

(Tetraoxidoselenato- κ O)tris(thiourea- κ S)zinc(II)

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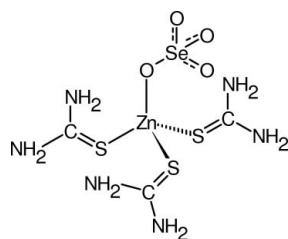
Received 7 January 2008; accepted 9 January 2008

Key indicators: single-crystal X-ray study; $T = 292$ K; mean $\sigma(\text{N}-\text{C}) = 0.003$ Å; R factor = 0.022; wR factor = 0.051; data-to-parameter ratio = 19.3.

The title structure, $[\text{Zn}(\text{SeO}_4)(\text{CH}_4\text{N}_2\text{S})_3]$, is isomorphous with sulfatotris(thiourea)zinc(II). In both structures, the Zn^{2+} cation is coordinated in a tetrahedral geometry. The corresponding intramolecular distances are quite similar except for the Se—O and S—O distances. Although the hydrogen-bonding patterns are similar, there are some differences; in the title structure all the H atoms are involved in the hydrogen-bond pattern, in contrast to the situation in sulfatotris(thiourea)zinc(II). No reproducible anomalies were detected by differential scanning calorimetry in the range 93–463 K until decomposition started at the higher temperature.

Related literature

For related literature, see: Krupková *et al.* (2007); Alex & Phillip (2001); Becker & Coppens (1974); PerkinElmer (2001); Ramabadran *et al.* (1992); Ushasree *et al.* (1998, 2000); Venkataraman *et al.* (1995).



Experimental

Crystal data

$[\text{Zn}(\text{SeO}_4)(\text{CH}_4\text{N}_2\text{S})_3]$	$V = 1395.08$ (4) Å ³
$M_r = 436.7$	$Z = 4$
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation
$a = 11.2045$ (2) Å	$\mu = 4.83$ mm ⁻¹
$b = 7.8824$ (1) Å	$T = 292$ K
$c = 15.7960$ (2) Å	$0.35 \times 0.25 \times 0.1$ mm

Data collection

Nonius KappaCCD diffractometer	23449 measured reflections
Absorption correction: Gaussian (Coppens & Hamilton, 1970)	3150 independent reflections
$T_{\min} = 0.223$, $T_{\max} = 0.602$	3004 reflections with $I > 3\sigma(I)$
	$R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$	$\Delta\rho_{\text{max}} = 0.36$ e Å ⁻³
$wR(F^2) = 0.050$	$\Delta\rho_{\text{min}} = -0.25$ e Å ⁻³
$S = 1.52$	Absolute structure: Flack (1983),
3150 reflections	1492 Friedel pairs
163 parameters	Flack parameter: -0.020 (6)
H-atom parameters constrained	

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1N1}\cdots\text{O4}^{\text{i}*}$	0.89	2.20	3.066 (3)	164
$\text{N1}-\text{H2N1}\cdots\text{O3}^{\text{ii}*}$	0.89	2.38	3.072 (3)	135
$\text{N2}-\text{H1N2}\cdots\text{O2}^{\text{ii}*}$	0.89	1.98	2.852 (3)	167
$\text{N2}-\text{H2N2}\cdots\text{S3}$	0.89	2.63	3.497 (3)	166
$\text{N3}-\text{H1N3}\cdots\text{O3}^{\text{*}}$	0.89	2.17	2.988 (3)	152
$\text{N3}-\text{H2N3}\cdots\text{O1}^{\text{iii}*}$	0.89	2.04	2.895 (3)	160
$\text{N4}-\text{H1N4}\cdots\text{O2}^{\text{iv}*}$	0.89	2.12	2.999 (3)	168
$\text{N4}-\text{H2N4}\cdots\text{S2}^{\text{iii}}$	0.89	2.86	3.643 (2)	148
$\text{N5}-\text{H1N5}\cdots\text{O3}^{\text{v}*}$	0.89	2.06	2.938 (3)	170
$\text{N5}-\text{H2N5}\cdots\text{O4}^{\text{vi}}$	0.89	2.57	3.297 (3)	139
$\text{N6}-\text{H1N6}\cdots\text{S1}$	0.89	2.73	3.577 (3)	159
$\text{N6}-\text{H2N6}\cdots\text{O4}^{\text{v}*}$	0.89	2.19	2.905 (3)	137

Symmetry codes: (i) $x + \frac{1}{2}, -y + 1, z$; (ii) $x, y + 1, z$; (iii) $x + \frac{1}{2}, -y, z$; (iv) $-x + 1, -y, z + \frac{1}{2}$; (v) $-x + 1, -y + 1, z + \frac{1}{2}$; (vi) $-x + \frac{1}{2}, y, z + \frac{1}{2}$. * indicates that the pertinent hydrogen bond is also present in $\text{Zn}[(\text{SC}(\text{NH}_2)_2)_3(\text{SO}_4)]$ (Krupková *et al.*, 2007).

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1997); program(s) used to refine structure: (*JANA2000*; Petříček *et al.*, 2000); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *JANA2000*.

Support under a CZ-US grant as part of the KONTAKT program (Czech Ministry of Education, Youth and Sports), No. 1P05ME 785, is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2062).

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supporting information

Acta Cryst. (2008). E64, m342–m343 [doi:10.1107/S1600536808000743]

(Tetraoxidoselenato- κ O)tris(thiourea- κ S)zinc(II)**Radmila Krupková, Jan Fábry, Ivana Císařová and Přemysl Vaněk****S1. Comment**

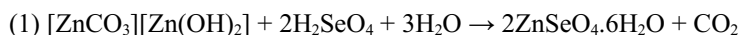
Zinc [tris(thiourea)]sulfate, isomorphous to the title structure, is reported to be a perspective semiorganic non-linear optical material (Ushasree *et al.*, 1998, 2000). It can substitute potassium dihydrogenphosphate in technical applications (Ramabadran *et al.*, 1992; Alex & Phillip, 2001). It has also an exceptionally wide acceptance angle for second harmonic generation (Ramabadran *et al.*, 1992). Its resistance against laser induced damage is good (Venkataramanan *et al.*, 1995).

We have synthesized the title compound since it is expected that it might show similar interesting properties as its known isostructural counterpart (Krupková *et al.*, 2007). As a part of our on-going study of the title compound we report here its structure determination. The investigation of dielectric and optical properties is in progress.

The common features and differences between the hydrogen-bond patterns in both isostructural compounds are shown in Tab. 1. This table shows that the stronger hydrogen bonds are common for both isostructural compounds.

S2. Experimental

The title compound has been prepared in a similar way as zinc[tris(thiourea)] sulfate. The preparation was carried out in two steps according to following equations:



5.0 g (0.222 M) of $\text{ZnCO}_3[\text{Zn}(\text{OH})_2]$ dissolved in 3.6 g (0.2 M) of distilled H_2O reacted with 6.45 g (96%) H_2SeO_4 (0.0427 M) at room temperature. After the neutralization white suspension was obtained. The suspension into which had been poured 50 ml of distilled H_2O was heated at 60°C for 30 minutes. The solution became clearer and its pH=4.

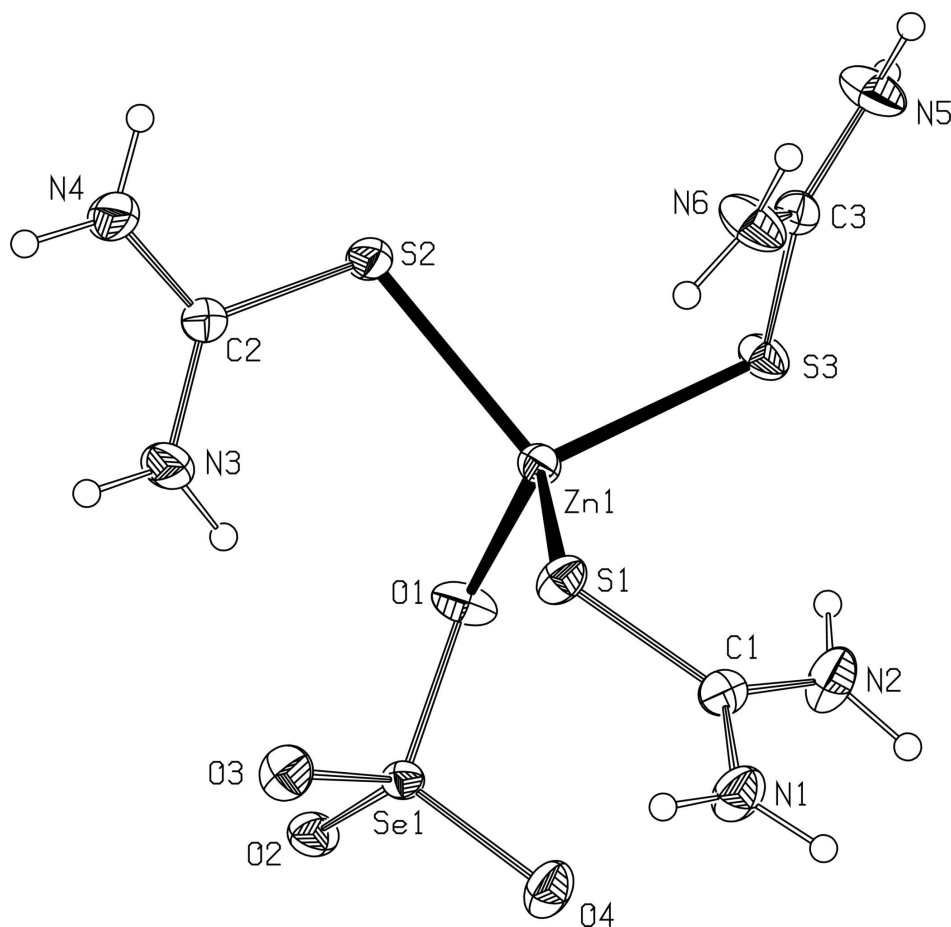
Then, at 50°C was added 10.14 g (0.1332 M) of thiourea. The solution became orange-coloured and under stirring it was kept at 50°C for another 10 minutes. An orange precipitate has developed to which another 100 ml of distilled water was added. The mixture was stirred for another 20 minutes and then cooled down to room temperature. After two days, transparent crystals of length of 0.5 mm appeared at the walls of the beaker while an orange precipitate covered its bottom. Next day the precipitate was filtered off, some orange-tinged crystals have been isolated as seeds that were introduced into the filtrate. After a week clear transparent crystals appeared of the size of 1 cm, of the similar *HABITUS* as zinc[tris(thiourea)] sulfate (Alex & Phillip, 2001).

S3. Refinement

All the H atoms were discernible in the difference Fourier map and even could be refined. Nevertheless, their coordinates were constrained in riding motion formalism: The pertinent distances equalled to 0.89 Å and $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{N})$.

The calorimetric experiments were performed on PerkinElmer DSC 7 and Pyris Diamond differential scanning calorimeters using PYRIS Software (PerkinElmer, 2001), with $m = 30$ mg, a temperature interval of 93–466 K and scanning rate of 10 K/min. No reproducible DSC anomalies were detected until the symptoms of decomposition at 463

K.

**Figure 1**

View of the title molecule with anisotropic displacement parameters shown at the 30% probability level.

(Tetraoxidoselenato- κ O)tris(thiourea- κ S)zinc(II)

Crystal data

[Zn(SeO₄)(CH₄N₂S)₃]

$M_r = 436.7$

Orthorhombic, *Pca*2₁

Hall symbol: P 2c -2ac

$a = 11.2045$ (2) Å

$b = 7.8824$ (1) Å

$c = 15.7960$ (2) Å

$V = 1395.08$ (4) Å³

$Z = 4$

$F(000) = 864$

$D_x = 2.079$ Mg m⁻³

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

Cell parameters from 14388 reflections

$\theta = 1.0$ – 27.5°

$\mu = 4.83$ mm⁻¹

$T = 292$ K

Prism, colourless

$0.35 \times 0.25 \times 0.1$ mm

Data collection

Nonius KappaCCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: gaussian
(Coppens & Hamilton, 1970)

$T_{\min} = 0.223$, $T_{\max} = 0.602$

23449 measured reflections

3150 independent reflections

3004 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.039$
 $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.2^\circ$
 $h = -14 \rightarrow 14$

$k = -10 \rightarrow 10$
 $l = -19 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.050$
 $S = 1.52$
 3150 reflections
 163 parameters
 0 restraints
 48 constraints
 H-atom parameters constrained

Weighting scheme based on measured s.u.'s $w =$
 $1/[\sigma^2(I) + 0.0004I^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.005$
 $\Delta\rho_{\text{max}} = 0.36 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.25 \text{ e } \text{\AA}^{-3}$
 Extinction correction: B-C type 1 Lorentzian
 isotropic (Becker & Coppens, 1974)
 Extinction coefficient: 1.65 (5)
 Absolute structure: Flack (1983), 1492 Friedel
 pairs
 Absolute structure parameter: -0.020 (6)

Special details

Refinement. The Flack parameter converged to the value -0.020 (6), so it was excluded from the final refinement.

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	0.43588 (3)	0.34032 (3)	0.42203 (2)	0.02479 (9)
Se1	0.37373 (2)	0.15124 (3)	0.247798	0.02293 (7)
O1	0.34191 (19)	0.1846 (2)	0.34926 (13)	0.0363 (6)
O2	0.29853 (18)	-0.0173 (2)	0.22066 (12)	0.0317 (6)
O3	0.51627 (17)	0.1169 (2)	0.23987 (16)	0.0372 (6)
O4	0.33169 (19)	0.3147 (2)	0.19315 (15)	0.0392 (6)
S1	0.57849 (6)	0.49589 (8)	0.34906 (5)	0.03060 (19)
C1	0.5054 (2)	0.6544 (2)	0.29483 (16)	0.0290 (8)
N1	0.5667 (2)	0.7339 (3)	0.23498 (16)	0.0401 (8)
N2	0.3957 (2)	0.7021 (3)	0.31154 (18)	0.0447 (9)
S2	0.52313 (7)	0.17226 (9)	0.52667 (5)	0.0327 (2)
C2	0.64030 (18)	0.0636 (3)	0.48127 (17)	0.0314 (8)
N3	0.6501 (2)	0.0405 (4)	0.39895 (16)	0.0468 (9)
N4	0.7222 (2)	0.0025 (3)	0.53155 (17)	0.0460 (9)
S3	0.29592 (6)	0.50137 (8)	0.49583 (5)	0.03039 (18)
C3	0.3845 (2)	0.5992 (3)	0.57094 (15)	0.0295 (7)
N5	0.3360 (3)	0.6436 (3)	0.64329 (16)	0.0453 (9)
N6	0.4979 (2)	0.6351 (3)	0.55684 (18)	0.0455 (9)
H1n1	0.63954	0.698311	0.22123	0.0482*
H2n1	0.534956	0.822806	0.208546	0.0482*
H1n2	0.359482	0.77757	0.278428	0.0536*
H2n2	0.35742	0.658874	0.355973	0.0536*
H1n3	0.59099	0.071809	0.364689	0.0562*
H2n3	0.71576	-0.006424	0.377612	0.0562*
H1n4	0.718708	0.022995	0.58691	0.0552*
H2n4	0.781526	-0.059533	0.510475	0.0552*
H1n5	0.373839	0.715311	0.677503	0.0543*

H2n5	0.265147	0.601891	0.658106	0.0543*
H1n6	0.535457	0.589501	0.512718	0.0546*
H2n6	0.536798	0.705007	0.591462	0.0546*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02747 (16)	0.02426 (15)	0.02265 (16)	0.00004 (11)	0.00160 (12)	-0.00106 (11)
Se1	0.02532 (13)	0.02427 (12)	0.01920 (13)	-0.00028 (8)	0.00161 (10)	0.00140 (11)
O1	0.0414 (12)	0.0444 (10)	0.0231 (9)	-0.0183 (9)	0.0063 (9)	-0.0069 (8)
O2	0.0396 (10)	0.0290 (9)	0.0264 (10)	-0.0047 (7)	-0.0031 (8)	-0.0027 (6)
O3	0.0268 (9)	0.0441 (10)	0.0408 (12)	0.0020 (8)	0.0042 (10)	0.0047 (10)
O4	0.0401 (11)	0.0336 (9)	0.0441 (12)	0.0049 (8)	0.0048 (10)	0.0138 (9)
S1	0.0252 (3)	0.0343 (3)	0.0323 (3)	0.0001 (2)	0.0004 (3)	0.0102 (3)
C1	0.0314 (15)	0.0266 (12)	0.0291 (14)	-0.0051 (10)	-0.0037 (11)	0.0013 (10)
N1	0.0423 (14)	0.0369 (12)	0.0412 (15)	0.0019 (10)	0.0037 (11)	0.0138 (11)
N2	0.0364 (14)	0.0400 (13)	0.0575 (18)	0.0084 (12)	0.0078 (13)	0.0189 (12)
S2	0.0354 (4)	0.0400 (4)	0.0227 (3)	0.0119 (3)	0.0055 (3)	0.0041 (2)
C2	0.0356 (14)	0.0326 (13)	0.0260 (14)	0.0060 (11)	0.0011 (11)	0.0012 (10)
N3	0.0477 (16)	0.0652 (17)	0.0276 (13)	0.0260 (14)	0.0023 (11)	-0.0063 (12)
N4	0.0435 (15)	0.0629 (17)	0.0315 (13)	0.0267 (12)	-0.0011 (11)	0.0021 (12)
S3	0.0228 (3)	0.0406 (3)	0.0279 (3)	0.0011 (2)	-0.0020 (3)	-0.0110 (3)
C3	0.0324 (13)	0.0296 (12)	0.0266 (14)	0.0035 (10)	-0.0047 (11)	-0.0045 (11)
N5	0.0384 (15)	0.0655 (17)	0.0320 (14)	-0.0047 (12)	0.0003 (12)	-0.0218 (12)
N6	0.0328 (14)	0.0620 (17)	0.0418 (16)	-0.0102 (11)	0.0010 (12)	-0.0253 (12)

Geometric parameters (Å, °)

Zn1—O1	1.984 (2)	C3—N5	1.313 (4)
Zn1—S1	2.3207 (8)	C3—N6	1.321 (3)
Zn1—S2	2.3330 (8)	N1—H1n1	0.89
Zn1—S3	2.3302 (7)	N1—H2n1	0.89
Se1—O1	1.663 (2)	N2—H1n2	0.89
Se1—O2	1.6307 (18)	N2—H2n2	0.89
Se1—O3	1.6246 (19)	N3—H1n3	0.89
Se1—O4	1.621 (2)	N3—H2n3	0.89
S1—C1	1.722 (2)	N4—H1n4	0.89
C1—N1	1.326 (3)	N4—H2n4	0.89
C1—N2	1.313 (4)	N5—H1n5	0.89
S2—C2	1.724 (2)	N5—H2n5	0.89
C2—N3	1.317 (4)	N6—H1n6	0.89
C2—N4	1.306 (3)	N6—H2n6	0.89
S3—C3	1.729 (2)		
Se1—Zn1—S1	88.22 (2)	H1n1—N1—H2n1	120.0
Se1—Zn1—S2	115.80 (2)	C1—N2—H1n2	120.0
Se1—Zn1—S3	122.45 (2)	C1—N2—H2n2	120.0
S1—Zn1—S2	111.31 (3)	H1n2—N2—H2n2	120.0

S1—Zn1—S3	115.09 (3)	C2—N3—H1n3	120.0
S2—Zn1—S3	103.70 (3)	C2—N3—H2n3	120.0
O1—Se1—O2	105.75 (10)	H1n3—N3—H2n3	120.0
O1—Se1—O3	108.14 (11)	C2—N4—H1n4	120.0
O1—Se1—O4	108.98 (11)	C2—N4—H2n4	120.0
O2—Se1—O3	110.62 (10)	H1n4—N4—H2n4	120.0
O2—Se1—O4	110.95 (10)	C3—N5—H1n5	120.0
O3—Se1—O4	112.15 (11)	C3—N5—H2n5	120.0
S1—C1—N1	116.84 (19)	H1n5—N5—H2n5	120.0
S1—C1—N2	123.6 (2)	C3—N6—H1n6	120.0
N1—C1—N2	119.5 (2)	C3—N6—H2n6	120.0
S2—C2—N3	122.86 (19)	H1n6—N6—H2n6	120.0
S2—C2—N4	117.7 (2)	H1n1—N1—H2n1	120.0
N3—C2—N4	119.4 (2)	H1n2—N2—H2n2	120.0
S3—C3—N5	118.6 (2)	H1n3—N3—H2n3	120.0
S3—C3—N6	122.2 (2)	H1n4—N4—H2n4	120.0
N5—C3—N6	119.2 (2)	H1n5—N5—H2n5	120.0
C1—N1—H1n1	120.0	H1n6—N6—H2n6	120.0
C1—N1—H2n1	120.0		
