Contribution from the Escuela de Química Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela.

The Crystal Structure of a Five-Coordinated Cadmium(II) Complex: Tristhiourea-Cadmium Sulphate

E. Corao* and S. Baggio

Received July 19, 1969

The crystal structure of tristhiourea-cadmium sulphate, $Cd(SC(NH_2)_2)_3SO_4$, has been determined by three dimensional X-ray analysis. Crystals are triclinic ($P\bar{1}$) with cell dimensions $a = 9.06(2)$, $b = 9.80(2)$, $c = 8.78(2)$ Å, $\alpha = 110.6(5)$, $\beta = 95.1(5)$, and $\gamma = 92.0(5)°$. The measured and calculated values for the density (for $Z=2$) are 2.02 and 2.00 g/cm³, respectively. A total of 1568 non-zero reflexions has been obtained by photographic methods. The structure was solved by Patterson methods and refined by the full-matrix least square method to a conventional R factor of 0.097. The crystal structure shows that the molecule is a dimer, and that the coordination around the metal atom is intermediate between square pyramidal and trigonal bipyramidal, although somewhat closer to the former. One sulphur atom from a thiourea molecule coordinates to two adjacent cadmium atoms at distances 2.627(7) and 2.870(7). The other three bond lengths in the coordination polyhedra are: Cd–S(2) = 2.538(6), Cd–S(3) = 2.627(6) (both S from thiourea molecules) and Cd–O(1) = 2.339(15) (the O belonging to the sulphate group).

Introduction

Nardelli and Chierici[1] obtained three complexes of cadmium sulphate with thiourea (hereafter tu); $Cdtu\text{-}SO_4 \cdot 2H_2O$, $Cd(tu)_4SO_4$ and $Cd(tu)_3SO_4$. The first compound was studied by X-ray diffraction[2] and the crystal structure showed that it was polymeric with octahedral coordination around the cadmium atom.

In this work, the analysis of the crystal structure of $Cd(tu)_3SO_4$ is undertaken, in order to investigate the coordination around the metal atom and the binding of its ligands, since it seems that these cannot be determined from the chemical composition alone.

Experimental Section

The crystals of $Cd(tu)_3SO_4$ were kindly supplied by Dr. R. Levitus.

Crystals are triclinic, with cell dimensions a = 9.06(2) Å, b = 9.80(2) Å, c = 8.78(2) Å, α = 110.6(5)°, β = 95.1(5)°, γ = 92.0(5)°. These values were obtained from calibrated precession photographs, taken with Mo kα radiation (λ = 0.7107 Å) at 20°C, and standard deviations were estimated from repeated film measurements; they are slightly different from those reported previously by Nardelli *et. al.*[1] The space group is $P\bar{1}$, as determined by crystal analysis. They are two molecules per cell and the observed and calculated density are 2.02 and 2.00 g/cm³, respectively. The volume of the unit cell is 724 Å.³

The intensities were collected with a single crystal of roughly spherical shape and mean radius of 0.01 cm, which was mounted with the *c* axis parallel to the spindle axis.

The layers hk0 to hk8 were recorded in a Weissenberg camera using the equi-inclination technique; the h0l and 0kl layers with a precession camera (all with Mo Kα radiation).

The intensities were estimated visually on the Weissenberg photographs by comparison with a calibrated scale; for the integrated precession photographs a microdensitometer was used. A total of 1568 non-zero reflexions was obtained within a 2,000: 1 ratio of maximum to minimum intensity.

Lorentz and polarization corrections were taken into account and the Phillips spot-shape factor[3] was apllied to the extended half of the upper level Weissenberg photographs.

The data from the different layers were put on the same scale using the h0l and 0kl levels.

No absorption correction was applied ($\mu_{MoK\alpha}$ = 21.4 cm⁻¹) because if the crystal is assumed to absorb as a sphere of radius 0.01 cm, the largest variation in intensity for a given layer is less than 2 per cent.

Structure Determination and Refinement. The cadmium and sulphur atoms were located in a three dimensional Patterson synthesis. The positions of the other atoms were obtained from successive electron density maps.

The initial reliability index $R = (\Sigma(|F_o|-|F_c|))/\Sigma|F_o|$ with all atoms was 0.29. A full matrix least square refinement was begun at this point, refining the positional parameters, isotropic temperature factor and a scale factor, one for each layer. After four cycles, convergence was achieved with reliability indexes $R = 0.122$ and $R' = (\Sigma\omega(F_o^2-F_c^2))/\Sigma\omega F_o^2 = 0.142$. The weighting scheme used was $\sigma=1$ when

(*) Present address: Centro de Ciencias U.L.A. Mérida, Venezuela.
(1) M. Nardelli and I. Chierici, *Ric. Sci.*, *28*, 1016, (1958).
(2) L. Cavalca, P. Domiano, G. Fava and P. Boldrini, *Acta Cryst.* 22, 878 (1967).
(3) D. C. Phillips, *Acta Cryst.*, 7 ,746 (1954).

$|F_o|<50.0$ and $\sigma=(1+0.1(|F_o|-50.0))^{1/2}$ when $|F_o|>50.0$, which gave a fairly constant value of $\omega\Delta^2$ in ranges of $|F_o|$ and $\sin\vartheta/\lambda$.

The refinement was continued allowing for anisotropic temperature factors of the Cd and S atoms and reducing the number of variable scale factors to one overall scale factor. This new series of refinement cycles converged after three cycles with $R = 0.097$ and $R' = 0.123$. With the coordinates obtained in the last cycle of refinement a difference Fourier synthesis was computed. The resulting electron density map showed no peaks exceeding ± 0.8 e. Å^{-3}.

The atomic scattering factors for neutral atoms used during the refinement were taken from a paper of Cromer and Waber.[4]

No attempt was made to locate hydrogen atoms. Theoretical positions for H were calculated assuming an sp^2 configuration for the nitrogen atoms and distances N–H of 1.03 Å. These positions are given in Table I.

Table I. Theoretical Positions for Hydrogen Atoms

Atom	x	y	z
H(1)	0.580	0.340	0.089
H(2)	0.741	0.384	0.009
H(3)	0.141	0.060	0.566
H(4)	0.179	0.224	0.785
H(5)	0.573	0.132	0.626
H(6)	0.568	0.333	0.738
H(7)	0.551	0.125	0.127
H(8)	0.700	–0.012	0.074
H(9)	–0.076	0.452	0.688
H(10)	0.061	0.421	0.834
H(11)	0.426	0.468	0.638
H(12)	0.300	0.385	0.431

Table II. Coordinates and Isotropic Temperature Factors. Standard deviations given in parentheses are in units of the last decimal place.

Atom	x	y	z	B
Cd	0.1125(2)	0.1331(2)	0.2211(2)	*
S(1)	0.0991(6)	–0.1450(6)	0.0367(7)	*
S(2)	–0.0798(7)	0.2003(7)	0.4235(8)	*
S(3)	0.3728(7)	0.0977(6)	0.3546(7)	*
S(4)	0.2732(6)	0.3657(5)	0.1057(7)	*
O(1)	0.1887(16)	0.3711(15)	0.2456(18)	2.8(2)
O(2)	0.4260(20)	0.4310(19)	0.1671(22)	4.3(3)
O(3)	0.1961(19)	0.4512(18)	0.0162(21)	4.0(3)
O(4)	0.2737(18)	0.2085(18)	–0.0056(21)	3.9(3)
N(1)	0.3205(23)	–0.3123(22)	–0.0465(25)	4.0(4)
N(2)	0.1220(23)	0.1795(22)	0.6631(26)	3.6(4)
N(3)	0.5316(22)	0.2425(24)	0.6384(29)	4.5(4)
N(4)	0.3464(22)	–0.0956(20)	–0.0837(26)	3.5(4)
N(5)	0.0018(24)	0.3880(22)	0.7208(26)	4.0(4)
N(6)	0.3843(23)	0.3805(23)	0.5340(27)	4.1(4)
C(1)	0.2695(22)	–0.1826(21)	0.0354(26)	2.3(3)
C(2)	0.0256(23)	0.2592(22)	0.6096(26)	2.6(4)
C(3)	0.4351(29)	0.2513(26)	0.5137(31)	3.7(4)

* were refined anisotropically

Results

Table II gives the positional parameters and the isotropic temperature factor; Table III gives the anisotropic thermal parameters for the Cd and S atoms. The observed and calculated structure factors using the numbers given in Tables II and III are given in Table IV. Table V gives the least squares planes passing through the thiourea molecules and the deviations of the atoms from them. Table VI gives the most important bond distances and angles.

Table III. Anisotropic Temperature Factors. Thermal parameters ($\times 10^4$). Standard deviations given in parentheses are in units of the last decimal place.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd	100(2)	84(2)	103(3)	6(1)	31(2)	25(2)
S(1)	63(6)	76(6)	113(10)	3(5)	17(6)	31(6)
S(2)	84(7)	127(8)	122(11)	23(6)	8(6)	13(7)
S(3)	110(8)	78(6)	109(10)	13(6)	–6(7)	15(6)
S(4)	77(6)	72(6)	96(10)	4(5)	13(6)	32(6)

The form of the anisotropic temperature expression is $\exp(-\sum_i \sum_j \beta_{ij} h_i h_j)$

Discussion

Figure 1 gives a projection of the structure on the (100) plane of a set of orthogonal cordinates obtained by the transformation given in the footnote of Table V. Figure 2 shows a schematic view of the molecule.

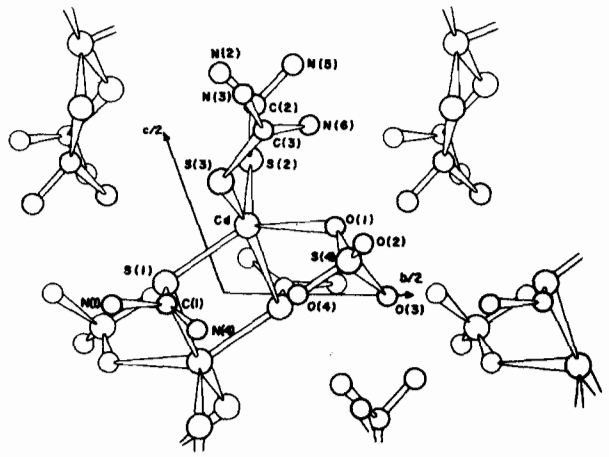

Figure 1. Orthogonal projection of the structure on the plane (100).

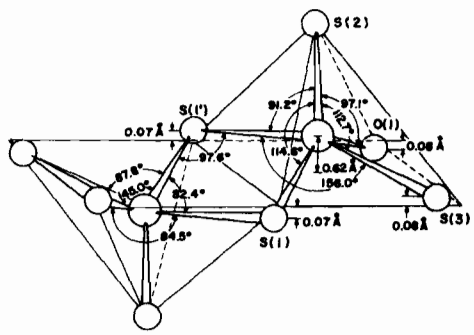

Figure 2. Schematic view of the molecule.

(4) D. T. Cromer and J. T. Waber, *Acta Cryst.*, *18*, 104 (1965).

Table IV. Observed and calculated structure factors. The five columns contain values of h, k, l, $10|F_o|$ and $10 F_o$

0	1	0	606	561
0	2	0	827	-694
0	3	0	1176	-948
0	4	0	1451	-1144
0	6	0	107	84
0	7	0	195	204
0	8	0	382	400
0	12	0	198	-139
1	-9	0	206	208
1	-8	0	106	139
1	-6	0	242	246
1	-5	0	205	-262
1	-4	0	731	-611
1	-3	0	87	-75
1	-2	0	358	-351
1	-1	0	1247	1257
1	0	0	566	775
1	1	0	225	-193
1	2	0	272	-256
1	3	0	1458	-1415
1	4	0	372	-404
1	5	0	295	312
1	6	0	461	460
1	7	0	545	586
1	8	0	245	261
1	9	0	245	-246
1	10	0	156	-170
1	11	0	220	-223
2	-10	0	151	149
2	-9	0	199	243
2	-8	0	151	196
2	-7	0	185	155
2	-6	0	567	-546
2	-5	0	422	-389
2	-4	0	197	173
2	-3	0	136	-90
2	-2	0	333	253
2	-1	0	468	461
2	0	0	49	30
2	2	0	651	-560
2	3	0	521	-468
2	5	0	250	274
2	6	0	274	290
2	7	0	267	247
2	9	0	195	-210
2	10	0	178	-171
3	-10	0	250	300
3	-7	0	472	-484
3	-6	0	675	-680
3	-4	0	201	207
3	-3	0	919	849
3	-2	0	576	531
3	0	0	75	-94
3	1	0	249	-273
3	2	0	464	-503
3	5	0	89	132
3	6	0	285	313
3	8	0	210	-205
4	-8	0	177	-180
4	-7	0	487	-516
4	-5	0	232	315
4	-4	0	814	835
4	-3	0	737	696
4	-1	0	981	-988
4	0	0	789	-780
4	1	0	558	-591
4	2	0	172	-150
4	3	0	712	697
4	4	0	468	458
4	5	0	441	469
4	7	0	217	-241
4	8	0	154	-184
4	9	0	164	-199
5	-8	0	152	-189
5	-7	0	196	-215
5	-6	0	217	-225
5	-5	0	180	184
5	-4	0	502	530
5	-3	0	477	483
5	-2	0	101	-67
5	-1	0	780	-735
5	0	0	615	-650
5	1	0	343	-388
5	2	0	616	783
5	3	0	570	625
5	4	0	292	282
5	6	0	386	-427
5	7	0	157	-237
5	8	0	160	-154
6	-5	0	145	170
6	-4	0	322	330
6	-3	0	277	271
6	-1	0	324	-405
6	0	0	458	-452
6	2	0	365	403
6	3	0	375	420
6	4	0	101	117
6	5	0	273	-324
6	6	0	187	-227
7	-7	0	169	154
7	-6	0	180	227
7	-5	0	289	261
7	-4	0	105	-137
7	-3	0	124	-142
7	-2	0	281	-281
7	-1	0	355	-367
7	2	0	176	194
7	3	0	315	292
7	5	0	114	-118
8	-6	0	155	206
8	-5	0	116	-134
8	-4	0	365	-379
8	-3	0	205	-263
8	-2	0	107	-118
8	-1	0	385	393
8	0	0	151	296
8	1	0	53	108
8	3	0	97	-110
8	4	0	248	-279
8	5	0	121	-139
9	-7	0	205	255
9	-5	0	214	-225
9	-4	0	120	-196
9	-3	0	228	-262
9	-2	0	116	130
9	-1	0	346	355
9	0	0	182	157
9	3	0	160	-242
10	-3	0	166	-220
10	-2	0	124	184
10	-1	0	164	197
10	0	0	152	221
11	-1	0	162	178
-12	-3	1	160	-127
-11	-4	1	218	-210
-11	-3	1	151	-114
-11	-1	1	255	201
-11	0	1	207	242
-10	-4	1	206	-141
-10	-3	1	284	-230
-10	-1	1	308	297
-10	0	1	137	138
-10	3	1	159	-186
-9	-6	1	207	-153
-9	-5	1	159	-142
-9	-4	1	193	-153
-9	-2	1	260	263
-9	-1	1	288	281
-9	2	1	259	-256
-9	3	1	186	-217
-8	-7	1	288	-202
-8	-3	1	124	138
-8	-2	1	242	236
-8	1	1	238	-155
-8	2	1	397	-394
-8	5	1	261	227
-8	6	1	235	228
-7	-8	1	203	-183
-7	-7	1	335	-313
-7	-5	1	248	238
-7	-4	1	287	315
-7	-3	1	230	217
-7	-2	1	153	-187
-7	-1	1	269	-263
-7	0	1	242	-224
-7	1	1	345	-290
-7	3	1	229	260
-7	4	1	265	245
-7	5	1	390	389
-7	7	1	358	-310
-7	8	1	284	-222
-6	-8	1	420	-388
-6	-7	1	349	-359
-6	-4	1	609	637
-6	-3	1	301	292
-6	-1	1	324	-322
-6	0	1	474	-476
-6	2	1	206	198
-6	3	1	260	252
-6	4	1	248	220
-6	6	1	246	-244
-6	7	1	183	-202
-6	8	1	273	-212
-5	-9	1	157	-157
-5	-8	1	262	-226
-5	-5	1	600	577
-5	-4	1	500	517
-5	-2	1	210	-196
-5	-1	1	851	-970
-5	0	1	554	-539
-5	1	1	182	160
-5	2	1	457	439
-5	3	1	472	461
-5	4	1	389	375
-5	6	1	117	-136
-5	7	1	304	-281
-5	8	1	264	-243
-4	-6	1	269	245
-4	-5	1	323	296
-4	-3	1	179	-195
-4	-2	1	655	-652
-4	-1	1	498	-502
-4	1	1	550	589
-4	2	1	664	677
-4	3	1	223	237
-4	4	1	275	-244
-4	5	1	180	-199
-4	6	1	198	-131
-4	7	1	415	-393
-3	-11	1	148	-191
-3	-10	1	197	-186
-3	-7	1	226	241
-3	-6	1	209	183
-3	-5	1	193	-196
-3	-3	1	346	-368
-3	-2	1	187	-216
-3	-1	1	613	575
-3	0	1	540	492
-3	1	1	442	475
-3	3	1	401	-385
-3	4	1	512	-560
-3	5	1	434	-414
-3	7	1	349	319
-2	-11	1	385	-361
-2	-8	1	458	492
-2	-7	1	670	723
-2	-6	1	100	76
-2	-5	1	502	-495
-2	-4	1	927	-905
-2	-3	1	534	-551
-2	-2	1	696	661
-2	0	1	417	-337
-2	1	1	1014	1106
-2	3	1	189	-218
-2	4	1	475	-463
-2	5	1	419	-380
-2	6	1	350	362
-2	7	1	381	392
-2	8	1	127	144
-2	10	1	260	-230
-1	-12	1	216	-194
-1	-11	1	143	-114
-1	-9	1	177	213
-1	-8	1	635	655
-1	-7	1	267	244
-1	-6	1	396	-376
-1	-5	1	838	-810
-1	-4	1	745	-827
-1	-3	1	299	-293
-1	-2	1	982	1166
-1	-1	1	645	704
-1	0	1	927	1073
-1	2	1	636	-653
-1	3	1	327	-323
-1	4	1	957	-938
-1	6	1	389	380
-1	7	1	350	369
-1	8	1	344	287
-1	10	1	266	-296
0	-9	1	214	207
0	-8	1	162	21
0	-5	1	572	-657
0	-4	1	406	-442
0	-3	1	668	732
0	-2	1	770	585
0	-1	1	663	797
0	1	1	1189	-953
0	2	1	555	-498
0	3	1	858	-931
0	4	1	395	-365
0	5	1	476	425
0	6	1	559	583
0	7	1	363	371
0	9	1	177	-200
0	10	1	237	-265
1	-10	1	156	176
1	-9	1	222	227
1	-8	1	97	-137
1	-6	1	128	-111
1	-5	1	234	-275
1	-2	1	284	219
1	-1	1	200	282
1	0	1	894	-712
1	1	1	275	-291
1	2	1	208	-194
1	3	1	145	100
1	4	1	726	690
1	5	1	232	268
1	8	1	127	-147
1	9	1	280	-305
1	10	1	127	-130
2	-12	1	215	178
2	-11	1	247	220
2	-10	1	232	267
2	-9	1	216	-203
2	-8	1	493	-465
2	-7	1	214	-197
2	-6	1	354	-419
2	-5	1	238	224
2	-4	1	562	506
2	-3	1	431	445
2	-2	1	515	907
2	-1	1	221	-184
2	0	1	1305	-1255
2	1	1	244	-226
2	3	1	196	224
2	4	1	451	460
2	7	1	139	-186
2	8	1	205	-185
2	9	1	58	100
3	-11	1	205	209
3	-9	1	379	-444
3	-8	1	353	-395
3	-7	1	327	-319
3	-6	1	250	213
3	-5	1	656	785
3	-4	1	638	578
3	-3	1	270	268
3	-2	1	217	-217
3	-1	1	856	-900
3	0	1	516	-571
3	1	1	133	-124
3	2	1	322	-322
3	3	1	1029	952
3	4	1	437	449
3	6	1	81	-93
3	7	1	529	-564
3	9	1	142	125
4	-8	1	323	-307
4	-7	1	158	-167
4	-6	1	559	552
4	-5	1	523	511
4	-4	1	154	167
4	-3	1	366	-332
4	-2	1	734	-738
4	-1	1	833	-797
4	0	1	209	193
4	1	1	79	113
4	2	1	517	542
4	3	1	684	657
4	4	1	169	190
4	5	1	103	102
4	6	1	653	-618
4	7	1	431	-463
4	10	1	276	267
5	-6	1	251	244
5	-5	1	229	255
5	-4	1	272	270
5	-3	1	228	-250
5	-2	1	225	-272
5	0	1	195	-167
5	1	1	200	208
5	2	1	358	374
5	3	1	128	-114
5	5	1	236	-240
5	6	1	267	-307
5	9	1	262	240
5	10	1	160	162
6	-7	1	354	327
6	-3	1	380	-377
6	-2	1	187	-187
6	-1	1	150	-192
6	0	1	245	255
6	1	1	358	418
6	5	1	139	-168
7	-9	1	204	185
7	-8	1	307	270
7	-5	1	176	-208
7	-4	1	448	-471
7	-3	1	143	-132
7	-1	1	233	238
7	0	1	523	520
7	1	1	217	259
7	3	1	338	-311
7	4	1	258	-277
8	-8	1	122	141
8	-6	1	138	-151
8	-5	1	280	-291
8	-1	1	326	352
8	0	1	158	169
8	2	1	352	-356
8	3	1	363	-419
8	4	1	153	-164
8	5	1	127	175
8	6	1	208	232
8	7	1	191	200
9	-6	1	223	-217
9	-5	1	232	-233
9	-2	1	212	233
10	-3	1	145	192
10	-2	1	144	168
10	2	1	148	-143
-12	3	2	269	-190
-11	3	2	254	-201
-10	3	2	239	-170
-9	-4	2	280	210
-9	-3	2	315	265
-9	-2	2	219	195
-9	-1	2	217	-191
-9	0	2	306	-329
-9	3	2	275	182
-9	4	2	163	161
-8	-5	2	271	220
-8	-3	2	268	250
-8	-2	2	144	-152
-8	-1	2	413	-461
-8	0	2	246	-264
-8	3	2	557	516
-8	4	2	217	167
-8	7	2	300	-257
-7	-9	2	251	-139
-7	-6	2	216	227
-7	-4	2	375	362
-7	-2	2	452	-430
-7	0	2	386	-386
-7	2	2	531	515
-7	3	2	395	336
-7	5	2	150	-183
-7	6	2	502	-476
-7	7	2	166	-152
-6	-9	2	240	-177
-6	-8	2	228	-212
-6	-7	2	152	152
-6	-6	2	290	263
-6	-5	2	275	250
-6	-4	2	426	384
-6	-3	2	327	-292
-6	-2	2	212	-213
-6	-1	2	334	-335
-6	0	2	410	-384
-6	1	2	122	123
-6	2	2	347	328
-6	3	2	486	446
-6	4	2	153	178
-6	5	2	443	-400
-6	6	2	390	-364
-5	-8	2	267	224
-5	-7	2	347	257
-5	-4	2	452	-466
-5	-3	2	410	-401
-5	-2	2	219	-188
-5	-1	2	154	-172
-5	0	2	354	364
-5	1	2	507	500
-5	2	2	431	407
-5	3	2	121	122
-5	5	2	459	-481
-5	6	2	283	-277
-4	-8	2	296	210
-4	-5	2	171	-144
-4	-4	2	427	-380
-4	-3	2	512	-452
-4	-1	2	843	955
-4	0	2	642	697
-4	2	2	515	-473
-4	3	2	497	-494
-4	4	2	394	-310
-4	6	2	197	155
-4	7	2	210	169
-3	-9	2	259	255
-3	-8	2	246	205
-3	-7	2	304	282
-3	-5	2	437	-409
-3	-4	2	558	-544
-3	-3	2	297	-260
-3	-1	2	883	1033
-3	0	2	741	797
-3	1	2	188	-178
-3	2	2	774	-814
-3	3	2	728	-820
-3	4	2	164	-57
-3	5	2	449	404
-3	6	2	458	411
-3	9	2	154	-173
-3	10	2	116	-149
-2	-10	2	312	253
-2	-9	2	359	372
-2	-8	2	418	375
-2	-7	2	181	-167
-2	-6	2	439	-407
-2	-5	2	645	-695
-2	-4	2	542	-554
-2	-3	2	333	-283
-2	-2	2	552	615
-2	-1	2	1158	1572
-2	0	2	522	516
-2	2	2	827	-1056
-2	3	2	571	-539
-2	5	2	344	170
-2	6	2	232	372
-2	7	2	208	225
-2	8	2	150	-150
-2	9	2	194	-208
-2	10	2	141	-151
-1	-7	2	366	-319
-1	-6	2	440	-385
-1	-5	2	310	-230
-1	-4	2	433	393
-1	-3	3	501	516
-1	-2	2	804	562
-1	-1	2	148	121
-1	0	2	195	-110
-1	1	2	665	-860
-1	2	2	783	-944
-1	3	2	406	-470
-1	5	2	887	818
-1	6	2	642	565
-1	7	2	65	60
-1	8	2	172	-208
-1	9	2	153	-215
-1	10	2	151	-166
0	-9	2	205	150
0	-8	2	269	-237
0	-7	2	391	-405
0	-5	2	203	158
0	-4	2	643	636
0	-3	2	340	340
0	-2	2	675	-789
0	1	2	851	-797
0	2	2	54	113
0	4	2	705	570
0	5	2	440	412
0	7	2	179	-179
0	8	2	346	-336
0	9	2	228	-245
1	-12	2	220	247
1	-7	2	257	-236
1	-5	2	315	281
1	-4	2	938	918
1	-2	2	250	-234
1	-1	2	484	-556
1	0	2	907	-922
1	1	2	855	637
1	2	2	635	561
1	3	2	259	237
1	4	2	378	374
1	5	2	382	-356
1	6	2	276	-271
1	8	2	210	-205
1	10	2	166	200
2	-13	2	153	196
2	-10	2	136	-162
2	-9	2	451	-486
2	-8	2	135	-173
2	-5	2	1188	1105
2	-4	2	757	675
2	-3	2	285	246
2	-2	2	604	-507
2	-1	2	1319	-1531
2	0	2	1024	-1120
2	1	2	371	342
2	2	2	820	749
2	3	2	838	819
2	4	2	83	74
2	5	2	535	-486
2	7	2	126	-151
2	9	2	143	168
3	-10	2	168	-242
3	-9	2	120	-144
3	-8	2	126	142
3	-6	2	481	469
3	-5	2	166	193
3	-4	2	120	97
3	-2	2	1035	-1102
3	-1	2	661	-638
3	0	2	132	123
3	1	2	713	647
3	2	2	1043	956
3	3	2	681	639
3	4	2	564	-501
3	5	2	453	-445
3	6	2	396	-396
3	7	2	235	-193
3	8	2	140	171
3	9	2	79	154
3	10	2	120	165
4	-10	2	142	-185
4	-8	2	115	-106
4	-7	2	108	125
4	-6	2	419	364
4	-5	2	147	-150
4	-3	2	347	-325
4	-2	2	317	-321
4	0	2	221	208
4	1	2	382	361
4	2	2	570	527
4	3	2	194	-202
4	4	2	326	-350
4	5	2	335	-331
4	6	2	299	-265
4	7	2	201	232
4	8	2	156	186
4	9	2	130	139
5	-11	2	155	-202
5	-8	2	178	209
5	-7	2	413	353
5	-5	2	119	-158
5	-4	2	118	-143
5	-3	2	451	-393
5	-2	2	103	119
5	-1	2	305	300
5	0	2	124	-135
5	1	2	76	101
5	3	2	170	-175
5	5	2	169	-182
5	6	2	100	88
5	7	2	229	251
6	-12	2	142	-128
6	-9	2	193	203
6	-8	2	226	275
6	-7	2	159	175
6	-6	2	292	-296
6	-5	2	563	-512
6	-4	2	573	-555
6	-2	2	652	644
6	-1	2	492	500
6	0	2	230	216
6	2	2	235	-250
6	3	2	145	-157
6	4	2	140	-149
6	6	2	189	207
7	-9	2	112	140
7	-7	2	89	-104
7	-6	2	110	-150
7	-5	2	244	-259
7	-4	2	290	-273
7	-3	2	257	269
7	-2	2	381	395
7	-1	2	445	493
7	0	2	77	91
7	1	2	463	-469
7	2	2	456	-525
7	3	2	133	-140
7	5	2	246	274
7	6	2	203	230
8	-5	2	133	-155
8	-2	2	222	236
8	-1	2	260	291
8	0	2	155	-201
8	1	2	266	-313
8	2	2	191	-204
8	4	2	149	202
8	5	2	257	285
9	-2	2	136	164
9	-1	2	73	93
10	-1	2	111	-102
-9	-6	3	166	185
-9	-5	3	361	362
-9	-2	3	263	-320
-9	-1	3	451	-433
-9	1	3	152	141
-9	2	3	218	242
-9	3	3	316	291
-9	6	3	347	-116
-8	-6	3	272	268
-8	-5	3	263	230
-8	-2	3	504	-497
-8	-1	3	158	-220
-8	0	3	198	188
-8	1	3	323	320
-8	2	3	385	401
-8	4	3	152	-197
-7	-6	3	288	331
-7	-5	3	142	162
-7	-4	3	136	117
-7	-3	3	353	-343
-7	-2	3	458	-486
-7	1	3	383	388
-7	2	3	331	292
-7	3	3	139	-140
-7	4	3	145	-162
-6	-8	3	219	196
-6	-7	3	294	290
-6	-5	3	188	-215
-6	-4	3	180	-187
-6	-3	3	302	-302
-6	0	3	338	327
-6	1	3	459	457
-6	3	3	227	-210
-6	4	3	194	-244
-6	5	3	250	-222
-5	-9	3	222	213
-5	-8	3	354	373
-5	-6	3	403	-396
-5	-5	3	436	-416
-5	-4	3	547	-547
-5	-3	3	364	328
-5	-2	3	653	704
-5	-1	3	298	295
-5	0	3	349	341
-5	2	3	350	-323
-5	3	3	348	-331
-5	4	3	390	-379
-5	6	3	358	344
-5	7	3	219	210
-4	-9	3	360	329
-4	-8	3	377	353
-4	-6	3	319	-325
-4	-5	3	584	-606
-4	-4	3	250	-249
-4	-3	3	613	653
-4	-2	3	419	397
-4	-1	3	221	217
-4	1	3	610	-635
-4	2	3	289	-288
-4	3	3	390	-365
-4	5	3	639	646
-4	6	3	346	320
-4	9	3	398	-319
-3	-10	3	313	316
-3	-9	3	328	301
-3	-7	3	180	-204
-3	-6	3	546	-517
-3	-5	3	578	-605
-3	-3	3	638	672
-3	-2	3	520	569
-3	-1	3	781	879
-3	0	3	472	-414
-3	1	3	600	-675
-3	2	3	325	-323
-3	3	3	268	-239
-3	4	3	356	307
-3	5	3	222	214
-3	6	3	234	178
-3	8	3	332	-224
-3	9	3	313	-230
-2	-10	3	152	150
-2	-9	3	143	-147
-2	-7	3	253	-304
-2	-6	3	328	-318
-2	-5	3	245	-212
-2	-4	3	361	349
-2	-3	3	756	910
-2	-2	3	776	907
-2	-1	3	354	-416
-2	0	3	657	-807
-2	1	3	378	-333
-2	2	3	512	-496
-2	3	3	314	285
-2	4	3	325	288
-2	5	3	286	240
-2	6	3	162	140
-1	-10	3	150	-150
-1	-9	3	199	-218
-1	-6	3	318	326
-1	-5	3	418	435
-1	-4	3	208	239
-1	-3	3	146	180
-1	-2	3	398	-385
-1	-1	3	769	-841
-1	0	3	507	-512
-1	1	3	548	-564
-1	2	3	684	655
-1	3	3	777	651
-1	4	3	367	383
-1	5	3	269	205
-1	6	3	294	-302
-1	7	3	303	-256
0	-12	3	256	251
0	-11	3	57	141
0	-9	3	384	-368
0	-8	3	546	-515
0	-6	3	501	517
0	-5	3	378	372
0	-4	3	412	385
0	-3	3	359	-350
0	-2	3	710	-776
0	0	3	205	174
0	1	3	328	330
0	2	3	610	422
0	4	3	76	97
0	5	3	288	-278
0	6	3	481	-461
0	7	3	189	-214
0	9	3	218	235
0	10	3	157	214
1	-10	3	162	-215
1	-9	3	537	-510
1	-8	3	327	-326
1	-7	3	355	403
1	-6	3	640	670
1	-5	3	931	921
1	-4	3	239	-205
1	0	3	455	394
1	1	3	453	442
1	2	3	376	352

Table IV. (Continued)

1	3	3	258	244
1	5	3	420	-390
1	6	3	320	-336
1	8	3	134	169
1	9	3	235	252
2	-10	3	175	-185
2	-9	3	252	-235
2	-8	3	308	321
2	-7	3	343	303
2	-6	3	537	530
2	-5	3	333	375
2	-4	3	747	-699
2	-3	3	625	-578
2	0	3	459	462
2	1	3	657	654
2	2	3	547	480
2	3	3	125	155
2	4	3	253	-234
2	5	3	390	-390
2	6	3	378	-257
2	8	3	210	244
2	9	3	158	207
3	-8	3	53	119
3	-6	3	205	172
3	-5	3	357	-393
3	-4	3	192	-216
3	-3	3	63	-57
3	-2	3	141	-149
3	-1	3	511	514
3	0	3	810	738
3	1	3	135	153
3	2	3	180	-159
3	3	3	380	-400
3	4	3	534	-519
3	8	3	260	272
4	-9	3	320	316
4	-8	3	128	118
4	-5	3	290	-269
4	-3	3	155	-164
4	-1	3	485	470
4	0	3	256	304
4	1	3	150	-128
4	2	3	291	-274
4	3	3	440	-445
4	4	3	167	162
4	5	3	207	227
4	7	3	188	205
5	-10	3	292	310
5	-9	3	296	284
5	-8	3	160	170
5	-7	3	116	-91
5	-6	3	559	-571
5	-5	3	355	-362
5	-3	3	79	99
5	-2	3	548	578
5	-1	3	140	156
5	2	3	431	-380
5	3	3	225	-245
5	5	3	88	133
5	6	3	238	235
5	8	3	173	-143
6	-9	3	111	125
6	-8	3	130	95
6	-7	3	342	-377
6	-6	3	567	-582
6	-4	3	125	170
6	-2	3	411	404
6	1	3	478	-520
6	2	3	366	-371
6	5	3	233	268
6	6	3	225	255
7	-7	3	207	-198
7	-5	3	85	-106
7	-4	3	136	147
7	-3	3	413	420
7	-2	3	149	-158
7	0	3	253	-226
7	1	3	208	-218
7	4	3	164	185
7	5	3	256	274
8	-4	3	232	245
8	0	3	136	-143
9	-1	3	190	-208
9	0	3	136	-103
10	-2	3	155	-187
-10	-2	4	163	-223
-10	-1	4	162	-208
-10	2	4	235	270
-9	2	4	221	232
-9	4	4	287	-263
-9	5	4	256	-308
-8	-4	4	207	-199
-8	-1	4	200	192
-7	-5	4	245	-242
-7	-3	4	418	-385
-7	-2	4	132	133
-7	-1	4	389	389
-7	2	4	156	-211
-6	-10	4	254	263
-6	-4	4	221	-196
-6	-2	4	688	755
-6	-1	4	280	305
-6	0	4	173	165
-6	1	4	455	-440
-6	2	4	621	-606
-6	6	4	314	304
-5	-9	4	218	212
-5	-7	4	351	-383
-5	-6	4	261	-287
-5	-5	4	215	-174
-5	-3	4	590	643
-5	-2	4	411	408
-5	1	4	681	-746
-5	2	4	556	-498
-5	4	4	331	307
-5	5	4	535	595
-5	6	4	262	215
-4	-10	4	224	199
-4	-9	4	258	263
-4	-8	4	242	-222
-4	-7	4	348	-305
-4	-6	4	275	-269
-4	-4	4	188	206
-4	-3	4	179	201
-4	-2	4	174	208
-4	-1	4	335	306
-4	0	4	324	-308
-4	1	4	629	-572
-4	4	4	448	444
-4	5	4	458	449
-3	-10	4	154	134
-3	-9	4	250	-237
-3	-8	4	357	-373
-3	-7	4	218	-221
-3	-6	4	145	-113
-3	-5	4	431	444
-3	-4	4	617	641
-3	-3	4	270	270
-3	0	4	481	-498
-3	1	4	242	-216
-3	2	4	401	-335
-3	4	4	395	411
-2	-10	4	151	-129
-2	-9	4	245	-225
-2	-6	4	370	335
-2	-5	4	460	530
-2	-4	4	226	179
-2	-3	4	411	-355
-2	-2	4	251	-289
-2	-1	4	764	-868
-2	0	4	235	-220
-2	1	4	478	422
-2	2	4	469	372
-2	3	4	619	622
-1	-10	4	258	-293
-1	-7	4	147	165
-1	-6	4	324	291
-1	-5	4	334	366
-1	-4	4	150	-122
-1	-3	4	480	-418
-1	-2	4	523	-611
-1	-1	4	741	-674
-1	0	4	440	417
-1	1	4	565	745
-1	2	4	921	785
0	-13	4	144	143
0	-11	4	274	-291
0	-10	4	363	-339
0	-9	4	138	-177
0	-7	4	371	400
0	-6	4	455	498
0	-5	4	347	287
0	-4	4	100	86
0	-3	4	503	-552
0	-2	4	476	-675
0	0	4	435	410
0	1	4	525	520
0	2	4	450	456
1	-11	4	211	-287
1	-8	4	245	241
1	-7	4	431	455
1	-4	4	821	-731
1	-3	4	753	-683
1	-2	4	231	-230
1	0	4	750	625
1	1	4	886	756
2	-8	4	305	355
2	-6	4	207	-225
2	-5	4	374	-383
2	-4	4	540	-511
2	-3	4	343	339
2	-2	4	454	426
2	-1	4	256	237
2	0	4	127	138
2	1	4	217	154
3	-9	4	267	252
3	-7	4	106	-98
3	-6	4	150	-159
3	-5	4	447	-401
3	-4	4	130	121
3	-3	4	354	347
3	-2	4	451	437
3	-1	4	376	363
3	0	4	326	-312
3	1	4	685	-621
4	-11	4	157	125
4	-10	4	375	380
4	-9	4	148	157
4	-8	4	57	-114
4	-6	4	440	-412
4	-5	4	358	-394
4	-3	4	246	201
4	-2	4	722	680
4	-1	4	184	197
4	0	4	345	-301
4	1	4	227	-230
5	-11	4	172	180
5	-10	4	152	170
5	-9	4	54	-94
5	-8	4	114	-169
5	-7	4	297	-308
5	-6	4	333	-275
5	-5	4	239	229
5	-4	4	111	123
5	-3	4	419	363
5	-2	4	701	672
5	-1	4	161	-182
5	0	4	364	-364
5	1	4	568	-601
6	-3	4	348	360
6	-1	4	247	-249
6	0	4	288	-276
6	1	4	369	-355
7	-6	4	135	169
7	-2	4	179	-189
7	-1	4	98	95
8	-7	4	116	164
8	-6	4	180	222
8	-5	4	226	231
8	-3	4	291	-286
8	-2	4	165	-190
8	1	4	173	206
9	-6	4	84	122
9	-5	4	101	101
9	-4	4	99	-153
9	-3	4	313	-293
9	-2	4	161	-155
9	0	4	209	243
9	1	4	246	266
10	0	4	257	291
-11	0	5	171	148
-11	1	5	243	237
-10	0	5	278	302
-10	1	5	282	293
-8	-5	5	255	-293
-7	-6	5	379	-425
-7	-4	5	189	253
-7	-3	5	294	292
-7	-2	5	469	505
-7	0	5	278	-259
-7	1	5	134	-185
-7	2	5	240	-273
-6	-7	5	282	-310
-6	-6	5	270	-296
-6	-4	5	384	392
-6	-3	5	624	622
-6	-2	5	208	204
-6	-1	5	418	-389
-6	0	5	426	-456
-6	1	5	464	-492
-6	3	5	335	324
-6	4	5	320	330
-6	5	5	212	231
-5	-8	5	200	-176
-5	-7	5	232	-263
-5	-5	5	170	-117
-5	-4	5	304	307
-5	-3	5	527	524
-5	-1	5	359	-355
-5	0	5	425	-469
-5	1	5	235	-262
-5	2	5	301	320
-5	3	5	390	392
-5	4	5	194	189
-4	-9	5	204	-163
-4	-8	5	270	-259
-4	-5	5	158	196
-4	-4	5	357	404
-4	-2	5	281	-277
-4	-1	5	174	-163
-4	0	5	381	-406
-4	2	5	284	276
-4	4	5	295	290
-3	-11	5	224	-150
-3	-9	5	342	-357
-3	-7	5	470	474
-3	-6	5	421	462
-3	-5	5	390	379
-3	-3	5	736	-750
-3	-2	5	398	-419
-3	-1	5	156	-151
-3	1	5	483	501
-3	3	5	336	322
-3	5	5	295	-325
-2	-10	5	252	-241
-2	-9	5	236	-198
-2	-8	5	283	238
-2	-7	5	388	351
-2	-6	5	388	376
-2	-4	5	670	-739
-2	-3	5	616	-630
-2	-2	5	137	-108
-2	-1	5	115	75
-2	0	5	831	915
-2	1	5	516	494
-2	4	5	375	-609
-2	5	5	379	-391
-2	8	5	295	293
-1	-11	5	217	-181
-1	-10	5	352	-367
-1	-8	5	277	290
-1	-7	5	379	379
-1	-6	5	390	491
-1	-5	5	297	-284
-1	-4	5	476	-486
-1	-3	5	515	-481
-1	-2	5	285	-296
-1	-1	5	604	540
-1	1	5	159	194
-1	3	5	358	-426
-1	4	5	280	-301
-1	7	5	79	267
-1	8	5	282	267
0	-11	5	152	-158
0	-9	5	188	222
0	-7	5	392	656
0	-5	5	294	-312
0	-4	5	298	-280
0	-3	5	867	-823
0	0	5	603	502
0	1	5	120	120
0	2	5	300	-291
0	3	5	361	-383
0	7	5	144	157
1	-11	5	91	112
1	-1	5	418	509
1	0	5	457	385
1	1	5	130	-121
1	2	5	636	-600
1	3	5	321	-348
1	6	5	180	226
2	-1	5	69	-72
2	0	5	548	-509
2	1	5	422	-380
2	2	5	250	-243
2	3	5	137	151
2	4	5	176	236
2	6	5	156	162
3	-1	5	304	-271
3	0	5	428	-368
3	1	5	196	-155
3	3	5	129	153
3	4	5	329	286
3	5	5	179	200
3	7	5	188	-181
3	8	5	200	-187
4	0	5	459	-330
4	1	5	126	-109
4	3	5	203	147
4	4	5	203	209
5	0	5	112	-136
5	2	5	245	235
5	3	5	259	282
6	1	5	109	114
6	2	5	273	296
6	4	5	163	-172
6	5	5	133	-153
7	1	5	163	172
7	3	5	147	-140
8	0	5	138	142
0	1	5	167	182
9	-1	5	119	149
-9	1	6	221	-243
-8	-4	6	250	247
-8	0	6	288	-325
-8	1	6	207	-243
-8	4	6	229	218
-7	-5	6	310	326
-7	-4	6	270	333
-7	-1	6	265	-248
-7	0	6	270	-318
-7	1	6	156	-203
-7	3	6	254	267
-7	4	6	346	356
-6	-6	6	190	210
-6	-5	6	258	260
-6	-2	6	262	-249
-6	-1	6	302	-303
-6	2	6	234	260
-6	3	6	282	304
-5	-6	6	178	249
-5	-4	6	201	167
-5	-2	6	311	-316
-5	2	6	222	260
-4	-7	6	359	447
-4	-4	6	238	-236
-4	-3	6	457	-541
-4	-2	6	302	-312
-4	1	6	578	563
-4	2	6	210	191
-4	3	6	225	-201
-3	-8	6	387	407
-3	-7	6	269	257
-3	-5	6	147	-134
-3	-4	6	531	-576
-3	-3	6	429	-441
-3	-1	6	233	261
-3	0	6	569	656
-3	1	6	459	484
-3	2	6	165	-135
-3	3	6	307	-295
-3	4	6	489	-499
-3	5	6	109	-159
-3	6	6	117	175
-2	-8	6	332	312
-2	-5	6	389	-408
-2	-4	6	370	-388
-2	-3	6	286	217
-2	-1	6	341	322
-2	0	6	437	438
-2	2	6	102	-152
-2	3	6	474	-470
-2	4	6	500	-454
-2	6	6	255	287
-2	7	6	256	316
-1	-9	6	351	366
-1	-8	6	174	204
-1	-5	6	578	-620
-1	-4	6	150	-138
-1	-1	6	295	285
-1	3	6	319	-302
-1	4	6	88	-100
-1	5	6	95	133
-1	7	6	147	183
0	-10	6	245	207
0	-8	6	173	-173
0	-6	6	473	-474
0	-5	6	186	-181
0	-4	6	276	292
0	-1	6	195	148
0	0	6	230	-195
0	1	6	230	-240
0	2	6	184	-204
0	4	6	125	149
1	-11	6	181	225
1	-10	6	137	165
1	-9	6	184	-204
1	-8	6	325	-308
1	-7	6	317	-298
1	-5	6	334	293
1	-4	6	223	220
1	-3	6	516	523
1	-2	6	252	249
1	-1	6	327	-296
1	0	6	679	-576
1	1	6	460	-370
1	2	6	91	-99
1	3	6	330	332
1	4	6	294	298
1	7	6	139	-136
2	-12	6	139	153
2	-11	6	218	252
2	-7	6	279	-237
2	-4	6	228	188
2	-3	6	445	371
2	-2	6	154	-141
2	-1	6	461	-435
2	0	6	354	-369
2	1	6	154	-137
2	2	6	363	341
2	3	6	443	462
2	4	6	167	214
2	6	6	287	-300
2	7	6	217	-233
3	-12	6	141	157
3	-9	6	200	-235
3	-8	6	349	-318
3	-6	6	225	200
3	-5	6	130	162
3	-4	6	386	354
3	-3	6	169	174
3	-2	6	96	-99
3	-1	6	82	-110
3	0	6	537	-476
3	1	6	137	-136
3	2	6	273	248
3	3	6	186	199
3	4	6	181	176
3	6	6	223	-224
4	-7	6	262	202
4	-6	6	257	269
4	-5	6	181	175
4	-3	6	335	-273
4	-2	6	164	-177
4	-1	6	227	-234
4	1	6	132	132
4	2	6	150	50
4	4	6	143	132
4	6	6	141	-137
5	-6	6	152	175
5	-4	6	463	-403
5	-3	6	230	-216
5	-2	6	81	-110
5	-1	6	110	123
5	0	6	346	348
5	2	6	106	105
5	4	6	151	-130
6	-5	6	165	-175
6	-3	6	85	-78
6	-1	6	275	277
6	0	6	146	140
6	2	6	101	-100
6	3	6	274	-277
7	-7	6	139	174
7	-4	6	176	-170
7	-3	6	206	-203
7	-1	6	178	207
7	0	6	190	201
7	2	6	172	-160
7	3	6	179	-177
8	-4	6	118	-124
8	0	6	189	180
8	2	6	183	-197
8	3	6	146	-140
-9	-4	7	217	260
-9	-3	7	215	268
-9	0	7	154	-231
-8	-4	7	288	350
-8	-1	7	286	-323
-8	0	7	252	-312
-8	2	7	215	187
-8	3	7	223	240
-7	-1	7	232	-264
-7	2	7	205	248
-7	3	7	213	209
-6	-6	7	189	203
-6	-3	7	175	-171
-6	0	7	180	184
-5	-7	7	349	376
-5	-5	7	170	-213
-5	-4	7	333	-331
-5	-3	7	254	-241
-5	-1	7	231	225
-5	0	7	168	224
-5	3	7	155	-161
-4	-8	7	326	371
-4	-7	7	217	215
-4	-6	7	205	-203
-4	-5	7	336	-352
-4	-4	7	539	-584
-4	-3	7	255	-236
-4	-2	7	341	338
-4	-1	7	580	588
-4	0	7	352	382
-4	2	7	331	-330
-4	3	7	266	-288
-3	-8	7	222	230
-3	-5	7	180	-160
-3	-4	7	380	-329
-3	-2	7	393	381
-3	-1	7	517	458
-3	0	7	276	268
-3	1	7	404	-387
-3	2	7	450	-537
-3	3	7	166	-179
-3	6	7	241	239
-2	-9	7	189	164
-2	-7	7	163	-206
-2	-5	7	243	-229
-2	-4	7	136	-93
-2	-3	7	343	274
-2	-2	7	139	116
-2	-1	7	253	254
-2	1	7	364	-393
-2	2	7	141	-160
-2	5	7	210	266
-1	-8	7	300	-272
-1	-7	7	299	-303
-1	-6	7	255	-271
-1	-4	7	620	490
-1	1	7	123	-131
-1	4	7	157	215
0	-9	7	263	-298
0	-8	7	323	-339
0	-7	7	160	-141
0	-5	7	718	718
0	-4	7	631	450
0	0	7	352	-350
0	1	7	94	-89
0	3	7	260	278
0	4	7	251	252
0	7	7	182	-159
1	-11	7	160	166
1	-9	7	149	-200
1	-8	7	110	-143
1	-7	7	302	-290
1	-6	7	170	203
1	-5	7	584	543
1	-4	7	172	169
1	-2	7	514	-562
1	-1	7	459	-468
1	1	7	257	135
1	2	7	314	299
1	3	7	345	341
1	6	7	188	-171
1	7	7	183	-197
2	-8	7	205	-196
2	-7	7	130	-113
2	-6	7	250	240
2	-5	7	227	223
2	-4	7	226	156
2	-2	7	422	-368
2	-1	7	247	-207
2	1	7	157	205
2	2	7	450	388
2	4	7	174	-176
3	-8	7	134	159
3	-7	7	208	220
3	-6	7	89	114
3	-5	7	76	87
3	-4	7	113	92
3	-3	7	277	-260
3	-2	7	263	-291
3	-1	7	134	-125
3	1	7	245	260
3	2	7	150	173
4	-8	7	227	216
4	-7	7	111	121
4	-6	7	80	-74
4	-5	7	209	-203
4	-4	7	295	-318
4	-3	7	186	-180
4	-2	7	227	167
4	-1	7	122	160
4	0	7	277	293
4	1	7	109	132
4	4	7	202	-157
5	-9	7	123	137
5	-8	7	184	198
5	-6	7	86	-94
5	-5	7	229	-220
5	-4	7	240	-256
5	-3	7	108	118
5	-2	7	242	232
5	-1	7	225	210
5	0	7	117	122
5	1	7	118	-132
5	2	7	139	-144
5	3	7	137	-165
6	-9	7	140	173
6	-8	7	135	173
6	-7	7	97	92
6	-6	7	53	-130
6	-5	7	284	-264
6	-4	7	162	-130
6	-2	7	193	187
6	-1	7	140	166
6	1	7	126	-129
7	-6	7	142	-189
7	-5	7	140	-138
7	-3	7	120	124
7	-1	7	123	143
-8	1	8	230	235
-7	-4	8	145	-210
-7	0	8	259	253
-6	-9	8	230	202
-6	-8	8	220	200
-6	-5	8	240	-258
-6	-4	8	135	-203
-6	0	8	199	221
-5	-9	8	271	272
-5	-6	8	301	-338
-5	-5	8	366	-400
-5	-3	8	176	161
-5	-2	8	216	278
-5	-1	8	295	272
-5	2	8	206	-192
-5	3	8	265	-285
-4	-6	8	336	-381
-4	-3	8	302	289
-4	-2	8	346	401
-4	1	8	186	-154
-4	2	8	312	-342
-4	3	8	86	-120
-4	6	8	190	210
-3	-7	8	181	-145
-3	-3	8	284	268
-3	-1	8	153	-167
-3	0	8	167	-155
-3	1	8	126	-193
-3	3	8	96	122
-3	5	8	126	188
-2	-8	8	265	-310
-2	-7	8	175	-151
-2	-4	8	687	390
-2	-3	8	182	167
-2	-1	8	103	-125
-2	0	8	271	-270
-2	2	8	136	141
-2	3	8	54	130
-1	-9	8	281	-326
-1	-8	8	226	-260
-1	-7	8	172	172
-1	-6	8	160	136
-1	-5	8	364	324
-1	-4	8	227	297
-1	0	8	282	-305
-1	1	8	136	158
-1	2	8	194	238
-1	3	8	287	236
-1	5	8	136	-137
0	-9	8	243	-276
0	-7	8	172	190
0	-6	8	226	221
0	-5	8	384	392
0	-4	8	148	-183
0	-2	8	230	-330
0	-1	8	308	-299
0	0	8	111	96
0	1	8	160	218
0	2	8	220	281
0	3	8	258	286
0	5	8	210	-225
0	6	8	150	-184
1	-9	8	139	-165
1	-7	8	142	121
1	-6	8	321	305
1	-4	8	205	-175
1	-3	8	60	-72
1	-2	8	113	-147
1	0	8	133	193
1	4	8	183	-180
1	5	8	114	-127
2	-10	8	127	-60
2	-8	8	88	110
2	-7	8	273	211
2	-6	8	126	103
2	-5	8	120	-133
2	-4	8	109	-130
2	-3	8	230	-164
2	-2	8	121	-129
2	-1	8	264	166
3	-9	8	173	181
3	-8	8	167	186
3	-7	8	105	109
3	-6	8	259	-223
3	-5	8	325	-203
3	-4	8	136	-132
3	-3	8	221	-177
3	-2	8	302	240
3	-1	8	296	295
3	0	8	112	98
3	1	8	121	100
3	2	8	158	-183
3	3	8	118	-113
4	-7	8	92	-107
4	-6	8	324	-239
4	-3	8	137	126
4	-2	8	343	309
4	-1	8	141	145
4	0	8	146	155
4	1	8	233	-227
4	2	8	420	-357
5	-7	8	132	-129
5	-3	8	112	111
5	1	8	210	-159
6	-6	8	180	-161
6	-4	8	158	168
7	-5	8	165	156
7	-4	8	154	144

Table V. Equations of least-squares planes and deviations (Å) from these planes. (In this calculations an unitary weighting scheme was used). Coefficients are direction cosines relative to orthogonal axes. X, Y, X are also orthogonal coordinates, in Å [a].

Equation of plane	Atom	Deviation
(−0.358)X+(−0.096)Y+(−0.929)Z+2.78 = 0	S(1)	−0.0044(6)
	C(1)	0.01(2)
	N(1)	0.00(2)
	N(4)	0.00(2)
(0.743)X+(0.570)Y+(−0.350)Z−1.669 = 0	S(2)	−0.012(6)
	C(2)	0.04(3)
	N(2)	−0.01(2)
	N(5)	−0.01(2)
(0.793)X+(0.358)Y+(−0.484)Z−0.986 = 0	S(3)	−0.011(6)
	C(3)	0.04(3)
	N(3)	−0.01(2)
	N(6)	−0.01(2)

[a] Orthogonal coordinates in angstroms are obtained by transforming the fractional coordinates with the matrix (a, b. cos γ, c. cos β//0, b. sin γ, c.(cos α −cos β cos γ)/sin γ//0,0,V/(a.b.sin γ)). X is along the axis, Y in the (a, b) plane and Z along the c-axis.

Table VI. Distances (Å) and Angles (°) in $Cd(tu)_3SO_4$. Standard deviations, given in parentheses, are in units of the last decimal place. For numbering of atoms see Figure 1.

Coordination Polyhedra

Cd—S(1)	2.627(7)	S(1)—Cd—S(1′)	82.4(2)	S(1′)—Cd—S(3)	156.0(2)
Cd—S(1′)	2.870(7)	S(1)—Cd—S(2)	114.6(2)	S(1′)—Cd—O(1)	84.5(4)
Cd—S(2)	2.538(6)	S(1)—Cd—S(3)	87.8(2)	S(2)—Cd—S(3)	112.7(2)
Cd—S(3)	2.627(6)	S(1)—Cd—O(1)	145.0(4)	S(2)—Cd—O(1)	97.1(14)
Cd—O(1)	2.339(15)	S(1′)—Cd—S(2)	91.2(2)	S(3)—Cd—O(1)	91.6(4)

Sulphate Group:

S(4)—O(1)	1.491(15)	O(1)—S(4)—O(2)	110.0(1.0)	O(2)—S(4)—O(3)	109.4(1.0)
S(4)—O(2)	1.476(19)	O(1)—S(4)—O(3)	108.0(1.0)	O(2)—S(4)—O(4)	111.0(1.0)
S(4)—O(3)	1.487(19)	O(1)—S(4)—O(4)	108.4(1.0)	O(3)—S(4)—O(4)	109.0(1.0)
S(4)—O(4)	1.507(19)				
S—O (mean value)	1.490				

Thiourea Molecules:

S(1)—C(1)	1.724(21)	S(1)—C(1)—N(1)	117.3(1.6)
C(1)—N(1)	1.342(31)	S(1)—C(1)—N(4)	123.5(1.7)
C(1)—N(4)	1.287(30)	N(1)—C(1)—N(4)	119.1(2.0)
S(2)—C(2)	1.713(22)	S(2)—C(2)—N(2)	125.5(1.7)
C(2)—N(2)	1.351(31)	S(2)—C(2)—N(5)	118.8(1.7)
C(2)—N(5)	1.335(31)	N(2)—C(2)—N(5)	115.2(2.0)
S(3)—C(3)	1.690(27)	S(3)—C(3)—N(3)	119.7(2.0)
C(3)—N(3)	1.368(34)	S(3)—C(3)—N(6)	123.3(2.0)
C(3)—N(6)	1.321(36)	N(3)—C(3)—N(6)	116.6(2.3)
S—C (mean value)	1.709	C—N (mean value)	1.336

In the following discussion atoms are labelled as follow:

Superscript	Coordinates
none	x, y, z
′	−x, −y, −z
″	1−x, 1−y, 1−z
‴	1−x, −y, 1−z
iv	x, y, 1+z
v	x, 1−y, z
vi	1+x, −y, −z
vii	−x, 1−y, 1−z
viii	x, y, 1+z

It is seen that in $Cd(tu)_3SO_4$, the cadmium atom is five-coordinated. Coordination can best be described in terms of a distorted square pyramid. Four sulphur atoms from thiourea molecules and one oxygen atom from the sulphate group surround the metal atom. The atoms S(1), S(3), S(1′) and O(1) determine the base of the distorted pyramid, while S(2) is at the apex. The least squares plane passing through S(1), S(3), S(1′) and O(1) is (0.664)X+(0.208)Y+(−0.718)Z+0.001 = 0 where X, Y, Z are orthogonal coordinates (see footnote of Table V). The distances of the atoms to this plane are: S(1) = −0.074(6); S(3) = 0.076(6); S(1′) = 0.077(6) and O(1) = −0.078(6). For Cd and S(2) the distances are 0.624(2) and 3.099(6) Å, respectively. As can be seen in Figure 2, atoms S(1′) and S(3) that are 0.077 and 0.076 Å above the mean plane, respectively, make the angle S(1′)—Cd—S(3) greater than S(1)—Cd—O(1). The angles S(2)—Cd—O(1) and S(2)—Cd—S(1′) are smaller than S(2)—Cd—S(1) and S(2)—Cd—S(3). This indicates that the S(2)—Cd bond is tilted with respect to the basal plane in the direction of the S(1′)—O(1) edge of the base. Two pyramids related by an inver-

sion center are joined through the S(1′)–S(1) edge, resulting in a dimer molecule. The angles around S(1): Cd–S(1)–Cd′ = 97.6(7), Cd–S(1)–C(1) = 107.8(7) and Cd′–S(1)–C(1) = 109.6(7)°, indicate a distorted tetrahedral environment. The S(1) atom coordinates to two adjacent Cd atoms with somewhat different distances: 2.627(7) and 2.870(7) Å. The other distances between Cd and S in the coordination polyhedra are: Cd–S(2) = 2.538(6) and Cd–S(3) = 2.627(6) Å.

The ligand thiourea acts as a bridge in other Cd^{II} complexes with distances Cd–S of 2.64 and 2.65 Å in monothiourea cadmium sulphate,[2] and 2.74 and 2.71 in bisthiourea cadmium formate.[5] Some of these values are significatly different from those obtained by us, and in all cases they are intermediate between the sum of Pauling's covalent and ionic radii, 2.52 and 2.87 Å, respectively.

The Cd–O(1) distance, 2.339(15) Å, is greater than the sum of Pauling's covalent radii, 2.22 Å, and it differs by less than three e.s.d. from the mean value obtained in $Cd(tu)SO_4 . 2H_2O$.[2]

It is convenient at this point to emphasize that $Cd(tu)_3SO_4$ is the first reported five-coordinated Cd^{II} complex; it is also the first reported structure where thiourea acts as a bridge in a dimer molecule. Distorted square pyramidal coordination has been also found in some Zn^{II} complexes, *i.e.* $Zn(acac)_2 . H_2O$,[6] and the angles obtained in the coordination polyhedra are rather similar to those found by us.

Distances and angles in the sulphate group are in good agreement with those observed in other sulphate complexes and are practically equal to those found in the ionic sulphate.[7] The orientation of the sulphate group is mainly determined by the intra and intermolecular hydrogen bonds involving the oxygen atoms and the NH_2 groups. The angle Cd–O(1)–S(4) is 109.3(8)°. One of the oxygen atoms, O(4), is located at 2.84 Å from Cd atom. This is a relatively short distance for non bonded atoms; a tentative explanation for this fact is that O(4) participates strongly in intra and intermolecular hydrogen bonding with H(8) and $H(4^{IV})$.

The three independent thiourea molecules are planar, and their least square planes are given in Table V. The dimensions in the thiourea molecules are not significantly different from those reported previously for the free ligand.[8] The S–C bond lengths are between 1.690 and 1.724 Å (mean value 1.709(14) Å), compared with a value of 1.720(9) Å in the free ligand; while the mean value of the C–N bond length, 1.336(15) Å, differs by less than one e.s.d. from 1.340(6) Å, which is the value found in the free thiourea.

The thiourea molecules are tilted with respect to the Cd–S bond. The values of the angles are: Cd–S(1)–C(1) = 107.8(7), Cd–S(1′)–C(1) = 109.6(7), Cd–S(2)–C(2) = 103.2(8) and Cd–S(3)–C(3) = 100.0(9). The values are consistent with those obtained in other thiourea complexes, *i.e.* 101.9, 107.7 and 107.0° in tristhiourea zinc sulphate;[7] 100.6 and 101.2° in bisthiourea zinc acetate[9] and 113.0° in bisthiourea cadmium chloride.[10]

Apparently the molecules in the crystal are held together by hydrogen bonds involving oxygen atoms from the SO_4 group, the NH_2 group of the thiourea molecules and probably S atoms of the same ligand. The distances that can be considered as hydrogen bonds are listed below, as well as the N–H–X angle, where X is O or S. In this calculation the theoretical positions for H atoms, as are given in Table I, were used. The distances and angles are:

N(1)–O(2^{vi})	2.74(2) Å	N(1)–H(1)–O(2^{vi})	165°
N(1)–O(3^{v})	2.79(3)	N(1)–H(2)–O(3^{v})	161
N(2)–O(4^{iv})	3.02(3)	N(2)–H(4)–O(4^{iv})	153
N(3)–S(3″)	3.49(3)	N(3)–H(5)–S(3″)	168
N(3)–O(2″)	3.04(3)	N(3)–H(6)–O(2″)	143
N(4)–O(4)	2.93(3)	N(4)–H(8)–O(4)	161
N(5)–O(1^{vii})	2.92(3)	N(5)–H(9)–O(1^{vii})	148
N(5)–O(3^{viii})	2.86(3)	N(5)–H(10)–O(3^{viii})	167
N(6)–O(1)	2.93(3)	N(6)–H(12)–O(1)	170
N(6)–O(2″)	2.97(3)	N(6)–H(11)–O(2″)	154

Acknowledgments. We are grateful to the Director and staff of the Departmento de Computación of U.C.V. for generous allocation of computing time. We are also indebted to Drs. F. R. Ahmed, B. Foxman, M. E. Pippy, C. T. Prewit, D. P. Shoemaker and A. Zaldkin, for making available to us the Fortran IV programmes we used in the calculations. One of us (E.C.) thanks to the Universidad de Los Andes for a fellowship.

(5) M. Nardelli, G. Fava and P. Boldrini, *Acta Cryst.*, *18*, 618 (1965).
(6) H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, *16*, 748 (1963).
(7) D. Andreetti, L. Cavalca and A. Musatti, *Acta Cryst.*, *B24*, 683 (1968).
(8) M. R. Truter, *Acta Cryst.*, *22*, 556 (1967).
(9) L. Cavalca, G. Fava, D. Andretti and P. Domiano, *Acta Cryst.*, *22*, 90 (1967).
(10) M. Nardelli, L. Cavalca and A. Braibanti, *Gazz. Chim. Ital.*, *87*, 137 (1957).