

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

(μ -*trans*-1,2-Di-4-pyridylethylene- κ^2 N:N')bis[bis(*N,N*-diethyldithiocarbamato- κ^2 S,S')zinc(II)] chloroform solvate

Hadi D. Arman,^a Pavel Poplaukhin^b and Edward R. T. Tiekink^{c*}

^aDepartment of Chemistry, The University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698, USA, ^bChemical Abstracts Service, 2540 Olenangy River Rd, Columbus, Ohio 43202, USA, and ^cDepartment of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: edward.tiekink@gmail.com

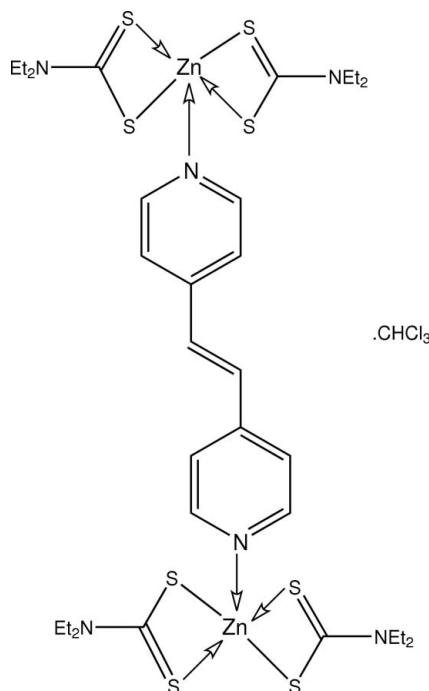
Received 23 October 2009; accepted 24 October 2009

Key indicators: single-crystal X-ray study; $T = 98$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.034; wR factor = 0.075; data-to-parameter ratio = 19.4.

The dinuclear title solvate, $[\text{Zn}_2(\text{C}_5\text{H}_{10}\text{NS}_2)_4(\text{C}_{12}\text{H}_{10}\text{N}_2)] \cdot \text{CHCl}_3$, features two five-coordinate Zn atoms; both coordination polyhedra are distorted, but one has an NS_4 donor set approximating to a square pyramid (with the N atom in the apical site), while the other is closer to a ZnNS_4 trigonal-bipyramidal arrangement (with the N atom in an equatorial site). In both cases, the Zn^{II} atom is chelated by two S,S' -bidentate dithiolate ligands. In the crystal, the chloroform solvent molecules reside in cavities defined by the dinuclear species and are held in place *via* $\text{C}-\text{H} \cdots \text{S}$ contacts.

Related literature

For background to supramolecular polymers of zinc 1,1-dithiolates, see: Lai *et al.* (2002); Chen *et al.* (2006); Benson *et al.* (2007). For a related structure and the synthesis, see: Lai & Tiekink (2003). For additional geometrical analysis, see: Addison *et al.* (1984).



Experimental

Crystal data

$[\text{Zn}_2(\text{C}_5\text{H}_{10}\text{NS}_2)_4(\text{C}_{12}\text{H}_{10}\text{N}_2)] \cdot \text{CHCl}_3$	$V = 4618.5(14)$ Å ³
$M_r = 1025.37$	$Z = 4$
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 17.443(3)$ Å	$\mu = 1.61$ mm ⁻¹
$b = 15.739(3)$ Å	$T = 98$ K
$c = 16.823(3)$ Å	$0.35 \times 0.21 \times 0.09$ mm

Data collection

Rigaku AFC12K/SATURN724 diffractometer	36476 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	9260 independent reflections
$T_{\min} = 0.824$, $T_{\max} = 1$	8995 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	H-atom parameters constrained
$wR(F^2) = 0.075$	$\Delta\rho_{\text{max}} = 0.83$ e Å ⁻³
$S = 1.07$	$\Delta\rho_{\text{min}} = -0.40$ e Å ⁻³
9260 reflections	Absolute structure: Flack (1983),
477 parameters	3766 Friedel pairs
1 restraint	Flack parameter: $-0.004(8)$

Table 1

Selected bond lengths (Å).

Zn1—N5	2.069(3)	Zn2—N6	2.075(3)
Zn1—S1	2.3567(9)	Zn2—S7	2.3381(10)
Zn1—S3	2.3659(9)	Zn2—S5	2.3526(9)
Zn1—S2	2.5629(9)	Zn2—S6	2.4934(10)
Zn1—S4	2.5654(9)	Zn2—S8	2.6575(9)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C33—H33 \cdots S8 ⁱ	1.00	2.72	3.598 (4)	149

Symmetry code: (i) $-x + 1, -y + 2, z + \frac{1}{2}$.

Data collection: *CrystalClear* (Rigaku/MS, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5173).

References

- Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
- Benson, R. E., Ellis, C. A., Lewis, C. E. & Tiekink, E. R. T. (2007). *CrystEngComm*, **9**, 930–940.
- Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Chen, D., Lai, C. S. & Tiekink, E. R. T. (2006). *CrystEngComm*, **8**, 51–58.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Lai, C. S., Lim, Y. X., Yap, T. C. & Tiekink, E. R. T. (2002). *CrystEngComm*, **4**, 596–600.
- Lai, C. S. & Tiekink, E. R. T. (2003). *Appl. Organomet. Chem.* **17**, 251–252.
- Rigaku/MS (2005). *CrystalClear*. Rigaku/MS Inc., The Woodlands, Texas, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

Acta Cryst. (2009). E65, m1472-m1473 [doi:10.1107/S1600536809044237]

**(μ -*trans*-1,2-Di-4-pyridylethylene- $\kappa^2N:N'$)bis[bis(*N,N*-diethyldithiocarbamato- κ^2S,S')zinc(II)]
chloroform solvate**

H. D. Arman, P. Poplaukhin and E. R. T. Tiekink

Comment

The title compound (I) was prepared in connection with crystal engineering studies of zinc(II) 1,1-dithiolates (Lai *et al.*, 2002; Chen *et al.*, 2006; Benson *et al.* 2007). The dinuclear compound features two five coordinate Zn atoms, each being coordinated by two dithiocarbamate ligands and a pyridine-N atom. The dithiocarbamate ligands are chelating but form disparate Zn—S bond distances that range from 2.3381 (10) to 2.6575 (9) Å. The coordination geometries for the Zn1 and Zn2 atoms are each based on a NS₄ donor set but are distinct. Thus, the geometries for the Zn1 and Zn2 atoms are distorted towards trigonal bipyramidal (TB) and square pyramidal (SP), respectively. This is quantified by the values of $\tau = 0.56$ and 0.36, respectively, compared with the ideal values of 1.0 and 0.0 for TB and SP, respectively (Addison *et al.*, 1984).

The most closely related structure available for comparison is the diethyldithiocarbamate analogue of (I) which was crystallized with a *trans*-1,2-bis(4-pyridyl)ethylene molecule (Lai & Tiekink, 2003) rather than a solvent chloroform molecule as for (I). In the former, the range of Zn—S bond distances was considerably narrower, *i.e.* 2.4100 (10) to 2.4914 (11) Å, and the coordination geometry for Zn (the dinuclear molecule is centrosymmetric) was close to SP ($\tau = 0.13$).

The solvent chloroform molecules in (I) reside in cavities defined by the dinuclear molecules and are held in place by C—H \cdots S interactions, Table 1,

Experimental

Compound (I) was prepared by following a standard literature procedure (Lai & Tiekink, 2003) whereby two equivalents of Zn(S₂CNEt₂)₂ were added to *trans*-1,2-bis(4-pyridyl)ethylene. Crystals were obtained from slow evaporation of a chloroform solution. When heated, the crystals turned opaque at 349–351 K and melted at 401–403 K.

Refinement

The H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$.

Figures

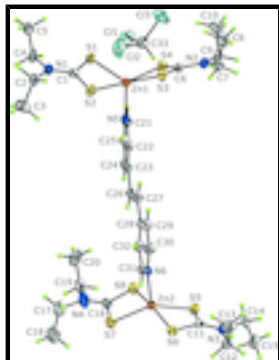


Fig. 1. The molecular structure of (I) showing displacement ellipsoids at the 70% probability level.

(μ -*trans*-1,2-Di-4-pyridylethylene- $\kappa^2N:N'$)bis[bis(*N,N*-diethyldithiocarbamato- κ^2S,S')zinc(II)] chloroform solvate

Crystal data

$[Zn_2(C_5H_{10}NS_2)_4(C_{12}H_{10}N_2)] \cdot CHCl_3$

$M_r = 1025.37$

Orthorhombic, *Pna*2₁

Hall symbol: P 2c -2n

$a = 17.443$ (3) Å

$b = 15.739$ (3) Å

$c = 16.823$ (3) Å

$V = 4618.5$ (14) Å³

$Z = 4$

$F_{000} = 2120$

$D_x = 1.475$ Mg m⁻³

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

Cell parameters from 19833 reflections

$\theta = 2.1$ – 40.8°

$\mu = 1.61$ mm⁻¹

$T = 98$ K

Block, yellow

$0.35 \times 0.21 \times 0.09$ mm

Data collection

Rigaku AFC12K/SATURN724 diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 98$ K

ω scans

Absorption correction: multi-scan (ABSCOR; Higashi, 1995)

$T_{\min} = 0.824$, $T_{\max} = 1$

36476 measured reflections

9260 independent reflections

8995 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\max} = 27.5^\circ$

$\theta_{\min} = 2.1^\circ$

$h = -22 \rightarrow 22$

$k = -20 \rightarrow 20$

$l = -17 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 3.3574P]$

$wR(F^2) = 0.075$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{\max} = 0.001$
9260 reflections	$\Delta\rho_{\max} = 0.83 \text{ e } \text{Å}^{-3}$
477 parameters	$\Delta\rho_{\min} = -0.40 \text{ e } \text{Å}^{-3}$
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 3766 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: $-0.004 (8)$

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.48561 (2)	0.46529 (2)	0.25986 (2)	0.01771 (8)
Zn2	0.52421 (2)	1.04699 (2)	-0.32727 (2)	0.01811 (8)
S1	0.37402 (5)	0.47688 (5)	0.33808 (5)	0.02142 (17)
S2	0.39216 (5)	0.35268 (5)	0.20769 (5)	0.02060 (16)
S3	0.60161 (4)	0.38777 (5)	0.26719 (5)	0.01975 (16)
S4	0.58224 (5)	0.55975 (5)	0.33339 (5)	0.02023 (16)
S5	0.64756 (4)	1.10741 (5)	-0.32528 (6)	0.02142 (16)
S6	0.59961 (5)	0.96317 (5)	-0.42580 (5)	0.02180 (17)
S7	0.40173 (5)	1.06415 (6)	-0.38140 (6)	0.02441 (18)
S8	0.45491 (5)	1.17094 (5)	-0.24764 (5)	0.02131 (16)
N1	0.25911 (16)	0.38216 (17)	0.28033 (17)	0.0202 (6)
N2	0.71730 (16)	0.47956 (17)	0.32773 (17)	0.0202 (6)
N3	0.74526 (16)	1.01190 (18)	-0.40881 (17)	0.0220 (6)
N4	0.30787 (18)	1.1551 (2)	-0.2899 (2)	0.0353 (8)
N5	0.47859 (15)	0.54237 (15)	0.16051 (18)	0.0165 (6)
N6	0.51719 (15)	0.95913 (15)	-0.2356 (2)	0.0179 (5)
C1	0.33315 (19)	0.40127 (18)	0.2750 (2)	0.0193 (6)
C2	0.22382 (19)	0.3145 (2)	0.2327 (2)	0.0214 (7)
H2A	0.1822	0.2877	0.2639	0.026*
H2B	0.2627	0.2704	0.2212	0.026*
C3	0.1911 (3)	0.3475 (2)	0.1547 (2)	0.0349 (9)
H3A	0.1549	0.3937	0.1655	0.052*
H3B	0.1644	0.3013	0.1271	0.052*

supplementary materials

H3C	0.2329	0.3688	0.1212	0.052*
C4	0.2053 (2)	0.4269 (2)	0.3333 (2)	0.0259 (7)
H4A	0.1555	0.4337	0.3059	0.031*
H4B	0.2256	0.4842	0.3452	0.031*
C5	0.1932 (2)	0.3788 (3)	0.4108 (2)	0.0343 (9)
H5A	0.1758	0.3209	0.3992	0.051*
H5B	0.1543	0.4081	0.4428	0.051*
H5C	0.2415	0.3766	0.4404	0.051*
C6	0.64211 (18)	0.4769 (2)	0.3119 (2)	0.0182 (6)
C7	0.7699 (2)	0.4104 (2)	0.3059 (2)	0.0254 (7)
H7A	0.8193	0.4351	0.2886	0.030*
H7B	0.7480	0.3788	0.2603	0.030*
C8	0.7845 (2)	0.3483 (3)	0.3742 (3)	0.0358 (9)
H8A	0.8133	0.3771	0.4164	0.054*
H8B	0.8143	0.2998	0.3546	0.054*
H8C	0.7354	0.3282	0.3954	0.054*
C9	0.7508 (2)	0.5538 (2)	0.3680 (2)	0.0243 (7)
H9A	0.7268	0.6059	0.3464	0.029*
H9B	0.8062	0.5562	0.3555	0.029*
C10	0.7411 (3)	0.5535 (3)	0.4577 (2)	0.0343 (9)
H10A	0.6868	0.5466	0.4709	0.051*
H10B	0.7599	0.6074	0.4796	0.051*
H10C	0.7705	0.5064	0.4806	0.051*
C11	0.67278 (19)	1.0258 (2)	-0.3888 (2)	0.0185 (6)
C12	0.7677 (2)	0.9474 (2)	-0.4679 (2)	0.0278 (8)
H12A	0.8156	0.9656	-0.4944	0.033*
H12B	0.7272	0.9430	-0.5090	0.033*
C13	0.7798 (2)	0.8609 (2)	-0.4302 (2)	0.0340 (9)
H13A	0.8204	0.8647	-0.3900	0.051*
H13B	0.7948	0.8199	-0.4712	0.051*
H13C	0.7321	0.8421	-0.4049	0.051*
C14	0.80844 (19)	1.0610 (2)	-0.3729 (2)	0.0274 (8)
H14A	0.8547	1.0247	-0.3698	0.033*
H14B	0.7940	1.0773	-0.3180	0.033*
C15	0.8274 (2)	1.1405 (2)	-0.4197 (2)	0.0322 (8)
H15A	0.8483	1.1245	-0.4716	0.048*
H15B	0.8654	1.1741	-0.3905	0.048*
H15C	0.7807	1.1742	-0.4272	0.048*
C16	0.38029 (19)	1.1340 (2)	-0.3040 (2)	0.0212 (7)
C17	0.2414 (2)	1.1077 (3)	-0.3288 (3)	0.0414 (10)
H17A	0.2569	1.0485	-0.3405	0.050*
H17B	0.1971	1.1061	-0.2921	0.050*
C18	0.2196 (3)	1.1518 (3)	-0.4038 (3)	0.0451 (11)
H18A	0.2003	1.2087	-0.3914	0.068*
H18B	0.1795	1.1191	-0.4309	0.068*
H18C	0.2646	1.1564	-0.4384	0.068*
C19	0.2882 (2)	1.2217 (2)	-0.2313 (2)	0.0301 (8)
H19A	0.2416	1.2521	-0.2493	0.036*
H19B	0.3306	1.2633	-0.2283	0.036*

C20	0.2740 (2)	1.1845 (3)	-0.1493 (3)	0.0383 (10)
H20A	0.2313	1.1440	-0.1519	0.058*
H20B	0.2611	1.2302	-0.1121	0.058*
H20C	0.3202	1.1551	-0.1309	0.058*
C21	0.47506 (18)	0.62720 (19)	0.1688 (2)	0.0187 (6)
H21	0.4723	0.6503	0.2209	0.022*
C22	0.47521 (19)	0.6821 (2)	0.1050 (2)	0.0199 (7)
H22	0.4718	0.7417	0.1136	0.024*
C23	0.48044 (18)	0.6501 (2)	0.0279 (2)	0.0185 (6)
C24	0.48146 (19)	0.5615 (2)	0.0190 (2)	0.0209 (7)
H24	0.4826	0.5366	-0.0324	0.025*
C25	0.48072 (18)	0.5108 (2)	0.0864 (2)	0.0199 (7)
H25	0.4818	0.4509	0.0798	0.024*
C26	0.48606 (19)	0.7044 (2)	-0.0429 (2)	0.0197 (7)
H26	0.4815	0.6784	-0.0937	0.024*
C27	0.4971 (2)	0.7877 (2)	-0.0400 (2)	0.0212 (7)
H27	0.5004	0.8129	0.0113	0.025*
C28	0.50485 (19)	0.8446 (2)	-0.10882 (19)	0.0170 (6)
C29	0.5127 (2)	0.9317 (2)	-0.0959 (2)	0.0233 (7)
H29	0.5140	0.9536	-0.0433	0.028*
C30	0.51845 (19)	0.9857 (2)	-0.1599 (2)	0.0208 (7)
H30	0.5236	1.0448	-0.1500	0.025*
C31	0.51125 (18)	0.87512 (19)	-0.2482 (2)	0.0197 (6)
H31	0.5119	0.8549	-0.3014	0.024*
C32	0.5043 (2)	0.8172 (2)	-0.1877 (2)	0.0212 (7)
H32	0.4992	0.7585	-0.1995	0.025*
C33	0.4971 (2)	0.7614 (3)	0.4505 (2)	0.0313 (8)
H33	0.5306	0.7820	0.4063	0.038*
Cl1	0.44088 (7)	0.84716 (6)	0.48451 (7)	0.0425 (2)
Cl2	0.43669 (6)	0.68037 (8)	0.41320 (8)	0.0503 (3)
Cl3	0.55577 (7)	0.72255 (6)	0.52699 (7)	0.0431 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01558 (16)	0.02010 (16)	0.01744 (19)	-0.00015 (13)	0.00102 (15)	0.00359 (15)
Zn2	0.01462 (16)	0.02072 (17)	0.01900 (19)	-0.00070 (13)	0.00125 (15)	0.00434 (15)
S1	0.0177 (4)	0.0264 (4)	0.0202 (4)	-0.0051 (3)	0.0021 (3)	-0.0059 (3)
S2	0.0192 (4)	0.0200 (4)	0.0226 (4)	-0.0006 (3)	0.0035 (3)	-0.0026 (3)
S3	0.0168 (3)	0.0178 (3)	0.0247 (4)	-0.0009 (3)	0.0000 (3)	0.0002 (3)
S4	0.0200 (4)	0.0203 (4)	0.0204 (4)	0.0006 (3)	-0.0014 (3)	-0.0009 (3)
S5	0.0165 (3)	0.0225 (3)	0.0253 (4)	-0.0024 (3)	0.0019 (3)	-0.0017 (3)
S6	0.0208 (4)	0.0244 (4)	0.0202 (4)	-0.0017 (3)	0.0016 (3)	-0.0008 (3)
S7	0.0187 (4)	0.0318 (4)	0.0227 (4)	0.0054 (3)	-0.0028 (3)	-0.0070 (4)
S8	0.0191 (4)	0.0207 (3)	0.0241 (4)	-0.0002 (3)	-0.0003 (3)	-0.0009 (3)
N1	0.0179 (13)	0.0221 (13)	0.0206 (15)	-0.0028 (10)	0.0016 (11)	-0.0041 (11)
N2	0.0175 (13)	0.0220 (13)	0.0210 (15)	-0.0029 (10)	0.0000 (11)	0.0011 (11)
N3	0.0175 (14)	0.0279 (14)	0.0205 (15)	0.0030 (11)	0.0009 (11)	0.0035 (12)

supplementary materials

N4	0.0213 (16)	0.0437 (19)	0.041 (2)	0.0091 (14)	-0.0024 (14)	-0.0157 (16)
N5	0.0147 (12)	0.0169 (12)	0.0178 (16)	-0.0021 (9)	-0.0002 (10)	0.0002 (10)
N6	0.0172 (12)	0.0188 (12)	0.0179 (14)	0.0014 (9)	-0.0004 (11)	0.0018 (11)
C1	0.0212 (15)	0.0160 (13)	0.0206 (17)	-0.0023 (11)	-0.0013 (12)	0.0031 (12)
C2	0.0191 (15)	0.0206 (15)	0.0246 (18)	-0.0026 (12)	-0.0009 (13)	-0.0035 (13)
C3	0.043 (2)	0.0285 (18)	0.034 (2)	0.0029 (16)	-0.0098 (18)	-0.0050 (16)
C4	0.0174 (16)	0.0299 (17)	0.030 (2)	-0.0014 (13)	0.0040 (14)	-0.0107 (15)
C5	0.0229 (18)	0.054 (2)	0.026 (2)	-0.0052 (17)	0.0018 (15)	-0.0114 (18)
C6	0.0171 (15)	0.0217 (14)	0.0159 (16)	-0.0040 (12)	0.0006 (12)	0.0020 (12)
C7	0.0163 (16)	0.0306 (17)	0.029 (2)	0.0020 (13)	0.0011 (14)	-0.0009 (15)
C8	0.031 (2)	0.035 (2)	0.041 (3)	0.0033 (16)	-0.0037 (18)	0.0049 (18)
C9	0.0196 (17)	0.0286 (17)	0.0249 (19)	-0.0063 (13)	-0.0022 (14)	0.0006 (14)
C10	0.039 (2)	0.040 (2)	0.024 (2)	-0.0037 (18)	-0.0075 (17)	-0.0049 (17)
C11	0.0173 (15)	0.0226 (15)	0.0156 (15)	0.0035 (12)	0.0038 (12)	0.0048 (12)
C12	0.0229 (18)	0.0343 (19)	0.026 (2)	0.0108 (14)	0.0054 (15)	0.0014 (16)
C13	0.041 (2)	0.037 (2)	0.024 (2)	0.0156 (17)	-0.0002 (17)	-0.0029 (16)
C14	0.0120 (15)	0.042 (2)	0.028 (2)	0.0027 (14)	-0.0019 (13)	0.0044 (16)
C15	0.0198 (17)	0.042 (2)	0.035 (2)	-0.0045 (15)	0.0030 (16)	0.0036 (18)
C16	0.0192 (16)	0.0223 (15)	0.0222 (19)	0.0017 (12)	-0.0007 (13)	-0.0006 (13)
C17	0.0250 (19)	0.052 (2)	0.047 (3)	0.0083 (17)	0.007 (2)	-0.008 (2)
C18	0.034 (2)	0.050 (3)	0.051 (3)	0.0033 (19)	-0.002 (2)	-0.006 (2)
C19	0.0235 (17)	0.0352 (18)	0.032 (2)	0.0109 (14)	-0.0013 (15)	-0.0086 (17)
C20	0.035 (2)	0.035 (2)	0.046 (3)	-0.0018 (17)	0.0116 (19)	-0.0060 (19)
C21	0.0184 (14)	0.0202 (14)	0.0174 (16)	0.0011 (11)	-0.0007 (13)	-0.0028 (13)
C22	0.0213 (16)	0.0183 (14)	0.0201 (18)	0.0009 (12)	-0.0032 (13)	-0.0008 (13)
C23	0.0150 (15)	0.0225 (16)	0.0181 (17)	-0.0012 (12)	-0.0005 (12)	0.0012 (13)
C24	0.0198 (16)	0.0209 (15)	0.0218 (18)	-0.0029 (12)	-0.0012 (13)	-0.0035 (14)
C25	0.0210 (16)	0.0191 (15)	0.0197 (17)	-0.0008 (12)	0.0002 (13)	0.0026 (13)
C26	0.0222 (17)	0.0220 (15)	0.0149 (16)	-0.0010 (12)	-0.0016 (12)	0.0019 (13)
C27	0.0250 (17)	0.0225 (15)	0.0161 (16)	0.0000 (13)	0.0006 (13)	-0.0021 (13)
C28	0.0166 (15)	0.0185 (14)	0.0159 (16)	0.0014 (12)	0.0021 (12)	0.0023 (12)
C29	0.0290 (19)	0.0216 (16)	0.0192 (18)	0.0011 (13)	0.0012 (14)	0.0007 (14)
C30	0.0227 (16)	0.0171 (15)	0.0227 (18)	-0.0007 (11)	0.0005 (13)	0.0013 (13)
C31	0.0217 (15)	0.0206 (14)	0.0167 (17)	-0.0012 (12)	0.0002 (13)	-0.0006 (13)
C32	0.0262 (17)	0.0178 (14)	0.0196 (17)	-0.0029 (12)	0.0005 (14)	-0.0003 (13)
C33	0.0268 (19)	0.040 (2)	0.027 (2)	-0.0002 (16)	0.0031 (16)	0.0057 (17)
Cl1	0.0430 (6)	0.0343 (5)	0.0501 (7)	0.0026 (4)	0.0076 (5)	0.0064 (5)
Cl2	0.0277 (5)	0.0651 (7)	0.0579 (7)	-0.0034 (5)	0.0009 (5)	-0.0286 (6)
Cl3	0.0532 (7)	0.0335 (5)	0.0426 (6)	-0.0029 (4)	-0.0174 (5)	0.0094 (4)

Geometric parameters (Å, °)

Zn1—N5	2.069 (3)	C9—H9B	0.9900
Zn1—S1	2.3567 (9)	C10—H10A	0.9800
Zn1—S3	2.3659 (9)	C10—H10B	0.9800
Zn1—S2	2.5629 (9)	C10—H10C	0.9800
Zn1—S4	2.5654 (9)	C12—C13	1.517 (5)
Zn2—N6	2.075 (3)	C12—H12A	0.9900
Zn2—S7	2.3381 (10)	C12—H12B	0.9900

Zn2—S5	2.3526 (9)	C13—H13A	0.9800
Zn2—S6	2.4934 (10)	C13—H13B	0.9800
Zn2—S8	2.6575 (9)	C13—H13C	0.9800
S1—C1	1.746 (3)	C14—C15	1.514 (5)
S2—C1	1.711 (3)	C14—H14A	0.9900
S3—C6	1.741 (3)	C14—H14B	0.9900
S4—C6	1.709 (3)	C15—H15A	0.9800
S5—C11	1.728 (3)	C15—H15B	0.9800
S6—C11	1.728 (3)	C15—H15C	0.9800
S7—C16	1.745 (3)	C17—C18	1.490 (7)
S8—C16	1.712 (3)	C17—H17A	0.9900
N1—C1	1.329 (4)	C17—H17B	0.9900
N1—C2	1.468 (4)	C18—H18A	0.9800
N1—C4	1.473 (4)	C18—H18B	0.9800
N2—C6	1.339 (4)	C18—H18C	0.9800
N2—C7	1.470 (4)	C19—C20	1.519 (6)
N2—C9	1.472 (4)	C19—H19A	0.9900
N3—C11	1.326 (4)	C19—H19B	0.9900
N3—C14	1.476 (4)	C20—H20A	0.9800
N3—C12	1.473 (5)	C20—H20B	0.9800
N4—C16	1.327 (4)	C20—H20C	0.9800
N4—C19	1.479 (5)	C21—C22	1.377 (5)
N4—C17	1.525 (5)	C21—H21	0.9500
N5—C25	1.343 (5)	C22—C23	1.396 (5)
N5—C21	1.344 (4)	C22—H22	0.9500
N6—C30	1.341 (5)	C23—C24	1.402 (4)
N6—C31	1.343 (4)	C23—C26	1.470 (5)
C2—C3	1.523 (5)	C24—C25	1.386 (5)
C2—H2A	0.9900	C24—H24	0.9500
C2—H2B	0.9900	C25—H25	0.9500
C3—H3A	0.9800	C26—C27	1.326 (4)
C3—H3B	0.9800	C26—H26	0.9500
C3—H3C	0.9800	C27—C28	1.470 (5)
C4—C5	1.522 (6)	C27—H27	0.9500
C4—H4A	0.9900	C28—C29	1.395 (5)
C4—H4B	0.9900	C28—C32	1.395 (5)
C5—H5A	0.9800	C29—C30	1.375 (5)
C5—H5B	0.9800	C29—H29	0.9500
C5—H5C	0.9800	C30—H30	0.9500
C7—C8	1.530 (5)	C31—C32	1.372 (5)
C7—H7A	0.9900	C31—H31	0.9500
C7—H7B	0.9900	C32—H32	0.9500
C8—H8A	0.9800	C33—Cl3	1.754 (4)
C8—H8B	0.9800	C33—Cl1	1.764 (4)
C8—H8C	0.9800	C33—Cl2	1.769 (4)
C9—C10	1.519 (5)	C33—H33	1.0000
C9—H9A	0.9900		
N5—Zn1—S1	110.90 (8)	H10A—C10—H10C	109.5
N5—Zn1—S3	113.27 (8)	H10B—C10—H10C	109.5

supplementary materials

S1—Zn1—S3	135.82 (4)	N3—C11—S6	121.3 (3)
N5—Zn1—S2	95.23 (8)	N3—C11—S5	121.4 (3)
S1—Zn1—S2	73.70 (3)	S6—C11—S5	117.29 (19)
S3—Zn1—S2	101.84 (3)	N3—C12—C13	111.9 (3)
N5—Zn1—S4	95.08 (7)	N3—C12—H12A	109.2
S1—Zn1—S4	103.21 (3)	C13—C12—H12A	109.2
S3—Zn1—S4	73.25 (3)	N3—C12—H12B	109.2
S2—Zn1—S4	169.66 (3)	C13—C12—H12B	109.2
N6—Zn2—S7	108.20 (8)	H12A—C12—H12B	107.9
N6—Zn2—S5	108.23 (8)	C12—C13—H13A	109.5
S7—Zn2—S5	142.61 (4)	C12—C13—H13B	109.5
N6—Zn2—S6	99.94 (8)	H13A—C13—H13B	109.5
S7—Zn2—S6	106.51 (3)	C12—C13—H13C	109.5
S5—Zn2—S6	74.98 (3)	H13A—C13—H13C	109.5
N6—Zn2—S8	95.04 (8)	H13B—C13—H13C	109.5
S7—Zn2—S8	72.29 (3)	N3—C14—C15	112.5 (3)
S5—Zn2—S8	96.44 (3)	N3—C14—H14A	109.1
S6—Zn2—S8	164.46 (3)	C15—C14—H14A	109.1
C1—S1—Zn1	86.85 (12)	N3—C14—H14B	109.1
C1—S2—Zn1	81.19 (11)	C15—C14—H14B	109.1
C6—S3—Zn1	87.36 (11)	H14A—C14—H14B	107.8
C6—S4—Zn1	81.79 (11)	C14—C15—H15A	109.5
C11—S5—Zn2	85.61 (11)	C14—C15—H15B	109.5
C11—S6—Zn2	81.30 (11)	H15A—C15—H15B	109.5
C16—S7—Zn2	88.75 (12)	C14—C15—H15C	109.5
C16—S8—Zn2	79.48 (12)	H15A—C15—H15C	109.5
C1—N1—C2	122.3 (3)	H15B—C15—H15C	109.5
C1—N1—C4	123.5 (3)	N4—C16—S8	122.7 (3)
C2—N1—C4	114.2 (3)	N4—C16—S7	119.7 (3)
C6—N2—C7	122.5 (3)	S8—C16—S7	117.67 (19)
C6—N2—C9	120.4 (3)	C18—C17—N4	109.2 (4)
C7—N2—C9	117.1 (3)	C18—C17—H17A	109.8
C11—N3—C14	121.5 (3)	N4—C17—H17A	109.8
C11—N3—C12	122.5 (3)	C18—C17—H17B	109.8
C14—N3—C12	116.1 (3)	N4—C17—H17B	109.8
C16—N4—C19	121.1 (3)	H17A—C17—H17B	108.3
C16—N4—C17	121.6 (3)	C17—C18—H18A	109.5
C19—N4—C17	117.1 (3)	C17—C18—H18B	109.5
C25—N5—C21	117.7 (3)	H18A—C18—H18B	109.5
C25—N5—Zn1	122.1 (2)	C17—C18—H18C	109.5
C21—N5—Zn1	120.1 (2)	H18A—C18—H18C	109.5
C30—N6—C31	117.2 (3)	H18B—C18—H18C	109.5
C30—N6—Zn2	119.8 (2)	N4—C19—C20	111.7 (3)
C31—N6—Zn2	123.0 (3)	N4—C19—H19A	109.3
N1—C1—S2	121.9 (3)	C20—C19—H19A	109.3
N1—C1—S1	120.6 (3)	N4—C19—H19B	109.3
S2—C1—S1	117.47 (19)	C20—C19—H19B	109.3
N1—C2—C3	112.4 (3)	H19A—C19—H19B	107.9
N1—C2—H2A	109.1	C19—C20—H20A	109.5

C3—C2—H2A	109.1	C19—C20—H20B	109.5
N1—C2—H2B	109.1	H20A—C20—H20B	109.5
C3—C2—H2B	109.1	C19—C20—H20C	109.5
H2A—C2—H2B	107.9	H20A—C20—H20C	109.5
C2—C3—H3A	109.5	H20B—C20—H20C	109.5
C2—C3—H3B	109.5	N5—C21—C22	122.9 (3)
H3A—C3—H3B	109.5	N5—C21—H21	118.6
C2—C3—H3C	109.5	C22—C21—H21	118.6
H3A—C3—H3C	109.5	C21—C22—C23	119.8 (3)
H3B—C3—H3C	109.5	C21—C22—H22	120.1
N1—C4—C5	111.7 (3)	C23—C22—H22	120.1
N1—C4—H4A	109.3	C22—C23—C24	117.4 (3)
C5—C4—H4A	109.3	C22—C23—C26	123.2 (3)
N1—C4—H4B	109.3	C24—C23—C26	119.4 (3)
C5—C4—H4B	109.3	C25—C24—C23	119.0 (3)
H4A—C4—H4B	107.9	C25—C24—H24	120.5
C4—C5—H5A	109.5	C23—C24—H24	120.5
C4—C5—H5B	109.5	N5—C25—C24	123.1 (3)
H5A—C5—H5B	109.5	N5—C25—H25	118.4
C4—C5—H5C	109.5	C24—C25—H25	118.4
H5A—C5—H5C	109.5	C27—C26—C23	123.7 (3)
H5B—C5—H5C	109.5	C27—C26—H26	118.2
N2—C6—S4	122.2 (2)	C23—C26—H26	118.2
N2—C6—S3	120.6 (2)	C26—C27—C28	125.9 (3)
S4—C6—S3	117.27 (19)	C26—C27—H27	117.1
N2—C7—C8	112.9 (3)	C28—C27—H27	117.1
N2—C7—H7A	109.0	C29—C28—C32	116.9 (3)
C8—C7—H7A	109.0	C29—C28—C27	119.0 (3)
N2—C7—H7B	109.0	C32—C28—C27	124.1 (3)
C8—C7—H7B	109.0	C30—C29—C28	119.6 (3)
H7A—C7—H7B	107.8	C30—C29—H29	120.2
C7—C8—H8A	109.5	C28—C29—H29	120.2
C7—C8—H8B	109.5	N6—C30—C29	123.3 (3)
H8A—C8—H8B	109.5	N6—C30—H30	118.3
C7—C8—H8C	109.5	C29—C30—H30	118.3
H8A—C8—H8C	109.5	N6—C31—C32	123.0 (3)
H8B—C8—H8C	109.5	N6—C31—H31	118.5
N2—C9—C10	114.3 (3)	C32—C31—H31	118.5
N2—C9—H9A	108.7	C31—C32—C28	120.0 (3)
C10—C9—H9A	108.7	C31—C32—H32	120.0
N2—C9—H9B	108.7	C28—C32—H32	120.0
C10—C9—H9B	108.7	Cl3—C33—Cl1	110.7 (2)
H9A—C9—H9B	107.6	Cl3—C33—Cl2	110.9 (2)
C9—C10—H10A	109.5	Cl1—C33—Cl2	109.6 (2)
C9—C10—H10B	109.5	Cl3—C33—H33	108.5
H10A—C10—H10B	109.5	Cl1—C33—H33	108.5
C9—C10—H10C	109.5	Cl2—C33—H33	108.5
N5—Zn1—S1—C1	84.10 (13)	C9—N2—C6—S4	2.7 (4)
S3—Zn1—S1—C1	-95.67 (11)	C7—N2—C6—S3	2.5 (4)

supplementary materials

S2—Zn1—S1—C1	-5.33 (11)	C9—N2—C6—S3	-177.9 (2)
S4—Zn1—S1—C1	-175.12 (11)	Zn1—S4—C6—N2	174.3 (3)
N5—Zn1—S2—C1	-104.77 (13)	Zn1—S4—C6—S3	-5.19 (17)
S1—Zn1—S2—C1	5.50 (11)	Zn1—S3—C6—N2	-173.9 (3)
S3—Zn1—S2—C1	140.11 (11)	Zn1—S3—C6—S4	5.58 (18)
S4—Zn1—S2—C1	79.5 (2)	C6—N2—C7—C8	-96.2 (4)
N5—Zn1—S3—C6	84.91 (14)	C9—N2—C7—C8	84.2 (4)
S1—Zn1—S3—C6	-95.33 (12)	C6—N2—C9—C10	81.3 (4)
S2—Zn1—S3—C6	-174.04 (11)	C7—N2—C9—C10	-99.1 (4)
S4—Zn1—S3—C6	-3.45 (11)	C14—N3—C11—S6	-175.4 (2)
N5—Zn1—S4—C6	-109.25 (13)	C12—N3—C11—S6	4.8 (4)
S1—Zn1—S4—C6	137.86 (11)	C14—N3—C11—S5	4.9 (4)
S3—Zn1—S4—C6	3.54 (11)	C12—N3—C11—S5	-174.8 (2)
S2—Zn1—S4—C6	66.5 (2)	Zn2—S6—C11—N3	172.1 (3)
N6—Zn2—S5—C11	90.19 (14)	Zn2—S6—C11—S5	-8.27 (16)
S7—Zn2—S5—C11	-103.21 (12)	Zn2—S5—C11—N3	-171.6 (3)
S6—Zn2—S5—C11	-5.53 (11)	Zn2—S5—C11—S6	8.69 (17)
S8—Zn2—S5—C11	-172.33 (11)	C11—N3—C12—C13	-88.1 (4)
N6—Zn2—S6—C11	-100.79 (13)	C14—N3—C12—C13	92.1 (4)
S7—Zn2—S6—C11	146.70 (11)	C11—N3—C14—C15	-90.3 (4)
S5—Zn2—S6—C11	5.58 (11)	C12—N3—C14—C15	89.5 (4)
S8—Zn2—S6—C11	63.49 (16)	C19—N4—C16—S8	8.8 (5)
N6—Zn2—S7—C16	81.52 (14)	C17—N4—C16—S8	-166.8 (3)
S5—Zn2—S7—C16	-85.08 (13)	C19—N4—C16—S7	-172.7 (3)
S6—Zn2—S7—C16	-171.80 (12)	C17—N4—C16—S7	11.7 (5)
S8—Zn2—S7—C16	-8.02 (11)	Zn2—S8—C16—N4	166.5 (3)
N6—Zn2—S8—C16	-99.21 (14)	Zn2—S8—C16—S7	-12.03 (17)
S7—Zn2—S8—C16	8.31 (12)	Zn2—S7—C16—N4	-165.1 (3)
S5—Zn2—S8—C16	151.76 (12)	Zn2—S7—C16—S8	13.47 (19)
S6—Zn2—S8—C16	96.33 (16)	C16—N4—C17—C18	-92.5 (5)
S1—Zn1—N5—C25	-118.7 (2)	C19—N4—C17—C18	91.7 (5)
S3—Zn1—N5—C25	61.1 (2)	C16—N4—C19—C20	-92.2 (5)
S2—Zn1—N5—C25	-44.2 (2)	C17—N4—C19—C20	83.6 (4)
S4—Zn1—N5—C25	135.0 (2)	C25—N5—C21—C22	-1.4 (5)
S1—Zn1—N5—C21	64.2 (2)	Zn1—N5—C21—C22	175.8 (2)
S3—Zn1—N5—C21	-116.0 (2)	N5—C21—C22—C23	-1.1 (5)
S2—Zn1—N5—C21	138.7 (2)	C21—C22—C23—C24	3.1 (5)
S4—Zn1—N5—C21	-42.0 (2)	C21—C22—C23—C26	-175.9 (3)
S7—Zn2—N6—C30	-103.6 (2)	C22—C23—C24—C25	-2.8 (5)
S5—Zn2—N6—C30	67.9 (2)	C26—C23—C24—C25	176.2 (3)
S6—Zn2—N6—C30	145.2 (2)	C21—N5—C25—C24	1.7 (5)
S8—Zn2—N6—C30	-30.6 (2)	Zn1—N5—C25—C24	-175.4 (3)
S7—Zn2—N6—C31	76.4 (3)	C23—C24—C25—N5	0.4 (5)
S5—Zn2—N6—C31	-112.2 (2)	C22—C23—C26—C27	9.5 (5)
S6—Zn2—N6—C31	-34.8 (3)	C24—C23—C26—C27	-169.5 (3)
S8—Zn2—N6—C31	149.4 (2)	C23—C26—C27—C28	178.6 (3)
C2—N1—C1—S2	4.0 (4)	C26—C27—C28—C29	177.0 (4)
C4—N1—C1—S2	-175.4 (3)	C26—C27—C28—C32	-2.5 (6)
C2—N1—C1—S1	-175.2 (2)	C32—C28—C29—C30	0.8 (5)

C4—N1—C1—S1	5.4 (5)	C27—C28—C29—C30	-178.7 (3)
Zn1—S2—C1—N1	172.7 (3)	C31—N6—C30—C29	-1.1 (5)
Zn1—S2—C1—S1	-8.05 (16)	Zn2—N6—C30—C29	178.8 (3)
Zn1—S1—C1—N1	-172.1 (3)	C28—C29—C30—N6	-0.2 (5)
Zn1—S1—C1—S2	8.67 (17)	C30—N6—C31—C32	1.9 (5)
C1—N1—C2—C3	-91.9 (4)	Zn2—N6—C31—C32	-178.0 (3)
C4—N1—C2—C3	87.6 (4)	N6—C31—C32—C28	-1.3 (5)
C1—N1—C4—C5	-97.5 (4)	C29—C28—C32—C31	-0.1 (5)
C2—N1—C4—C5	83.0 (4)	C27—C28—C32—C31	179.4 (3)
C7—N2—C6—S4	-176.9 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C33—H33...S8 ⁱ	1.00	2.72	3.598 (4)	149

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

Fig. 1

