17)	0.088 (2)	0.0214 (12)	−0.0107 (16)	0.0011 (11)	−0.0106 (14)
C22	0.0181 (10)	0.0125 (10)	0.0171 (9)	0.0022 (8)	−0.0001 (8)	0.0006 (8)
C23	0.0185 (10)	0.0207 (11)	0.0173 (10)	0.0017 (8)	−0.0004 (8)	−0.0010 (9)
C24	0.0213 (11)	0.0280 (12)	0.0224 (11)	0.0044 (9)	−0.0029 (9)	−0.0020 (9)
C25	0.0291 (12)	0.0303 (13)	0.0188 (10)	0.0037 (10)	−0.0021 (9)	−0.0071 (10)
C26	0.0293 (12)	0.0386 (14)	0.0219 (11)	0.0030 (11)	−0.0036 (9)	−0.0076 (10)
C27	0.0323 (14)	0.0544 (18)	0.0293 (13)	0.0014 (12)	0.0050 (10)	−0.0133 (13)
C28	0.0453 (16)	0.0587 (19)	0.0228 (12)	−0.0010 (14)	0.0055 (11)	−0.0167 (13)
C29	0.0453 (16)	0.0574 (18)	0.0230 (12)	0.0018 (14)	−0.0090 (11)	−0.0131 (12)
C30	0.0309 (13)	0.0492 (16)	0.0259 (12)	0.0036 (12)	−0.0050 (10)	−0.0121 (12)
C31	0.0177 (10)	0.0199 (11)	0.0144 (9)	−0.0007 (8)	−0.0047 (8)	−0.0005 (8)
C32	0.0204 (10)	0.0201 (11)	0.0198 (10)	0.0004 (8)	−0.0037 (8)	−0.0011 (9)
C33	0.0200 (11)	0.0282 (12)	0.0269 (11)	0.0085 (9)	−0.0038 (9)	−0.0002 (10)
C34	0.0148 (10)	0.0368 (14)	0.0376 (13)	−0.0014 (10)	−0.0021 (9)	−0.0004 (11)
C35	0.0229 (11)	0.0263 (12)	0.0351 (13)	−0.0058 (10)	−0.0039 (10)	0.0023 (10)
C36	0.0184 (10)	0.0210 (11)	0.0257 (11)	0.0011 (9)	−0.0051 (8)	−0.0027 (9)
Zn2	0.01392 (11)	0.01808 (12)	0.01235 (11)	0.00177 (9)	0.00010 (8)	0.00002 (9)
S3	0.0247 (3)	0.0162 (2)	0.0153 (2)	0.0031 (2)	0.00224 (19)	0.0012 (2)
S4	0.0124 (2)	0.0311 (3)	0.0151 (2)	0.0007 (2)	−0.00026 (18)	0.0001 (2)
N7	0.0209 (9)	0.0161 (9)	0.0155 (8)	0.0032 (7)	0.0034 (7)	−0.0007 (7)
N8	0.0176 (8)	0.0169 (9)	0.0130 (8)	0.0020 (7)	0.0015 (6)	−0.0028 (7)
N9	0.0147 (8)	0.0189 (9)	0.0125 (7)	0.0019 (7)	−0.0004 (6)	−0.0019 (7)
N10	0.0151 (9)	0.0583 (14)	0.0210 (9)	0.0013 (9)	−0.0034 (8)	−0.0149 (10)
N11	0.0154 (8)	0.0270 (10)	0.0132 (8)	0.0012 (7)	−0.0013 (6)	−0.0030 (7)
N12	0.0161 (8)	0.0166 (9)	0.0122 (7)	−0.0002 (7)	−0.0004 (6)	−0.0010 (7)
C37	0.0115 (9)	0.0182 (10)	0.0158 (9)	0.0005 (8)	0.0028 (7)	−0.0009 (8)
C38	0.0265 (11)	0.0252 (12)	0.0144 (9)	0.0023 (9)	0.0029 (8)	−0.0030 (9)
C39	0.0297 (13)	0.0444 (15)	0.0208 (11)	0.0048 (11)	−0.0039 (9)	−0.0037 (11)
C40	0.0132 (9)	0.0185 (10)	0.0156 (9)	0.0018 (8)	0.0010 (7)	−0.0006 (8)
C41	0.0201 (10)	0.0197 (11)	0.0145 (9)	−0.0012 (8)	−0.0022 (8)	0.0020 (8)
C42	0.0213 (10)	0.0203 (11)	0.0155 (9)	−0.0034 (8)	0.0015 (8)	0.0018 (9)
C43	0.0378 (13)	0.0163 (11)	0.0166 (10)	−0.0101 (9)	0.0087 (9)	−0.0013 (9)
C44	0.0567 (16)	0.0177 (11)	0.0269 (12)	−0.0043 (11)	0.0189 (11)	0.0011 (10)
C45	0.116 (3)	0.0187 (13)	0.0368 (16)	−0.0011 (16)	0.0347 (17)	−0.0045 (12)

C46	0.158 (4)	0.0300 (16)	0.0247 (14)	−0.023 (2)	0.0151 (19)	−0.0127 (13)
C47	0.116 (3)	0.0389 (18)	0.0225 (13)	−0.0262 (19)	−0.0109 (15)	−0.0036 (13)
C48	0.0559 (17)	0.0258 (13)	0.0224 (11)	−0.0146 (12)	−0.0042 (11)	−0.0001 (10)
C49	0.0235 (10)	0.0158 (10)	0.0140 (9)	0.0056 (8)	−0.0017 (8)	−0.0019 (8)
C50	0.0258 (11)	0.0193 (11)	0.0213 (10)	0.0063 (9)	0.0030 (9)	−0.0003 (9)
C51	0.0472 (15)	0.0202 (12)	0.0250 (11)	0.0106 (11)	0.0119 (11)	0.0057 (10)
C52	0.0688 (19)	0.0274 (13)	0.0181 (11)	0.0112 (13)	−0.0101 (12)	0.0009 (10)
C53	0.0571 (18)	0.0342 (15)	0.0349 (14)	−0.0029 (13)	−0.0286 (13)	0.0050 (12)
C54	0.0344 (13)	0.0257 (12)	0.0292 (12)	−0.0015 (10)	−0.0114 (10)	0.0051 (10)
C55	0.0170 (10)	0.0225 (11)	0.0171 (9)	0.0009 (8)	−0.0008 (8)	0.0000 (9)
C56	0.0274 (13)	0.0653 (19)	0.0252 (12)	−0.0023 (13)	−0.0055 (10)	−0.0137 (13)
C57	0.066 (2)	0.055 (2)	0.0391 (16)	0.0093 (16)	0.0059 (14)	−0.0032 (15)
C58	0.0140 (9)	0.0160 (10)	0.0151 (9)	−0.0012 (8)	0.0009 (7)	0.0016 (8)
C59	0.0173 (10)	0.0168 (10)	0.0149 (9)	−0.0005 (8)	0.0013 (8)	−0.0017 (8)
C60	0.0181 (10)	0.0160 (10)	0.0148 (9)	−0.0003 (8)	0.0017 (8)	−0.0010 (8)
C61	0.0178 (10)	0.0163 (10)	0.0177 (10)	−0.0015 (8)	−0.0020 (8)	0.0032 (8)
C62	0.0195 (10)	0.0215 (11)	0.0194 (10)	−0.0002 (9)	−0.0029 (8)	0.0003 (9)
C63	0.0326 (12)	0.0253 (12)	0.0179 (10)	−0.0010 (10)	−0.0009 (9)	−0.0035 (9)
C64	0.0332 (13)	0.0322 (13)	0.0193 (10)	−0.0073 (10)	−0.0105 (9)	0.0005 (10)
C65	0.0205 (11)	0.0367 (14)	0.0223 (11)	−0.0051 (10)	−0.0070 (9)	0.0061 (10)
C66	0.0202 (10)	0.0274 (12)	0.0187 (10)	0.0000 (9)	0.0001 (8)	0.0038 (9)
C67	0.0127 (9)	0.0197 (10)	0.0131 (9)	0.0017 (8)	−0.0026 (7)	−0.0006 (8)
C68	0.0177 (10)	0.0203 (11)	0.0222 (10)	−0.0014 (8)	0.0012 (8)	0.0005 (9)
C69	0.0278 (11)	0.0148 (10)	0.0254 (11)	0.0024 (9)	−0.0008 (9)	−0.0028 (9)
C70	0.0255 (11)	0.0242 (12)	0.0214 (10)	0.0047 (9)	0.0060 (9)	−0.0045 (9)
C71	0.0212 (11)	0.0227 (11)	0.0228 (10)	−0.0010 (9)	0.0070 (8)	−0.0017 (9)
C72	0.0195 (10)	0.0159 (10)	0.0222 (10)	−0.0004 (8)	0.0004 (8)	−0.0018 (9)

Geometric parameters (Å, º)

Zn1—N6	2.0522 (16)	Zn2—N12	2.0496 (15)
Zn1—N3	2.0528 (16)	Zn2—N9	2.0727 (16)
Zn1—S2	2.2688 (5)	Zn2—S3	2.2707 (6)
Zn1—S1	2.2827 (6)	Zn2—S4	2.2823 (5)
S1—C1	1.745 (2)	S3—C37	1.761 (2)
S2—C19	1.753 (2)	S4—C55	1.751 (2)
N1—C1	1.344 (2)	N7—C37	1.351 (3)
N1—C2	1.453 (3)	N7—C38	1.464 (3)
N1—H1N	0.871 (10)	N7—H7N	0.870 (9)
N2—C1	1.323 (2)	N8—C37	1.311 (3)
N2—N3	1.385 (2)	N8—N9	1.378 (2)
N3—C4	1.315 (2)	N9—C40	1.307 (3)
N4—C19	1.347 (2)	N10—C55	1.356 (3)
N4—C20	1.457 (3)	N10—C56	1.477 (3)
N4—H4N	0.863 (9)	N10—H10N	0.874 (10)
N5—C19	1.321 (2)	N11—C55	1.309 (2)
N5—N6	1.374 (2)	N11—N12	1.378 (2)
N6—C22	1.311 (2)	N12—C58	1.308 (2)

C2—C3	1.508 (3)	C38—C39	1.521 (3)
C2—H2A	0.9900	C38—H38A	0.9900
C2—H2B	0.9900	C38—H38B	0.9900
C3—H3A	0.9800	C39—H39A	0.9800
C3—H3B	0.9800	C39—H39B	0.9800
C3—H3C	0.9800	C39—H39C	0.9800
C4—C5	1.448 (3)	C40—C41	1.444 (3)
C4—C13	1.489 (3)	C40—C49	1.489 (3)
C5—C6	1.342 (3)	C41—C42	1.339 (3)
C5—H5	0.9500	C41—H41	0.9500
C6—C7	1.469 (3)	C42—C43	1.458 (3)
C6—H6	0.9500	C42—H42	0.9500
C7—C8	1.397 (3)	C43—C48	1.397 (3)
C7—C12	1.403 (3)	C43—C44	1.398 (3)
C8—C9	1.383 (3)	C44—C45	1.381 (4)
C8—H8	0.9500	C44—H44	0.9500
C9—C10	1.383 (3)	C45—C46	1.372 (5)
C9—H9	0.9500	C45—H45	0.9500
C10—C11	1.385 (3)	C46—C47	1.385 (5)
C10—H10	0.9500	C46—H46	0.9500
C11—C12	1.382 (3)	C47—C48	1.382 (4)
C11—H11	0.9500	C47—H47	0.9500
C12—H12	0.9500	C48—H48	0.9500
C13—C14	1.394 (3)	C49—C54	1.387 (3)
C13—C18	1.397 (3)	C49—C50	1.389 (3)
C14—C15	1.388 (3)	C50—C51	1.394 (3)
C14—H14	0.9500	C50—H50	0.9500
C15—C16	1.390 (3)	C51—C52	1.379 (4)
C15—H15	0.9500	C51—H51	0.9500
C16—C17	1.383 (3)	C52—C53	1.377 (4)
C16—H16	0.9500	C52—H52	0.9500
C17—C18	1.389 (3)	C53—C54	1.380 (3)
C17—H17	0.9500	C53—H53	0.9500
C18—H18	0.9500	C54—H54	0.9500
C20—C21	1.487 (3)	C56—C57	1.462 (4)
C20—H20A	0.9900	C56—H56A	0.9900
C20—H20B	0.9900	C56—H56B	0.9900
C21—H21A	0.9800	C57—H57A	0.9800
C21—H21B	0.9800	C57—H57B	0.9800
C21—H21C	0.9800	C57—H57C	0.9800
C22—C23	1.443 (3)	C58—C59	1.444 (3)
C22—C31	1.497 (3)	C58—C67	1.494 (3)
C23—C24	1.336 (3)	C59—C60	1.344 (3)
C23—H23	0.9500	C59—H59	0.9500
C24—C25	1.469 (3)	C60—C61	1.460 (3)
C24—H24	0.9500	C60—H60	0.9500
C25—C26	1.396 (3)	C61—C66	1.397 (3)
C25—C30	1.395 (3)	C61—C62	1.401 (3)

C26—C27	1.380 (3)	C62—C63	1.384 (3)
C26—H26	0.9500	C62—H62	0.9500
C27—C28	1.389 (3)	C63—C64	1.387 (3)
C27—H27	0.9500	C63—H63	0.9500
C28—C29	1.382 (4)	C64—C65	1.380 (3)
C28—H28	0.9500	C64—H64	0.9500
C29—C30	1.386 (3)	C65—C66	1.383 (3)
C29—H29	0.9500	C65—H65	0.9500
C30—H30	0.9500	C66—H66	0.9500
C31—C32	1.391 (3)	C67—C72	1.386 (3)
C31—C36	1.393 (3)	C67—C68	1.395 (3)
C32—C33	1.391 (3)	C68—C69	1.385 (3)
C32—H32	0.9500	C68—H68	0.9500
C33—C34	1.383 (3)	C69—C70	1.383 (3)
C33—H33	0.9500	C69—H69	0.9500
C34—C35	1.389 (3)	C70—C71	1.382 (3)
C34—H34	0.9500	C70—H70	0.9500
C35—C36	1.388 (3)	C71—C72	1.389 (3)
C35—H35	0.9500	C71—H71	0.9500
C36—H36	0.9500	C72—H72	0.9500
S1—Zn1—S2	118.67 (2)	S3—Zn2—S4	124.97 (2)
S1—Zn1—N3	87.25 (5)	S3—Zn2—N9	85.99 (5)
S1—Zn1—N6	126.78 (5)	S3—Zn2—N12	131.29 (5)
S2—Zn1—N3	134.00 (5)	S4—Zn2—N9	124.42 (5)
S2—Zn1—N6	87.00 (5)	S4—Zn2—N12	87.23 (5)
N3—Zn1—N6	107.95 (6)	N9—Zn2—N12	105.85 (6)
C1—S1—Zn1	92.96 (7)	C37—S3—Zn2	93.84 (7)
C19—S2—Zn1	91.99 (7)	C55—S4—Zn2	92.29 (7)
C1—N1—C2	126.29 (18)	C37—N7—C38	121.72 (18)
C1—N1—H1N	116.4 (15)	C37—N7—H7N	114.2 (15)
C2—N1—H1N	116.8 (15)	C38—N7—H7N	117.6 (15)
C1—N2—N3	115.89 (16)	C37—N8—N9	114.79 (16)
C4—N3—N2	115.61 (16)	C40—N9—N8	115.50 (16)
C4—N3—Zn1	125.47 (12)	C40—N9—Zn2	126.72 (13)
N2—N3—Zn1	116.26 (12)	N8—N9—Zn2	117.76 (12)
C19—N4—C20	126.77 (18)	C55—N10—C56	122.08 (18)
C19—N4—H4N	114.5 (16)	C55—N10—H10N	117.9 (17)
C20—N4—H4N	118.2 (16)	C56—N10—H10N	118.7 (17)
C19—N5—N6	114.62 (16)	C55—N11—N12	115.50 (16)
C22—N6—N5	116.88 (16)	C58—N12—N11	114.72 (15)
C22—N6—Zn1	126.45 (13)	C58—N12—Zn2	128.03 (13)
N5—N6—Zn1	116.52 (12)	N11—N12—Zn2	116.56 (12)
N2—C1—N1	113.83 (17)	N8—C37—N7	117.06 (18)
N2—C1—S1	127.62 (15)	N8—C37—S3	127.47 (15)
N1—C1—S1	118.55 (15)	N7—C37—S3	115.44 (15)
N1—C2—C3	112.14 (19)	N7—C38—C39	112.11 (17)
N1—C2—H2A	109.2	N7—C38—H38A	109.2

C3—C2—H2A	109.2	C39—C38—H38A	109.2
N1—C2—H2B	109.2	N7—C38—H38B	109.2
C3—C2—H2B	109.2	C39—C38—H38B	109.2
H2A—C2—H2B	107.9	H38A—C38—H38B	107.9
C2—C3—H3A	109.5	C38—C39—H39A	109.5
C2—C3—H3B	109.5	C38—C39—H39B	109.5
H3A—C3—H3B	109.5	H39A—C39—H39B	109.5
C2—C3—H3C	109.5	C38—C39—H39C	109.5
H3A—C3—H3C	109.5	H39A—C39—H39C	109.5
H3B—C3—H3C	109.5	H39B—C39—H39C	109.5
N3—C4—C5	123.26 (17)	N9—C40—C41	117.21 (18)
N3—C4—C13	115.20 (17)	N9—C40—C49	121.76 (18)
C5—C4—C13	121.49 (17)	C41—C40—C49	121.04 (18)
C6—C5—C4	124.01 (18)	C42—C41—C40	125.62 (19)
C6—C5—H5	118.0	C42—C41—H41	117.2
C4—C5—H5	118.0	C40—C41—H41	117.2
C5—C6—C7	127.24 (18)	C41—C42—C43	124.9 (2)
C5—C6—H6	116.4	C41—C42—H42	117.6
C7—C6—H6	116.4	C43—C42—H42	117.6
C8—C7—C12	118.24 (18)	C48—C43—C44	118.2 (2)
C8—C7—C6	118.42 (17)	C48—C43—C42	122.6 (2)
C12—C7—C6	123.30 (18)	C44—C43—C42	119.2 (2)
C9—C8—C7	121.16 (19)	C45—C44—C43	120.8 (3)
C9—C8—H8	119.4	C45—C44—H44	119.6
C7—C8—H8	119.4	C43—C44—H44	119.6
C10—C9—C8	120.0 (2)	C46—C45—C44	120.2 (3)
C10—C9—H9	120.0	C46—C45—H45	119.9
C8—C9—H9	120.0	C44—C45—H45	119.9
C9—C10—C11	119.6 (2)	C45—C46—C47	120.0 (3)
C9—C10—H10	120.2	C45—C46—H46	120.0
C11—C10—H10	120.2	C47—C46—H46	120.0
C12—C11—C10	120.9 (2)	C48—C47—C46	120.3 (3)
C12—C11—H11	119.6	C48—C47—H47	119.9
C10—C11—H11	119.6	C46—C47—H47	119.9
C11—C12—C7	120.1 (2)	C47—C48—C43	120.4 (3)
C11—C12—H12	119.9	C47—C48—H48	119.8
C7—C12—H12	119.9	C43—C48—H48	119.8
C14—C13—C18	119.38 (17)	C54—C49—C50	119.25 (19)
C14—C13—C4	120.00 (17)	C54—C49—C40	120.62 (19)
C18—C13—C4	120.55 (17)	C50—C49—C40	120.10 (18)
C15—C14—C13	120.42 (19)	C49—C50—C51	119.9 (2)
C15—C14—H14	119.8	C49—C50—H50	120.0
C13—C14—H14	119.8	C51—C50—H50	120.0
C14—C15—C16	119.71 (19)	C52—C51—C50	120.1 (2)
C14—C15—H15	120.1	C52—C51—H51	119.9
C16—C15—H15	120.1	C50—C51—H51	119.9
C17—C16—C15	120.26 (18)	C53—C52—C51	119.9 (2)
C17—C16—H16	119.9	C53—C52—H52	120.1

C15—C16—H16	119.9	C51—C52—H52	120.1
C16—C17—C18	120.16 (19)	C52—C53—C54	120.4 (2)
C16—C17—H17	119.9	C52—C53—H53	119.8
C18—C17—H17	119.9	C54—C53—H53	119.8
C17—C18—C13	120.02 (18)	C53—C54—C49	120.4 (2)
C17—C18—H18	120.0	C53—C54—H54	119.8
C13—C18—H18	120.0	C49—C54—H54	119.8
N5—C19—N4	115.66 (17)	N11—C55—N10	115.82 (18)
N5—C19—S2	127.95 (15)	N11—C55—S4	128.40 (15)
N4—C19—S2	116.36 (15)	N10—C55—S4	115.77 (15)
N4—C20—C21	111.0 (2)	C57—C56—N10	111.2 (2)
N4—C20—H20A	109.4	C57—C56—H56A	109.4
C21—C20—H20A	109.4	N10—C56—H56A	109.4
N4—C20—H20B	109.4	C57—C56—H56B	109.4
C21—C20—H20B	109.4	N10—C56—H56B	109.4
H20A—C20—H20B	108.0	H56A—C56—H56B	108.0
C20—C21—H21A	109.5	C56—C57—H57A	109.5
C20—C21—H21B	109.5	C56—C57—H57B	109.5
H21A—C21—H21B	109.5	H57A—C57—H57B	109.5
C20—C21—H21C	109.5	C56—C57—H57C	109.5
H21A—C21—H21C	109.5	H57A—C57—H57C	109.5
H21B—C21—H21C	109.5	H57B—C57—H57C	109.5
N6—C22—C23	117.06 (17)	N12—C58—C59	118.20 (17)
N6—C22—C31	122.24 (17)	N12—C58—C67	120.79 (17)
C23—C22—C31	120.69 (17)	C59—C58—C67	121.00 (17)
C24—C23—C22	126.2 (2)	C60—C59—C58	123.84 (18)
C24—C23—H23	116.9	C60—C59—H59	118.1
C22—C23—H23	116.9	C58—C59—H59	118.1
C23—C24—C25	124.7 (2)	C59—C60—C61	127.06 (18)
C23—C24—H24	117.6	C59—C60—H60	116.5
C25—C24—H24	117.6	C61—C60—H60	116.5
C26—C25—C30	118.2 (2)	C66—C61—C62	118.10 (18)
C26—C25—C24	122.8 (2)	C66—C61—C60	119.34 (18)
C30—C25—C24	119.0 (2)	C62—C61—C60	122.56 (18)
C27—C26—C25	120.9 (2)	C63—C62—C61	120.5 (2)
C27—C26—H26	119.6	C63—C62—H62	119.8
C25—C26—H26	119.6	C61—C62—H62	119.8
C26—C27—C28	120.3 (2)	C62—C63—C64	120.4 (2)
C26—C27—H27	119.9	C62—C63—H63	119.8
C28—C27—H27	119.9	C64—C63—H63	119.8
C29—C28—C27	119.6 (2)	C65—C64—C63	119.9 (2)
C29—C28—H28	120.2	C65—C64—H64	120.0
C27—C28—H28	120.2	C63—C64—H64	120.0
C28—C29—C30	120.1 (2)	C64—C65—C66	119.9 (2)
C28—C29—H29	119.9	C64—C65—H65	120.1
C30—C29—H29	119.9	C66—C65—H65	120.1
C29—C30—C25	120.9 (2)	C65—C66—C61	121.3 (2)
C29—C30—H30	119.5	C65—C66—H66	119.4

C25—C30—H30	119.5	C61—C66—H66	119.4
C32—C31—C36	119.14 (19)	C72—C67—C68	119.29 (18)
C32—C31—C22	119.82 (18)	C72—C67—C58	121.08 (18)
C36—C31—C22	121.04 (18)	C68—C67—C58	119.61 (18)
C33—C32—C31	120.2 (2)	C69—C68—C67	120.59 (19)
C33—C32—H32	119.9	C69—C68—H68	119.7
C31—C32—H32	119.9	C67—C68—H68	119.7
C34—C33—C32	120.4 (2)	C70—C69—C68	119.6 (2)
C34—C33—H33	119.8	C70—C69—H69	120.2
C32—C33—H33	119.8	C68—C69—H69	120.2
C33—C34—C35	119.6 (2)	C71—C70—C69	120.3 (2)
C33—C34—H34	120.2	C71—C70—H70	119.8
C35—C34—H34	120.2	C69—C70—H70	119.8
C36—C35—C34	120.2 (2)	C70—C71—C72	120.2 (2)
C36—C35—H35	119.9	C70—C71—H71	119.9
C34—C35—H35	119.9	C72—C71—H71	119.9
C35—C36—C31	120.4 (2)	C67—C72—C71	120.02 (19)
C35—C36—H36	119.8	C67—C72—H72	120.0
C31—C36—H36	119.8	C71—C72—H72	120.0
C1—N2—N3—C4	−161.61 (18)	C37—N8—N9—C40	178.13 (17)
C1—N2—N3—Zn1	0.9 (2)	C37—N8—N9—Zn2	−3.3 (2)
C19—N5—N6—C22	178.11 (17)	C55—N11—N12—C58	−172.63 (18)
C19—N5—N6—Zn1	−6.0 (2)	C55—N11—N12—Zn2	−1.4 (2)
N3—N2—C1—N1	179.06 (17)	N9—N8—C37—N7	−177.12 (16)
N3—N2—C1—S1	−0.8 (3)	N9—N8—C37—S3	4.9 (3)
C2—N1—C1—N2	−177.69 (19)	C38—N7—C37—N8	7.1 (3)
C2—N1—C1—S1	2.2 (3)	C38—N7—C37—S3	−174.65 (14)
Zn1—S1—C1—N2	0.30 (19)	Zn2—S3—C37—N8	−3.59 (18)
Zn1—S1—C1—N1	−179.60 (16)	Zn2—S3—C37—N7	178.41 (14)
C1—N1—C2—C3	82.8 (3)	C37—N7—C38—C39	−86.1 (2)
N2—N3—C4—C5	8.6 (3)	N8—N9—C40—C41	−178.13 (16)
Zn1—N3—C4—C5	−152.08 (15)	Zn2—N9—C40—C41	3.5 (3)
N2—N3—C4—C13	−173.99 (16)	N8—N9—C40—C49	1.8 (3)
Zn1—N3—C4—C13	25.3 (2)	Zn2—N9—C40—C49	−176.55 (14)
N3—C4—C5—C6	−168.14 (19)	N9—C40—C41—C42	−163.6 (2)
C13—C4—C5—C6	14.6 (3)	C49—C40—C41—C42	16.4 (3)
C4—C5—C6—C7	−178.40 (18)	C40—C41—C42—C43	177.55 (19)
C5—C6—C7—C8	−176.6 (2)	C41—C42—C43—C48	17.1 (3)
C5—C6—C7—C12	5.6 (3)	C41—C42—C43—C44	−163.1 (2)
C12—C7—C8—C9	−0.2 (3)	C48—C43—C44—C45	−0.5 (3)
C6—C7—C8—C9	−178.13 (19)	C42—C43—C44—C45	179.7 (2)
C7—C8—C9—C10	0.7 (3)	C43—C44—C45—C46	1.0 (4)
C8—C9—C10—C11	−0.7 (3)	C44—C45—C46—C47	−0.8 (5)
C9—C10—C11—C12	0.2 (3)	C45—C46—C47—C48	0.2 (5)
C10—C11—C12—C7	0.3 (3)	C46—C47—C48—C43	0.3 (4)
C8—C7—C12—C11	−0.3 (3)	C44—C43—C48—C47	−0.2 (4)
C6—C7—C12—C11	177.55 (19)	C42—C43—C48—C47	179.7 (2)

N3—C4—C13—C14	52.5 (2)	N9—C40—C49—C54	61.8 (3)
C5—C4—C13—C14	−130.1 (2)	C41—C40—C49—C54	−118.2 (2)
N3—C4—C13—C18	−124.4 (2)	N9—C40—C49—C50	−116.2 (2)
C5—C4—C13—C18	53.0 (3)	C41—C40—C49—C50	63.7 (3)
C18—C13—C14—C15	1.0 (3)	C54—C49—C50—C51	−0.7 (3)
C4—C13—C14—C15	−175.98 (18)	C40—C49—C50—C51	177.40 (19)
C13—C14—C15—C16	1.1 (3)	C49—C50—C51—C52	1.7 (3)
C14—C15—C16—C17	−1.9 (3)	C50—C51—C52—C53	−0.8 (4)
C15—C16—C17—C18	0.7 (3)	C51—C52—C53—C54	−1.0 (4)
C16—C17—C18—C13	1.4 (3)	C52—C53—C54—C49	2.0 (4)
C14—C13—C18—C17	−2.2 (3)	C50—C49—C54—C53	−1.2 (3)
C4—C13—C18—C17	174.75 (18)	C40—C49—C54—C53	−179.2 (2)
N6—N5—C19—N4	175.76 (16)	N12—N11—C55—N10	−179.60 (19)
N6—N5—C19—S2	−6.5 (3)	N12—N11—C55—S4	1.4 (3)
C20—N4—C19—N5	−178.6 (2)	C56—N10—C55—N11	−7.7 (3)
C20—N4—C19—S2	3.4 (3)	C56—N10—C55—S4	171.4 (2)
Zn1—S2—C19—N5	13.04 (19)	Zn2—S4—C55—N11	−0.6 (2)
Zn1—S2—C19—N4	−169.19 (15)	Zn2—S4—C55—N10	−179.63 (17)
C19—N4—C20—C21	175.9 (2)	C55—N10—C56—C57	84.5 (3)
N5—N6—C22—C23	174.90 (16)	N11—N12—C58—C59	−177.58 (17)
Zn1—N6—C22—C23	−0.5 (3)	Zn2—N12—C58—C59	12.4 (3)
N5—N6—C22—C31	−4.2 (3)	N11—N12—C58—C67	3.2 (3)
Zn1—N6—C22—C31	−179.56 (14)	Zn2—N12—C58—C67	−166.85 (14)
N6—C22—C23—C24	−177.1 (2)	N12—C58—C59—C60	−172.94 (19)
C31—C22—C23—C24	1.9 (3)	C67—C58—C59—C60	6.3 (3)
C22—C23—C24—C25	177.8 (2)	C58—C59—C60—C61	178.86 (19)
C23—C24—C25—C26	−16.0 (4)	C59—C60—C61—C66	171.7 (2)
C23—C24—C25—C30	164.3 (2)	C59—C60—C61—C62	−8.0 (3)
C30—C25—C26—C27	−1.0 (4)	C66—C61—C62—C63	−1.9 (3)
C24—C25—C26—C27	179.4 (2)	C60—C61—C62—C63	177.8 (2)
C25—C26—C27—C28	−0.3 (4)	C61—C62—C63—C64	0.3 (3)
C26—C27—C28—C29	0.7 (5)	C62—C63—C64—C65	1.0 (3)
C27—C28—C29—C30	0.4 (5)	C63—C64—C65—C66	−0.9 (3)
C28—C29—C30—C25	−1.7 (4)	C64—C65—C66—C61	−0.7 (3)
C26—C25—C30—C29	2.0 (4)	C62—C61—C66—C65	2.0 (3)
C24—C25—C30—C29	−178.3 (2)	C60—C61—C66—C65	−177.6 (2)
N6—C22—C31—C32	−74.8 (3)	N12—C58—C67—C72	−112.5 (2)
C23—C22—C31—C32	106.1 (2)	C59—C58—C67—C72	68.2 (3)
N6—C22—C31—C36	105.0 (2)	N12—C58—C67—C68	66.0 (3)
C23—C22—C31—C36	−74.1 (3)	C59—C58—C67—C68	−113.2 (2)
C36—C31—C32—C33	−1.8 (3)	C72—C67—C68—C69	0.1 (3)
C22—C31—C32—C33	178.02 (18)	C58—C67—C68—C69	−178.50 (19)
C31—C32—C33—C34	−0.6 (3)	C67—C68—C69—C70	1.3 (3)
C32—C33—C34—C35	2.2 (3)	C68—C69—C70—C71	−1.5 (3)
C33—C34—C35—C36	−1.4 (3)	C69—C70—C71—C72	0.2 (3)
C34—C35—C36—C31	−1.0 (3)	C68—C67—C72—C71	−1.4 (3)
C32—C31—C36—C35	2.6 (3)	C58—C67—C72—C71	177.18 (19)
C22—C31—C36—C35	−177.24 (19)	C70—C71—C72—C67	1.3 (3)

Hydrogen-bond geometry (Å, º)

*Cg*1 and *Cg*2 are the centroids of the C31–C36 and C13—C18 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···S3	0.87 (2)	2.65 (2)	3.5077 (19)	170 (2)
N7—H7*N*···N2	0.87 (2)	2.10 (2)	2.941 (2)	164 (2)
N10—H10*N*···S2ⁱ	0.87 (1)	2.59 (2)	3.318 (2)	142 (2)
C11—H11···S4	0.95	2.86	3.715 (2)	151
C8—H8···*Cg*1ⁱⁱ	0.95	2.73	3.608 (2)	154
C32—H32···*Cg*2ⁱⁱⁱ	0.95	2.64	3.532 (2)	157

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