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

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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  $P\bar{I}$  with the following crystal data:  $Cd[SC(NH_2)_2]_3SO_4$ ;  $M = 436.8$ ;  $a = 8.77(2)$ ,  $b = 9.05(2)$ ,  $c = 9.83(1) \text{ \AA}$ .  $\alpha = 91.3(2)^\circ$ ,  $\beta = 111.9(1)^\circ$ ,  $\gamma = 95.5(2)^\circ$ ,  $V = 718.9 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_o = 2.02$ ,  $D_c = 2.06 \text{ g cm}^{-3}$ ,  $F(000) = 432$ ,  $\mu = 179.5 \text{ cm}^{-1}$  (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 ( $Cd-S = 2.52(1)$ ,  $2.60(1)$ ,  $2.63(2) \text{ \AA}$ ) and one oxygen atom ( $Cd-O(2) = 2.29(2) \text{ \AA}$ ) of a sulphate group, at the corners of a severely distorted tetrahedron. Two long contacts  $Cd-S = 2.85(2) \text{ \AA}$  and  $Cd-O = 2.88(2) \text{ \AA}$  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  $NH \dots O$  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 $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ), are as follows:



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

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

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

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

(1) M. Nardelli and I. Chierici, *Ric. Sci.*, 5, 1017 (1958).

Space group:  $P\bar{I}$  (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] ( $r = 0.08 \text{ mm}, \mu r = 1.5$ ) and as a sphere for the reflections taken around [010] ( $r = 0.15 \text{ mm}, \mu r = 2.7$ ). 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  $B = 2.13 \text{ \AA}^2$ .

*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 »

(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(ethylene-thiourea)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. Boldrini, *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.** Observed and calculated structure factors. A minus sign for  $F_o$  means «less than»

$h$	$k$	$l$	$10F_o$	$10F_c$	$h$	$k$	$l$	$10F_o$	$10F_c$	$h$	$k$	$l$	$10F_o$	$10F_c$	$h$	$k$	$l$	$10F_o$	$10F_c$	$h$	$k$	$l$	$10F_o$	$10F_c$	$h$	$k$	$l$	$10F_o$	$10F_c$					
2	0	0	100	-62	2	6	0	365	-377	4	1	1	851	851	3	4	I	265	240	4	7	1	136	59	5	0	2	45-	53	6	3	2	348	345
3	0	0	268	180	3	6	0	82-	-3	4	1	1	791	816	4	4	I	319	-273	4	7	1	148	124	6	0	2	248	-218	6	3	2	177	-165
4	0	0	468	410	3	6	0	334	-367	4	1	I	23-	2	4	I	668	-590	4	7	I	154	93	6	0	2	448	490	6	3	2	131	-127	
5	0	0	574	572	4	6	0	274	-362	4	1	I	711	-711	4	4	I	257	232	4	7	I	436	405	7	0	2	94	78	6	3	2	45	-36
6	0	0	254	-244	4	6	0	199	182	5	1	1	165	-166	4	4	I	391	296	5	7	1	231	248	7	0	2	139	-129	7	3	2	225	245
7	0	0	416	-419	5	6	0	111	95	5	1	I	177	191	5	4	I	177	-154	5	7	1	199	-200	8	0	2	302	358	7	3	2	688	-649
8	0	0	111	106	5	6	0	525	-508	5	1	I	674	598	5	4	I	22	25	5	7	I	168	178	8	0	2	362	-384	7	3	2	382	-377
9	0	0	297	343	6	6	0	202	207	5	1	I	585	602	5	4	I	354	-130	5	7	I	91-	10	9	0	2	39-	31	7	3	2	442	425
10	0	0	37-	2	6	5	0	99	-91	6	1	I	454	-436	5	4	I	168	-165	6	7	1	102	131	9	0	2	99	-111	8	3	2	291	-279
0	1	0	848	754	7	6	0	91	-91	6	1	I	99	97	6	4	I	188	187	6	7	I	197	-267	10	0	2	122	131	8	3	2	51-	20
1	1	0	784	-704	7	6	0	197	178	6	1	I	405	-361	6	4	I	619	617	6	7	I	268	286	0	1	2	328	-263	8	3	2	251	324
1	1	0	1062	1052	8	6	0	111	-106	7	1	I	191	163	6	4	I	319	-302	6	7	I	265	-264	0	1	2	302	-377	8	3	2	485	508
2	1	0	960	-946	0	7	0	68-	66	7	1	I	216	-153	6	4	I	77	36	7	7	I	162	-171	1	1	2	257	-202	9	3	2	485	508
2	1	0	102	-92	1	7	0	575	619	7	1	I	582	-583	7	4	I	197	189	7	7	I	197	203	1	1	2	620	-680	10	3	2	57	-70
3	1	0	499	444	1	7	0	239	-275	8	1	I	99	77	7	4	I	102	101	7	7	I	239	215	1	1	2	311	231	0	4	2	214	-171
3	1	0	577	-562	2	7	0	148	126	8	1	I	65-	63	7	4	I	182	201	7	7	I	265	1	1	2	1109	1172	0	4	2	108	53	
4	1	0	685	643	2	7	0	382	-394	9	1	I	91	-82	7	7	I	645	641	0	8	1	145	157	2	1	2	634	611	1	4	2	629	617
4	1	0	468	427	3	7	0	285	-316	9	1	I	188	199	8	4	I	337	-347	0	8	1	402	403	2	1	2	901	-984	705	671			
5	1	0	465	428	3	7	0	25-	4	10	1	I	197	193	8	4	I	188	202	1	8	I	85-	32	2	1	2	262	-220	1	4	2	736	-790
5	1	0	588	590	4	7	0	25-	5	0	2	I	54-	71	8	4	I	62-	47	1	8	I	222	-236	2	1	2	879	940	740	-710			
6	1	0	674	-668	4	7	0	119	129	0	2	I	477	468	9	4	I	108	-110	8	8	I	342	426	3	1	2	457	409	2	4	2	632	598
6	1	0	57	-73	5	7	0	99	54	1	2	I	314	-238	0	5	I	462	-415	1	8	I	74-	-19	3	1	2	697	731	2	4	2	531	-491
7	1	0	114	93	5	7	0	268	-267	1	2	I	1100	1109	0	5	I	751	-758	2	8	I	334	-378	3	1	2	679	-768	2	4	2	357	-351
7	1	0	288	-275	6	7	0	277	292	1	2	I	277	-199	1	5	I	274	264	2	8	I	148	-158	3	1	2	454	-376	139	-64			
8	1	0	205	246	6	7	0	322	-308	1	2	I	91	18	1	5	I	165	158	2	8	I	294	327	4	1	2	431	398	3	4	2	382	-320
9	1	0	97	94	7	7	0	94	-99	2	2	I	414	345	1	5	I	117	-52	2	8	I	474	-528	4	1	2	837	854	3	4	2	348	-318
10	1	0	99	-97	7	7	0	25-	23	2	2	I	54-	43	1	5	I	951	-1004	3	8	I	70-	39	4	1	2	245	-233	3	4	2	111	-91
0	2	0	34-	32	0	8	0	309-	304	2	2	I	1519	-1579	2	5	I	182	162	3	8	I	337	328	4	1	2	602	-635	508	632			
1	2	0	1031	-1266	1	8	0	161	179	2	2	I	1508	1547	2	5	I	499	529	3	8	I	85-	-86	5	1	2	754	-724	4	4	2	434	-417
1	2	0	466	-337	1	8	0	114	80	3	2	I	771	756	2	5	I	317	304	3	8	I	256-	-230	5	1	2	68-	-30	100	-85			
2	2	0	1108	-1144	2	8	0	245	-254	3	2	I	405	-358	2	5	I	174	-149	4	8	I	211	272	5	1	2	494	460	6	4	2	748	765
2	2	0	568	529	2	8	0	259	-297	3	2	I	57-	-68	3	5	I	85-	48	4	8	I	82	59	5	1	2	339	-333	4	4	2	222	167
3	2	0	585	516	3	8	0	148	-206	3	2	I	511	-421	3	5	I	74-	-50	4	8	I	62-	109	6	1	2	142	-161	85	-61			
3	2	0	814	-831	3	8	0	234	227	4	2	I	254	191	3	5	I	182	198	4	8	I	211	206	6	1	2	122	99	5	4	2	348	335
4	2	0	185	173	4	8	0	77-	33	4	2	I	482	441	3	5	I	382	320	5	8	I	242	260	6	1	2	301	281	79	50			
4	2	0	242	-191	4	8	0	119	114	4	2	I	297	249	4	5	I	717	-729	5	8	I	77-	7	1	2	428	413	5	4	2	319	-244	
5	2	0	617	58	5	8	0	191	213	4	2	I	948	-898	4	5	I	771	-746	5	8	I	139	155	7	1	2	82	-62	77	37			
5	2	0	956	1000	5	8	0	77-	61	4	2	I	479	-463	4	5	I	202	140	2	9	I	68-	-75	1	2	2	68-	-35	8	4	2	371	397
5	2	0	526	-502	1	10	0	151	172	3	3	I	365	-303	6	5	I	105	-86	0	9	I	94-	87	1	2	2	51-	12	156	165			
5	3	0	486	-446	2	10	0	74-	-110	0	3	I	45-	-39	0	6	I	74	37	2	9	I	88-	86	3	2	2	537	-491	2	5	2	425	428
5	3	0	171	-134	2	10	0	79-	80	1	3	I	191	-131	0	6	I	414	-440	2	9	I	197-	204	3	2	2	937	-1017	137	105			
6	3	0	562	-591	3	10	0	151	-186	1	3	I	511	491	1	6	I	468	469	3	9	I	77-	92	3	2	2	988	953	2	5	2	245	-207
7	3	0	688	-721	4	10	0	37-	47	1	3	I	951	-923	1	6	I	71	-50	3	9	I	191	179	4	2	2	174	-143	528	-497			
7	3	0	377	324	0	11	0	225	214	2	3	I	737	695	1	6	I	362	-348	4	9	I	34-	380	4	2	2	465	454	3	5	2	611	659
3	4	0	57-	47	2	0	1	708	-834	6	3	I	354	-220	4	6	I	425	-437	0	10	I	79-	-102	3	6	2	225	-176	5	5	2	294	312
4	4	0	380	-355	2	0	1	339	218	4	3	I	408	398	4	6	I	657	-461	0	10	I	219	234	7	2	2	548	572</					

Table III. (Continued)

$h$	$k$	$l$	$10F_{\bar{Q}}$	$10F_{\bar{S}}$	$h$	$k$	$l$	$10F_{\bar{Q}}$	$10F_{\bar{S}}$	$h$	$k$	$l$	$10F_{\bar{Q}}$	$10F_{\bar{S}}$	$h$	$k$	$l$	$10F_{\bar{Q}}$	$10F_{\bar{S}}$	$h$	$k$	$l$	$10F_{\bar{Q}}$	$10F_{\bar{S}}$
5	6	2	268	221	0	11	2	257	-236	10	2	3	172	231	0	6	3	505	473	3	9	3	79-	-10
6	6	2	142	-147	0	11	2	219	154	0	3	3	68-	15	3	311	295	3	9	3	88-	-44		
6	5	2	245	250	1	11	2	25-	22	0	3	3	828	903	1	6	3	105	43	4	9	3	174	167
6	6	2	82	-91	1	11	2	74	-59	1	3	3	1054	1041	1	6	3	291	300	5	9	3	202	-217
6	5	2	337	-294	1	11	2	39-	11	1	3	3	477	-435	1	6	3	423	-450	5	9	3	63-	55
7	6	2	51	-82	1	11	2	39-	-19	1	3	3	308	316	1	6	3	357	327	6	9	3	79	90
7	5	2	131	126	2	11	2	102	-118	1	3	3	408	-395	2	6	3	225	-219	6	9	3	177	187
7	6	2	257	271	2	11	2	51-	45	2	3	3	779	730	2	6	3	451	454	7	9	3	251	270
7	5	2	128	-127	3	11	2	42-	-34	2	3	3	857	-896	2	6	3	68-	-49	0	10	3	117	-142
8	6	2	88	87	3	11	2	48-	56	2	3	3	91	-63	2	6	3	328	-326	0	10	3	251	-243
8	5	2	62-	67	0	0	3	983	-963	2	3	3	308	-279	3	6	3	111	-29	1	10	3	45-	52
10	6	2	22-	-16	1	0	3	913	-913	1	3	3	514	-654	3	6	3	228	-242	1	10	3	208	-223
0	7	2	239	248	1	0	3	672	738	3	3	3	311	-250	3	6	3	645	779	1	10	3	242	-259
0	7	2	331	-324	2	0	3	84	39	3	3	3	111	-117	3	6	3	357	-347	2	10	3	168	-188
1	7	2	131	-91	2	0	3	374	347	3	3	3	768	682	4	6	3	366	369	2	10	3	74-	80
1	7	2	119	73	3	0	3	139	121	4	3	3	139	-136	4	6	3	317	-132	3	10	3	62-	84
1	7	2	54	-37	3	0	3	362	-330	4	3	3	94	62	4	6	3	377	420	3	10	3	68-	-23
1	7	2	251	-198	4	0	3	325	-285	4	3	3	382	361	4	6	3	165	160	4	10	3	191	204
2	7	2	597	-625	4	0	3	543	-558	4	3	3	302	253	5	6	3	65-	64	4	10	3	219	-225
2	7	2	499	538	5	0	3	502	-481	5	3	3	222	212	5	6	3	357	393	5	10	3	257	-286
2	7	2	371	450	5	0	3	789	-875	5	3	3	414	379	5	6	3	62-	-43	6	10	3	19-	26
2	7	2	439	-463	6	0	3	277	-264	5	3	3	488	491	5	6	3	688	664	0	11	3	51-	-55
3	7	2	179	66	6	0	3	371	357	5	3	3	834	-773	6	6	3	437	-421	1	11	3	179	-180
3	7	2	334	307	7	0	3	371	375	6	3	3	285	258	6	6	3	360	338	2	11	3	191	-216
3	7	2	157	-159	7	0	3	48	58	6	3	3	374	-357	6	6	3	108	-116	0	10	4	1150	-1216
4	7	2	151	143	8	0	3	339	-332	6	3	3	471	-442	7	6	3	48-	42	1	10	4	422	-474
4	7	2	219	-215	9	0	3	188	-220	7	3	3	62-	-5	7	6	3	105	91	2	10	4	634	-644
4	7	2	199	-225	9	0	3	99	-109	7	3	3	262	-220	7	6	3	162	-145	2	10	4	597	-670
4	7	2	188	163	10	0	3	97	97	7	3	3	329	-329	8	6	3	94	103	3	10	4	131	-93
5	7	2	111	66	11	0	3	222	282	7	3	3	68-	-1	8	6	3	65-	45	0	10	4	414	-469
5	7	2	282	-286	0	1	3	1396	-1469	8	3	3	194	-116	0	7	3	374	365	4	10	4	674	-699
5	7	2	102	-98	0	1	3	112	-94	8	3	3	234	-222	0	7	3	174	-201	2	10	4	102	-80
5	7	2	534	525	1	1	3	171	133	9	3	3	359	361	1	7	3	391	-391	5	10	4	77-	-21
6	7	2	251	-238	1	1	3	397	-345	10	3	3	71	81	1	7	3	302	290	5	10	4	328	-329
6	7	2	51-	-51	1	1	3	85	-19	0	4	3	828	751	1	7	3	154	-152	6	10	4	225	-206
6	7	2	74	63	1	1	3	325	-290	0	4	3	737	748	1	7	3	297	283	2	10	4	274	-305
6	7	2	68-	5	2	1	3	294	261	1	4	3	831	761	2	7	3	245	-240	7	10	4	357	-362
7	7	2	302	292	2	1	3	522	-524	1	4	3	291	251	2	7	3	397	384	7	10	4	475	-511
7	7	2	428	394	2	1	3	51-	30	1	4	3	371	-342	2	7	3	328	323	8	10	4	372	-571
7	7	2	131	-136	2	1	3	528	525	1	4	3	222	-186	2	7	3	119	131	8	10	4	177	-167
8	7	2	79-	59	3	1	3	348	275	2	4	3	265	-220	3	7	3	122	92	9	10	4	219	-217
0	8	2	185	188	3	1	3	671	701	2	4	3	574	-538	3	7	3	191	-177	10	10	4	88	-92
0	8	2	145	-147	3	1	3	781	790	2	4	3	379	-372	3	7	3	457	506	11	10	4	142	-143
1	8	2	362	-412	3	1	3	157	175	2	4	3	562	-484	3	7	3	371	-381	0	10	4	537	-537
1	8	2	408	-431	4	1	3	268	-230	3	4	3	577	-559	4	7	3	119	141	0	10	4	492	-680
1	8	2	145	154	4	1	3	114	105	3	4	3	437	-382	4	7	3	157	-142	1	10	4	837	-756
1	8	2	248	277	4	1	3	706	-700	3	4	3	222	-201	4	7	3	119	-126	1	10	4	899	-810
2	8	2	239	-252	4	1	3	431	-404	3	4	3	751	681	4	7	3	437	-413	1	10	4	77	-644
2	8	2	357	336	5	1	3	442	-418	4	4	3	79	56	5	7	3	248	-229	3	10	4	861	-886
2	8	2	251	288	5	1	3	471	-519	4	4	3	139	-139	5	7	3	91	-29	2	10	4	497	-500
2	8	2	137	-127	5	1	3	259	226	4	4	3	274	-254	5	7	3	259	-254	2	10	4	131	-176
3	8	2	94-	71	5	1	3	557	-545	4	4	3	242	-201	5	7	3	314	-308	2	10	4	918	-935
3	8	2	439	449	6	1	3	445	-432	5	4	3	319	298	6	7	3	279	-283	2	10	4	422	-429
3	8	2	94-	-34	6	1	3	377	-379	5	4	3	97	83	6	7	3	274	-279	3	10	4	111	-111
3	8	2	468	-520	6	1	3	603	593	5	4	3	285	-291	6	7	3	268	-268	3	10	4	445	-439
4	8	2	65-	64	6	1	3	68	78	5	4	3	97	78	6	7	3	111	-111	7	10	4	262	-262
4	8	2	168	-120	7	1	3	508	503	6	4	3	331	-322	7	7	3	288	-283	2	10	4	237	-251
4	8	2	194-	186	10	1	3	168	153	4	4	3	348	-344	8	8	3	91	-53	6	10	4	425	-425
2	9	2	237	219	0	2	3	597	-530	10	4	3	174	-174	1	8	3	142	178	6	10	4	148	-150
2	9	2	85	112	0	2	3	137	-122	0	5	3	542	508	2	8	3	545	573	6	10	4	234	-234
2	9	2	134	-129	1	2	3	277	213	0	5	3	457	-437	4	8	3	142	-136	10	10	4	91-	91
0	9	2	177	-194	1	2	3	222	-242	1	5	3	194	-137	2	8	3	508	515</					

Table III. (Continued)

$h$	$k$	$l$	$10F_g$	$10F_{\bar{g}}$	$h$	$k$	$l$	$10F_g$	$10F_{\bar{g}}$	$h$	$k$	$l$	$10F_g$	$10F_{\bar{g}}$	$h$	$k$	$l$	$10F_g$	$10F_{\bar{g}}$	$h$	$k$	$l$	$10F_g$	$10F_{\bar{g}}$
7	8	4	328	365	3	2	5	234	-232	4	5	5	297	287	0	9	5	294	-272	6	2	5	85	69
6	8	4	71-	-38	4	2	5	160	-131	4	5	5	671	650	1	6	5	122	-92	6	2	5	94	72
0	9	4	154	-168	4	2	5	228	-227	4	5	5	262	253	1	6	5	142	-170	7	2	6	114	103
0	9	4	228	-223	4	2	5	411	-429	4	5	5	202	-186	2	6	5	108	-72	7	2	6	274	290
1	9	4	57-	-48	4	2	5	598	594	5	5	5	57-	-24	2	6	5	74-	116	7	2	6	91-	8
1	8	4	68-	-3	5	2	5	429	440	5	5	5	68-	-21	3	8	5	119	-107	8	2	6	134	142
1	9	4	68-	-78	5	2	5	534	-538	5	5	5	382	-407	3	8	5	362	-400	8	2	6	105-	65
1	8	4	159-	-193	5	2	5	71-	32	5	5	5	168-	-142	4	5	5	345	-363	9	2	6	339	-349
2	8	4	176	185	5	2	5	88-	14	6	5	5	171	-180	4	5	5	79	90	10	2	6	228	-230
2	9	4	88-	127	6	2	5	79	60	6	5	5	94-	-89	5	9	5	68-	-85	0	3	6	437	405
2	8	4	211	257	6	2	5	99	51	6	5	5	56-	-17	6	5	5	25-	-50	0	3	6	806	-815
3	8	4	71-	-3	6	2	5	111	110	6	5	5	131	-108	7	9	5	45	70	11	3	6	174	-124
3	9	4	79-	110	6	2	5	418	-433	7	5	5	91	-87	0	10	5	42-	-16	1	3	6	119	-87
3	8	4	134	138	7	2	5	228	-233	7	5	5	228	-295	0	10	5	62-	-81	1	3	6	277	248
4	8	4	322	-320	7	2	5	642	392	7	5	5	225	-224	1	10	5	42-	-44	1	3	6	277	244
4	9	4	154	-164	7	2	5	234	265	8	5	5	137	-121	1	10	5	148	-160	2	3	6	542	-502
5	9	4	179	-206	7	2	5	222	-240	9	5	5	151	-111	2	10	5	51-	74	2	3	6	537	515
5	9	4	65-	-104	8	2	5	162	-157	0	6	5	431	-391	2	10	5	139	-159	2	3	6	545	554
6	8	4	28-	11	8	2	5	111-	39	0	6	5	234	218	3	10	5	28-	-5	2	3	6	82-	-18
7	8	4	254	273	9	2	5	408	-419	1	6	5	268	-220	3	10	5	248	292	3	6	6	108	-92
0	10	4	57-	-42	10	2	5	105	129	1	6	5	62-	-10	4	10	5	174	211	3	6	6	251	223
0	10	4	437	-392	0	3	5	182	149	1	6	5	125	-82	5	10	5	37-	35	3	3	6	222	213
1	10	4	34-	27	0	3	5	114	-122	1	6	5	194	181	6	10	5	38-	-55	3	3	6	576	-580
1	10	4	51-	-70	1	3	5	114	92	2	6	5	97-	-64	0	6	6	122	102	4	3	6	219	201
1	10	4	51-	-15	1	3	5	525	-478	2	6	5	448	-461	1	0	6	695	711	4	3	6	125	101
1	10	4	125	-157	1	3	5	799	842	2	6	5	563	-580	1	0	6	168	-160	4	3	6	177	-179
2	10	4	57-	82	1	3	5	231	-214	2	6	5	319	-303	2	0	6	88-	18	4	3	6	134	-117
2	10	4	65-	111	2	3	5	608	-553	3	6	5	405	-387	2	0	6	85	-92	5	3	6	102	-134
2	10	4	102	77	2	3	5	462	434	3	6	5	279	-258	3	0	6	611	-618	5	3	6	99	-79
3	10	4	194	184	2	3	5	208	216	3	6	5	31-	-43	3	0	6	537	550	3	3	6	491	-518
3	10	4	202	235	2	3	5	439	-461	3	6	5	211	-204	4	0	6	62-	-45	3	3	6	494	-506
4	10	4	17-	-41	3	3	5	88-	25	4	6	5	299	261	4	0	6	508	546	6	3	6	354	-280
4	10	4	34-	-15	3	3	5	251	264	4	6	5	179	-160	5	0	6	56	157	1	3	6	239	236
5	10	4	139	-167	3	3	5	439	-414	4	6	5	142	-142	5	0	6	71-	35	6	3	6	268	-302
6	7	4	74-	-104	3	3	5	637	-673	4	6	5	134	-114	6	0	6	162	148	6	3	6	57-	42
0	0	5	159	-61	4	3	5	485	465	5	6	5	257	-246	6	0	6	538	-560	7	3	6	339	-367
1	0	5	436	480	4	5	5	291	268	5	6	5	268	-251	7	0	6	31-	-5	7	3	6	111	-125
1	0	5	677	-735	4	3	5	462	-460	5	6	5	62-	-15	7	0	6	100	-45	7	3	6	105	-105
2	0	5	531	513	4	3	5	474	470	5	6	5	79-	-61	8	0	6	282	282	8	3	6	268	-269
2	0	5	199	190	5	3	5	337	301	6	8	5	79	-52	9	0	6	88	65	8	3	6	71-	-81
3	0	5	354	-330	5	3	5	428	-424	6	6	5	202	-211	10	0	6	77	-72	9	3	6	434	-399
4	0	5	399	435	5	3	5	65-	-37	6	8	5	299	289	11	0	6	162	-167	10	3	6	34-	-30
4	0	5	385	-359	5	3	5	422	418	7	6	5	85-	-163	0	1	6	552	548	4	6	6	91-	-50
4	0	5	322	302	6	3	5	151	-138	7	6	5	408	-366	0	1	6	252	287	0	4	6	157	-136
5	0	5	99-	36	6	3	5	202-	-189	7	6	5	74-	-35	1	1	6	85-	-65	1	4	6	111	-125
5	0	5	325	-329	6	3	5	191	-210	8	6	5	62-	-40	1	1	6	679	482	3	4	6	205	-157
6	0	5	117	106	6	3	5	168-	-173	0	7	5	185-	-179	1	1	6	179	-165	1	4	6	639	-633
6	0	5	194-	-203	7	3	5	145-	-161	0	7	5	337-	-327	1	1	6	462	-406	1	4	6	328	-285
7	0	5	85-	61	7	3	5	397	364	1	7	5	20-	-13	2	1	6	448	-373	2	4	6	428	-374
7	0	5	705	798	7	3	5	134	-116	1	7	5	660-	-560	1	6	6	252	-221	2	4	6	122	-111
8	0	5	385	384	7	3	5	176-	-160	1	7	5	251-	-237	2	1	6	122	-127	2	4	6	425	-445
9	1	5	62-	-1	8	3	5	348	305-	6	7	5	197-	-187	6	1	6	62-	-53	6	4	6	322	-321
3	1	5	471	456	3	4	5	305-	-308	6	7	5	177-	-177	6	1	6	141-	-164	1	4	6	191	-186
4	1	5	657-	658	3	4	5	657-	-662	6	7	5	191-	-199	7	1	6	279	-314	7	4	6	108	-80
4	1	5	488-	-450	4	4	5	257	225	6	7	5	331-	-354	7	1	6	148-	-146	7	4	6	208-	-213
4	1	5	48-	-14	4	4	5	619	602	7	7	5	239-	-217	7	1	6	214	-217	8	4	6	311	-304
4	1	5	339	366	4	4	5	439-	-453	7	7	5	194-	165	7	1	6	257-	-304	8	4	6	414	-403
5	1	5	21-	15	4	4	5	88-	-76	8	7	5	265-	-244	8	1	6	374	390	9	4	6	77-	-59
5	1	5	157-	-171	5	4	5	145-	-142	0	8	5	197-	-197	9	1	6	68-	52	0	5	6	565-	-533
5	1	5	285	-260	5	4	5	368	377	4	8	5	148-	-127	10	1	6	217	-196	0	5	6	331-	-278
6	1	5	139	113	5	4	5	185-	178	1	8	5	237-	224	0	2	6	422	-365	1	5	6	465-	-414
6	1	5	205	191	6	4	5	142-	-134	1	8	5	277-	262	0	2	6	615	-651	1	5	6	174-	-156
6	1	5	317	331	6	4	5	157-	-218															

Table III. (Continued)

$h$	$k$	$l$	$10F_{\alpha}$	$10F_{\beta}$	$h$	$k$	$l$	$10F_{\alpha}$	$10F_{\beta}$	$h$	$k$	$l$	$10F_{\alpha}$	$10F_{\beta}$	$h$	$k$	$l$	$10F_{\alpha}$	$10F_{\beta}$	$h$	$k$	$l$	$10F_{\alpha}$	$10F_{\beta}$	
6	3	7	279	294	2	7	7	151	-126	3	2	8	157	-160	0	6	8	82	-66	0	2	9	291	280	
7	3	7	271	285	2	7	7	174	-142	3	2	8	368	362	0	6	8	234	-220	1	2	9	162	149	
7	3	7	77	-38	3	7	7	94	92	3	2	8	137	-128	1	6	8	125	83	1	2	9	68-	-70	
8	3	7	139	131	3	7	7	239	-269	4	2	8	448	431	1	6	8	297	-272	1	2	9	291	-306	
8	3	7	168	-141	3	7	7	197	179	4	2	8	171	-160	1	6	8	274	202	1	2	9	111	100	
9	3	7	219	-188	4	7	7	99	111	4	2	8	437	431	1	6	8	528	-514	2	2	9	291	288	
9	3	7	57	-110	4	7	7	57	-13	4	2	8	85	-70	2	6	8	42-	-4	2	2	9	322	-339	
10	3	7	239	-213	4	7	7	179	184	5	2	8	454	441	2	6	8	91	100	2	2	9	599	-639	
0	4	7	368	-322	5	7	7	379	363	5	2	8	79	-41	2	6	8	311	352	2	2	9	491	487	
0	4	7	642	-653	5	7	7	216	-234	5	2	8	274	262	2	6	8	299	-292	3	2	9	357	342	
1	4	7	674	-595	6	7	7	277	216	6	2	8	168	-194	3	6	8	42-	4	3	2	9	182	-193	
1	4	7	571	-493	6	7	7	251	-232	6	2	8	322	361	3	6	8	159	122	3	2	9	302	-396	
1	4	7	254	-234	7	7	7	68	-48	7	2	8	257	-255	3	6	8	251	243	3	2	9	188	-196	
1	4	7	111	117	7	7	7	68	65	7	2	8	101	-20	4	6	8	105	-136	4	2	9	31	51	
2	4	7	337	301	8	7	7	57	-30	8	2	8	139	132	4	6	8	99	60	4	2	9	97	92	
2	4	7	228	207	0	8	7	137	110	8	2	8	285	-337	5	6	8	85	67	4	2	9	319	-273	
2	4	7	165	176	0	8	7	185	165	9	2	8	65	68	5	6	8	91	-35	5	2	9	242	256	
2	4	7	128	120	1	8	7	317	309	10	2	8	202	-192	6	6	8	108	130	5	2	9	265	-251	
3	4	7	339	321	1	8	7	139	-93	0	3	8	334	-314	6	5	8	194	-169	6	2	9	139	-139	
3	4	7	174	152	1	8	7	65	-29	0	3	8	82	-15	7	6	8	299	242	6	2	9	219	232	
3	4	7	77	57	1	8	7	277	-288	1	3	8	171	-117	7	6	8	137	116	7	2	9	131	-82	
3	4	7	82	-13	2	8	7	322	-345	1	3	8	388	346	8	6	8	265	218	7	2	9	179	200	
4	4	7	228	-200	2	8	7	77	-80	1	3	8	482	-504	5	6	8	25-	-1	8	2	9	116	96	
4	4	7	343	-349	2	8	7	194	-196	1	3	8	74	-39	0	7	8	59-	77	8	2	9	117	-138	
4	4	7	122	-132	3	8	7	139	-142	2	3	8	294	268	0	7	8	159	125	9	2	9	311	276	
4	4	7	365	-368	3	8	7	114	-91	2	3	8	59	-37	1	7	8	88	108	10	2	9	22-	-27	
5	4	7	137	-197	3	8	7	117	-80	2	3	8	185	139	1	7	8	299	-273	0	3	9	119	-125	
5	4	7	91	-77	4	8	7	219	209	2	3	8	282	264	1	7	8	348	350	8	3	9	74-	63	
5	4	7	525	-528	4	8	7	128	147	3	3	8	479	443	1	7	8	277	-261	1	3	9	219	213	
5	4	7	165	134	5	8	7	354	360	3	3	8	322	-324	2	7	8	119	88	1	3	9	197	188	
6	4	7	274	266	5	8	7	71	-76	3	3	8	134	133	2	7	8	194	165	1	3	9	539	-554	
6	4	7	654	462	6	8	7	128	-123	3	3	8	88	-0	2	7	8	331	-318	1	3	9	114	98	
7	4	7	159	155	6	8	7	257	-281	4	3	8	82	-69	3	7	8	94	112	2	3	9	291	274	
7	4	7	237	244	7	8	7	54	-41	4	3	8	308	-301	3	7	8	71	-2	2	3	9	248	-233	
8	4	7	162	-153	0	9	7	445	336	4	3	8	96	69	3	7	8	77-	-84	2	3	9	194	-203	
8	4	7	177	-174	1	9	7	125	129	4	3	8	437	-452	4	7	8	216	-218	2	3	9	345	345	
9	4	7	171	-156	1	9	7	31	35	5	3	8	31	-31	52	4	7	8	194	161	3	3	9	197	192
9	4	7	45	-106	2	8	7	37	-13	5	3	8	239	-227	5	7	8	74	64	3	3	9	351	-331	
0	5	7	317	-303	2	9	7	140	-157	5	3	8	77	-17	15	5	7	8	114	96	1	3	9	539	-554
0	5	7	316	-276	3	8	7	51	-68	6	3	8	411	-419	6	7	8	191	215	3	3	9	394	373	
1	5	7	119	-57	4	8	7	108	129	6	3	8	468	480	6	7	8	237	-243	6	3	9	19	10	
1	5	7	388	-348	3	9	7	39	-39	7	3	8	194	182	7	7	8	37-	16	3	3	9	317	313	
1	5	7	139	-122	0	0	8	502	504	7	3	8	231	234	2	7	8	37-	26	4	3	9	311	305	
1	5	7	102	-68	1	0	8	148	139	8	3	8	262	-233	0	8	8	191	161	1	3	9	199	180	
2	5	7	388	374	1	0	8	77	-5	8	3	8	59-	8	1	8	88	205	201	5	3	9	445	-435	
2	5	7	134	-80	2	0	8	439	-446	9	3	8	102	89	1	8	88	48-	-38	6	3	9	311	-305	
2	5	7	425	451	2	0	8	302	-304	10	3	8	19-	-43	2	8	8	65-	-19	6	3	9	101	-111	
2	5	7	374	371	3	0	8	122	121	0	4	8	265	-254	145	123	7	3	9	62-	-37				
3	5	7	97	56	3	0	8	614	-641	0	4	8	228	-218	3	8	8	165	-165	7	3	9	94	103	
3	5	7	271	248	4	0	8	405	385	1	4	8	88	-73	3	8	8	151	-136	8	3	9	231	200	
3	5	7	142	-117	4	0	8	142	146	2	4	8	205	293	1	0	9	259	-247	1	4	8	171	-158	
3	5	7	105	-62	5	0	8	34-	32	1	4	8	417	-403	4	8	8	62-	-43	2	4	9	271	-246	
4	5	7	217	-217	1	1	8	177	-162	3	4	8	448	428	3	0	9	382	-363	2	4	9	381	-361	
4	5	7	402	-402	1	1	8	188	-170	4	5	8	491	-480	4	0	9	179	206	2	4	9	168	-163	
4	5	7	214	-197	1	1	8	851	830	4	4	8	148	-155	4	0	9	217	-218	3	4	9	451	-483	
4	5	7	62	-22	2	1	8	368	-337	4	4	8	274	-257	5	0	9	268	261	3	4	9	417	416	
4	5	7	94	-76	2	1	8	291	-286	5	4	8	19-	-32	3	6	8	91	58	3	4	9	434	430	
0	6	7	182	-191	2	1	8	637	-648	5	4	8	454	-425	7	0	8	345	340	4	4	9	219	215	
0	6	7	105	-71	2	1	8	99-	94-	5	4	8	285	-273	1	1	8	328	-332	6	4	8	351	477	
1	6	7	82	-41	3	1	8	262	251	6	4	8	59-	-64	9	0	9	45-	15	5	4	9	99-	-91	
1	6	7	265	-256	3	1	8	194	-168	191	208	0	0	9	185	158	3	1	9	348	-327				
1	6	7	411	411	3	1	8	385	-385	7	4	8	277	299	0	1	9	311	-346	7	1	9	291	-268	
1	6	7	451	-451	3	1	8	111	-120	7	4	8	385	401	0	1									

**Table III.** (Continued)

h	k	l	10F <sub>2</sub>	10F <sub>5</sub>	h	k	l	10F <sub>2</sub>	10F <sub>5</sub>	h	k	l	10F <sub>2</sub>	10F <sub>5</sub>	h	k	l	10F <sub>2</sub>	10F <sub>5</sub>	h	k	l	10F <sub>2</sub>	10F <sub>5</sub>										
5	1	11	222	-237	3	2	11	85	-81	2	3	11	54-	39	1	4	11	274	266	1	5	11	54	-35	4	0	12	34-	20	6	1	12	99	97
6	1	11	342	304	3	2	11	214	222	2	3	11	279	-275	2	4	11	25-	-29	2	5	11	245	-295	3	0	12	151	-154	6	1	12	103	-102
6	1	11	99	-95	4	2	11	48-	-12	3	3	11	54-	-40	2	4	11	85	-122	2	5	11	60-	-72	6	0	12	94	78	1	2	12	180	271
7	1	11	245	208	4	2	11	57-	-26	3	3	11	54-	33	2	2	11	151	-150	3	3	11	45-	61	1	1	12	105	81	2	2	12	202	205
7	1	11	176	167	3	2	11	159	184	4	3	11	39-	-32	3	4	11	208	-199	3	5	11	74-	-84	1	1	12	320	-333	3	2	12	79	-92
8	1	11	31-	19	5	2	11	68	-73	4	3	11	39-	-39	3	4	11	43-	-41	4	5	11	271	273	2	1	12	348	394	4	2	12	116	-129
8	1	11	39-	28	6	2	11	374	362	5	3	11	203	225	4	4	11	199	195	4	5	11	102	194	2	1	12	85	112	5	2	12	39-	-49
0	2	11	176	-195	6	2	11	162	-171	5	3	11	203	-198	4	4	11	174	152	5	5	11	74	63	3	1	12	148	179	6	2	12	262	250
0	2	11	139	-139	7	2	11	90	-23	6	3	11	99	98	5	6	11	194	172	5	5	11	154	206	3	1	12	111	133	2	3	12	93	95
1	2	11	277	-331	7	2	11	119	116	6	3	11	242	-216	5	8	11	42-	-22	6	5	11	19-	12	4	1	12	151	-164	3	3	12	74	-77
1	2	11	299	337	8	2	11	45	-193	7	3	11	322	-296	6	4	11	45-	-36	1	0	12	91	-121	4	1	12	117	124	2	3	12	28-	-18
1	2	11	531	-542	0	3	11	271	239	7	3	11	42-	-2	6	4	11	354	-379	2	0	12	136	141	5	1	12	39-	-50	4	3	12	94	-95
2	2	11	65-	-11	1	3	11	259	325	0	4	11	303	280	7	4	11	168	-151	3	0	12	357	384	5	1	12	45-	-64	5	3	12	20-	4

**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) = 1.53(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>i</sup> ) = 3.00(2)	N(5)HO(4 <sup>i</sup> ) = 141.6
N(6) ... O(2) = 2.89(3)	N(6)HO(2) = 165.0
N(6) ... O(4 <sup>i</sup> ) = 2.91(2)	N(6)HO(4 <sup>i</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>ii</sup> ) = 3.29(2) Å
S(3) ... O(1 <sup>i</sup> ) = 3.39(3)	O(3) ... C(1 <sup>ii</sup> ) = 3.48(3)
S(3) ... O(2 <sup>i</sup> ) = 3.49(2)	O(3) ... N(1 <sup>ii</sup> ) = 3.03(3)
S(4) ... N(5 <sup>i</sup> ) = 3.47(2)	O(4) ... C(3 <sup>i</sup> ) = 3.37(2)

i    x, y, z	v    1-x, 1-y, 1-z
ii   x+1, y, z	vi  1-x, 1-y, z
iii  i-x, y, 1-z	vii x-1, y, z
iv  x, 1-y, z	

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*(ethylenthiourea)-cadmium thiocyanate.<sup>14</sup>

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*<sup>10</sup> configuration of Cd<sup>2+</sup> it is impossible to make any sound discussion on the nature of the metal-ligands interactions.

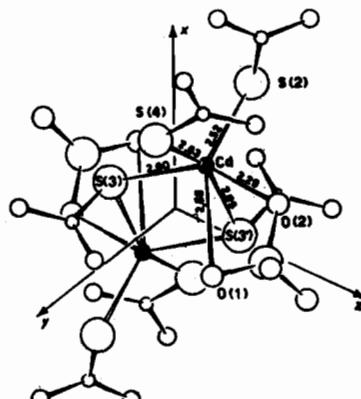


Figure 1. Clinographic projection of a dimer.

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<sup>3</sup> 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).

character for S(3)-C(2). This is also confirmed by the angles around S(3): CdS(3)C(2)=107.0°, CdS(3)Cd<sup>i</sup>=97.5°, Cd<sup>i</sup>S(3)C(2)=109.2°. Nor any  $\pi$  interaction seems probable as indicated by the dihedral angles: CdS(3)C(2)  $\wedge$  S(3)C(2)N(3)N(4)=38.6°

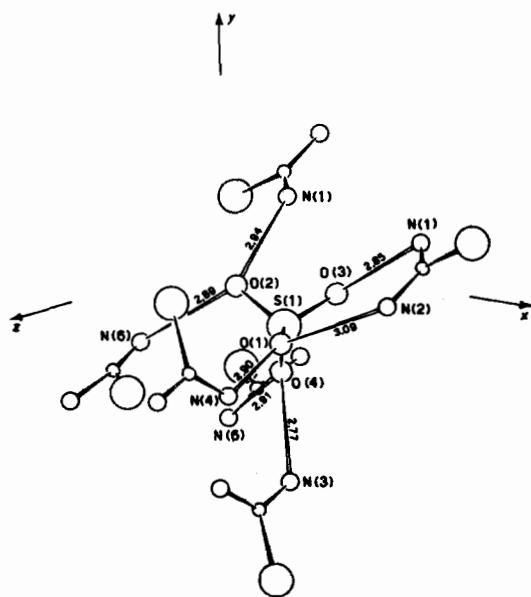


Figure 2. Clinographic projection of the  $\text{SO}_4^{2-}$  environment.

and  $\text{Cd}^i\text{S}(3)\text{C}(2) \wedge \text{S}(3)\text{C}(2)\text{N}(3)\text{N}(4) = 24.5^\circ$  which are far from 90°. 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: CdS(2)-C(1)=103.0, 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: CdS(2)C(1)  $\wedge$  S(2)C(1)N(1)N(2)=54.9°, CdS(4)C(3)  $\wedge$  S(4)C(3)N(5)N(6)=22.6°.

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 Å.\*

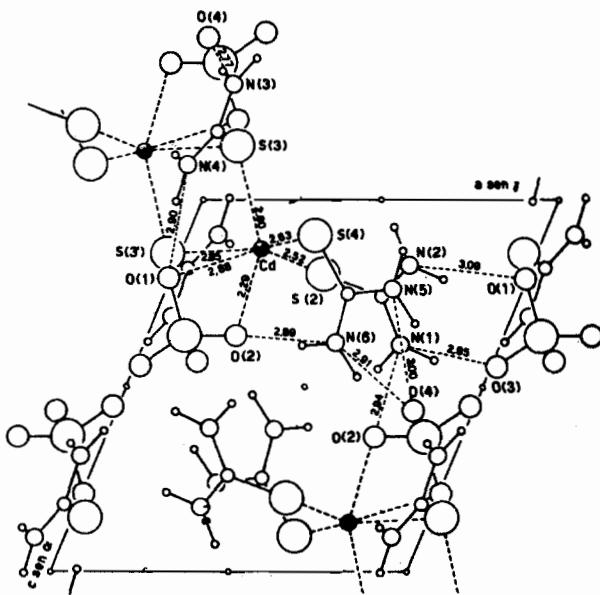


Figure 3. Projection of the structure down to [010].

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 (S(1)-O(2)=1.51(2) Å) corresponds to the shorter Cd-O contact (Cd-O(2)=2.29(2) Å) 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 CdO(2)S(1)=112.4(1.1)°.

Packing is mainly due to the hydrogen bonds (see Table IV) formed by the NH<sub>2</sub> 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'+0.7903 Y'+0.1530 Z'=0.9319. The orthogonal X', Y', Z' coordinates are expressed in Å and are obtained from the x, y, z triclinic ones using the matrix:  $(\begin{matrix} \sin \gamma & 0 & -\sin \alpha \cos \beta^* \\ 0 & \cos \gamma & \sin \alpha \cos \beta^* \\ 0 & -\sin \gamma & \sin \alpha \end{matrix})$