

The Crystal Structure of *tris*(thiourea)cadmium Sulphate

L. Cavalca, A. Chiesi Villa, A. Mangia, and C. Palmieri

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The crystal structure of *tris*(thiourea)cadmium sulphate has been determined by an X ray three-dimensional analysis. The crystals are triclinic  $P\bar{1}$  with the following crystal data:  $Cd[SC(NH_2)_2]_3SO_4$ ;  $M = 436.8$ ;  $a = 8.77(2)$ ,  $b = 9.05(2)$ ,  $c = 9.83(1)$  Å,  $\alpha = 91.3(2)^\circ$ ,  $\beta = 111.9(1)^\circ$ ,  $\gamma = 95.5(2)^\circ$ ,  $V = 718.9$  Å<sup>3</sup>,  $Z = 2$ ,  $D_o = 2.02$ ,  $D_c = 2.06$  g cm<sup>-3</sup>,  $F(000) = 432$ ,  $\mu = 179.5$  cm<sup>-1</sup> (CuK $\alpha$ ). The structure was solved by standard Patterson and Fourier three-dimensional methods and refined by differential synthesis down to  $R = 8.3\%$ . Coordination around cadmium involves three sulphur atoms from three thiourea molecules ( $Cd-S = 2.52(1)$ ,  $2.60(1)$ ,  $2.63(2)$  Å) and one oxygen atom ( $Cd-O(2) = 2.29(2)$  Å) of a sulphate group, at the corners of a severely distorted tetrahedron. Two long contacts  $Cd-S = 2.85(2)$  Å and  $Cd-O = 2.88(2)$  Å complete the coordination around the metal atom to a distorted octahedron. The  $SO_4^{2-}$  group behaves as a bidentate ligand but the bonds it makes with the metal atom have quite different lengths. The coordination octahedra are joined in dimers sharing an S-S edge. Packing is mainly due to NH...O hydrogen bonds.

## Introduction

The crystal structure of *tris*(thiourea)cadmium sulphate,  $Cd[SC(NH_2)_2]_3SO_4$ , has been determined to study the coordination around the metal atom, particularly in connection with the behaviour of the  $SO_4^{2-}$  group which could play the role of an uncoordinated ion, or a monodentate ligand or a chelating agent or could be in a bridging situation.

## Experimental Section

Crystals of *tris*(thiourea)cadmium sulphate were obtained as thick triclinic prisms by slow concentration of an aqueous solution of the components.<sup>1</sup> Crystal data, determined by rotation and Weissenberg methods (CuK $\alpha$ ,  $\lambda = 1.5418$  Å), are as follows:

$$Cd[SC(NH_2)_2]_3SO_4, M = 436.8$$

$$a = 8.77(2), b = 9.05(2), c = 9.83(1) \text{ \AA}$$

$$\alpha = 91.3(2)^\circ, \beta = 111.9(1)^\circ, \gamma = 95.5(2)^\circ$$

$$V = 718.9 \text{ \AA}^3, Z = 2, D_o = 2.02, D_c = 2.06 \text{ g cm}^{-3}$$

$$F(000) = 432, \mu = 179.5 \text{ cm}^{-1} \text{ (CuK}\alpha\text{)}$$

Space group:  $P\bar{1}$  (from the structure analysis, in agreement with the lack of piezoelectricity).

Three-dimensional intensity data was collected at room temperature from integrated Weissenberg photographs (multiple film technique) around [100] and [010]. The total number of observed independent reflections was 2919 from 3226 possible ones.

Absorption effects were corrected as continuous, considering the crystal as a cylinder for the reflections taken around [100] ( $r = 0.08$  mm,  $\mu r = 1.5$ ) and as a sphere for the reflections taken around [010] ( $r = 0.15$  mm,  $\mu r = 2.7$ ). Correction for the shape of the spots in non-equatorial layers was applied using the formula  $I_{\text{corr}} = I(1 \pm K \cos \vartheta)$  where  $K$  is a constant determined empirically from the upper and lower parts of the photograph. After correction for Lorentz and polarization factors the structure amplitudes were put first in the same scale following Rollett and Sparks,<sup>2</sup> then in absolute scale by Wilson's<sup>3</sup> method, the mean isotropic temperature factor being  $B = 2.13$  Å<sup>2</sup>.

*Structure analysis and refinement.* The structure was solved using the heavy atom technique starting from a three-dimensional Patterson map. The value of the conventional reliability index, when all the atoms from the Fourier synthesis were considered, was 17.7%. Refinement was carried out by Booth's differential synthesis with isotropic thermal parameters down to  $R = 14.8\%$ , then anisotropically down to the final  $R = 8.3\%$  value. At this point an  $F_o-F_c$  synthesis was calculated to look for the hydrogen atoms, but their direct location was impossible. The calculated positions for the hydrogen atoms correspond to high positive electron density regions, which nevertheless were too smeared to be used for a direct location of the peaks. Introduction of hydrogen atoms contributions did not improve the  $R$  value, so they were not taken into further consideration.

In Table I the final positional and thermal parameters, with their standard deviations and ratios e.s.d./coordinate shift, are quoted. A comparison of observed and calculated values for electron density and its second derivatives on the atomic peaks (Table II) gives an idea of the reliability of the analysis. No reliable discussion on the anisotropic parameters can be made, as the absorption effects were corrected only isotropically. In Table III observed and calculated structure factors are compared. The « less than »

(1) M. Nardelli and I. Chierici, *Ric. Sci.*, 5, 1017 (1958).(2) J. S. Rollett and R. A. Sparks, *Acta Cryst.*, 13, 273 (1960).(3) A. J. C. Wilson, *Nature, Lond.*, 150, 151 (1942).

**Table I.** Final atomic fractional coordinates ( $\times 10^4$ ), thermal parameters<sup>a</sup> ( $\times 10 \text{ \AA}^2$ ) with e.s.d.'s and ratios (e.s.d.)/(coordinate shift)

	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	$B_{11}(\sigma)$	$B_{22}(\sigma)$	$B_{33}(\sigma)$	$B_{12}(\sigma)$	$B_{13}(\sigma)$	$B_{23}(\sigma)$	$ r(x) $	$ r(z) $	$ r(y) $
Cd	2210(1)	1122(1)	1334(1)	16(0)	24(0)	13(0)	2(0)	0(1)	0(0)	2	2	2
S(1)	1054(4)	2733(3)	3645(3)	15(1)	19(1)	9(1)	-1(1)	1(2)	-1(1)	41	3	8
S(2)	4229(5)	-794(4)	2007(5)	16(1)	26(1)	30(2)	1(2)	1(2)	4(2)	24	3	48
S(3)	368(4)	980(3)	-1449(3)	17(1)	18(1)	11(1)	1(1)	1(2)	0(1)	5	7	15
S(4)	3543(4)	3735(4)	963(4)	18(1)	30(1)	16(1)	-4(2)	-1(2)	2(1)	7	35	18
O(1)	-39(20)	2755(10)	2109(17)	25(4)	46(5)	15(4)	5(6)	-3(6)	6(6)	5	3	5
O(2)	2469(17)	1903(15)	3653(23)	19(4)	31(3)	20(5)	3(5)	5(6)	3(5)	4	2	1
O(3)	161(18)	1933(15)	4475(12)	38(4)	45(4)	25(5)	-3(5)	13(6)	4(5)	5	37	41
O(4)	1692(22)	4232(12)	4347(14)	29(4)	18(2)	29(4)	1(5)	-6(6)	-5(4)	17	6	14
N(1)	7195(17)	10(22)	3898(20)	23(4)	55(8)	24(6)	4(9)	-8(8)	13(9)	5	27	5
N(2)	6527(12)	1225(10)	1768(13)	16(3)	31(4)	34(8)	-2(6)	2(8)	13(7)	17	17	5
N(3)	-470(22)	3192(14)	-3135(17)	34(6)	30(4)	14(5)	5(7)	1(8)	6(6)	10	14	16
N(4)	-837(16)	3436(9)	-933(13)	25(5)	28(4)	15(5)	9(7)	2(7)	5(6)	6	3	44
N(5)	6348(18)	5321(18)	2407(17)	44(6)	68(5)	29(8)	-21(8)	7(10)	1(8)	6	13	15
N(6)	5366(17)	3839(13)	3842(12)	32(4)	41(3)	17(5)	-18(5)	-4(7)	2(5)	10	12	6
C(1)	6130(19)	277(13)	2607(15)	15(4)	33(4)	14(5)	-3(6)	3(7)	3(6)	2	2	2
C(2)	-386(13)	2723(10)	-1841(11)	13(4)	22(3)	12(5)	-2(5)	-2(6)	1(5)	7	2	4
C(3)	5195(15)	4351(13)	2545(13)	22(5)	23(2)	20(6)	-7(5)	6(8)	-5(5)	6	133	3

<sup>a</sup> The anisotropic temperature factor is:  $\exp -1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)$ .

**Table II.** Atomic peak heights ( $e \cdot \text{\AA}^{-3}$ ), curvatures ( $e \cdot \text{\AA}^{-5}$ ) and e.s.d.'s

	$\rho$	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	$A_{kl}$	$A_{hl}$	$A_{hk}$	
Cd	obs.	142.4	1263	1309	1577	46	390	77
	calc.	141.5	1265	1324	1566	50	398	76
S(1)	obs.	42.3	379	403	486	27	130	8
	calc.	42.5	381	404	486	26	133	12
S(2)	obs.	35.6	329	351	327	31	93	14
	calc.	35.7	329	350	334	28	98	17
S(3)	obs.	43.9	390	449	518	22	121	14
	calc.	43.8	391	449	519	20	122	16
S(4)	obs.	37.2	322	331	405	22	84	-10
	calc.	37.3	324	333	405	17	87	-5
O(1)	obs.	12.8	98	118	102	-3	40	10
	calc.	12.8	96	120	101	-4	40	11
O(2)	obs.	13.8	122	114	85	26	37	-6
	calc.	13.7	119	114	83	24	35	-7
O(3)	obs.	11.8	88	84	114	-3	25	12
	calc.	12.0	88	87	110	-4	24	12
O(4)	obs.	11.8	68	97	106	0	24	7
	calc.	12.1	71	96	106	0	24	8
N(1)	obs.	9.7	80	52	68	7	9	6
	calc.	10.1	85	69	79	8	13	5
N(2)	obs.	14.0	154	135	127	12	41	16
	calc.	13.8	153	134	129	9	44	18
N(3)	obs.	10.7	74	104	99	12	25	8
	calc.	11.0	75	104	99	10	26	8
N(4)	obs.	12.5	104	122	124	-7	42	7
	calc.	12.5	103	119	125	-5	41	4
N(5)	obs.	9.3	81	56	76	-1	16	-6
	calc.	9.2	84	57	77	0	19	-5
N(6)	obs.	10.4	79	75	99	-1	12	-10
	calc.	10.6	79	77	97	1	12	-10
C(1)	obs.	10.3	87	78	94	-1	28	-12
	calc.	10.2	87	80	93	-2	30	-13
C(2)	obs.	12.3	109	140	134	12	25	9
	calc.	12.3	110	141	133	10	25	11
C(3)	obs.	10.9	104	89	117	9	30	-7
	calc.	10.9	105	86	118	9	29	-6
e.s.d.'s	e.s.d.'s	0.3	4	5	5	3	3	3

values are referred to the reflections which are too weak to be observed, taken as equal to  $I_{\min}-1$ .

Standard deviations have been calculated following Cruickshank<sup>4</sup> for the electron density and its derivatives, Ahmed and Cruickshank<sup>5</sup> for bond lengths,

(4) D. W. J. Cruickshank, *Acta Cryst.*, **2**, 65 (1949).

Darlow<sup>6</sup> for angles; the effects of the errors in the cell parameters were considered following Darlow and Cochran.<sup>7</sup>

The atomic factors used throughout the calculations were those of Cromer and Mann.<sup>8</sup>

Table IV gives the more interesting distances and angles.

Calculations were performed on the Olivetti Elea 6001/S computer of the *Centro di Calcolo Elettronico dell'Università di Parma*.

## Discussion

Coordination around the metal atom involves three sulphur atoms from three thiourea molecules and one oxygen atom from a  $\text{SO}_4^{2-}$  group in a severely distorted tetrahedral arrangement (Figure 1). The Cd-O(2) distance is a little longer than the sum of the Pauling covalent radii (2.22 Å) and is in agreement with those found in *bis*(acetamide)cadmium chloride<sup>9</sup> (2.23 Å) and in *bis*(thiourea)cadmium formate<sup>10</sup> (2.28 Å). The Cd-S distances are of two kinds: one shorter (Cd-S(2) = 2.52 Å) and two longer (Cd-S(3) = 2.60, Cd-S(4) = 2.63 Å). The first one is equal to the sum of Pauling covalent radii (2.52 Å) and is in agreement with those found in other cadmium tetrahedral complexes: 2.45 Å in *bis*(thiourea)cadmium chloride;<sup>11</sup> 2.52 Å in *bis*(ethylenethiourea)cadmium chloride.<sup>12</sup> The other two distances are not significantly different and their values are intermediate between the sum of the covalent and the sum of the ionic radii (2.87 Å). They are in agree-

(5) F. R. Ahmed and D. W. J. Cruickshank, *Acta Cryst.*, **6**, 385 (1953).

(6) S. F. Darlow, *Acta Cryst.*, **13**, 683 (1960).

(7) S. F. Darlow and W. Cochran, *Acta Cryst.*, **14**, 1250 (1961).

(8) D. T. Cromer and J. B. Mann, *Acta Cryst.*, **A24**, 321 (1968).

(9) L. Cavalca, M. Nardelli, and L. Coghi, *Nuovo Cimento*, **10**, 278 (1957).

(10) M. Nardelli, G. Fava Gasparri, and P. Bolchini, *Acta Cryst.*, **18**, 618 (1965).

(11) M. Nardelli, L. Cavalca, and A. Braibanti, *Gazz. Chim.*, **87**, 137 (1957).

(12) L. Cavalca, P. Domiano, A. Musatti, and P. Sgarabotto, *Chem. Comm.*, p. 1136 (1968).









Table III. (Continued)

h	k	l	10 $\sigma$ <sub>Q</sub>	10 $\sigma$ <sub>E</sub>	h	k	l	10 $\sigma$ <sub>Q</sub>	10 $\sigma$ <sub>E</sub>	h	k	l	10 $\sigma$ <sub>Q</sub>	10 $\sigma$ <sub>E</sub>	h	k	l	10 $\sigma$ <sub>Q</sub>	10 $\sigma$ <sub>E</sub>	h	k	l	10 $\sigma$ <sub>Q</sub>	10 $\sigma$ <sub>E</sub>	h	k	l	10 $\sigma$ <sub>Q</sub>	10 $\sigma$ <sub>E</sub>	h	k	l	10 $\sigma$ <sub>Q</sub>	10 $\sigma$ <sub>E</sub>	
5	1	1	222	-237	3	2	1	85	-81	2	3	1	54	-39	1	4	1	274	266	1	5	1	54	-33	4	0	1	34	-20	6	1	1	99	97	
6	1	1	342	304	3	2	1	214	222	2	3	1	279	-275	1	4	1	25	-29	2	5	1	245	-295	3	0	1	151	-154	6	1	1	105	-102	
6	1	1	99	-95	4	2	1	48	-12	3	3	1	54	-40	2	4	1	85	-122	2	5	1	60	-72	6	0	1	94	78	1	2	1	180	271	
7	1	1	245	208	4	2	1	57	-26	3	3	1	54	-33	2	4	1	151	-150	3	5	1	45	-61	1	1	1	105	81	2	2	1	202	205	
7	1	1	174	167	5	2	1	159	184	4	3	1	39	-32	3	4	1	208	-199	3	5	1	74	-84	1	1	1	320	-333	3	2	1	79	-92	
8	1	1	31	-19	5	2	1	68	-73	4	3	1	39	-39	3	4	1	45	-41	4	5	1	271	273	2	1	1	348	394	4	2	1	114	-129	
8	1	1	39	-28	6	2	1	374	362	5	3	1	205	225	4	4	1	199	195	4	5	1	102	194	2	1	1	85	-112	5	2	1	39	-49	
0	2	1	174	-195	6	2	1	162	-171	5	3	1	205	-198	4	4	1	174	152	5	5	1	74	63	3	1	1	148	179	6	2	1	262	250	
0	2	1	139	-139	7	2	1	90	-23	6	3	1	99	98	5	4	1	194	172	5	5	1	154	206	3	1	1	111	133	2	3	1	93	95	
1	2	1	277	-331	7	2	1	119	116	6	3	1	242	-216	5	4	1	42	-22	6	5	1	19	-19	-12	4	1	117	124	3	3	1	74	-77	
1	2	1	299	-337	8	2	1	45	-193	7	3	1	122	-296	6	4	1	45	-36	1	0	1	91	-121	4	1	1	117	39	-50	4	3	1	94	-95
1	2	1	531	-542	0	3	1	271	239	7	3	1	42	-2	6	4	1	354	-379	2	0	1	134	141	5	1	1	39	-50	4	3	1	94	-95	
2	2	1	65	-11	1	3	1	259	325	0	4	1	305	280	7	4	1	168	-151	3	0	1	357	384	5	1	1	45	-64	5	3	1	20	4	
2	2	1	68	-59	1	3	1	254	-310																										

Table IV. Distances and angles.

Cd—O(2) = 2.29(2) Å	S(2)CdS(4) = 112.9(1)°
Cd—S(2) = 2.52(1)	S(3)CdS(4) = 87.5(1)
Cd—S(3) = 2.60(1)	S(2)CdO(2) = 98.8(4)
Cd—S(4) = 2.63(2)	S(3)CdO(2) = 145.7(4)
S(2)CdS(3) = 113.3(1)°	S(4)CdO(2) = 91.0(4)

## (b) in the thiourea molecules

S(2)—C(1) = 1.73(2) Å	S(2)C(1)N(2) = 121.8(1.1)°
N(1)—C(1) = 1.31(2)	S(2)C(1)N(1) = 116.3(1.2)
N(2)—C(1) = 1.31(2)	N(2)C(1)N(1) = 121.7(1.6)
S(3)—C(2) = 1.76(2)	S(3)C(2)N(4) = 121.1(8)
N(3)—C(2) = 1.33(2)	S(3)C(2)N(3) = 114.5(9)
N(4)—C(2) = 1.29(2)	N(3)C(2)N(4) = 124.4(1.1)
S(4)—C(3) = 1.72(1)	S(4)C(3)N(5) = 116.8(1.0)
N(5)—C(3) = 1.32(2)	S(4)C(3)N(6) = 122.4(1.1)
N(6)—C(3) = 1.33(2)	N(5)C(3)N(6) = 120.7(1.3)

(c) in the SO<sub>4</sub><sup>2-</sup> group

S(1)—O(1) = 1.46(2) Å	O(1)S(1)O(2) = 106.1(1.0)°
S(1)—O(2) = 1.51(2)	O(1)S(1)O(3) = 109.9(8)
S(1)—O(3) = 1.48(2)	O(1)S(1)O(4) = 112.6(7)
S(1)—O(4) = 1.47(2)	O(2)S(1)O(3) = 109.7(9)
	O(2)S(1)O(4) = 109.8(1.0)
	O(3)S(1)O(4) = 108.8(8)

## (d) hydrogen-bonds

N(1) ... O(3 <sup>ii</sup> ) = 2.85(3) Å	N(1)HO(3 <sup>ii</sup> ) = 158.8°
N(1) ... O(2 <sup>iii</sup> ) = 2.94(3)	N(1)HO(2 <sup>iii</sup> ) = 147.5
N(2) ... O(1 <sup>ii</sup> ) = 3.09(3)	N(2)HO(1 <sup>ii</sup> ) = 161.5
N(3) ... O(4 <sup>iv</sup> ) = 2.77(3)	N(3)HO(4 <sup>iv</sup> ) = 167.8
N(4) ... O(1) = 2.90(2)	N(4)HO(1) = 160.7
N(5) ... O(4 <sup>*</sup> ) = 3.00(2)	N(5)HO(4 <sup>*</sup> ) = 141.6
N(6) ... O(2) = 2.89(3)	N(6)HO(2) = 165.0
N(6) ... O(4 <sup>*</sup> ) = 2.91(2)	N(6)HO(4 <sup>*</sup> ) = 147.0

## (e) contacts less than 3.5 Å

S(2) ... N(4 <sup>i</sup> ) = 3.44(2) Å	O(3) ... N(2 <sup>iii</sup> ) = 3.29(2) Å
S(3) ... O(1 <sup>i</sup> ) = 3.39(3)	O(3) ... C(1 <sup>iii</sup> ) = 3.48(3)
S(3) ... O(2 <sup>i</sup> ) = 3.49(2)	O(3) ... N(1 <sup>iii</sup> ) = 3.03(3)
S(4) ... N(5 <sup>iv</sup> ) = 3.47(2)	O(4) ... C(3 <sup>v</sup> ) = 3.37(2)

i $\bar{x}, \bar{y}, \bar{z}$	v $1-x, 1-y, 1-z$
ii $x+1, y, z$	vi $1-x, 1-y, \bar{z}$
iii $1-x, \bar{y}, 1-z$	vii $x-1, y, z$
iv $\bar{x}, 1-y, \bar{z}$	

Further analysis of the cadmium environment shows stant from the metal respectively. The long Cd—S(3<sup>i</sup>) contact corresponds well to the sum of the ionic radii, while the Cd—O(1) distance is much longer than the sum of their ionic radii (2.43 Å). Considering these interactions too, the coordination polyhedron around the metal is a very distorted octahedron. The S(3) and S(3<sup>i</sup>) atoms act as bridges between two centrosymmetrical cadmium atoms, giving origin to a dimer formed by two octahedra sharing the S(3)—S(3<sup>i</sup>) edge. The sulphate group behaves as a bidentate ligand, the two bonds it forms being quite different in length. Considering these distances and  $d^{10}$  configuration of Cd<sup>2+</sup> it is impossible to make any sound discussion on the nature of the metal-ligands interactions.

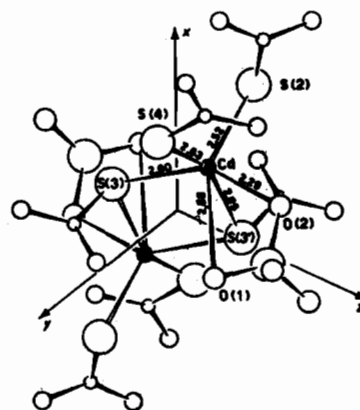


Figure 1. Clinographic projection of a dimer.

Concerning bond distances and angles in the thiourea molecules it seems interesting to observe that the longer S—C distance (S(3)—C(2) = 1.76(2) Å is found in the thiourea molecule whose sulphur is in a bridging position, while the shorter ones (S(2)—C(1) = 1.73(2) and S(4)—C(3) = 1.72(1) Å) are present in the monocoordinate molecules, confirming the idea that coordination can influence the S—C distance in thiourea.<sup>13</sup> In fact the bridging behaviour implies an  $sp^3$  bond configuration for sulphur and a single bond

(13) L. Cavalca, P. Domiano, G. Fava Gasparri, and P. Boldrini, *Acta Cryst.*, 22, 878 (1967).

(14) L. Cavalca, M. Nardelli, and G. Fava Gasparri, *Acta Cryst.*, 13, 125 (1960).

ment with those generally found in octahedral cadmium complexes: 2.65 Å in *mono*(thiourea)cadmium sulphate dihydrate;<sup>13</sup> 2.60 Å in *bis*(ethylthiourea)-cadmium thiocyanate.<sup>14</sup>

character for S(3)–C(2). This is also confirmed by the angles around S(3):  $\text{CdS(3)C(2)} = 107.0^\circ$ ,  $\text{CdS(3)Cd}^1 = 97.5^\circ$ ,  $\text{Cd}^1\text{S(3)C(2)} = 109.2^\circ$ . Nor any  $\pi$  interaction seems probable as indicated by the dihedral angles:  $\text{CdS(3)C(2)} \wedge \text{S(3)C(2)N(3)N(4)} = 38.6^\circ$

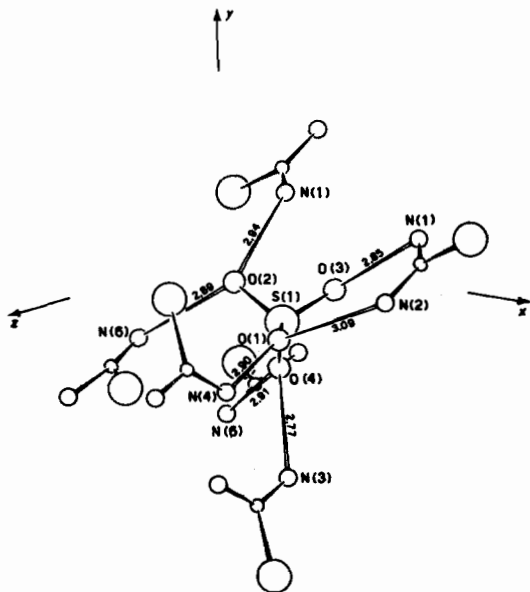


Figure 2. Clinographic projection of the  $\text{SO}_4^{2-}$  environment.

and  $\text{Cd}^1\text{S(3)C(2)} \wedge \text{S(3)C(2)N(3)N(4)} = 24.5^\circ$  which are far from  $90^\circ$ . Also for the other thiourea molecules coordination to the metal atom occurs through interactions concerning pairs of electrons which are in molecular orbitals not much different from the  $sp^3$  sulphur hybrids, as indicated by the angles:  $\text{CdS(2)C(1)} = 103.0$ ,  $\text{CdS(4)C(3)} = 109.3$ . For these molecules too, no interactions between metal and  $\pi$  electrons of the ligands seem implied as indicated by the dihedral angles the molecules of thiourea form with the CdSC planes:  $\text{CdS(2)C(1)} \wedge \text{S(2)C(1)N(1)N(2)} = 54.9^\circ$ ,  $\text{CdS(4)C(3)} \wedge \text{S(4)C(3)N(5)N(6)} = 22.6^\circ$ .

The thiourea molecules are planar excepting S(2)–C(1)N(1)N(2), which shows a small but statistically significant deviation: C(1) is out of the mean plane by

$-0.03 \text{ \AA}^*$

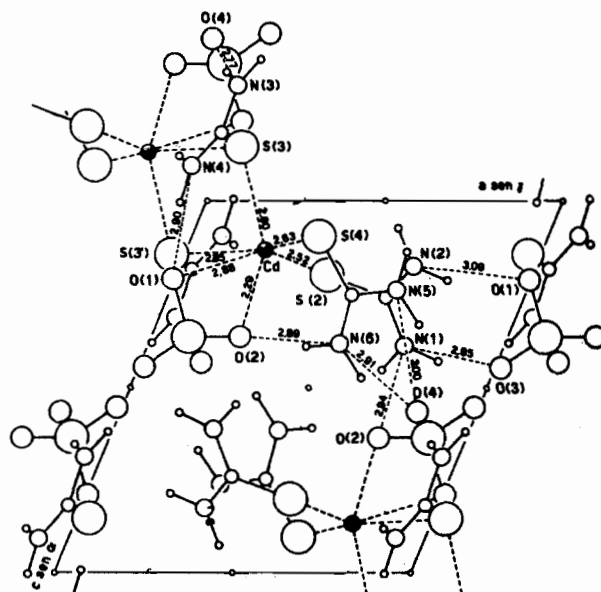


Figure 3. Projection of the structure down to  $[010]$ .

Bond distances and angles in the  $\text{SO}_4^{2-}$  group, agree well with those generally found in other sulphates. It may be pointed out that the longer S–O distance ( $\text{S(1)–O(2)} = 1.51(2) \text{ \AA}$ ) corresponds to the shorter Cd–O contact ( $\text{Cd–O(2)} = 2.29(2) \text{ \AA}$ ) and this indicates a reduced double-bond character for the S(1)–O(2) bond as a consequence of the binding with the metal. The coordinated electronpair is in a  $\text{SO}_4^{2-}$  molecular orbital which is essentially an  $sp^3$  hybrid of oxygen, as indicated by the angle  $\text{CdO(2)S(1)} = 112.4(1.1)^\circ$ .

Packing is mainly due to the hydrogen bonds (s. Table IV) formed by the  $\text{NH}_2$  groups and the oxygen atoms, as shown in Figure 2 and 3.

(\*) The least-squares planes of the three molecules are: S(2)C(1)–N(1)N(2)  $0.5422 X' - 0.7413 Y' - 0.3957 Z' = 1.7015$ ; S(3)C(2)N(3)N(4)  $0.8277 X' + 0.3552 Y' + 0.4344 Z' = 0.4529$ ; S(4)C(3)N(5)N(6)  $-0.5934 X' + 0.7902 Y' + 0.1530 Z' = 0.9319$ . The orthogonal  $X', Y', Z'$  coordinates are expressed in  $\text{\AA}$  and are obtained from the  $x, y, z$  triclinic ones using the matrix:  $(\sin \gamma \ 0 \ -\sin \alpha \cos \beta^* \mid \cos \gamma \ 1 \ \cos \alpha \mid 0 \ 0 \ \sin \alpha \sin \beta^*)$ .