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Poly[bis(μ_2-5-thioxo-1*H*-1,2,4-thiadiazole-3-thiolato-κ^2S^3:S^5)zinc(II)]

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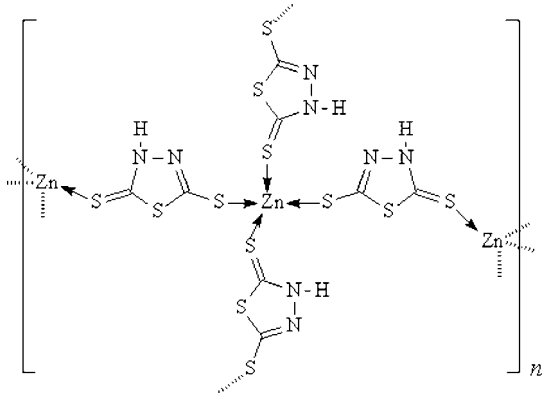
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(N–C) = 0.002 Å; R factor = 0.019; wR factor = 0.047; data-to-parameter ratio = 17.8.

In the crystal structure of the neutral polymeric title compound, $[Zn(C_2HN_2S_3)_2]_n$, the Zn^{II} atom is located at a site of 2 symmetry and is coordinated by four S atoms of four symmetry-related 5-thioxo-1*H*-1,2,4-thiadiazole-3-thiolate ligands in a tetrahedral geometry, with S—Zn distances of 2.3343 (6) and 2.3560 (6) Å, and S—Zn—S angles ranging from 103.78 (3) to 112.572 (17)°. Each of the ligands bridges two Zn^{II} atoms through two terminal S atoms, leading to the formation of a chiral two-dimensional layer containing homochiral helical chains. However, in the crystal structure, adjacent layers have opposite chirality and are connected into a three-dimensional network by N—H···S hydrogen bonds.

Related literature

For related literature, see: Bats (1976); Li *et al.* (2005); Ma *et al.* (2004*a*, *b*); Mura *et al.* (1985); Qiu *et al.* (2006); Tannai *et al.* (2003, 2005, 2006); Tzeng *et al.* (2007).



Experimental

Crystal data

$[Zn(C_2HN_2S_3)_2]$
M_r = 363.83
Orthorhombic, *Pbcn*
a = 12.983 (3) Å
b = 11.448 (2) Å
c = 7.6035 (15) Å
V = 1130.1 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.25 mm^{-1}
T = 293 (2) K
0.20 × 0.12 × 0.10 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.863, T_{max} = 1.000
(expected range = 0.623–0.723)
10211 measured reflections
1298 independent reflections
1213 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.047
S = 1.08
1298 reflections
73 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—S3^{i}	2.3343 (6)	Zn1—S2	2.3560 (6)
S3^{ii}—Zn1—S3^{i}	103.78 (3)	S3^{i}—Zn1—S2	112.572 (17)
S3^{ii}—Zn1—S2	110.807 (18)	S2^{iii}—Zn1—S2	106.44 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···S3^{iv}	0.89 (1)	2.57 (2)	3.339 (2)	146 (2)
N1—H1···S3^{i}	0.89 (1)	2.83 (2)	3.378 (2)	121 (2)

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2441).

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supplementary materials

Acta Cryst. (2007). E**63**, m2432-m2433 [**doi:10.1107/S1600536807041797**]

Poly[bis(μ_2-5-thioxo-1*H*-1,2,4-thiadiazole-3-thiolato-κ^2S^3:S^5)zinc(II)]

X.-L. Zhang, N. An, Y.-E. Qiu, C.-L. Zhang and Y.-C. Wang

Comment

The structures of free 2,5-dimercapto-1,3,4-thiodiazole (Bats, 1976) and some of its metal-complexes (Li *et al.*, 2005; Mura *et al.*, 1985; Ma *et al.*, 2004*a*,b; Qiu *et al.*, 2006; Tannai *et al.*, 2003, 2005, 2006; Tzeng *et al.*, 2007) have been reported. In such complexes, the 2,5-dimercapto-1,3,4-thiodiazole ligand shows different valences and different coordination modes. Herein, we report a neutral Zn^{II} complex, $[Zn(C_2HN_2S_3)_2]_n$, with the above ligand.

As shown in Fig. 1, the Zn^{II} atom lies at a site of 2 symmetry. It is four-coordinated by four symmetry related 5-thioxo-1*H*-1,2,4-thiadiazole-3-thiolate ligands through their S atoms to form a tetrahedral geometry. The S—Zn distances are 2.3343 (6) and 2.3560 (6) Å, and S—Zn—S angles range from 103.78 (3) to 112.572 (17)° (Table 1). Each of the ligand coordinates to two Zn^{II} atoms through the two terminal S atoms to form a chiral two-dimensional layer (Fig. 2) containing homochiral helical chains (left- or right-hand single helical chain). The separation of Zn^{II} atom across the ligand is 7.779 (6) Å and the screw-pitch is 7.604 (5) Å. However, in the crystal structure, adjacent layers have opposite chirality, and were connected into a three-dimensional network by N—H···S hydrogen bonds (see Table 2).

Experimental

The title compound was synthesized by the hydrothermal method. A mixture of $ZnCl_2$ (27 mg, 0.2 mmol) and 2,5-dimercapto-1,3,4-thiodiazole (60 mg, 0.4 mmol) in water (10 ml) was placed in a Teflon-lined stainless-steel Parr bomb. The bomb was heated at 413 K for 30 h and then allowed to cool to room temperature; colourless crystals were isolated in about 20% yield. FT—IR (KBr pellets, cm^{-1}): 3157*m*, 1593w, 1478 s, 1411*m*, 1297*m*, 1124 s, 1103 s, 1036 s, 734*m*, 668w, 581w, 544*m*.

Refinement

Atom H1 was located in a difference map and refined isotropically, with an N—H distance restraint of 0.90 (1) Å.

Figures

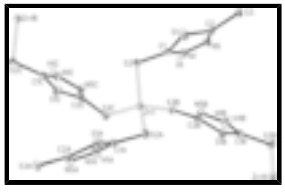


Fig. 1. Part of a two-dimensional network in the title compound. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes: (A) $1-x, y, 1/2-z$; (B) $3/2-x, 1/2-y, 1/2+z$; (C) $-1/2+x, 1/2-y, -z$.

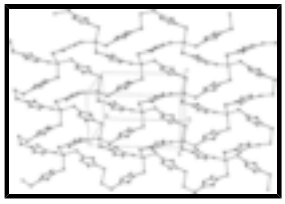


Fig. 2. Two-dimensional network structure in the title compound.

Poly[bis(μ$_2$-5-thioxo-1*H*-1,2,4-thiadiazole-3-thiolato-κ^2*S*^{3}:*S*^{5})zinc(II)]

Crystal data

$[Zn(C_2HN_2S_3)_2]$	F_{000} = 720
M_r = 363.83	D_x = 2.138 Mg m^{-3}
Orthorhombic, *Pbcn*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2n 2ab	Cell parameters from 9116 reflections
a = 12.983 (3) Å	θ = 3.1–27.5º
b = 11.448 (2) Å	μ = 3.25 mm^{-1}
c = 7.6035 (15) Å	*T* = 293 (2) K
V = 1130.1 (4) Å^3	Block, colourless
Z = 4	0.20 × 0.12 × 0.10 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	1298 independent reflections
Radiation source: fine-focus sealed tube	1213 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.030
T = 293(2) K	θ_{max} = 27.5º
φ and ω scans	θ_{min} = 3.1º
Absorption correction: multi-scan (SADABS; Bruker, 1998)	*h* = −16→16
T_{min} = 0.863, T_{max} = 1.000	*k* = −14→14
10211 measured reflections	*l* = −8→9

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.019	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.047	$w = 1/[\sigma^2(F_o^2) + (0.0201P)^2 + 0.66P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.08	$(\Delta/\sigma)_{max}$ = 0.001
1298 reflections	$\Delta\rho_{max}$ = 0.34 e Å^{-3}
73 parameters	$\Delta\rho_{min}$ = −0.31 e Å^{-3}

1 restraint
Primary atom site location: structure-invariant direct methods

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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_{iso}*/U_{eq}
Zn1	0.5000	0.16347 (3)	0.2500	0.02437 (9)
S2	0.47751 (3)	0.28669 (5)	0.00481 (7)	0.03425 (13)
S1	0.64938 (3)	0.44469 (4)	−0.11880 (7)	0.03453 (13)
S3	0.85977 (3)	0.46238 (4)	−0.28194 (6)	0.02663 (11)
N1	0.66827 (11)	0.23028 (13)	−0.1150 (2)	0.0291 (3)
N5	0.76058 (11)	0.26501 (13)	−0.1854 (2)	0.0297 (3)
C2	0.76163 (12)	0.37822 (15)	−0.1961 (2)	0.0223 (3)
C1	0.59931 (13)	0.30944 (15)	−0.0721 (2)	0.0248 (3)
H1	0.6565 (19)	0.1542 (9)	−0.109 (4)	0.058 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02160 (14)	0.02878 (16)	0.02272 (15)	0.000	−0.00047 (10)	0.000
S2	0.0217 (2)	0.0482 (3)	0.0329 (3)	0.00767 (18)	0.00397 (18)	0.0153 (2)
S1	0.0295 (2)	0.0264 (2)	0.0477 (3)	0.00416 (17)	0.0111 (2)	−0.00510 (19)
S3	0.0236 (2)	0.0240 (2)	0.0323 (2)	0.00054 (15)	0.00432 (17)	0.00029 (16)
N1	0.0241 (7)	0.0247 (7)	0.0386 (8)	0.0021 (6)	0.0049 (6)	0.0062 (6)
N5	0.0232 (7)	0.0263 (8)	0.0395 (8)	0.0037 (6)	0.0069 (7)	0.0030 (6)
C2	0.0201 (7)	0.0256 (8)	0.0211 (7)	0.0029 (6)	0.0005 (6)	−0.0027 (6)
C1	0.0239 (8)	0.0303 (8)	0.0203 (8)	0.0023 (6)	−0.0010 (6)	0.0037 (6)

Geometric parameters (Å, °)

Zn1—S3^{i}	2.3343 (6)	S3—C2	1.7258 (17)
Zn1—S3^{ii}	2.3343 (6)	S3—Zn1^{iv}	2.3343 (6)
Zn1—S2^{iii}	2.3560 (6)	N1—C1	1.315 (2)
Zn1—S2	2.3560 (6)	N1—N5	1.371 (2)
S2—C1	1.7060 (17)	N1—H1	0.885 (10)

S1—C1	1.7164 (18)	N5—C2	1.299 (2)
S1—C2	1.7458 (16)		
S3^{i}—Zn1—S3^{ii}	103.78 (3)	C1—N1—H1	123.2 (17)
S3^{i}—Zn1—S2^{iii}	112.572 (17)	N5—N1—H1	117.1 (17)
S3^{ii}—Zn1—S2^{iii}	110.807 (17)	C2—N5—N1	108.84 (14)
S3^{i}—Zn1—S2	110.807 (18)	N5—C2—S3	126.06 (12)
S3^{ii}—Zn1—S2	112.572 (17)	N5—C2—S1	113.90 (12)
S2^{iii}—Zn1—S2	106.44 (3)	S3—C2—S1	120.02 (10)
C1—S2—Zn1	104.35 (6)	N1—C1—S2	127.66 (14)
C1—S1—C2	89.58 (8)	N1—C1—S1	108.20 (12)
C2—S3—Zn1^{iv}	101.07 (6)	S2—C1—S1	124.04 (10)
C1—N1—N5	119.47 (15)		
S3^{i}—Zn1—S2—C1	−147.61 (7)	C1—S1—C2—N5	−0.51 (14)
S3^{ii}—Zn1—S2—C1	−31.90 (7)	C1—S1—C2—S3	177.92 (11)
S2^{iii}—Zn1—S2—C1	89.68 (7)	N5—N1—C1—S2	175.91 (13)
C1—N1—N5—C2	0.2 (2)	N5—N1—C1—S1	−0.5 (2)
N1—N5—C2—S3	−178.01 (13)	Zn1—S2—C1—N1	53.89 (17)
N1—N5—C2—S1	0.31 (19)	Zn1—S2—C1—S1	−130.19 (10)
Zn1^{iv}—S3—C2—N5	−23.57 (17)	C2—S1—C1—N1	0.55 (13)
Zn1^{iv}—S3—C2—S1	158.20 (8)	C2—S1—C1—S2	−176.05 (12)

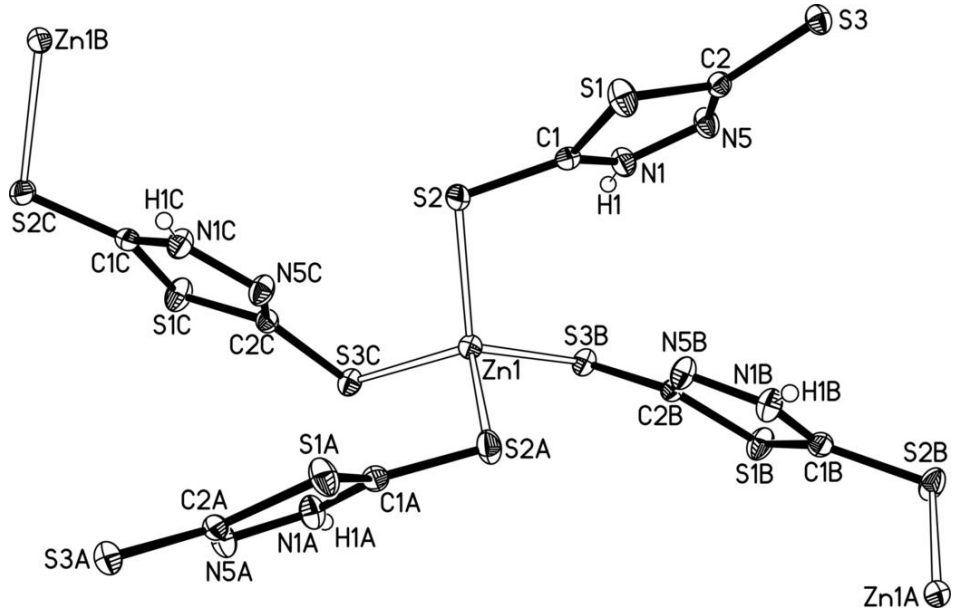
Symmetry codes: (i) *x*−1/2, −*y*+1/2, −*z*; (ii) −*x*+3/2, −*y*+1/2, *z*+1/2; (iii) −*x*+1, *y*, −*z*+1/2; (iv) −*x*+3/2, −*y*+1/2, *z*−1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···S3^{v}	0.89 (1)	2.57 (2)	3.339 (2)	146 (2)
N1—H1···S3^{ii}	0.89 (1)	2.83 (2)	3.378 (2)	121 (2)

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

Fig. 1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S1
C1
N5
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H1
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S2C
N1C
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S1A
S2A
S1B
C1B
S2B
C2A
C1A
S3A
N1A
H1A
N5A
Zn1A

Fig. 2