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The Crystal Structure of *mono*-Thiosemicarbazide-Zinc Chloride

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Mono-thiosemicarbazide-zinc chloride, $Zn[SC(NH_2)NHNH_2]Cl_2$, is orthorhombic with cell constants

$$a = 11{\cdot}92,\ b = 7{\cdot}28,\ c = 15{\cdot}46\ \text{Å}\,.$$

The eight molecules in a unit cell lie in two four-fold positions of the *Pnma* space group. The X-ray analysis has been carried out by Fourier methods using *h*0*l*, *h*1*l* and 0*kl* reflections. The complex is molecular, each Zn atom being tetrahedrally coordinated to two Cl atoms and to one thiosemicarbazide molecule, which behaves as a bidentate ligand. In the coordination polyhedron the bond distances (average of two crystallographically non-equivalent molecules) are:

$$\text{Zn–Cl} = 2{\cdot}24 \pm 0{\cdot}01,\ \text{Zn–S} = 2{\cdot}29 \pm 0{\cdot}01,\ \text{Zn–N} = 2{\cdot}09 \pm 0{\cdot}02\ \text{Å}\,.$$

Introduction

From neutral aqueous solutions containing $ZnCl_2$ and thiosemicarbazide, two complex compounds can be obtained:

$$\text{Zn}\textit{Thio}\text{Cl}_2 \quad \text{and} \quad \text{Zn}\textit{Thio}_3\text{Cl}_2$$
$$(\textit{Thio} = \text{SC(NH}_2\text{)NHNH}_2)\,.$$

The structure of *mono*-thiosemicarbazide-zinc chloride has been investigated as part of a programme for studying the coordination by divalent metal atoms of organic molecules containing sulphur. The results achieved in the present study have confirmed, in accordance with the work of Jensen & Rancke-Madsen (1934) on the chemical behaviour of substituted thiosemicarbazides, that thiosemicarbazide acts as a bidentate ligand.

Unit cell and space group

Mono-thiosemicarbazide-zinc chloride crystallizes in colourless well-formed needles showing only the {101} prism. Rotation and Weissenberg photographs (around [010] and [100]) indicated that the crystals are orthorhombic with:

$$a = 11{\cdot}92 \pm 0{\cdot}01,\ b = 7{\cdot}28 \pm 0{\cdot}02,\ c = 15{\cdot}46 \pm 0{\cdot}02\ \text{Å}\,.$$

The X-ray axial ratio *a*/*c* (0·771) agreed with that determined goniometrically (0·774). Systematically absent reflections were 0*kl* for *k*+*l* odd and *hk*0 for *h* odd, indicating space group D_{2h}^{16}–*Pnma* or C_{2v}^{9}–$Pn2_1a$. The density, determined by flotation, was 2·18 g.cm.$^{-3}$, whilst that calculated assuming 8 units of Zn*Thio*Cl_2 per cell was 2·25 g.cm.$^{-3}$.

Intensity data

Intensity data were obtained photometrically from *h*0*l*, *h*1*l* and 0*kl* integrated and non-integrated Weissenberg photographs taken with Cu *Kα* radiation. A multiple-film technique was used and the various photographs were related and corrected for geometrical and polarization factors. The final set of data consisted of 167 (*h*0*l*), 175 (*h*1*l*) and 52 (0*kl*) (possible 235, 234, 76 respectively) measured structure factors. As the μr values were small, only the cylindrical absorption correction was used. The first scale and temperature factors were found by Wilson's (1942) method.

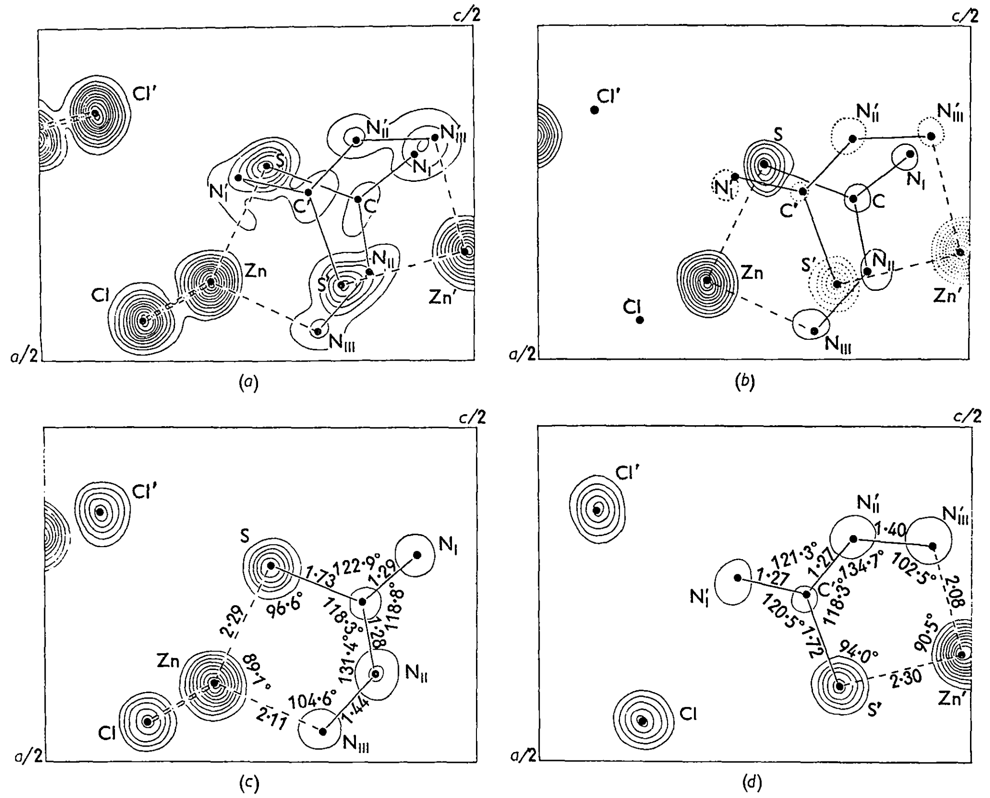
Table 1. *Final atomic coordinates and their standard deviations*

	x/*a*	*y*/*b*	*z*/*c*	*x*	*y*	*z*	σ(*x*)	σ(*y*)	σ(*z*)
Zn	0·3830	$\frac{1}{4}$	0·1945	4·565	1·820	3·007	0·005	—	0·002
Zn′	0·3370	$\frac{3}{4}$	0·4881	4·017	5·460	7·546	0·004	—	0·002
Cl	0·4383	0·0040	0·1189	5·225	0·029	1·838	0·003	0·016	0·004
Cl′	0·3720	0·4960	0·5661	4·434	3·611	8·752	0·003	0·015	0·004
S	0·2112	$\frac{1}{4}$	0·2603	2·518	1·820	4·024	0·005	—	0·003
S′	0·3867	$\frac{3}{4}$	0·3445	4·609	5·460	5·326	0·005	—	0·005
C	0·261	$\frac{1}{4}$	0·365	3·106	1·820	5·651	0·031	—	0·023
C′	0·250	$\frac{3}{4}$	0·308	2·980	5·460	4·766	0·021	—	0·035
N_{I}	0·195	$\frac{1}{4}$	0·432	2·324	1·820	6·680	0·032	—	0·012
N_{II}	0·367	$\frac{1}{4}$	0·378	4·373	1·820	5·839	0·029	—	0·017
N_{III}	0·459	$\frac{1}{4}$	0·317	5·475	1·820	4·907	0·028	—	0·018
N'_{I}	0·229	$\frac{3}{4}$	0·228	2·726	5·460	3·519	0·026	—	0·015
N'_{II}	0·172	$\frac{3}{4}$	0·364	2·050	5·460	5·626	0·019	—	0·015
N'_{III}	0·168	$\frac{3}{4}$	0·454	2·003	5·460	7·027	0·031	—	0·028

Table 2. *Observed and calculated structure factors*

A minus sign after an $|F_o|$ means 'less than'. Values corrected for extinction are starred

l	$10\lvert F_o\rvert$	$10F_c$
	0 0 1	
2	190	158
4	379	-321
6	293	316
8	79-	166
10	369	292
12	105-	-122
14	376	264
16	780	920
18	84-	17
	1 0 1	
1	402	445
2	39-	-21
* 3	1516	1383
4	101	-165
5	402	356
6	407	-339
7	224	177
8	978	966
9	812	-765
10	685	691
11	100-	153
12	105-	14
13	962	1012
14	807	756
15	111-	-17
16	105-	60
17	96-	-42
18	84-	37
19	133	124
	2 0 1	
0	953	-886
* 1	1167	1313
2	47-	13
3	603	-553
* 4	1720	-1560
* 5	2169	-2057
6	105	180
7	405	517
8	214	-172
9	269	233
10	285	298
11	1490	1485
12	435	-423
13	524	504
14	249	-244
15	110-	22
16	105-	19
17	155	191
18	81-	119
19	115	-52
	3 0 1	
* 1	1360	-1581
* 2	1320	-1724
* 3	1134	-1127
4	391	-343
5	494	407
6	344	-330
7	864	-869
8	770	731
9	414	-368
10	97-	-79
11	245	-119
12	202	-191
13	440	-501
14	728	782
15	270	-230
16	102-	-46
17	232	-248
18	425	-407
19	186	-163
	4 0 1	
* 0	2374	-2327
* 1	1600	1780
2	881	-953
3	460	368
4	211	174
5	224	-275
6	512	-596
7	704	-734
8	867	846
9	95-	27
10	294	-247
11	187	-88
12	110-	-51
13	288	-351
14	484	-437
15	498	-605
16	321	-329
17	91	-56
18	73-	15
19	49-	2
	5 0 1	
1	293	-237
2	395	-347
3	347	-257
4	422	-346
5	867	915
6	1040	1056
7	210	233
8	389	-439
9	730	732
10	1148	-1195
11	668	556
12	360	-393
13	774	-718
14	338	-294
15	230	188
16	94-	88
17	83	-96
18	66-	-88
	6 0 1	
0	77-	-19
1	580	-734
2	1095	1260
3	1239	1448
4	908	986
5	155	198
6	345	360
7	374	-384
8	174	139
9	125	-70
10	109-	41
11	246	-131
12	462	404
13	342	-336
14	294	273
15	213	-160
16	88-	-31
17	74-	-9
18	60-	28
	7 0 1	
1	1117	1256
2	271	335
3	378	318
4	146	178
5	549	-558
6	1250	1244
7	178	214
8	263	-121
9	456	335
10	214	-221
11	111-	-161
12	189	218
13	306	234
14	133	-113
15	91-	155
16	281	313
17	436	426
	8 0 1	
0	478	458
1	96-	26
2	347	-387
3	212	-229
4	100-	103
5	516	487
6	105-	95
7	258	-206
8	1041	-1187
9	473	387
10	111-	-102
11	111-	157
12	106-	137
13	384	378
14	342	320
15	81-	107
16	66-	49
	9 0 1	
1	209	200
2	169	-91
3	465	-453
4	194	-308
5	1225	-1300
6	522	-530
7	213	119
8	243	199
9	373	-286
10	342	369
11	590	-612
12	420	357
13	91-	12
14	81-	23
15	68-	-57
	10 0 1	
0	209	-342
1	110-	60
2	584	-596
3	387	-490
4	194	160
5	651	-666
6	176	-137
7	408	417
8	355	-401
9	237	-265
10	319	-254
11	155	117
12	186	161
13	153	-43
14	67-	-11
	11 0 1	
1	111-	-190
2	111-	20
3	111-	-61
4	111-	-18
5	111-	197
6	683	-770
7	311	305
8	103-	-82
9	332	353
10	247	219
11	84-	110
12	312	-265
13	61-	-155
	12 0 1	
0	502	-471
1	108-	78
2	463	457
3	369	-392
4	105-	199
5	103-	130
6	342	401
7	262	342
8	358	510
9	142	-242
10	203	188
11	288	-263
12	51-	-4
	13 0 1	
1	98-	40
2	452	512
3	96-	91
4	243	263
5	420	466
6	85-	-18
7	81-	-39
8	74-	74
9	254	241
10	53-	60
	14 0 1	
0	82-	-51
1	258	-227
2	81-	66
3	79-	184
4	76-	-34
5	462	426
6	375	-367
7	57-	106
	15 0 1	
1	56-	-148
2	54-	146
3	49-	48
	0 1 1	
1	1175	-996
3	1017	984
5	184	-133
7	570	459
9	1088	1051
11	132	-54
13	207	278
15	696	713
17	212	-228
19	234	297
	1 1 1	
1	996	-1188
2	554	588
3	212	-130
4	637	-655
5	1356	-1394
6	655	673
7	790	-712
8	66-	108
9	81	37
10	78-	-14
11	673	-683
12	240	252
13	154	226
14	166	122
15	409	-363
16	281	277
17	228	216
18	67-	38
19	208	-156
	2 1 1	
0	96	3
1	143	-56
2	1120	-1224
3	43-	-79
4	730	-745
5	185	167
6	301	-316
7	689	-672
8	1148	-1086
9	258	181
10	406	416
11	478	-482
12	817	-839
13	91-	-82
14	328	-283
15	149	-104
16	241	265
17	77-	-72
18	199	-267
19	69	-78
	3 1 1	
1	603	-614
2	442	-564
3	854	886
4	631	608
5	727	-705
6	920	-1018
7	181	224
8	129	-111
9	90-	-51
10	90-	-52
11	90-	72
12	368	-393
13	156	-118
14	368	-355
15	88-	-53
16	328	-285
17	74-	52
18	241	-253
19	46-	32
	4 1 1	
0	979	1015
1	254	244
2	155	228
3	554	-619
4	1032	1078
5	61-	-78
6	230	223
7	175	165
8	281	250
9	1115	-1048
10	504	420
11	585	533
12	355	379
13	282	-292
14	91-	8
15	390	-371
16	261	251
17	112	117
18	59-	-34
	5 1 1	
1	1012	1128
2	574	-683
3	60-	75
4	848	912
5	1110	1088
6	129	-84
7	393	363
8	275	-219
9	241	274
10	408	424
11	181	196
12	208	-202
13	257	159
14	367	391
15	164	132
16	229	-154
17	66-	21
18	292	265
	6 1 1	
0	582	-439
1	191	108
2	588	443
3	178	181
4	448	-399
5	216	228
6	424	397
7	313	317
8	275	304
9	261	316
10	394	-327
11	360	425
12	201	193
13	201	168
14	168	159
15	80-	130
16	410	-333
17	257	273
18	131	213
	7 1 1	
1	218	-241
2	73-	86
3	1087	-1186
4	206	-184
5	303	302
6	191	192
7	546	-597
8	345	307
9	447	-494
10	92-	-100
11	155	213
12	394	406
13	249	-263
14	81-	-12
15	73-	43
16	287	294
17	151	-125
	8 1 1	
0	79-	-186
1	208	-186
2	525	-502
3	81-	24
4	432	-462
5	85-	57
6	480	-489
7	190	-253
8	91-	-96
9	240	203
10	590	-601
11	422	-519
12	87-	-8
13	82-	75
14	163	-169
15	117	87
16	86	-78
	9 1 1	
1	158	-123
2	504	532
3	87-	-31
4	733	-742
5	250	-299
6	281	265
7	143	167
8	177	-191
9	91-	-14
10	226	-267
11	135	-117
12	226	-191
13	74-	-40
14	129	-218
15	54-	-29
	10 1 1	
0	280	467
1	229	-245
2	176	101
3	230	191
4	212	307
5	423	-425
6	301	334
7	91-	-118
8	90-	-139
9	87-	38
10	542	565
11	191	-190
12	75	-82
13	65	-122
14	52	56
	11 1 1	
1	176	247
2	92-	13
3	628	709
4	91-	100
5	90-	16
6	93	-103
7	92	196
8	84-	105
9	282	295
10	75-	-21
11	68-	-24
12	60-	82
13	160	205
	12 1 1	
0	88-	63
1	418	435
2	87-	-23
3	185	-160
4	269	214
5	234	245
6	81-	77
7	78-	198
8	74-	-76
9	68-	-20
10	177	215
11	176	263
12	38-	-33
	13 1 1	
1	206	-264
2	266	-261
3	78-	-107
4	243	276
5	165	-164
6	70-	-54
7	66-	-98
8	59-	27
9	93	-122
10	97	182
	14 1 1	
0	131	-220
1	66-	-60
2	66-	-117
3	63-	-32
4	170	-205
5	57-	-34
6	168	-244
7	87	108
	15 1 1	
1	44-	45
2	42-	18
	0 2 1	
0	2885	-2454
2	1555	1450
4	1785	-1735
6	1760	-1781
8	117	-164
10	442	-388
12	422	-367
14	121-	14
16	119-	85
18	369	314
	0 3 1	
1	636	718
3	753	-736
5	87-	148
7	229	-240
9	713	-816
11	118-	-31
13	207	-215
15	582	-472
17	216	162
	0 4 1	
0	3808	3958
2	91-	99
4	96-	-38
6	171	222
8	112	99
10	228	181
12	120-	-72
14	271	158
16	574	532
	0 5 1	
1	437	-467
3	335	477
5	113-	20
7	281	243
9	424	483
11	119	-79
13	108-	132
15	383	369
	0 6 1	
0	522	-781
2	397	471
4	619	-707
6	706	-758
8	119-	-79
10	239	-189
12	205	-189
14	76-	9
	0 7 1	
1	130	241
3	224	-265
5	117-	98
7	111-	-69
9	201	-339
11	84-	-45
13	51-	-99
	0 8 1	
0	720	1200
2	104-	38
4	99-	-14
6	92-	66
8	78-	36
10	53-	64



(*a*) (*b*) (*c*) (*d*)

Fig. 1. Final projection of: (*a*) ϱ_0, (*b*) S_1, (*c*) $\frac{1}{2}(\varrho_0+S_1)$, (*d*) $\frac{1}{2}(\varrho_0-S_1)$ on (010). Contours at intervals of 5 e.Å^{-2}, zero contours omitted, negative contours dotted.

Structure determination

Since the unit cell contains eight molecules of Zn*Thio*Cl$_2$, they can be arranged for the *Pnma* space group on either the general eight-fold position (*d*) or on two special four-fold positions. For the *Pn*2$_1$*a* space group there is only the four-fold general position (*a*) available.

Projections of the Patterson function along the *a* and *b* axes were computed first, but their interpretation was obtained only *a posteriori*. To solve the phase problem, statistical sign relations were applied, following Grant, Howells & Rogers (1957). Using this method the signs of 56 *h*0*l* reflections with

$$U \geq 0{\cdot}12\ (U_{\text{max.}} = 0{\cdot}51)$$

were obtained. Subsequent refinement showed these signs were correct except for the 407 reflection.

With these reflections a first $\varrho_0(X, Z)$ projection was calculated. Four relevant peaks appeared in each asymmetric unit ($\frac{1}{2}a$, $\frac{1}{2}c$); they were similar in weight and appeared close together in pairs. The only possible interpretation of this was to admit in each asymmetric unit two non-equivalent molecules lying in two four-fold positions; the two Cl atoms of each molecule overlap in the projection giving peaks of weight similar to Zn. A successive $\varrho_0(X, Z)$ projection, calculated with all the observed reflections and the signs obtained approximately by placing a Zn atom at each of the four peaks, gave an idea of the region occupied by the organic molecules ($0 < x < \frac{1}{2}a$, $\frac{1}{4}c < z < \frac{1}{2}c$). This led us to attribute the two adjacent peaks to the Zn atoms; in this region two organic molecules overlap and so the two Zn atoms must be at different *y* levels.

The nearly perfect circular shape of the Cl peaks indicated that their overlapping was probably caused by the presence of mirror planes containing the Zn atoms and particularly the organic molecules. From these considerations the *Pnma* space group was assumed; the correctness of this assumption was

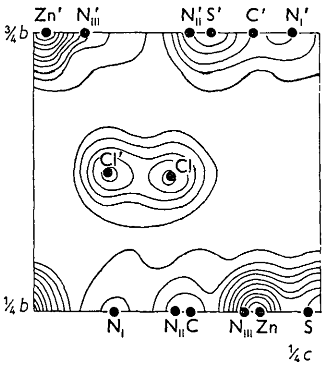


Fig. 2. Final projection of $\varrho_0(Y, Z)$; contours as in Fig. 1.

confirmed by the agreement between the observed and calculated structure factors.

The next step was a $S_1(X, Z)$ generalized projection calculated using the signs of the zinc contribution alone, putting Zn at $y=\frac{1}{4}$ and Zn′ at $y=\frac{3}{4}$. The y coordinates of the chlorine atoms, deduced from their distances from the zinc atoms in the projection, were approximately 0 and $\frac{1}{2}$, so that these atoms give no contributions to $S_1(X, Z)$. The $S_1(X, Z)$ projection showed well-resolved peaks of zinc and sulphur atoms. A successive $S_1(X, Z)$ projection, calculated using the signs of the contributions of all the heavy atoms, gave well-resolved organic molecules too. A better view of these appears on the projection of the functions $\frac{1}{2}\{\varrho_0+S_1\}(X, Z)$ and $\frac{1}{2}\{\varrho_0-S_1\}(X, Z)$, which correspond to the contributions of the $h0l$ and hll reflections to the three-dimensional sections of $\varrho(X, Y, Z)$ at $y=\frac{1}{4}$ and $y=\frac{3}{4}$ respectively.

Further refinement of x and z coordinates was carried out on these last projections and on the corresponding F_o-F_c syntheses. Fig. 1 shows the final ϱ_0, S_1, $\frac{1}{2}(\varrho_0+S_1)$ and $\frac{1}{2}(\varrho_0-S_1)$ projections on (010). The $\varrho_0(Y, Z)$ projection (Fig. 2) was used only to get the y coordinates of the chlorine atoms, which were very close to the anticipated positions.

In Table 1 the final atomic coordinates x/a, y/b, z/c and coordinates x, y, z (Å) with their standard deviations (Å) are reported. The standard deviations of the atomic coordinates were obtained by Cruickshank's (1949) method from $h0l$ and hll data, excepting chlorine for which $h0l$ and $0kl$ data were used. The standard deviations in electron densities are:

$$\sigma\{\varrho_0(X, Z)\}=1{\cdot}05,\ \ \sigma\{S_1(X, Z)\}=0{\cdot}76,$$
$$\sigma\{\varrho_0(Y, Z)\}=1{\cdot}27\ \text{e.Å}^{-2}.$$

In Table 2 the final values of $|F_o|$ and F_c are given. The conventional R indices (observed reflections only) are:

$$R(h0l)=0{\cdot}130,\ \ R(hll)=0{\cdot}117,\ \ R(0kl)=0{\cdot}137\ .$$

A correction for secondary extinction was applied to the reflections starred in Table 2, following the method of Pinnock, Taylor & Lipson (1956); this improved the $R(h0l)$ value to 0·114. The final overall isotropic temperature factor was 1·7 Å^{-2}, equal to that first obtained from Wilson's method.

Discussion

Fig. 3 shows diagrammatically the (010) projection of the unit cell. The structure is built up from molecular complexes Zn*Thio*Cl_2, in which the Zn atom coordinates tetrahedrally two chlorine atoms and one thiosemicarbazide molecule. This is illustrated by Fig. 4, which shows two crystallographically independent molecules. The bond distances and angles (Table 3) in these two molecules are in good agreement, indicating their chemical equivalence.

The distance Zn–Cl is equal to that found (2·25 Å) in $(NH_4)_3ZnCl_5$ by Klug & Alexander (1944) but a little shorter than that found (2·32 Å) in Zn[SC

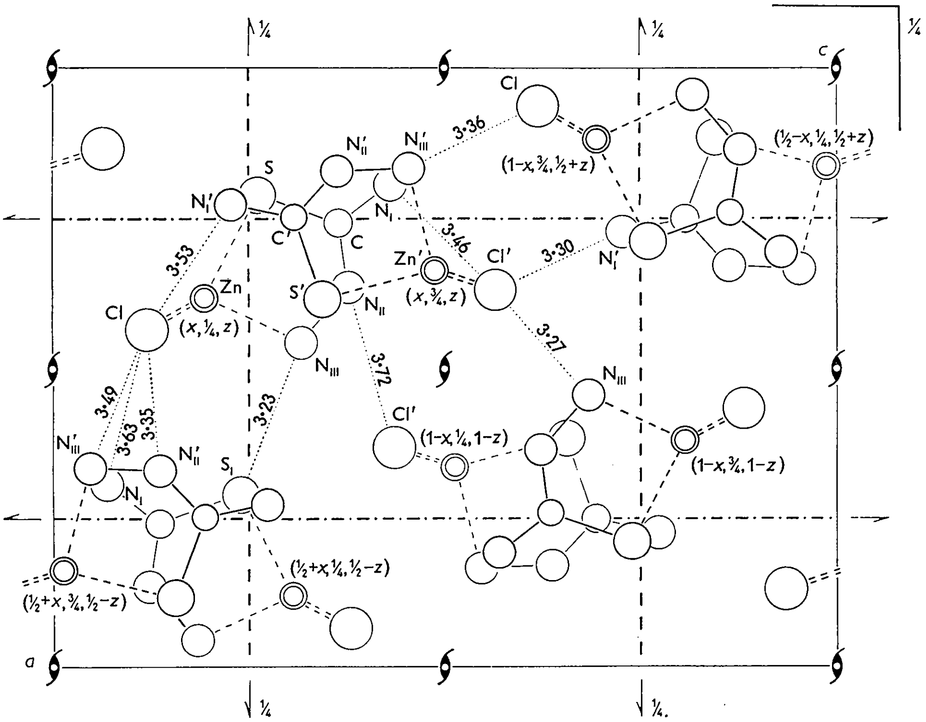


Fig. 3. Diagrammatic projection of a unit cell on (010).

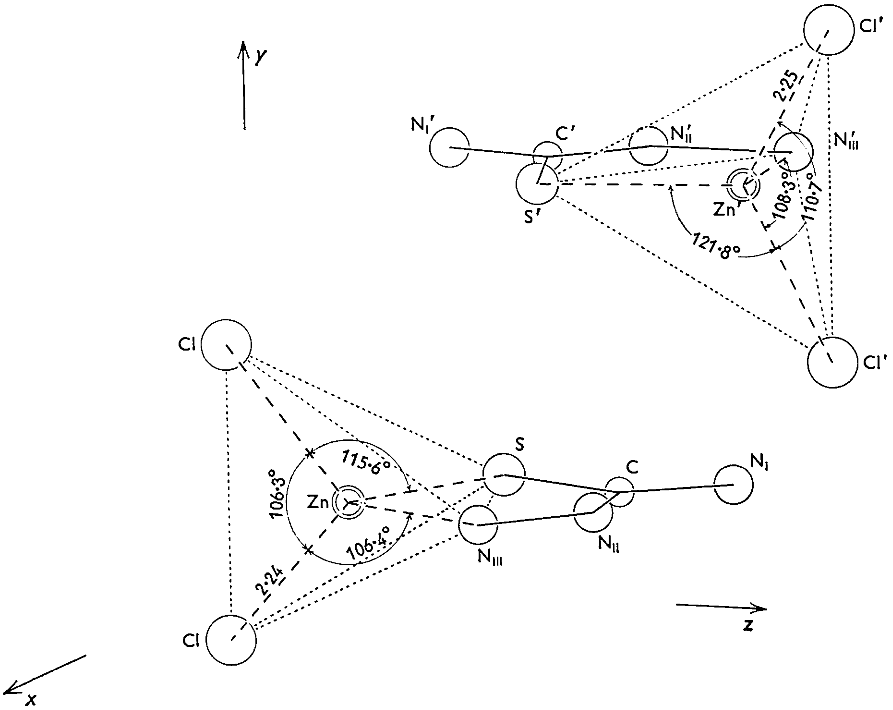


Fig. 4. Clinographic projection of an asymmotric unit.

$(NH_2)_2]_2Cl_2$ by Kunchur & Truter (1958); the Zn–S distance (2·35 Å) reported by Kunchur & Truter is a little larger than our value. The Zn–N distance agrees approximately with that found in $Zn(NH_3)_2Cl_2$ (2·04 Å) and $Zn(NH_3)_2Br_2$ (2·16 Å) by MacGillavry & Bijvoet (1936) and with that found in zinc 8-hydroxyquinolinate dihydrate (2·06 Å) by Merrit, Cady & Mundy (1954).

The planarity in the organic molecule follows from symmetry conditions and the bond distances are those to be expected.

Table 3. *Bond distances and angles with standard deviations*

	Molecule at	
	$(x, \frac{1}{4}, z)$	$(x, \frac{3}{4}, z)$
Zn–Cl	2·238 ± 0·010 Å	2·247 ± 0·009 Å
Zn–S	2·286 ± 0·006	2·298 ± 0·006
Zn–N_{III}	2·11 ± 0·02	2·08 ± 0·03
S–C	1·73 ± 0·02	1·72 ± 0·02
C–N_{I}	1·29 ± 0·03	1·27 ± 0·04
C–N_{II}	1·28 ± 0·04	1·27 ± 0·03
N_{II}–N_{III}	1·44 ± 0·03	1·40 ± 0·03
Cl–Zn–Cl	106·3 ± 0·5°	110·7 ± 0·5°
Cl–Zn–S	115·6 ± 0·2	121·8 ± 0·2
S–Zn–N_{III}	89·1 ± 0·7	90·5 ± 0·8
Cl–Zn–N_{III}	106·4 ± 0·4	108·3 ± 0·5
S–C–N_{I}	122·9 ± 1·6	120·5 ± 1·7
N_{I}–C–N_{II}	118·8 ± 2·3	121·3 ± 1·8
S–C–N_{II}	118·3 ± 1·5	118·3 ± 1·8
C–N_{II}–N_{III}	131·4 ± 2·4	134·7 ± 2·9
Zn–S–C	96·6 ± 1·0	94·0 ± 1·2
Zn–N_{III}–N_{II}	104·6 ± 1·4	102·5 ± 1·6

The angle Cl–Zn–Cl is practically tetrahedral but the angle S–Zn–N_{III} is considerably smaller. This fact can be justified considering the dimensions of the organic molecule in which is observed a relevant enlargement of the angle on N_{II} comparing with the expected trigonal value.

The van der Waals distances between the overlapping molecules in the (X, Z)-projection are all larger than $\frac{1}{2}b = 3{\cdot}64$ Å; the other most significant distances are:

N'_{I}–Cl$(x, \frac{1}{2}-y, z)$ = 3·53 ± 0·02 Å
Cl'–N_{I} = 3·46 ± 0·02
Cl$(x, \frac{1}{2}-y, z)$–$N'_{III}(\frac{1}{2}+x, \frac{3}{4}, \frac{1}{2}-z)$ = 3·49 ± 0·03
N'_{III}–Cl$(\frac{1}{2}-x, 1-y, \frac{1}{2}+z)$ = 3·36 ± 0·03
Cl'–$N'_{I}(\frac{1}{2}-x, \frac{1}{4}, \frac{1}{2}+z)$ = 3·30 ± 0·02
Cl'–$N_{III}(1-x, \frac{3}{4}, 1-z)$ = 3·27 ± 0·02
Cl–$N_{I}(1+x, \frac{1}{4}, \frac{1}{2}-z)$ = 3·63 ± 0·02
Cl$(x, \frac{1}{2}-y, z)$–$N'_{II}(\frac{1}{2}+x, \frac{3}{4}, \frac{1}{2}-z)$ = 3·35 ± 0·02
N_{II}–Cl'$(1-x, 1-y, 1-z)$ = 3·72 ± 0·03
N_{III}–S$(\frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z)$ = 3·23 ± 0·03

The distances between Cl and N atoms do not seem to indicate hydrogen bonding, especially in view of the large distance of the Cl atoms from the planes of the organic molecule. On the contrary, a hydrogen bonding may exist between $(NH_2)_{III}$ and S$(\frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z)$ which are coplanar; it is probable that this bonding is favoured by the distortion of the NH_2 group, caused by its coordination by Zn. An N–H · · · S hydrogen bond, 3·26 Å long, is described by Penfold (1953) in α-thiopyridone.

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The Crystal Structure of α-Pyrazinamide*

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α-Pyrazinamide, $C_5H_5N_3O$, obtained from alcohol–water solution, is monoclinic, space group $P2_1/a$, with four molecules in a unit cell of dimensions

$$a = 23{\cdot}07,\ b = 6{\cdot}73,\ c = 3{\cdot}73\ \text{Å},\ \beta = 101{\cdot}0°.$$

The detailed crystal structure has been determined by two-dimensional difference syntheses and least squares based on (*hk*0) and (*h*0*l*) reflexions.

The pyrazine ring is completely planar, with mean C–N = 1·348 and C–C = 1·383 Å, and makes an angle about 5° to the amide group (C–O = $1{\cdot}24_4$ and C–N = $1{\cdot}31_2$ Å). The molecules are connected by NH–O hydrogen bonds, 2·90 Å, forming dimers, and there are indications of NH–N hydrogen bonds, 3·14 Å, linking the dimers into endless chains extended along [011].

Anisotropic thermal vibration parameters of each atom were obtained, and they were interpreted by dividing into translational and angular oscillation of the rigid molecule. It was observed that the amide group makes probably a torsional motion.

Introduction

Structural investigation of pyrazinamide (pyrazine-2-carboxyamide), a potential antituberculosis drug, is a part of serial studies, attempted by us, on crystal structures of carboxyamides having rings with nitrogen. One of the main objects of these researches is to determine the accurate molecular configuration with special emphasis on the steric effects on the variation of bond lengths and angles.

Recently it has been reported (Tamura & Kuwano, 1959) that pyrazinamide has two modifications: one form is obtained from alcoholic solution and the other from melt. We shall call the former α and the latter β. On the other hand, crystal structures of a number of carboxyamides already reported can be grouped into two types of molecular arrangement. Therefore, it will be interesting to examine whether each of these two modifications has a related crystal structure to each of these types or not.

In the present paper will be reported a detailed crystal structure of the α-modification of pyrazinamide. An analysis of the anisotropic thermal motion of the molecule using Cruickshank's method (1956*a*) will also be given.

Experimental

Crystals were obtained from alcohol–water solution as fine colourless needles elongated along the *c* axis, sometimes as laths with (010) well developed. Twins were found frequently.

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* A preliminary note on this structure has been published (Takaki, Sasada & Watanabé 1959*a*).

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