

tations to fulfil the symmetry requirements. Theoretically this could also be the cause of the diffuse scattering. An *ORTEP* plot (Johnson, 1965) of one chain is presented in Fig. 3, showing one possible ligand orientation only and the splitting of the I position between two Pt atoms. A projection of the structure along the chains is given in Fig. 4.

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### References

- BEKAROGLU, Ö., BREER, H., ENDRES, H., KELLER, H. J. & NAM GUNG, H. (1977). *Inorg. Chim. Acta*, **21**, 183–186.  
 BERDESINSKI, W. & NUBER, B. (1966). *Neues Jahrb. Mineral. Abh.* **104**, 113–146.  
 HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 KELLER, H. J. (1977). *Chemistry and Physics of One-Dimensional Metals*. NATO-ASI-Series B25. New York: Plenum.  
 MILLER, J. S. & EPSTEIN, A. J. (1976). *Prog. Inorg. Chem.* **20**, 1–154.  
 STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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## Structure of Tetrakis(thiourea)zinc(II) Nitrate

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**Abstract.** Zn[SC(NH<sub>2</sub>)<sub>2</sub>]<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>, *M<sub>r</sub>* = 493, orthorhombic, *Pnaa*, *a* = 22.434 (23), *b* = 9.465 (2), *c* = 8.859 (1) Å, *V* = 1880.9 Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.72, *D<sub>c</sub>* = 1.73 g cm<sup>-3</sup>, *F*(000) = 1008, *μ* = 17.9 cm<sup>-1</sup>. The structure was solved by single-crystal X-ray diffraction with the heavy-atom technique and refined by full-matrix least squares to *R* = 0.072 for 1435 independent reflections [*I* > 2σ(*I*)]. Four S atoms from thiourea molecules coordinate to Zn in a tetrahedral arrangement: Zn–S = 2.361 (3) and 2.324 (3) Å. Packing is determined by N–H⋯O hydrogen bonds which the NH<sub>2</sub> thiourea groups form with the nitrate O atoms.

**Introduction.** This investigation was undertaken because of our interest in the molecular conformation of thiourea and selenourea complexes with divalent metal salts. We have already studied several complexes {Ni[SC(NH<sub>2</sub>)<sub>2</sub>]<sub>4</sub>Cl<sub>2</sub> (Truter & López-Castro, 1963), Hg[SC(NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(CN)<sub>2</sub> (Moreno & López-Castro, 1971) and Hg[SC(NH<sub>2</sub>)<sub>2</sub>]<sub>4</sub>Cl(SH) (Criado, Conde, Moreno & Márquez, 1975)} by three-dimensional X-ray analysis. In continuing this research, the crystal structure of

tetrakis(thiourea)zinc nitrate has been studied and the results of this analysis are reported here.

Single crystals were grown by slow evaporation of a 1:4 mixture of solutions of Zn(NO<sub>3</sub>)<sub>2</sub> and thiourea. They are colourless prisms elongated along *c*. The cell parameters were determined and the intensities of the reflections were recorded up to sin θ/λ = 0.70 Å<sup>-1</sup> with monochromated Mo *K*α radiation (λ = 0.7107 Å) on a Philips PW 1100 automatic four-circle diffractometer. Systematic absences of reflections were observed in the diffractometer data. The observed reflections obey the conditions: *hkl* (no condition), *0kl* (*k* + *l* = 2*n*), *hk0* (*h* = 2*n*), and *h0l* (*h* = 2*n*); the space group consistent with these observations is *Pnaa* [this corresponds to *Pccn* (*D*<sub>2h</sub><sup>10</sup>, No. 56) (*International Tables for X-ray Crystallography*, 1952) by a transformation involving a permutation of the *a* and *c* axes].

The intensities were only corrected for Lorentz and polarization factors. Of the 2734 independent reflections recorded, 1435 intensities greater than 2σ(*I*), as estimated from counting statistics, were regarded as 'observed' and used for the refinement. No absorption correction was applied.

The structure was solved by the heavy-atom technique. The three-dimensional Patterson synthesis was easily interpreted on the basis of the space group *Pnaa*. There are four molecules of  $\text{Zn}(\text{Tu})_4(\text{NO}_3)_2$  per cell; and there are four Zn atoms, eight  $\text{NO}_3$  groups and sixteen thiourea molecules in the unit cell. Therefore, the Zn would have to occupy a fourfold special set of the type 4(c)  $[\pm(x, \frac{1}{4}, \frac{1}{4}); \pm(\frac{1}{2} + x, \frac{3}{4}, \frac{1}{4})]$ ; the eight  $\text{NO}_3^-$  ions and the sixteen thiourea molecules were placed in an eightfold general set of the type 8(e)  $[\pm(x, y, z); \pm(x, \frac{1}{2} - y, \frac{1}{2} - z); \pm(\frac{1}{2} + x, \frac{1}{2} - y, z); \pm(\frac{1}{2} + x, y, \frac{1}{2} - z)]$ , so that it is necessary to place two independent thiourea molecules in general positions.

The Zn and S atom positions were determined from the Patterson function. The positions of the C and N atoms were obtained by subsequent Fourier syntheses and the structure, with all non-hydrogen atoms, was refined by the full-matrix least-squares method, minimizing  $\sum w \|F_o\| - |F_c|^2$  with  $w = 1/\sigma_{F_o}^2$ . A least-squares program (Busing, Martin & Levy, 1964) was used. All non-hydrogen atom coordinates, the scale factor and the thermal parameters (first isotropic and later anisotropic) were refined to an *R* of 0.076. At this stage a difference Fourier synthesis calculated with  $\sin \theta$  up to 0.35 revealed the positions of the H atoms. For two cycles the scale factor, the atomic coordinates for all atoms and the anisotropic thermal parameters for the heavy atoms (77 parameters in all) were varied. For H atoms the isotropic thermal parameters are those of the bonded atoms. The final agreement index,  $R_w = \sum \|F_o\| - |F_c| / \sum |F_o|$ , was 0.072 for observed reflec-

tions.\* The atomic scattering factors for Zn, S, O, N and C were taken from Cromer & Mann (1968) and for H from *International Tables for X-ray Crystallography* (1962).

The atomic positional parameters from the final least-squares cycle are given in Table 1. The standard deviations were determined from the diagonal elements of the inverse matrix in the least-squares procedure.

**Discussion.** The structure consists of  $\text{Zn}[\text{SC}(\text{NH}_2)_2]_4^{2+}$  cations and  $\text{NO}_3^-$  anions. The geometry around the Zn atoms is roughly tetrahedral. These atoms are surrounded by four S atoms from four thiourea molecules and the configuration is shown in Fig. 1. Distances and angles in the coordination polyhedron are: Zn—S(1) 2.361 (3), Zn—S(2) 2.324 (3) Å; S(1)—Zn—S(1') 106.0 (1), S(1)—Zn—S(2') 114.5 (1), S(2)—Zn—S(2') 121.5 (1), and S(1')—Zn—S(2) 100.0 (1)° [symmetry code: (i)  $x, -y + \frac{3}{2}, -z + \frac{3}{2}$ ].

The Zn—S bond distances are comparable to the sum of Pauling's (1960) covalent radii (2.35 Å) and to the values found in other tetrahedral Zn compounds [e.g. 2.311 (3), 2.355 (3) and 2.383 (2) Å in bis(diethylthiocarbamate)zinc (Bonamico, Mazzone, Vaciago & Zambonelli, 1965); 2.286 (6) and 2.298 (6) Å in

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33400 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates with their e.s.d.'s ( $\times 10^4$  for non-hydrogen atoms and  $\times 10^3$  for the H atoms)

	x	y	z
Zn	14 (1)	7500 (0)	7500 (0)
S(1)	-619 (1)	8235 (2)	9478 (3)
S(2)	520 (1)	5676 (2)	8702 (2)
O(1)	2558 (3)	992 (8)	8440 (3)
O(2)	3342 (3)	2057 (8)	9232 (3)
O(3)	2492 (3)	2659 (8)	10100 (3)
N(0)	2795 (3)	1911 (7)	9287 (3)
N(1)	1479 (4)	4185 (9)	8396 (10)
N(2)	1407 (4)	5943 (8)	6665 (10)
N(3)	815 (4)	10480 (9)	7692 (13)
N(4)	-1631 (3)	9252 (10)	8417 (11)
C(1)	-1050 (4)	9407 (10)	8472 (10)
C(2)	1183 (3)	5260 (9)	7841 (9)
H(11)	170 (5)	390 (5)	749 (5)
H(12)	120 (5)	360 (5)	890 (5)
H(21)	125 (5)	680 (5)	630 (5)
H(22)	175 (5)	570 (5)	610 (5)
H(31)	-95 (5)	1117 (5)	704 (5)
H(32)	-50 (5)	1060 (5)	780 (5)
H(41)	-195 (5)	870 (5)	785 (5)
H(42)	-180 (5)	980 (5)	760 (5)

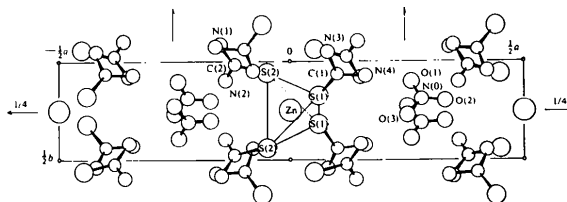


Fig. 1. Projection of the structure along *c*.

Table 2. Least-squares planes, bond distances (Å) and angles (°) for the thiourea molecules

Plane Tu(1):	S(1), C(1), N(3), N(4)	$-0.4833x + 0.6182y + 0.6199z = 8.6646$		
Plane Tu(2):	S(2), C(2), N(1), N(2)	$-0.0869x + 0.5830y + 0.8078z = 11.4495$		
	S—C	C—N	S—C—N	N—C—N
Tu(1)	1.72 (1)	1.37 (1)–	122.4 (8)–	117.3 (9)
		1.31 (1)	120.4 (8)	
Tu(2)	1.72 (1)	1.31 (1)–	116.8 (7)–	118.7 (8)
		1.33 (1)	124.5 (7)	
Tu*	1.720 (9)	1.340 (6)	120.5 (5)	119.0 (5)

\* Uncomplexed (Truter, 1967).

Table 3. Some intermolecular distances (Å) and angles (°)

N(4)—O(3 <sup>iv</sup> )	2.95	H(41)—O(3 <sup>iv</sup> )	2.54
N(1)—O(1 <sup>iii</sup> )	2.92	H(11)—O(1 <sup>iii</sup> )	2.10
N(2)—O(2 <sup>ii</sup> )	2.92	H(21)—O(2 <sup>ii</sup> )	2.32
N(4)—O(1 <sup>i</sup> )	2.95	H(42)—O(1 <sup>i</sup> )	2.05
N(3)—O(2 <sup>i</sup> )	2.95	H(31)—O(2 <sup>i</sup> )	2.12
N(2)—O(1 <sup>i</sup> )	3.17	H(22)—O(1 <sup>i</sup> )	2.45
N(2)—O(3 <sup>ii</sup> )	3.12	H(21)—O(3 <sup>ii</sup> )	2.47
N(4)—H(41)—O(3 <sup>iv</sup> )	104	N(3)—H(31)—O(2 <sup>i</sup> )	150
N(1)—H(11)—O(1 <sup>iii</sup> )	140	N(2)—H(22)—O(1 <sup>i</sup> )	133
N(2)—H(21)—O(2 <sup>ii</sup> )	121	N(2)—H(21)—O(3 <sup>ii</sup> )	126
N(4)—H(42)—O(1 <sup>i</sup> )	153		

## Symmetry code

- (i)  $x - \frac{1}{2}, y + 1, -z + \frac{3}{2}$       (iii)  $x, -y + \frac{1}{2}, -z + \frac{3}{2}$   
(ii)  $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$       (iv)  $-x, -y + 1, -z + 2$

mono(thiosemicarbazide)zinc chloride (Cavalca, Nardelli & Branchi, 1960); 2.35 (1) Å in bis(thiourea)zinc chloride (Kunchur & Truter, 1958); and 2.332 (4), 2.309 (4) and 2.323 (4) Å in tris(thiourea)zinc sulphate (Andreotti, Cavalca & Musatti, 1968)].

The orientation of the NO<sub>3</sub><sup>-</sup> group is determined by the hydrogen bonds involving the O atoms and the NH<sub>2</sub> groups. The NO<sub>3</sub><sup>-</sup> group is planar; the equation for the least-squares plane is 0.0942x - 0.6741y + 0.7327z = 5.3886 and the largest deviation from this plane is 0.010 Å.

The distances and angles in the NO<sub>3</sub><sup>-</sup> group are: N(0)—O(1) 1.26 (1), N(0)—O(2) 1.24 (1), N(0)—O(3) 1.22 (1) Å, O(1)—N(0)—O(2) 118.1 (8), O(2)—N(0)—O(3) 120.8 (8), O(1)—N(0)—O(3) 121.0 (8)°. These are in good agreement with those generally observed in nitrates, e.g. 1.25 (2), 1.22 (2) and 1.27 (2) Å in Zn(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (Petrović & Ribár, 1975), and 1.254 (2), 1.230 (2) and 1.209 (2) Å in tetrakis(urea)-calcium nitrate (Lebioda, 1977).

The two independent thiourea molecules are planar. Their least-squares planes are given in Table 2 with bond distances and angles. The largest deviations from the planes are 0.009 Å for Tu(1) and 0.002 Å for Tu(2). From these values, if compared with those found in uncomplexed thiourea, it is clear that coordination does not significantly influence the dimensions of the

ligand as observed for tris(thiourea)zinc(II) sulphate (Andreotti, Cavalca & Musatti, 1968).

The hydrogen-bonding scheme is shown in Table 3. It is not discussed in detail because of the low accuracy of the H positions, but distances and angles obtained with calculated H positions are given. The packing in the crystal and the orientation of the thiourea molecules are determined by these interactions (Fig. 1).

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## References

- ANDREOTTI, G. D., CAVALCA, L. & MUSATTI, A. (1968). *Acta Cryst.* B24, 683–690.  
BONAMICO, M., MAZZONE, G., VACIAGO, A. & ZAMBONELLI, L. (1965). *Acta Cryst.* 19, 898–909.  
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.  
CAVALCA, L., NARDELLI, M. & BRANCHI, G. (1960). *Acta Cryst.* 13, 688–693.  
CRIADO, A., CONDE, A., MORENO, E. & MÁRQUEZ, R. (1975). *Z. Kristallogr.* 141, 193–202.  
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.  
*International Tables for X-ray Crystallography* (1952). Vol. I. Birmingham: Kynoch Press.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
KUNCHUR, N. R. & TRUTER, M. R. (1958). *J. Chem. Soc.* pp. 3478–3484.  
LEBIODA, L. (1977). *Acta Cryst.* B33, 1583–1586.  
MORENO, E. & LÓPEZ-CASTRO, A. (1971). *An. Fis.* 67, 371–381.  
PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.  
PETROVIĆ, D. & RIBÁR, B. (1975). *Acta Cryst.* B31, 1795–1796.  
TRUTER, M. R. (1967). *Acta Cryst.* 22, 556–559.  
TRUTER, M. R. & LÓPEZ-CASTRO, A. (1963). *J. Chem. Soc.* pp. 1309–1317.