

## Short Communications

### The Crystal and Molecular Structure of Sulfato-bis(thiosemicarbazide)zinc(II)

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Earlier crystallographic investigations have shown that coordination compounds formed with the unsymmetrical ligand thiosemicarbazide (Htsc) often exist as different isomers. It is remarkable that the sulfate salts of bis(thiosemicarbazide) complexes with the divalent ions of Fe, Cd and Ni contain different geometrical isomers in the crystalline state. Cd(Htsc)<sub>2</sub>SO<sub>4</sub> and Fe(Htsc)<sub>2</sub>SO<sub>4</sub> are isostructural and contain hexacoordinated metal ions with *trans* sulfate groups, that bridge between different complexes with the two thiosemicarbazide ligands *cis* and *trans* respectively.<sup>1–3</sup> Ni is four coordinated in Ni(Htsc)<sub>2</sub>SO<sub>4</sub> but the crystals of this compound contain both *cis* and *trans* isomers of Ni(Htsc)<sub>2</sub><sup>2+</sup>. Bauer, Christensen and Larsen<sup>4</sup> have studied the  $\gamma$ -ray perturbed angular correlation spectra of the <sup>111</sup>Cd isotope in the surroundings of Cd in Cd(Htsc)<sub>2</sub>SO<sub>4</sub> and Zn in Zn(Htsc)<sub>2</sub>SO<sub>4</sub>. From the spectroscopic data they determined the electric field gradient for Cd in the two salts. The versatile stereochemistry of bis(thiosemicarbazide) complexes, combined with the lack of structural data for Zn(Htsc)<sub>2</sub>SO<sub>4</sub> initiated this structure determination for the latter compound. During the development of this work it was realized that the crystals of the Zn complex have unit cell dimensions similar to those of the analogous Cu complex, Cu(Htsc)<sub>2</sub>SO<sub>4</sub>.<sup>5</sup>

**Structure Determination.** A sample of the compound crystallized from aqueous solution was kindly supplied by Dr. Erik Larsen. The crystals were characterized by Weissenberg and precession photographs. The X-Ray intensity data were measured on the CAD4-4F four circle diffractometer at Chemical Laboratory B, The Technical University in Denmark, using monochromated MoK $\alpha$  radiation ( $\lambda=0.71073$  Å). A crystal of the size 0.2×0.1×0.3 mm was selected for the data collection performed at 23 °C. The unit cell dimensions were determined from the refinement of the setting angles of 23 reflections.

**Crystal data.** C<sub>2</sub>H<sub>10</sub>N<sub>6</sub>O<sub>4</sub>S<sub>3</sub>Zn, FW=343.70, triclinic, space group  $P\bar{1}$ , white needles,  $a=7.0020(15)$ ,  $b=12.465(2)$ ,  $c=6.4584(11)$  Å,  $\alpha=86.484(14)^\circ$ ,  $\beta=100.99(2)^\circ$ ,  $\gamma=86.08(2)^\circ$ ,  $V=550.5(3)$  Å<sup>3</sup>,  $D_c=2.074$  g/cm<sup>3</sup>,  $Z=2$ ,  $\mu=28.4$  cm<sup>-1</sup>. Developed faces {210}, {010} and {011}.

A choice of axes corresponding to Ref. 5 would be:  $a=6.458$ ,  $b=7.002$ ,  $c=12.465$  Å;  $\alpha=100.99$ ,  $\beta=93.92$  and  $\gamma=93.52^\circ$ .

Intensity data was collected by the  $\omega-2\theta$  scan mode. Three standard reflections measured after every 14 400 s showed a systematic decrease during the exposure time to a maximum of 10 %. The data was corrected for the degradation of the crystal and Lorentz, polarization and absorption effects. Of the 2514 reflections, the 1514 which had  $I/\sigma(I) \geq 2.0$  were classified as observed and used in the subsequent structure solution and refinement.

The structure was solved by the heavy atom method. The positions for zinc and two sulfur atoms were deduced from the Patterson function and the remaining non-hydrogen atoms by Fourier syntheses. The structure was refined by the method of least squares minimizing  $\sum w(|F_o| - |F_c|)^2$ . The hydrogen atoms were localized in a difference density. In the final refinement cycles, the weights employed followed the expression  $w^{-1} = 1.865 + 1.3 \cdot \sigma^2(F) + 0.0056 \cdot |F| + 0.00 \cdot |F|^2$ . The coefficients for the weight function were derived as

Table 1. Positional parameters with e.s.d.'s and equivalent isotropic thermal parameters in units of Å<sup>2</sup> for the non-hydrogen atoms of Zn(Htsc)<sub>2</sub>SO<sub>4</sub>.

Atom	x	y	z	$U_{iso}^a$
C(1)	0.2442(8)	0.0381(4)	0.0777(9)	0.024
C(2)	0.2483(8)	0.5219(4)	0.1166(10)	0.024
N(11)	0.2276(8)	0.1451(4)	0.3678(8)	0.024
N(12)	0.2576(8)	0.0448(4)	0.2836(9)	0.028
N(13)	0.2674(9)	-0.0605(4)	0.0143(9)	0.033
N(21)	0.2226(9)	0.3839(4)	0.3793(9)	0.029
N(22)	0.2489(7)	0.4914(4)	0.3176(8)	0.028
N(23)	0.2519(9)	0.6270(4)	0.0687(11)	0.035
O(1)	0.5781(6)	0.2573(4)	0.2372(7)	0.035
O(2)	0.8522(6)	0.3129(3)	0.4763(8)	0.035
O(3)	0.8174(6)	0.1245(3)	0.4313(7)	0.031
O(4)	0.6021(6)	0.2244(3)	0.6144(6)	0.030
S(1)	0.1982(3)	0.14805(11)	-0.1010(2)	0.031
S(2)	0.2446(2)	0.43489(11)	-0.0750(2)	0.028
S(3)	0.7139(2)	0.22942(10)	0.4429(2)	0.020
Zn	0.28381(10)	0.27415(5)	0.15042(11)	0.023
H(111)	0.124(10)	0.147(5)	0.393(11)	0.028
H(112)	0.301(10)	0.151(5)	0.467(12)	0.028
H(12)	0.244(9)	-0.005(6)	0.361(11)	0.029
H(131)	0.318(10)	-0.124(6)	0.114(12)	0.035
H(132)	0.253(10)	-0.062(6)	-0.111(13)	0.035
H(211)	0.103(11)	0.382(5)	0.397(11)	0.032
H(212)	0.289(10)	0.374(5)	0.495(12)	0.032
H(22)	0.235(10)	0.532(5)	0.409(11)	0.031
H(231)	0.289(11)	0.649(6)	0.162(13)	0.036
H(232)	0.279(19)	0.652(6)	-0.049(12)	0.036

<sup>a</sup> For the non-hydrogen atoms  $U_{iso}$  is calculated as  $U_{iso} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot \bar{a}_i \cdot \bar{a}_j$ .

described by K. Nielsen.<sup>6</sup> The positional parameters for the hydrogen atoms were included in the refinement but they were given a fixed isotropic thermal parameter equal to the isotropic temperature factor of the atom to which the hydrogen is bonded. In the last refinement cycle, the maximum shift is 0.19  $\sigma$ , the final unit weighted and weighted residuals are 0.038 and 0.041 respectively.

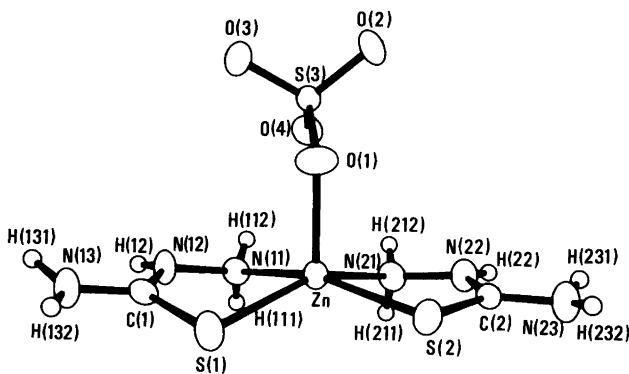


Fig. 1. The Zn(Htsc)<sub>2</sub>SO<sub>4</sub> unit showing the atomic labelling. The thermal ellipsoids enclose 50 % probability.

Table 2. Bond lengths (Å) and bond angles (deg) with e.s.d.'s.

Zn-N(11)	2.175(5)	Zn-N(21)	2.156(6)
Zn-S(1)	2.353(2)	Zn-S(2)	2.371(2)
S(1)-C(1)	1.708(6)	S(2)-C(2)	1.692(6)
C(1)-N(13)	1.327(8)	C(2)-N(23)	1.331(8)
C(1)-N(12)	1.324(8)	C(2)-N(22)	1.329(8)
N(12)-N(11)	1.412(7)	N(22)-N(21)	1.410(9)
Zn-O(1)	2.023(4)	O(4)-S(3)	1.474(5)
O(1)-S(3)	1.485(4)	O(2)-S(3)	1.467(5)
O(3)-S(3)	1.464(4)	N(21)-Zn-O(1)	98.6(2)
N(11)-Zn-O(1)	96.4(2)	S(2)-Zn-O(1)	99.93(14)
S(1)-Zn-O(1)	106.60(14)	N(11)-Zn-N(21)	86.9(2)
S(1)-Zn-S(2)	100.16(6)	S(2)-Zn-N(21)	82.82(15)
S(1)-Zn-N(11)	82.6(2)	Zn-N(21)-N(22)	112.2(4)
Zn-N(11)-N(12)	109.5(4)	N(21)-N(22)-C(2)	120.8(5)
N(11)-N(12)-C(1)	121.1(5)	N(22)-C(2)-S(2)	123.6(4)
N(12)-C(1)-S(1)	123.1(4)	N(22)-C(2)-N(23)	116.7(6)
N(12)-C(1)-N(13)	116.2(5)	N(23)-C(2)-S(2)	119.7(5)
N(13)-C(1)-S(1)	120.7(5)	C(2)-S(2)-Zn	96.8(2)
C(1)-S(1)-Zn	95.2(2)	O(1)-S(3)-O(2)	108.4(3)
Zn-O(1)-S(3)	133.3(3)	O(2)-S(3)-O(4)	110.2(3)
O(1)-S(3)-O(3)	107.9(3)	O(2)-S(3)-O(3)	110.4(2)
O(3)-S(3)-O(4)	110.4(2)		
O(1)-S(3)-O(4)	109.5(2)		

The X-Ray system<sup>7</sup> was used for the crystallographic computations and ORTEP II<sup>8</sup> for the illustrations. The atomic scattering factors were by Cromer and Mann<sup>9</sup> using the values for the uncharged atoms except for hydrogen where the values from Stewart *et al.*<sup>10</sup> were employed. The anomalous scattering corrections added to the scattering factors of Zn and S were those calculated by Cromer and Liberman.<sup>11</sup> The final coordinates and isotropic temperature factors are given in Table 1.

Lists of observed and calculated structure amplitudes as well as the anisotropic thermal parameters may be obtained upon request from the authors.

**Discussion.** The molecular structure is illustrated by the drawing in Fig. 1. and by the list of bond lengths and bond angles in Table 2. Zinc is five coordinated in Zn(Htsc)<sub>2</sub>SO<sub>4</sub>. The ligand atoms around zinc can be described as forming a distorted square pyramidal arrangement with the thiosemicarbazide groups in a *cis* configuration and an oxygen from the sulfate group in the axial position.

In other five coordinated zinc(II) complexes the coordination is often described as trigonal bipyramidal.<sup>12-14</sup> The structure of aqua-[3-ethoxy-2-oxo-butylaldehyde bis(thiosemicarbazone)]zinc(II) was classified by the authors as having the ligating atoms in an arrangement between a square pyramidal and a trigonal pyramidal<sup>15</sup> but in the present compound the irregular coordination around zinc seems closest to square pyramidal. Zn is displaced 0.42 Å towards O(1) from the least squares plane defined by S(1), S(2), N(11) and N(21).

In the isostructural Cu(II) complex, Cu(Htsc)<sub>2</sub>SO<sub>4</sub>, the two thiosemicarbazide ligands show much larger variations in their molecular dimensions than is observed in the present structure.<sup>5</sup> Here the two groups agree well internally, and with the results from other structures that contain thiosemicarbazide as a bidentate ligand.<sup>1-3,16</sup> However, the two thiosemicarbazide groups exhibit some conformational differences. These differences have been analysed by calculation of least squares planes for different groups of atoms within the molecule. The plane defined by S(1), C(1), N(12) and N(11), (N(13) is 0.05 Å and Zn 0.77 Å from the plane) shows a much smaller deviation from planarity (max. deviation=0.009 Å) than the equivalent defined by the atoms S(2), C(2), N(21) and N(22), where the maximum deviation is 0.034 Å, N(23) is 0.13 Å and Zn 0.49 Å from the plane. The first plane makes an

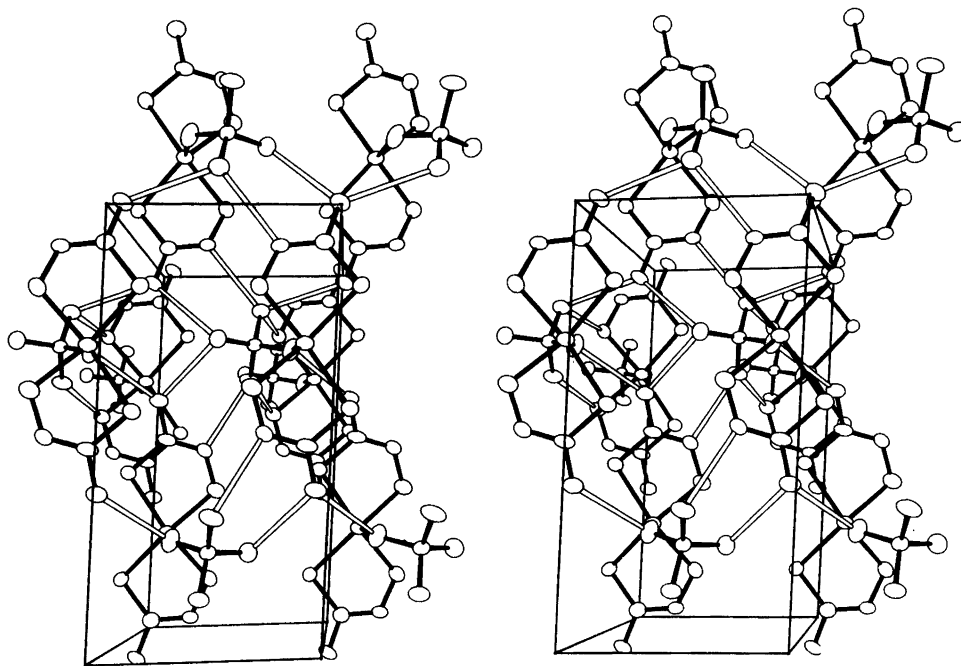


Fig. 2. A stereoscopic view of the unit cell viewed along  $\bar{a}^*$ . The hydrogen bonds are shown as open bonds. The thermal ellipsoids correspond to 50 % probability.

angle of  $14^\circ$  with the coordination plane S(1), S(2), N(11) and N(21) and the latter  $3^\circ$ . The angle between the planes of the two thiosemicarbazide ligands is  $17^\circ$ . The difference in conformation could be due to the formation of hydrogen bonds between the complex and seven neighbouring sulfate groups. The hydrogen bonds observed in the structure are listed in Table 3 and they are shown in the stereo pair in Fig. 2. In both thiosemicarbazide groups only one of the hydrogen atoms bonded to the coordinating nitrogen atom is not involved in hydrogen bonding. Though the hydrogen bond pattern is similar for the two ligands the N—O distances are slightly longer for the most planar thiosemicarbazide group (S(1), C(1), N(12), N(11)), indicating weaker hydrogen bonds.

The distances from zinc to the ligating atoms,  $\langle \text{Zn-S} \rangle = 2.362 \text{ \AA}$  and  $\langle \text{Zn-N} \rangle = 2.166 \text{ \AA}$  are similar to those observed in other five coordinated zinc complexes with sulfur and

Table 3. Hydrogen bonds ( $\text{\AA}$ ).

	Angles ( $^\circ$ )	Distance (H—O)	Distance (N—O)
N(11)—H(111)—O(3) <sup>a</sup>	169(7)	2.24(8)	3.004(8)
N(12)—H(12)—O(3) <sup>d</sup>	174(7)	2.07(7)	2.87(7)
N(13)—H(131)—O(4) <sup>d</sup>	162(6)	2.05(7)	3.011(7)
N(13)—H(132)—O(3) <sup>e</sup>	159(7)	2.23(8)	2.995(7)
N(21)—H(211)—O(2) <sup>a</sup>	156(6)	2.14(8)	2.961(8)
N(22)—H(22)—O(2) <sup>b</sup>	155(6)	2.20(7)	2.957(7)
N(23)—H(231)—O(4) <sup>b</sup>	159(8)	2.28(8)	2.931(8)
N(23)—H(232)—O(1) <sup>c</sup>	155(7)	2.05(8)	2.860(8)

<sup>a</sup>  $(x-1, y, z)$ . <sup>b</sup>  $(1-x, 1-y, 1-z)$ . <sup>c</sup>  $(1-x, 1-y, -z)$ . <sup>d</sup>  $(1-x, -y, 1-z)$ . <sup>e</sup>  $(1-x, -y, -y)$ .

nitrogen ligators.<sup>12-15</sup> It should be noted that the Zn-S distance is significantly longer in this complex than in the tetrahedral mono-thiosemicarbazide zinc(II) chloride<sup>17</sup> where Zn-S=2.292 Å. The geometry of the sulfate ion shows no deviation from the normally found values.

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