701. *The Crystal Structure of Dichlorobisthioureazinc.*

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An *X*-ray crystal structure analysis of dichlorobisthioureazinc, $[(NH_2)_2CS]_2ZnCl_2$, has shown that the complex is molecular, each zinc atom being tetrahedrally co-ordinated to two chlorine and two sulphur atoms. Three-dimensional refinement, with allowance for anisotropic thermal motion, gave the bond lengths Zn–Cl = 2·32 ± 0·01 Å, Zn–S = 2·35 ± 0·01 Å, S–C = 1·78 ± 0·02 Å, C–N = 1·28 ± 0·03 Å. The thiourea group is planar with angles S–C–N 121·2° ± 1·6° and 116·1° ± 1·6° and N–C–N 122·6° ± 2·0°. The bond angle Zn–S–C is 108·6° ± 0·7°. The zinc valency angles deviate slightly but significantly from the tetrahedral, the angles being Cl–Zn–Cl 107·3°, S–Zn–S 111·5°, S–Zn–Cl 109·0° and 110·6°, all ±0·2°.

Most of the known complexes of zinc are tetrahedral, but there are exceptions, *e.g.*, five-covalent dichloroterpyridylzinc.[1] Dichlorobisthioureazinc, $[(NH_2)_2CS]_2ZnCl_2$, could be either a molecular compound or a salt, or, since the thiourea ligands might be linked through either the sulphur or the nitrogen atoms, it could be polynuclear. It is sparingly soluble in hot water and its aqueous solution does not give a precipitate with silver nitrate, so it is likely that the chlorine is covalently linked. Although both sulphur and nitrogen atoms form co-ordinate links with zinc, the majority of ligands containing both atoms are linked through the sulphur; hence the molecule is probably neutral with the zinc tetrahedrally bound to two chlorine and two sulphur atoms. This arrangement has, in fact, been proved by the structure analysis described below.

[1] Corbridge and Cox, *J.*, 1956, 594.

As the crystal structure of thiourea has recently been accurately re-determined [2] the analysis of the structure of the zinc complex has been carried as far as possible to see if any conclusions could be drawn from changes in the molecular dimensions of thiourea on co-ordination.

EXPERIMENTAL

Crystals of dichlorobisthioureazinc were obtained by Maly's method: [3] hot saturated aqueous solutions of zinc chloride and thiourea were mixed, and cooled to give acicular crystals of the complex (Found: Zn, 22·9; Cl, 24·0; N, 20·4. Calc. for $ZnS_2Cl_2C_2H_8N_4$: Zn, 22·6; Cl, 24·8; N, 19·5%).

Accurate determination of the dimensions of the orthorhombic unit cell by Straumanis's method, Cu-K radiation being used, gave $a = 13{\cdot}065$, $b = 12{\cdot}722$, $c = 5{\cdot}890$ Å, all $\pm 0{\cdot}005$ Å ($v = 978{\cdot}92$ Å^3). The density calculated for 4 molecules (M, 288·6) per unit cell is 1·960 g./c.c., in satisfactory agreement with the value 1·965 g./c.c. obtained by flotation.

Reflections from the classes of planes ($0kl$) with $k + l = 2n + 1$ and ($hk0$) with $h = 2n + 1$ were absent systematically. This is consistent with the space groups $Pnma$—D_{2h}^{16} and $Pn2_1a$—C_{2v}^{9}. A piezoelectric test gave a negative result, and a centric distribution [4] was found for the intensities of the ($hk0$) planes, so that the space group was taken to be the centrosymmetrical $Pnma$.

For intensity measurements very small crystals (0·03 mm. in diameter) were photographed with Cu-K radiation, and no absorption correction was made (linear absorption coefficient, 127 cm.$^{-1}$). Equi-inclination Weissenberg photographs were taken about the principal axes for as many layers as possible, *viz.* up to ($hk3$), ($7kl$), and ($h7l$). Of the possible 739 reflections, 567 were observed. Intensities were estimated visually by comparison with a calibration slip, corrected for Lorentz and polarisation factors with the aid of a Cochran chart, and were correlated, and the resulting F^2 scaled by comparison with the absolute values of F^2 ($hk0$) determined by Wilson's method.[5] The square roots were extracted to give $|F_{obs}|$ and during the isotropic refinement a more accurate scale factor was obtained by making $\sum|F_{obs}| = \sum|F_{calc}|$, allowing for multiplicity, and during anisotropic refinement the scale factor was one of the parameters.

[Nardelli, Cavalca, and Braibanti [6] determined the unit-cell dimensions and space group, obtaining unit-cell dimensions not significantly different from ours, but a different space group because on their photographs there is a very weak reflection corresponding to (0,11,0) which violates the absences required for the n-glide but probably actually arises from double reflection by the pairs of planes ($\bar{2}40$), (270) and (240), ($\bar{2}70$).]

Three-dimensional Structure Analysis.—An approximate structure was obtained by two-dimensional methods, the projections along [001] and [010] being solved by Patterson and Fourier syntheses and refined until R was less than 0·22, where $R = \sum|(|F_{obs}| = |F_{calc}|)|/\sum|F_{obs}|$. The zinc and chlorine atoms lie in mirror planes at $y = 1/4$ and $3/4$; the thiourea molecules are in general positions, related in pairs by the mirror planes. The structure is shown in the Figure; each zinc atom is surrounded approximately tetrahedrally by two chlorine and two sulphur atoms.

Three-dimensional refinement of co-ordinates was by differential syntheses with a back-shift correction for finite series errors. Temperature factors were refined by changing the value of B in the exponential $-(B\sin^2\theta/\lambda^2)$ for each atom to make equal the curvatures of the electron-density distributions, $\partial^2\rho/\partial x_i^2$, derived from the observed and calculated structure factors.

The first set of three-dimensional structure factors was calculated from the co-ordinates given by the two-dimensional analysis with scattering factors for carbon and nitrogen (McWeeny [8]), chlorine and zinc (Berghuis *et al.*[9]) and sulphur (International Tables [10]) all

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[2] Kunchur and Truter, *J.*, 1958, 2551.

[3] Maly, *Ber.*, 1876, **9**, 172.

[4] Howells, Phillips, and Rogers, *Research*, 1949, **2**, 338.

[5] Wilson, *Acta Cryst.*, 1949, **2**, 318.

[6] Nardelli, Cavalca, and Braibanti, *Gazzetta*, 1956, **86**, 1037.

[7] Nardelli and Cavalca, personal communication.

[8] McWeeny, *Acta Cryst.*, 1951, **4**, 513.

[9] Berghuis, Ijbertha, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *ibid.*, 1955, **8**, 478.

[10] "International Tables for the Determination of Crystal Structures," Borntraeger, Berlin, 1935.

with $B = 1{\cdot}95\,\text{Å}^2$; these gave $R = 0{\cdot}30$. It was found that the temperature factor was correct for zinc but low for all the other atoms. Five cycles of refinement were required to reduce R to 0·182 and the last differential synthesis gave no shifts as large as the standard deviations so that isotropic refinement was complete. However, examination of the ratios between the observed curvatures and those calculated on the assumption of isotropic thermal motion shows that even for the heavy atoms the motions are markedly anisotropic. In Table 1 are shown the values of B used for the last isotropic calculation of structure factors, the observed peak electron density, ρ, the ratio between this and the calculated value, and $r(x_i) = (\partial^2\rho_0/\partial x_i^2)/(\partial^2\rho_c/\partial x_i^2)$.

TABLE 1.

	B, Å^2	ρ, e/Å^3	ρ_0/ρ_c	$r(x)$	$r(y)$	$r(z)$
Zn	2·10	64·1	0·95	0·90	1·00	0·95
S	2·60	29·6	0·96	0·87	1·03	0·99
Cl^1	2·50	31·1	0·96	0·94	0·90	0·98
Cl^2	2·50	28·8	0·91	0·75	1·02	0·93
C	2·50	8·0	1·00	0·96	0·99	1·02
N^1	3·20	8·2	0·89	0·78	0·91	0·90
N^2	3·20	7·6	0·90	0·75	1·03	0·87
	Weighted mean		0·95	0·86	0·99	0·96
					0·94	

The ratios correspond to values of $|F_{obs}|$ scaled to make $\sum|F_{obs}| = \sum|F_{calc}|$.

An interesting feature is the effect of anomalous dispersion on the temperature factor for zinc. From the atomic masses the ratio $B_{Zn} : B_{Cl}$ should be about 0·49 : 1·0 while that found is 0·84 : 1·0. Structure factors for the axial reflections were calculated with the correction for anomalous dispersion given by Dauben and Templeton [11]; a plot of log $([F_{corr}]/[F_{uncorr}])$ against $\sin^2\theta$ was linear and from the slope the value of the artificial temperature factor which allowed for anomalous dispersion was found to be $B = 0{\cdot}65$ Å^2. The value $B = 2{\cdot}10$ Å^2 empirically determined for zinc already includes this correction, $B = 0{\cdot}65$ Å^2, so that the contribution due to the thermal vibration of zinc is $B' = 1{\cdot}45$ Å^2. The $B'_{Zn} : B_{Cl}$ ratio is 0·58 : 1·0, in better agreement with expectation.

Anisotropic Refinement.—Cruickshank's method [12] for the successive refinement of anisotropic thermal parameters was used. The equations, which he gives, lead to the correct coefficients b_{ij} for each atom in the expression for the temperature factor $\exp - (b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2)$. Co-ordinates were refined by differential synthesis as before. The scale factor was refined to make the peak electron densities derived from the observed and calculated structure factors equal; this at first was different from the factor required to make $\sum|F_{obs}| = \sum|F_{calc}|$ allowing for multiplicity, but when refinement was complete the two factors were the same. The first set of structure factors calculated with allowance for anisotropy gave $R = 0{\cdot}153$; co-ordinate, and temperature factor shifts were applied to give new parameters (all $\times\ 10^5$), shown below, for which $R = 0{\cdot}148$.

	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Zn	0·16666	0·25000	0·31558	390	0	94	242	0	1598
S	0·09567	0·09791	0·15584	555	$\overline{262}$	$\overline{587}$	269	134	1619
Cl^1	0·34102	0·25000	0·25161	322	0	17	515	0	1588
Cl^2	0·14580	0·25000	$\bar{0}{\cdot}\overline{29428}$	776	0	812	245	0	1875
C	0·11794	$\bar{0}{\cdot}\overline{00811}$	0·34335	365	67	$\overline{320}$	390	$\overline{333}$	1210
N^1	0·14287	0·00597	$\bar{0}{\cdot}\overline{44571}$	757	$\overline{340}$	$\overline{275}$	555	$\overline{942}$	2612
N^2	0·10494	$\bar{0}{\cdot}\overline{09871}$	0·26297	769	$\overline{105}$	$\overline{1046}$	324	573	3313

(This table gives the parameters actually used although not all the figures are significant.) A list of structure factors calculated from these parameters is given in Table 2 together with the observed structure factors.

Differential syntheses based on the structure factors in Table 2 indicated a maximum shift of 0·017 Å in y_C and a corresponding standard deviation of 0·023 Å so that anisotropic refinement of co-ordinates was complete. The mean electron density ratio was 1·005, the mean curvature ratio 0·995, and the average deviation of the ratios from unity 1%; comparison with the values

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[11] Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.

[12] Cruickshank, *ibid.*, 1956, **9**, 747.

in Table 1 shows the improvement effected by anisotropic refinement. From the small differences between the observed and calculated curvatures the final changes in the thermal parameters were calculated, the largest (in b_{13} for Cl^2) being 1·2 times the corresponding standard deviation calculated from Cruickshank's formula.[12] Application of the shifts to the co-ordinates and temperature factors gave the final parameters which are shown in Table 3; the thermal parameters are quoted as the mean square amplitudes of vibration, U, where $U_{ii} = a_i^2 b_{ii}/2\pi^2$ and $U_{ij} = a_i a_j b_{ij}/4\pi^2$ $(i \neq j)$, the a's being unit-cell dimensions. Table 3 also shows the peak electron densities for the atoms; the standard deviation, $\sigma(\rho)$, was 0·5 e/Å^3. In Table 3 the estimated standard deviations[13] in the co-ordinates, $\sigma(x_i)$, are given; for the thermal parameters, the values of $\sigma(U_{ij})$ derived from $\sigma(b_{ij})$ were found to be approximately the same for all i and j for each atom so that only a mean $\sigma(U)$ is quoted.

Correction for Rotational Oscillation.—It has been shown[14] that rotational oscillations can cause appreciable errors in apparent atomic positions, and for some molecules which can be assumed to be rigid the thermal motions can be analysed[15] to give the translational and

TABLE 2. *Observed and calculated structure factors.*

Reflections which are too weak to be observed have been omitted.

hkl	F (calc.)	F (obs.)
000	(576)	—
020	−92	76
040	168	138
060	−198	169
080	173	154
0,12,0	114	99
0,14,0	−77	64
0,16,0	24	21
200	−53	51
210	−129	108
220	101	94
230	46	34
240	−116	125
250	−82	94
260	34	33
270	102	87
280	−46	49
290	−32	27
2,10,0	59	54
2,11,0	36	27
2,12,0	−27	23
2,13,0	−60	50
2,16,0	−27	19
400	−288	223
410	45	38
420	25	24
430	−97	86
440	−88	79
450	61	59
460	106	91
470	−21	23
480	−100	100
490	59	59
4,11,0	−45	45
4,12,0	−71	39
4,14,0	43	42
600	73	69
610	18	22
620	−150	128
640	181	171
650	16	17
660	−51	52
670	−18	21
680	78	68
6,10,0	−106	85
6,12,0	45	43
6,14,0	−23	16
810	−23	17
820	52	47
830	74	63
850	−39	30
860	23	30
890	−49	39
8,10,0	27	22
8,11,0	34	22
8,13,0	−6	12
10,0,0	−18	21
10,1,0	32	29
10,2,0	69	61
10,4,0	−87	63
10,7,0	−30	23
10,8,0	−37	32
10,10,0	59	42
10,12,0	−17	10
12,0,0	57	54
12,1,0	−7	16
12,2,0	−54	41
12,3,0	−12	16
12,4,0	26	27
12,6,0	−57	48
12,7,0	12	14
12,8,0	36	39
12,10,0	−23	26
14,0,0	−17	23
14,8,0	−2	5
16,0,0	−30	17
16,2,0	20	16
101	−32	36
111	31	35
131	−74	83
141	−86	91
151	38	47
161	−25	28
181	−26	28
191	40	34
1,10,1	26	20
1,11,1	−25	21
1,12,1	−11	13
1,13,1	6	8
1,15,1	−15	15
1,16,1	−18	17
301	85	89
311	−23	32
321	−12	15
331	−50	60
341	84	107
371	27	24
381	47	42
391	22	21
3,10,1	−20	21
3,11,1	−12	10
3,12,1	23	25
3,13,1	−16	23
501	−34	36
511	−43	54
521	18	17
531	31	36
541	26	27
551	−32	34
561	45	34
571	29	31
591	−24	31
5,11,1	13	19
5,12,1	−11	17
5,13,1	−17	23
701	−54	46
711	40	47
741	−26	31
751	23	31
761	10	10
771	−36	38
781	−28	34
7,12,1	−15	7
7,13,1	23	26
901	33	36
911	16	24
921	−19	22
931	13	18
961	−32	37
971	−16	13
981	14	13
9,12,1	15	19
9,13,1	12	10
11,0,1	17	14
11,1,1	−18	17
11,2,1	16	14
11,3,1	7	7
11,4,1	−7	10
11,5,1	−16	14
11,6,1	−1	1
11,7,1	15	15
11,10,1	15	21
11,11,1	8	7
13,2,1	7	10
13,3,1	−20	21
13,4,1	−5	7
13,9,1	10	13
002	−205	179
022	140	124
042	−72	64
062	150	124
082	−90	85
0,10,2	44	53
0,12,2	−61	50
0,14,2	55	46
202	33	29
212	43	45
222	−69	62
232	−51	51
242	59	58
252	36	38
262	−35	43
272	−45	45
282	29	27
292	24	24
2,10,2	−39	44
2,11,2	−31	27
2,12,2	18	16
2,13,2	23	24
2,14,2	−13	9
2,15,2	−21	13
402	110	91
412	−28	26
422	−73	71
432	40	49
442	36	35
452	−30	31
462	−87	89
472	20	16
482	51	63
492	−26	27
4,10,2	−22	27
4,11,2	24	27
4,12,2	37	41
4,13,2	−12	31
4,14,2	−32	28
602	−52	42
622	112	104
642	−98	97
662	59	67
682	−50	64
6,10,2	71	73
6,12,2	−32	36
6,14,2	24	22
802	11	8
812	17	13
822	−15	23
832	−28	31
842	15	18
852	18	19
862	−8	9
8,13,2	8	16
10,0,2	20	21
10,1,2	−16	21
10,2,2	−56	50
10,4,2	47	46
10,6,2	−28	35
10,7,2	14	8
10,8,2	25	29
10,10,2	−40	44
12,0,2	−41	40
12,2,2	36	29
12,4,2	−25	25
12,6,2	37	39
12,8,2	−26	30
12,10,2	18	16
16,0,2	20	16
103	9	12
113	−58	53
123	−57	47
133	116	79
143	86	65
153	−60	38
173	39	35
183	29	28
193	−61	64
1,10,3	−53	60
1,11,3	53	60
303	−75	71
313	27	28
323	87	72
333	70	76
343	−87	88
363	57	38
373	−31	21
383	−59	62
393	−29	36
3,10,3	53	56
3,11,3	25	23
3,12,3	−36	38
3,13,3	25	26
3,14,3	28	26
503	60	60
513	74	73
523	−20	26
533	−60	65
543	−22	26
553	53	47
563	−60	47
573	−64	65
583	17	16
593	38	18
703	57	54
713	−64	63
723	−32	38
743	20	23
753	−43	42
763	−43	46
773	55	46
783	35	26
903	−49	49
913	−27	29
923	41	45
933	−14	16
963	56	51
11,1,3	32	32
11,2,3	−15	25
11,3,3	−19	23
11,4,3	23	25
11,5,3	30	26
11,7,3	−25	31
13,2,3	−19	17
13,3,3	31	28
024	−49	52
044	42	36
204	−24	19
214	43	56
234	22	23
254	12	17
274	−48	42
424	35	41
434	37	31
444	−26	29
454	−12	12
604	49	40
614	−14	21
634	−17	23
804	−6	16
834	−39	29
854	10	12
10,04	−37	30
105	−27	21
115	46	51
125	30	37
135	−50	48
145	−32	29
155	44	33
175	−33	25
195	37	36
305	54	49
325	−49	51
335	−17	26
345	47	46
365	−44	40
505	−15	23
515	−49	52
535	35	35
555	−40	33
575	39	33
595	−30	28
705	−33	28
715	27	26
725	23	19
735	−21	17
905	22	22
925	−26	26
11,3,5	23	17
006	39	45

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[13] Cruickshank and Robertson, *Acta Cryst.*, 1953, **6**, 698.

[14] Cox, Cruickshank, and Smith, *Nature*, 1955, **175**, 766.

[15] Cruickshank, *Acta Cryst.*, 1956, **9**, 754.

TABLE 3. (*Continued.*)

hkl	F (calc.)	F (obs.)	*hkl*	F (calc.)	F (obs.)	*hkl*	F (calc.)	F (obs.)	*hkl*	F (calc.)	F (obs.)	*hkl*	F (calc.)	F (obs.)	*hkl*	F (calc.)	F (obs.)
216	−53	63	401	−57	59	10,6,1	−30	24	392	−31	37	033	−63	48	344	−25	24
256	−33	38	411	45	54	10,8,1	21	20	3,10,2	−26	34	053	30	17	354	27	22
276	51	41	421	−42	48	10,9,1	27	34	3,11,2	23	28				364	−37	38
			431	−18	19	10,10,1	−16	20	3,12,2	−14	16	213	−23	19			
406	−22	26	441	52	54				3,14,2	21	24	223	46	43	504	46	43
416	18	17	451	28	34	12,0,1	−48	40	3,15,2	17	13	233	11	14	514	−46	48
436	−45	41	461	13	21	12,1,1	−54	41				243	−20	24	544	30	29
456	26	30	471	−43	41	12,3,1	30	32	502	−32	25	253	−15	21	554	−26	12
			4,10,1	−44	31	12,5,1	−40	36	512	68	68	263	31	27	574	45	39
626	−13	14	4,11,1	−14	17	12,6,1	29	27	522	34	45						
			4,13,1	18	20	12,7,1	45	34	532	29	36	403	12	14	704	−47	45
836	42	28				12,8,1	−18	17	542	−20	29	423	−23	28	714	−15	21
			601	18	22	12,9,1	−28	28	552	36	40	433	36	38	724	34	32
10,0,6	17	16	611	−64	63	12,10,1	−5	7	562	29	31	453	−14	19	734	−12	11
			621	54	57	12,11,1	15	14	572	−59	59	463	−18	19	764	47	41
107	22	18	631	105	110				582	−23	33						
117	−19	19	641	−44	36	14,0,1	−12	10				613	40	42	904	−14	16
			651	−69	56	14,1,1	16	10	702	67	51	623	−22	27	914	35	37
307	−18	16	671	30	28	14,3,1	−10	10	712	22	22	633	−17	26	924	−23	29
			691	−60	34	14,4,1	11	7	722	−37	43	653	26	31			
527	−4	12	6,10,1	40	24	14,5,1	15	7	762	−68	69	663	−19	24	11,0,4	17	16
			6,11,1	45	34	14,6,1	16	7	772	−26	29	673	−32	31	11,2,4	−20	29
011	−125	106	6,13,1	−13	16	14,7,1	−15	7	782	24	32				11,3,4	35	32
031	62	69	6,15,1	19	17				7,12,2	25	23	813	−19	22			
051	−75	76				16,0,1	19	10	7,14,2	−27	21	823	28	32	035	40	40
071	96	89	801	60	64	16.1.1	22	21				843	−12	17			
091	−25	30	811	46	51				902	13	17	863	24	20	205	87	77
0,11,1	30	24	821	46	33	102	0	13	912	−47	38	873	20	17	235	17	18
0,13,1	−42	36	831	−34	34	112	−23	28	922	14	9				245	36	29
0,15,1	19	19	841	−31	34	122	−51	48	942	−29	38	10,1,3	−22	24	265	−39	28
			851	34	36	132	−80	70	952	−36	36	10,7,3	19	20			
201	−115	96	861	−29	38	142	64	64	962	−10	9				405	−17	18
211	46	48	871	−32	38	172	24	29	972	38	46	12,1,3	20	25	415	−16	17
221	−72	96	881	11	13	182	21	34	9,10,2	21	24	12,2,3	−18	17	425	37	37
231	−67	89	891	31	40	192	33	38				12,3,3	−18	24	435	−34	31
241	72	96	8,10,1	34	39	1,10,2	−42	44	11,0,2	−21	29				445	−49	45
251	45	48	8,11,1	−13	10	1,11,2	−26	28	11,2,2	25	22	104	−33	30			
261	54	49	8,12,1	11	13	1,13,2	−22	26	11,3,2	−42	38	114	6	10	605	−27	26
271	−22	22	8,13,1	20	21	1,15,2	−12	10	11,5,2	17	21	124	20	21	625	−14	10
281	−18	19	8,14,1	−10	10				11,6,2	33	38	134	44	50	635	−30	25
291	35	31				302	−62	64	11,9,2	26	28	144	−58	58			
2,10,1	−51	40	10,0,1	27	21	312	−32	24	11,11,2	−19	16	154	−10	17	825	−36	29
2,11,1	−27	24	10,1,1	16	14	332	58	52							835	13	17
2,12,1	−20	23	10,2,1	−32	36	342	43	55	13,2,2	−25	24	304	26	32	845	44	42
2,13,1	9	13	10,3,1	−43	34	352	−30	31	13,4,2	32	34	314	31	27			
2,14,1	18	19	10,4,1	13	14	362	53	60				324	−12	16	10,2,5	25	25
2,15,1	−11	15	10,5,1	21	24	372	24	28	013	18	19	334	−56	31			
2,16,1	18	17															

TABLE 3. *Final parameters and estimated standard deviations.*

	x/z	y/b	z/c	X (Å)	Y (Å)	Z (Å)	$\sigma(x)$ (10^3 Å)	$\sigma(y)$ (10^3 Å)	$\sigma(z)$ (10^3 Å)
Zn	0·1668	0·2500	0·3154	2·179	3·181	1·858	2	—	2
S	0·0959	0·0978	0·1560	1·253	1·244	0·919	5	5	5
Cl^1	0·3409	0·2500	0·2519	4·454	3·181	1·484	4	—	4
Cl$_2$	0·1458	0·2500	−0·2946	1·905	3·181	4·155	6	—	4
C	0·1177	−0·0095	0·3447	1·537	−0·120	2·030	15	23	19
N^1	0·1431	0·0062	0·5551	1·870	0·079	3·269	20	18	17
N^2	0·1043	−0·0995	0·2638	1·363	−1·265	1·554	20	15	22

	U_{11} (10^3Å^2)	U_{12} (10^3 Å^2)	U_{13} (10^3 Å^2)	U_{22} (10^3 Å^2)	U_{23} (10^3 Å^2)	U_{33} (10^3 Å^2)	$\sigma(U)$ (10^3 Å^2)	ρ (e/Å^3)
Zn	34	0	3	20	0	28	2	65·6
S	49	−26	−26	21	5	28	4	30·6
Cl^1	27	0	0	43	0	28	4	32·2
Cl^2	73	0	26	17	0	33	4	30·0
C	33	3	−11	31	−7	22	17	8·9
N^1	66	−33	−23	43	−36	47	19	8·9
N^2	67	−15	−40	24	23	63	19	8·3

rotational vibrations. A rigorous analysis for this complex is not possible because it is unlikely to be rigid and the standard deviations in the mean square amplitudes of oscillation are very large for the light atoms; it is, however, of interest to find an approximate value for the *maximum* correction for rotational oscillation. The procedure used was the same as that described for the ethyl sulphate anion [16] so that only the outline is given here. Cruickshank [17]

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[16] Truter, *Acta Cryst.*, 1958, in the press.

[17] Cruickshank, *ibid.*, 1956, **9**, 757.

has shown that the approximate correction, M, to the length OP from the mass centre O to an atom P is $M = (U_a + U_b)/2OP$ where U_a and U_b are the mean square amplitudes of oscillation about two axes through O orthogonal to OP. The zinc atom is only 0·2 Å from the mass centre of the molecule so that the motion of this atom may be taken as approximately the translational motion of the molecule as a whole. Subtraction of the thermal parameters for zinc (allowing for an apparent mean square amplitude of 8×10^{-3} Å^2 due to anomalous dispersion) gave mean square amplitudes, $U-U_{\text{Zn}}$, for the other atoms, which for the purpose of finding the maximum correction were taken as entirely due to rotational oscillation. The maximum, minimum, and intermediate values of the " oscillation " mean square amplitudes and their directions were calculated for each atom; the magnitudes are:

	S	Cl^1	Cl^2	C	N^1	N^2
$U_{\text{max.}}$ (10^3 Å^2)	37	32	65	20	53	67
$U_{\text{min.}}$ (10^3 Å^2)	0	1	5	5	0	8
$U_{\text{inter.}}$ (10^3 Å^2)	4	8	9	11	45	21

U_a was taken to be $U_{\text{max.}}$. For those atoms, Cl and S, for which $U_{\text{max.}}$ was approximately perpendicular to OP, U_b was taken to be the value of U in the third orthogonal direction, and a reliable correction was obtained. For the light atoms U_b was taken to be $U_{\text{inter.}}$; this procedure may overestimate M and probably underestimates the correction to the C–N bond length because it is likely that the nitrogen atoms rotate about the C–S bond axis, as in thiourea itself, as well as about the mass centre of the molecule. Corrected co-ordinates were obtained by increasing the distance of each atom from the mass centre by M along OP.

Interatomic Distances and Angles.—The bond lengths, with and without corrections for rotational oscillation, and their estimated standard deviations (e.s.d.) are shown in Table 4; as can be seen from the values of $\sigma(U)$ in Table 3, even if the procedure were rigorous some uncertainty in the corrections would be introduced by the inaccuracies in the thermal parameters so that for the final values the limits of error have been increased to allow for these deficiencies. Only one set of bond angles is given because they were not altered by the corrections. Some of the intramolecular non-bonded distances are also given in Table 4. In the Figure the intramolecular separations between nearest neighbours are shown. The thiourea group is planar to within ±0·01 Å as in thiourea.[2]

TABLE 4. *Interatomic distances and angles.*

Bond lengths	uncorr. Å	corr. Å	e.s.d. Å	final Å		Bond angles		e.s.d.	Distance Å	
Zn–S	2·343	2·352	0·005	2·35 ± 0·01		S–Zn–S′	111·5°	0·2	S...N^1	2·69
Zn–Cl^1	2·305	2·314	0·005	2·31	2·32 ± 0·01	S–Zn–Cl^1	109·0	0·2	S...N^2	2·59
Zn–Cl^2	2·313	2·328	0·005	2·32		S–Zn–Cl^2	110·6	0·2	N^1..N^2	2·24
S–C	1·78	1·78	0·022	1·78 ± 0·02		Cl^1–Zn–Cl^2	107·3	0·2	S...S′	3·87
C–N^1	1·30	1·30	0·027	1·30	1·28 ± 0·03	Zn–S–C	108·6	0·7	Cl^1.Cl^2	3·69
C–N^2	1·25	1·26	0·028	1·26		S–C–N^1	121·2	1·5	Zn..C	3·36
						S–C–N^2	116·1	1·5	N^1.Cl^2	3·23
						N^1–C–N^2	122·6	1·9		

It is noteworthy that even for bonds between heavy atoms the systematic error due to rotational oscillations may be twice the estimated standard deviation calculated to allow for random errors.

DISCUSSION

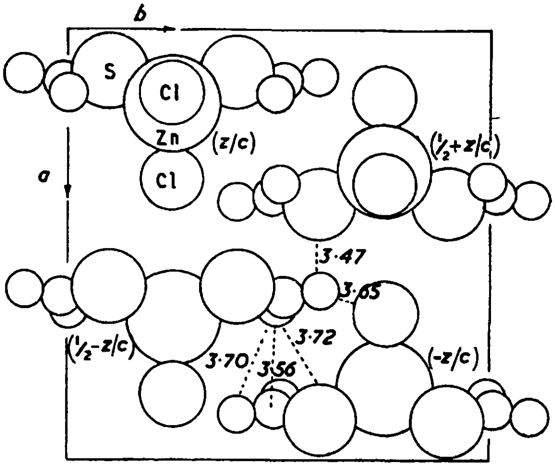
The structure as a whole is shown in the Figure. The packing is very efficient and there are many separations of about 3·5—4·0 Å but no unreasonably short ones and none that can be attributed to hydrogen bonding.

The significant departure of the bond angles around the zinc atom from those of a regular tetrahedron may indicate that the bonds are not formed from simple sp^3 hybrid orbitals but include some contribution from the d orbitals, or it may give rise to more efficient packing of the molecules in the solid. The Zn–S bond is not significantly longer than that in zinc blende but the Zn–Cl bond, which is the same as that (2·29 ± 0·02 Å) found in dichloroterpyridylzinc,[1] is significantly shorter than the sum of the ionic radii

(2·66 Å) as given by the separation in zinc chloride. Probably all the bonds to the zinc atom are partly ionic and partly covalent.

The S–C bond does not differ significantly from the value generally accepted for a single bond, 1·82 Å. A large variation in the bond angles for sulphur bonded to two other atoms has been observed[18] ranging from 65·8° to 119·0°; the angle found in the complex, 108·6° is approximately tetrahedral.

Comparison with unco-ordinated thiourea[2] shows that the molecule has retained its planarity, *i.e.*, that the carbon atom is in a state of sp^2 hybridisation. The C–S bond is lengthened and the C–N bonds are shortened. The change in the C–S bond is just significant; the bond in thiourea is 1·71 ± 0·01 Å, so that the probability that the increase of 0·07 Å has occurred as a result of random errors of observation is 1 in 100. The very large standard deviations in the C–N bond lengths mean that the difference between 1·28 ± 0·03 Å in the complex and 1·33 ± 0·01 Å in the molecule is not statistically significant. Qualitatively the changes appear reasonable; in thiourea three forms, two zwitterionic [$NH_2{\cdot}NH_2^+{:}C{\cdot}S^-$] and one uncharged [$(NH_2)_2C{:}S$], contribute to the bonding; a longer carbon-sulphur bond in the complex implies a greater contribution from the zwitterionic forms with more double-bond character for the carbon–nitrogen bonds. A very simple postulate is that the sulphur hybridisation is sp^2 in thiourea with an electron in a p_z orbital delocalised to participate in the π-bonding system of the molecule whereas in the complex, as in zinc blende, the sulphur atom is in sp^3 hybridisation. In the complex the angles round the carbon atom do not differ significantly from 120°, but they do differ significantly from those in thiourea for which S–C–N = 122·2° ± 0·6° and N–C–N = 115·6° ± 1·1°. The significance of these changes will be discussed later in connection with work now in progress[19] on thioacetamide and some of its co-ordination compounds.



Projection along [001]. *The heights of the molecules along the* c *axis are shown as fractional co-ordinates in parentheses. The numbers are distances in* Å *between nitrogen atoms and their nearest neighbours as indicated by the dotted lines.*

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[18] Abrahams, *Quart. Reviews*, 1956, **10**, 407.
[19] Truter, *Acta Cryst.*, 1957, **10**, 785.