

Poly[bis(μ_2 -pyrimidine- $\kappa^2N:N'$)bis-(selenocyanato- κN)zinc]

Jan Boeckmann,* Thorben Reinert and Christian Näther

 Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Max-Eyth
 Strasse 2, D-24098 Kiel, Germany

Correspondence e-mail: jboeckmann@ac.uni-kiel.de

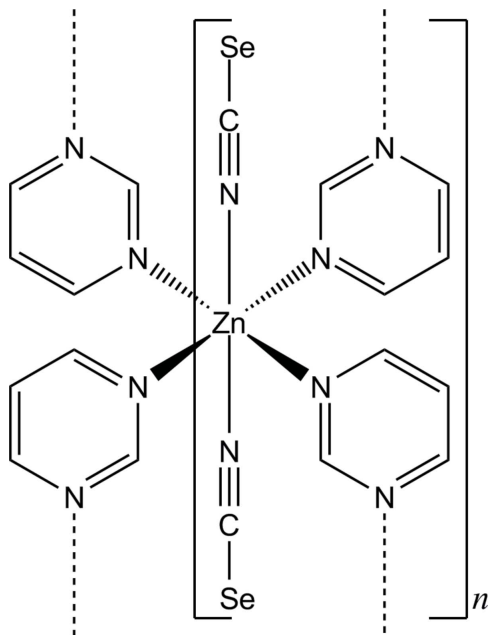
Received 10 June 2011; accepted 14 June 2011

 Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(C-C) = 0.003$ Å;
 R factor = 0.029; wR factor = 0.073; data-to-parameter ratio = 12.9.

The asymmetric unit of the title compound, $[Zn(NCSe)_2(C_4H_4N_2)_2]_n$, consists of one Zn^{2+} cation located on a special position with site symmetry $2/m$, one selenocyanate anion on a mirror plane and one pyrimidine ligand on a twofold rotation axis. The zinc cation is coordinated by six N atoms of four pyrimidine ligands and two N-bonded selenocyanate anions in mutually *trans* orientations within a slightly distorted octahedral coordination environment. The Zn atoms are μ -1,3-bridged *via* the pyrimidine ligands into a polymeric layer extending parallel to (100).

Related literature

For isotopic structures with different divalent transition metals and thiocyanate ligands, see: Bhosekar *et al.* (2010); Lloret *et al.* (1998, 1999); Wriedt *et al.* (2009); Wriedt & Näther (2010).



Experimental

Crystal data

$[Zn(NCSe)_2(C_4H_4N_2)_2]$
 $M_r = 435.51$
 Orthorhombic, $Cmca$
 $a = 9.4025$ (9) Å
 $b = 16.7146$ (10) Å
 $c = 8.7886$ (5) Å

$V = 1381.21$ (17) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 7.04$ mm⁻¹
 $T = 200$ K
 $0.28 \times 0.22 \times 0.16$ mm

Data collection

Stoe IPDS-1 diffractometer
 Absorption correction: numerical
 (*X-SHAPE* and *X-RED32*; Stoe
 & Cie, 2008)
 $T_{min} = 0.165$, $T_{max} = 0.321$

4502 measured reflections
 657 independent reflections
 638 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.073$
 $S = 1.15$
 657 reflections

51 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.40$ e Å⁻³
 $\Delta\rho_{min} = -0.81$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Zn1—N1	2.033 (3)	Zn1—N11	2.287 (2)
N1—C1—Se1	178.6 (3)		

Data collection: *X-AREA* (Stoe & Cie, 2008); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 2011); software used to prepare material for publication: *SHELXL97*.

We gratefully acknowledge financial support by the DFG (project number NA 720/3–1) and the State of Schleswig–Holstein. We thank Professor Dr Wolfgang Bensch for the opportunity to use his experimental facilities. Special thanks go to Inke Jess for her support of the single-crystal measurements.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2498).

References

- Bhosekar, G., Boeckmann, J., Jess, I. & Näther, C. (2010). *Z. Anorg. Allg. Chem.* **636**, 2595–2601.
 Brandenburg, K. (2011). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
 Lloret, F., De Munno, G., Julve, M., Cano, J., Ruiz, R. & Caneschi, A. (1998). *Angew. Chem. Int. Ed.* **37**, 135–138.
 Lloret, F., Julve, M., Cano, J. & De Munno, G. (1999). *Mol. Cryst. Liq. Cryst.* **334**, 569–585.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Stoe & Cie (2008). *X-AREA*, *X-RED32* and *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
 Wriedt, M. & Näther, C. (2010). *Z. Anorg. Allg. Chem.* **636**, 569–575.
 Wriedt, M., Sellmer, S. & Näther, C. (2009). *Inorg. Chem.* **48**, 6896–6903.

supplementary materials

Acta Cryst. (2011). E67, m948 [doi:10.1107/S1600536811023129]

Poly[bis(μ_2 -pyrimidine- $\kappa^2N:N'$)bis(selenocyanato- κN)zinc]

J. Boeckmann, T. Reinert and C. Näther

Comment

The structure determination of the title compound was performed as part of a project on the synthesis of new coordination polymers based on transition metal thiocyanates and the investigations of their thermal degradation products (Bhosekar *et al.*, 2010; Wriedt *et al.*, 2009; Wriedt & Näther, 2010)). Within this project we have reacted zinc(II) nitrate with potassium selenocyanate and pyrimidine in water, which leads to a single phase formation of the title compound, poly[bis(selenocyanato- κN)-bis(μ_2 -pyrimidine- N,N') zinc].

The title compound is isotypic with its zinc, manganese(II), iron(II), cobalt(II) and nickel(II) thiocyanato coordination polymer analogues (Bhosekar *et al.*, 2010; Lloret *et al.*, 1998; Lloret *et al.*, 1999; Wriedt *et al.*, 2009; Wriedt & Näther, 2010). In the crystal structure the zinc atoms are surrounded by six N-atoms of four pyrimidine ligands and two N-bonded selenocyanato anions in mutually *trans* orientations in a slightly distorted octahedral geometry (Fig. 1). The pyrimidine ligands bridge the metal cations forming layers which extend along the *ac* plane (Fig. 2). These layers are stacked in the direction of the crystallographic *b* axis. The Zn—Zn intralayer separation amounts to 6.4352 (4) Å, whereas the shortest Zn—Zn interlayer separation is 9.4422 (5) Å.

Experimental

The title compound was prepared by the reaction of 74.35 mg $Zn(NO_3)_2$ (0.25 mmol), 64.8 mg $KSeCN$ (0.45 mmol) and 78.8 μL pyrimidine (0.50 mmol) in 1.00 ml water at RT in a closed 3 ml snap cap vial. After one week colourless needles of the title compound were obtained.

Refinement

All H atoms were located in difference map but were positioned with idealized geometry and were refined isotropically with $U_{eq}(H) = 1.2 U_{eq}(C)$ of the parent atom using a riding model with C—H = 0.95 Å.

Figures

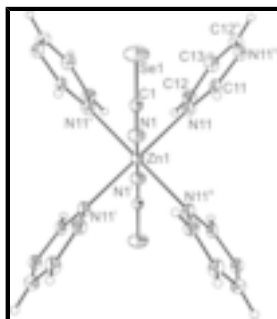


Fig. 1. : Part of the crystal structure of the title compound, showing the coordination around Zn^{2+} , with labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: i = -x, -y + 1, -z + 1; ii = -x, y, z; iii = x, -y + 1, -z + 1; iv = -x + 1/2, y, -z + 3/2.]

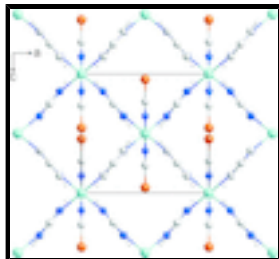


Fig. 2. : Packing diagram of the title compound with view along the crystallographic *b* axis onto the polymeric layer (aqua = zinc; orange = selenium; blue = nitrogen; grey = carbon; light-grey = hydrogen).

Poly[bis(μ_2 -pyrimidine- $\kappa^2N:N'$)bis(selenocyanato- κN)zinc]

Crystal data

[Zn(NCSe)₂(C₄H₄N₂)₂]

M_r = 435.51

Orthorhombic, *Cmca*

Hall symbol: -C 2bc 2

a = 9.4025 (9) Å

b = 16.7146 (10) Å

c = 8.7886 (5) Å

V = 1381.21 (17) Å³

Z = 4

F(000) = 832

D_x = 2.094 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

μ = 7.04 mm⁻¹

T = 200 K

Needle, colourless

0.28 × 0.22 × 0.16 mm

Data collection

Stoe IPDS-1
diffractometer

Radiation source: fine-focus sealed tube
graphite

φ scans

Absorption correction: numerical
(*X-SHAPE* and *X-RED32*; Stoe & Cie, 2008)

T_{min} = 0.165, *T_{max}* = 0.321

4502 measured reflections

657 independent reflections

638 reflections with *I* > 2σ(*I*)

R_{int} = 0.055

θ_{max} = 25.5°, θ_{min} = 3.4°

h = -11 → 11

k = -19 → 17

l = -9 → 10

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.029

wR(*F*²) = 0.073

S = 1.15

657 reflections

51 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0424*P*)² + 2.801*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.40 e Å⁻³

Δρ_{min} = -0.81 e Å⁻³

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.0000	0.5000	0.5000	0.0172 (2)
N1	0.0000	0.40527 (19)	0.6452 (4)	0.0220 (7)
C1	0.0000	0.3787 (2)	0.7666 (4)	0.0164 (7)
Se1	0.0000	0.34051 (3)	0.95337 (5)	0.0329 (2)
N11	0.1681 (2)	0.56159 (13)	0.6471 (2)	0.0191 (5)
C11	0.2500	0.5254 (2)	0.7500	0.0190 (7)
H11	0.2500	0.4685	0.7500	0.023*
C12	0.1740 (3)	0.64196 (17)	0.6445 (3)	0.0216 (6)
H12	0.1240	0.6699	0.5671	0.026*
C13	0.2500	0.6849 (2)	0.7500	0.0227 (8)
H13	0.2500	0.7417	0.7500	0.027*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0157 (3)	0.0225 (4)	0.0133 (4)	0.000	0.000	0.0033 (2)
N1	0.0240 (16)	0.0238 (17)	0.0182 (16)	0.000	0.000	0.0017 (13)
C1	0.0123 (15)	0.0190 (17)	0.0178 (18)	0.000	0.000	-0.0030 (14)
Se1	0.0494 (4)	0.0337 (3)	0.0156 (3)	0.000	0.000	0.00690 (16)
N11	0.0147 (11)	0.0240 (12)	0.0186 (11)	-0.0001 (8)	-0.0012 (9)	0.0001 (8)
C11	0.0113 (15)	0.0247 (19)	0.0210 (18)	0.000	-0.0013 (14)	0.000
C12	0.0186 (13)	0.0262 (14)	0.0198 (13)	0.0001 (11)	-0.0012 (11)	0.0026 (10)
C13	0.0192 (19)	0.0212 (19)	0.028 (2)	0.000	-0.0011 (16)	0.000

Geometric parameters (\AA , $^\circ$)

Zn1—N1 ⁱ	2.033 (3)	N11—C11	1.333 (3)
Zn1—N1	2.033 (3)	N11—C12	1.345 (4)
Zn1—N11	2.287 (2)	C11—N11 ^{iv}	1.333 (3)
Zn1—N11 ⁱ	2.287 (2)	C11—H11	0.9500
Zn1—N11 ⁱⁱ	2.287 (2)	C12—C13	1.373 (3)
Zn1—N11 ⁱⁱⁱ	2.287 (2)	C12—H12	0.9500

supplementary materials

N1—C1	1.156 (5)	C13—C12 ^{iv}	1.373 (3)
C1—Se1	1.761 (4)	C13—H13	0.9500
N1 ⁱ —Zn1—N1	180.00 (11)	C1—N1—Zn1	151.5 (3)
N1 ⁱ —Zn1—N11	90.23 (9)	N1—C1—Se1	178.6 (3)
N1—Zn1—N11	89.77 (9)	C11—N11—C12	116.2 (2)
N1 ⁱ —Zn1—N11 ⁱ	89.77 (9)	C11—N11—Zn1	125.3 (2)
N1—Zn1—N11 ⁱ	90.23 (9)	C12—N11—Zn1	117.95 (17)
N11—Zn1—N11 ⁱ	180.0	N11 ^{iv} —C11—N11	126.0 (4)
N1 ⁱ —Zn1—N11 ⁱⁱ	90.23 (9)	N11 ^{iv} —C11—H11	117.0
N1—Zn1—N11 ⁱⁱ	89.77 (9)	N11—C11—H11	117.0
N11—Zn1—N11 ⁱⁱ	87.46 (11)	N11—C12—C13	122.2 (3)
N11 ⁱ —Zn1—N11 ⁱⁱ	92.54 (11)	N11—C12—H12	118.9
N1 ⁱ —Zn1—N11 ⁱⁱⁱ	89.77 (9)	C13—C12—H12	118.9
N1—Zn1—N11 ⁱⁱⁱ	90.23 (9)	C12—C13—C12 ^{iv}	117.0 (4)
N11—Zn1—N11 ⁱⁱⁱ	92.54 (11)	C12—C13—H13	121.5
N11 ⁱ —Zn1—N11 ⁱⁱⁱ	87.45 (11)	C12 ^{iv} —C13—H13	121.5
N11 ⁱⁱ —Zn1—N11 ⁱⁱⁱ	180.0		

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

Fig. 1

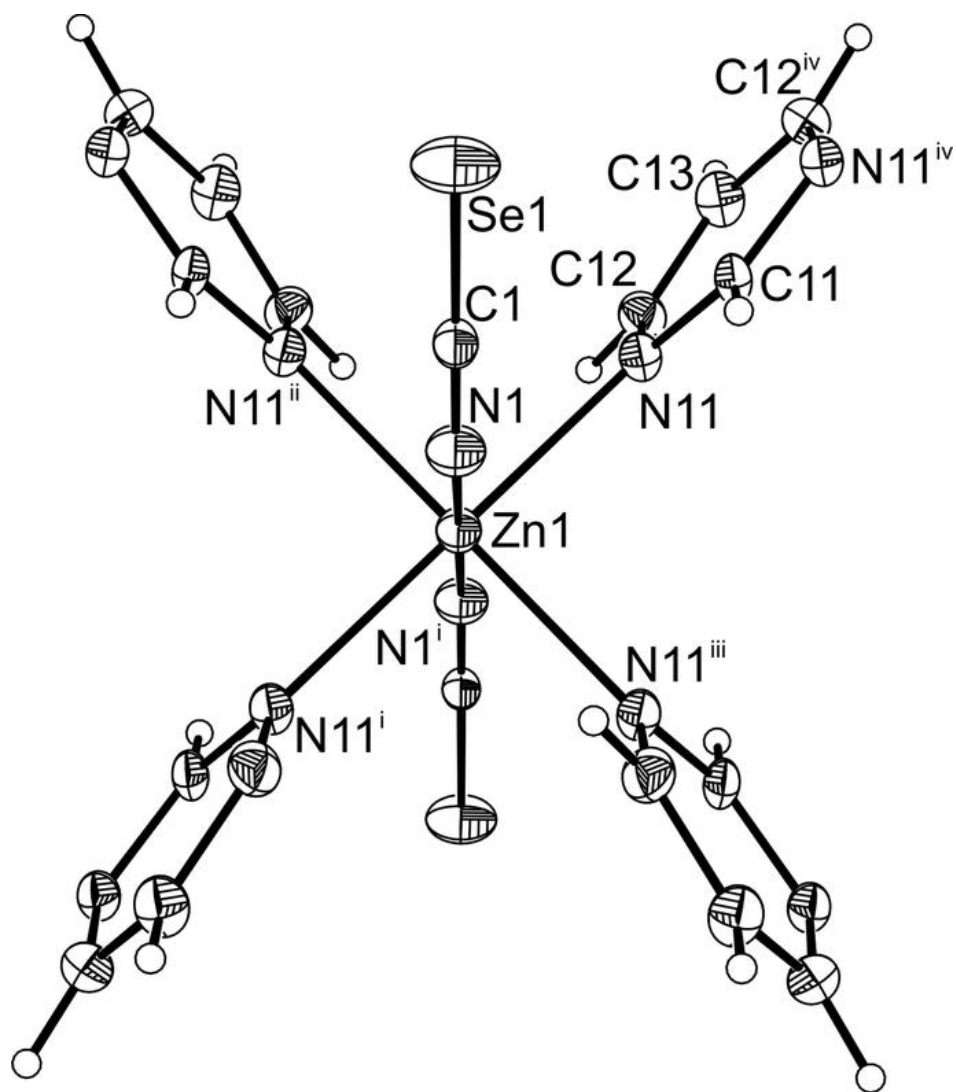


Fig. 2

