

Redetermination of sulfatotris(thiourea)zinc(II)

Radmila Krupková,^a Jan Fábry,^{a*} Ivana Císařová^b and Přemysl Vaněk^a^aInstitute of Physics, Czech Academy of Sciences, Na Slovance 2, 182 21 Praha 8, Czech Republic, and ^bDepartment of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 8, 128 43 Praha 2, Czech Republic
Correspondence e-mail: fabry@fzu.cz

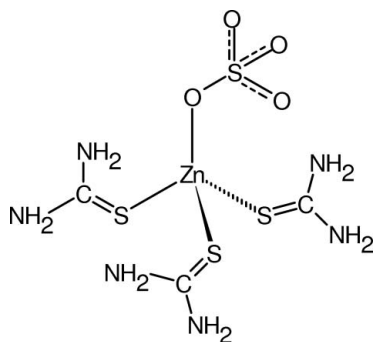
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Key indicators: single-crystal X-ray study; $T = 292$ K; mean $\sigma(\text{N}-\text{C}) = 0.003$ Å; R factor = 0.020; wR factor = 0.053; data-to-parameter ratio = 18.9.

In the title compound, $[\text{Zn}(\text{SO}_4)(\text{CH}_4\text{N}_2\text{S})_3]$, the Zn^{2+} cation is coordinated in a tetrahedral geometry by one O atom from a sulfate anion and the S atoms from three thiourea ligands. There are weak $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds in the structure, some of which are bifurcated. The same crystal has also been investigated at 110 K, below a reported phase transition at 120 K. No change in the space group below 120 K was observed. On the other hand, the differences between the fractional coordinates of the corresponding atoms in the determinations at 292 and 110 K are as large as about 0.007 for the non-H atoms. Differential scanning calorimetry did not detect reproducible anomalies in the interval 93–503 K up to the melting point.

Related literature

For previous structure determinations, see: Krupková *et al.* (2007); Andreetti *et al.* (1968). Ramabadran *et al.* (1992). For related literature, see: Alex & Philip (2001); Becker & Coppens (1974); Ouassaid *et al.* (1998); PerkinElmer (2001); Ushasree *et al.* (1998, 2000); Venkataramanan, Dhanaraj, Wadhawan *et al.* (1995); Venkataramanan, Subramanian & Bhat (1995).



Experimental

Crystal data

$[\text{Zn}(\text{SO}_4)(\text{CH}_4\text{N}_2\text{S})_3]$
 $M_r = 389.8$
 Orthorhombic, $Pca2_1$
 $a = 11.1738$ (2) Å
 $b = 7.8011$ (1) Å
 $c = 15.5424$ (2) Å
 $V = 1354.80$ (3) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 2.44$ mm⁻¹
 $T = 292$ K
 $0.2 \times 0.2 \times 0.2$ mm

Data collection

Nonius KappaCCD diffractometer
 Absorption correction: Gaussian (Coppens & Hamilton, 1970)
 $T_{\min} = 0.394$, $T_{\max} = 0.591$
 23153 measured reflections
 3081 independent reflections
 2961 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.053$
 $S = 1.77$
 3081 reflections
 163 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.22$ e Å⁻³
 $\Delta\rho_{\min} = -0.22$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1N1}\cdots\text{O4}^{\text{i}}$	0.89	2.18	3.064 (3)	171
$\text{N1}-\text{H2N1}\cdots\text{O3}^{\text{ii}}$	0.89	2.39	3.038 (2)	130
$\text{N1}-\text{H2N1}\cdots\text{S3}^{\text{iii}}$	0.89	2.85	3.467 (2)	128
$\text{N2}-\text{H1N2}\cdots\text{O2}^{\text{ii}}$	0.89	1.96	2.848 (2)	177
$\text{N2}-\text{H2N2}\cdots\text{S4}$	0.89	2.66	3.496 (2)	157
$\text{N3}-\text{H1N3}\cdots\text{O3}$	0.89	2.14	2.992 (2)	159
$\text{N3}-\text{H2N3}\cdots\text{O1}^{\text{iv}}$	0.89	2.04	2.903 (3)	163
$\text{N3}-\text{H2N3}\cdots\text{O2}^{\text{iv}}$	0.89	2.55	3.194 (2)	130
$\text{N4}-\text{H1N4}\cdots\text{O2}^{\text{v}}$	0.89	2.13	3.004 (3)	167
$\text{N4}-\text{H2N4}\cdots\text{S3}^{\text{iv}}$	0.89	2.83	3.601 (2)	146
$\text{N5}-\text{H1N5}\cdots\text{O3}^{\text{vi}}$	0.89	2.12	2.965 (3)	159
$\text{N6}-\text{H1N6}\cdots\text{S2}$	0.89	2.70	3.555 (2)	160
$\text{N6}-\text{H2N6}\cdots\text{O4}^{\text{vi}}$	0.89	2.14	2.895 (3)	143

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *HKL SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *JANA2000* (Petříček *et al.*, 2000); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *JANA2000*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2074).

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supplementary materials

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Redetermination of sulfatotris(thiourea)zinc(II)

R. Krupková, J. Fábry, I. Císarová and P. Vanek

Comment

The title structure is 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 & Philip, 2001). It has an exceptionally wide acceptance angle for second harmonic generation (Ramabadran *et al.*, 1992). Its resistance against laser induced damage is good (Venkataramanan, Subramanian & Bhat, 1995). However, the published structure determination (Andreetti *et al.*, 1968) does not meet today's demands: The intensities in the cited work were provided *via* film technique; the H atoms have not been observed directly and the *R*-factors are higher than 0.09.

The second structure determination (Ushasree *et al.*, 1998) has not provided the coordinates or the *R*-factors; the authors have only published the unit-cell parameters that corresponded to the those from the former structure determination though the the structure analysis has been performed.

Our structure determinations (this work and the low temperature study at 110 K (Krupková *et al.*, 2007) have confirmed the previous structural studies.

Ouassaid *et al.* (1998) have reported two phase transitions at 60±2 and 122±2 K. These phase transitions have been measured by polarized Raman scattering. Thermal gravimetric analysis (TGA) performed by Ushasree *et al.* (1998) revealed that the compound starts to decompose at 473 K. However, our experiments by differential scanning calorimetry revealed no phase transitions in the temperature interval 93–533 K. The comparison of the present structure determination with that at 110 K confirmed the same space group, however, some of the atoms were quite displaced with regard to the average value of the pertinent standard uncertainties (the largest displacement refers to the *y*-coordinate of N6 ($\Delta = 0.00721$ in fractional coordinates). The lattice parameters at 110 K are: *a* = 11.0661 (2), *b* = 7.7339 (3), *c* = 15.5524 (3) Å. The indicators of the refinement are: $R_{\text{obs}} = 0.0180$, $wR_{\text{obs}} = 0.0517$, $R_{\text{all}} = 0.0188$, $wR_{\text{all}} = 0.0519$, $S_{\text{all}} = 1.57$, $S_{\text{obs}} = 1.59$, $\rho_{\text{max}} = 0.17$, $\rho_{\text{min}} = -0.24$. The unconstrained refinement of the H atoms found in the difference Fourier map for the structure determination at 110 K yielded the positions of the H atoms that were displaced in the interval 0.71–0.98 Å from the carrier nitrogen.

The elastic properties were determined by Alex & Philip (2001).

Since our colleagues have been interested in the dielectric properties, we have grown the crystals that were also suitable for the structure determination. Here we report the redetermination of the structure at room temperature. A tendency to twinning should be stressed that is probably due to the ratio of the lattice parameters *b* and *c*.

Experimental

The preparation followed the procedure described by Venkataramanan, Dhanaraj, Wadhawan *et al.* (1995), i. e. according to the reaction scheme: $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + 3 \text{CS}(\text{NH}_2)_2 \rightarrow \text{Zn}[\text{CS}(\text{NH}_2)_2]_3\text{SO}_4$

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The used amounts were 40 g (0.139 M) of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 31.67 g (0.416 M) of $\text{CS}(\text{NH}_2)_2$ and 440 g (24.42 M) of H_2O . The mixture was stirred for ten minutes at 303 K. A clear solution was filtered yielding pH = 3.5. Then the mixture was left at 299–303 K for several days until crystals developed though the first crystals appeared at the surface after several hours.

The crystals were taken off, 20 g of them were dissolved at 323 K in 340 ml of distilled water. The solution was cooled down to room temperature and clear block-like crystals up to 5 mm as a maximal length developed in a course of several days.

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 absolute configuration could be clearly determined. The Flack parameter included into the refinement equalled to $-0.009(7)$, however, in the submitted refinement the Flack parameter has not been used because of unambiguity of its value and the crystal was supposed to be in one domain state of the inversion twin only.

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 93–533 K and scanning rate of 10 K/min. No reproducible DSC anomalies were detected until melting at 503 K. Before performing calorimetric measurement the sample was ground in an agate mortar and left in a desiccator for 5 days over P_4O_{10} .

Figures

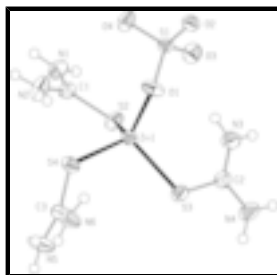


Fig. 1. View of the title molecule with anharmonic displacement parameters shown at the 50% probability level.

sulfatotris(thiourea)zinc(II)

Crystal data

$[\text{Zn}(\text{SO}_4)(\text{C}_1\text{H}_4\text{N}_2\text{S})_3]$

$M_r = 389.8$

Orthorhombic, $Pca2_1$

Hall symbol: P 2c -2ac

$a = 11.1738(2)$ Å

$b = 7.8011(1)$ Å

$c = 15.5424(2)$ Å

$V = 1354.80(3)$ Å³

$Z = 4$

$D_x = 1.910$ Mg m⁻³

Melting point: 533 K

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 14983 reflections

$\theta = 1\text{--}27.5^\circ$

$\mu = 2.44$ mm⁻¹

$T = 292$ K

Block, colourless

$0.2 \times 0.2 \times 0.2$ mm

$F_{000} = 792$

Data collection

Nonius KappaCCD diffractometer	3081 independent reflections
Radiation source: fine-focus sealed tube	2961 reflections with $I > 3\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.035$
$T = 292$ K	$\theta_{\text{max}} = 27.5^\circ$
ω scans	$\theta_{\text{min}} = 2.6^\circ$
Absorption correction: Gaussian (Coppens & Hamilton, 1970)	$h = -14 \rightarrow 14$
$T_{\text{min}} = 0.394$, $T_{\text{max}} = 0.591$	$k = -9 \rightarrow 10$
23153 measured reflections	$l = -20 \rightarrow 18$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.020$	Weighting scheme based on measured s.u.'s $w = 1/[\sigma^2(I) + 0.0004I^2]$
$wR(F^2) = 0.053$	$(\Delta/\sigma)_{\text{max}} = 0.026$
$S = 1.77$	$\Delta\rho_{\text{max}} = 0.22 \text{ e } \text{\AA}^{-3}$
3081 reflections	$\Delta\rho_{\text{min}} = -0.22 \text{ e } \text{\AA}^{-3}$
163 parameters	Extinction correction: B-C type 1 Lorentzian isotropic (Becker & Coppens, 1974)
48 constraints	Extinction coefficient: 1.25 (6)
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: difference Fourier map	

Special details

Refinement. The Flack parameter converged to the value -0.009 (7), 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	0.563754 (19)	0.65888 (3)	0.58241	0.02306 (7)
S1	0.62660 (5)	0.84508 (5)	0.75220 (3)	0.02168 (14)
O1	0.65466 (15)	0.81436 (18)	0.65829 (10)	0.0325 (5)
O2	0.69547 (13)	0.99703 (17)	0.77799 (10)	0.0299 (5)
O3	0.49795 (13)	0.8767 (2)	0.76043 (12)	0.0337 (5)
O4	0.66348 (15)	0.69514 (19)	0.80145 (11)	0.0353 (5)
S2	0.41946 (5)	0.49762 (7)	0.65242 (4)	0.02863 (15)
C1	0.49270 (18)	0.3368 (2)	0.70768 (14)	0.0271 (6)
N1	0.43115 (17)	0.2539 (2)	0.76720 (12)	0.0359 (6)
H1N1	0.355183	0.281748	0.777261	0.0431*

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H2N1	0.465667	0.170291	0.797218	0.0431*
N2	0.60402 (17)	0.2915 (2)	0.69193 (16)	0.0436 (7)
H1N2	0.63528	0.200505	0.718132	0.0523*
H2N2	0.648045	0.351947	0.655082	0.0523*
S3	0.47868 (5)	0.83168 (7)	0.47628 (4)	0.03033 (16)
C2	0.36195 (14)	0.9411 (3)	0.52285 (13)	0.0294 (6)
N3	0.34955 (16)	0.9625 (3)	0.60612 (11)	0.0423 (7)
N4	0.28047 (17)	1.0067 (3)	0.47049 (15)	0.0475 (7)
S4	0.70388 (4)	0.49833 (7)	0.50572 (4)	0.02851 (15)
C3	0.61496 (17)	0.3997 (2)	0.42887 (12)	0.0281 (6)
N5	0.6647 (2)	0.3571 (3)	0.35501 (13)	0.0485 (8)
H1N5	0.621843	0.303184	0.315059	0.0582*
H2N5	0.741154	0.382314	0.345092	0.0582*
N6	0.50170 (18)	0.3643 (3)	0.44185 (15)	0.0465 (7)
H1N6	0.464178	0.406556	0.487697	0.0558*
H2N6	0.462341	0.298047	0.404815	0.0558*
H1N3	0.406905	0.927697	0.641814	0.0508*
H2N3	0.283796	1.011784	0.626906	0.0508*
H1N4	0.284995	0.98732	0.414156	0.057*
H2N4	0.221175	1.070178	0.491633	0.057*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02518 (13)	0.02338 (12)	0.02062 (13)	-0.00010 (8)	0.00152 (9)	-0.00070 (9)
S1	0.0236 (2)	0.0245 (2)	0.0169 (2)	0.00020 (16)	0.00171 (17)	0.00148 (16)
O1	0.0370 (9)	0.0403 (8)	0.0203 (8)	-0.0149 (7)	0.0062 (6)	-0.0067 (6)
O2	0.0364 (8)	0.0289 (7)	0.0245 (8)	-0.0035 (6)	-0.0026 (6)	-0.0036 (5)
O3	0.0224 (8)	0.0409 (8)	0.0377 (9)	0.0022 (7)	0.0050 (6)	0.0041 (7)
O4	0.0373 (9)	0.0328 (7)	0.0359 (9)	0.0047 (7)	0.0032 (7)	0.0130 (6)
S2	0.0227 (2)	0.0332 (3)	0.0299 (3)	-0.00017 (19)	0.00000 (19)	0.0101 (2)
C1	0.0269 (11)	0.0266 (10)	0.0279 (11)	-0.0041 (7)	-0.0056 (9)	0.0024 (7)
N1	0.0383 (11)	0.0362 (11)	0.0333 (10)	-0.0010 (8)	-0.0006 (8)	0.0109 (9)
N2	0.0334 (10)	0.0385 (11)	0.0589 (14)	0.0058 (9)	0.0048 (10)	0.0201 (10)
S3	0.0316 (3)	0.0385 (3)	0.0209 (3)	0.0111 (2)	0.0057 (2)	0.00429 (19)
C2	0.0305 (10)	0.0316 (10)	0.0260 (11)	0.0045 (8)	0.0018 (9)	0.0029 (8)
N3	0.0422 (11)	0.0580 (12)	0.0269 (11)	0.0238 (10)	0.0024 (8)	-0.0043 (8)
N4	0.0446 (12)	0.0665 (14)	0.0313 (11)	0.0299 (10)	-0.0023 (10)	0.0023 (9)
S4	0.0208 (2)	0.0392 (3)	0.0255 (3)	0.00156 (19)	-0.00193 (19)	-0.01058 (18)
C3	0.0304 (10)	0.0297 (10)	0.0243 (10)	0.0040 (9)	-0.0034 (8)	-0.0049 (8)
N5	0.0403 (12)	0.0759 (16)	0.0291 (11)	-0.0023 (11)	0.0010 (9)	-0.0243 (10)
N6	0.0329 (11)	0.0620 (14)	0.0446 (14)	-0.0099 (10)	-0.0018 (10)	-0.0263 (10)

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

Zn1—O1	1.9732 (15)	N2—H1N2	0.89
Zn1—S2	2.3165 (6)	N2—H2N2	0.89
Zn1—S3	2.3326 (6)	C2—N3	1.312 (3)
Zn1—S4	2.3326 (6)	C2—N4	1.324 (3)

S1—O1	1.5120 (17)	N3—H1N3	0.89
S1—O2	1.4691 (14)	N3—H2N3	0.89
S1—O3	1.4641 (16)	N4—H1N4	0.89
S1—O4	1.4573 (16)	N4—H2N4	0.89
S2—C1	1.7266 (19)	C3—N5	1.318 (3)
S3—C2	1.7188 (18)	C3—N6	1.311 (3)
S4—C3	1.7336 (19)	N5—H1N5	0.89
C1—N1	1.322 (3)	N5—H2N5	0.89
C1—N2	1.316 (3)	N6—H1N6	0.89
N1—H1N1	0.89	N6—H2N6	0.89
N1—H2N1	0.89		
O1—Zn1—S2	114.29 (5)	H1N1—N1—H2N1	120.0
O1—Zn1—S3	106.09 (5)	C1—N2—H1N2	120.0
O1—Zn1—S4	106.85 (5)	C1—N2—H2N2	120.0
S2—Zn1—S3	111.24 (2)	H1N2—N2—H2N2	120.0
S2—Zn1—S4	114.56 (2)	N3—C2—N4	118.98 (18)
S3—Zn1—S4	102.86 (2)	C2—N3—H1N3	120.0
O1—S1—O2	106.41 (9)	C2—N3—H2N3	120.0
O1—S1—O3	108.34 (10)	H1N3—N3—H2N3	120.0
O1—S1—O4	108.74 (9)	C2—N4—H1N4	120.0
O2—S1—O3	110.76 (9)	C2—N4—H2N4	120.0
O2—S1—O4	110.87 (9)	H1N4—N4—H2N4	120.0
O3—S1—O4	111.53 (10)	N5—C3—N6	119.2 (2)
Zn1—S2—C1	107.35 (7)	C3—N5—H1N5	120.0
Zn1—S3—C2	107.37 (7)	C3—N5—H2N5	120.0
Zn1—S4—C3	101.86 (7)	H1N5—N5—H2N5	120.0
N1—C1—N2	119.39 (18)	C3—N6—H1N6	120.0
C1—N1—H1N1	120.0	C3—N6—H2N6	120.0
C1—N1—H2N1	120.0	H1N6—N6—H2N6	120.0

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1N1 \cdots O4 ⁱ	0.89	2.18	3.064 (3)	171
N1—H2N1 \cdots O3 ⁱⁱ	0.89	2.39	3.038 (2)	130
N1—H2N1 \cdots S3 ⁱⁱⁱ	0.89	2.85	3.467 (2)	128
N2—H1N2 \cdots O2 ⁱⁱ	0.89	1.96	2.848 (2)	177
N2—H2N2 \cdots S4	0.89	2.66	3.496 (2)	157
N3—H1N3 \cdots O3	0.89	2.14	2.992 (2)	159
N3—H2N3 \cdots O1 ^{iv}	0.89	2.04	2.903 (3)	163
N3—H2N3 \cdots O2 ^{iv}	0.89	2.55	3.194 (2)	130
N4—H1N4 \cdots O2 ^v	0.89	2.13	3.004 (3)	167
N4—H2N4 \cdots S3 ^{iv}	0.89	2.83	3.601 (2)	146
N5—H1N5 \cdots O3 ^{vi}	0.89	2.12	2.965 (3)	159
N6—H1N6 \cdots S2	0.89	2.70	3.555 (2)	160
N6—H2N6 \cdots O4 ^{vi}	0.89	2.14	2.895 (3)	143

supplementary materials

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

Fig. 1

