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The Crystal Structure of Bis(hydrazine)zinc Isothiocyanate

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The crystals of bis(hydrazine)zinc isothiocyanate are monoclinic, space group $P2_1/a$, and are twinned according to the (100) law. The structure is characterized by chains of octahedral complexes. The octahedra $[Zn(N_2H_4)_{4/2}(NCS)_2]$ are held together by bridges of hydrazine. The six bond lengths Zn–N are equal (2·17 Å). The hydrazine molecules are present in two enantiomorphous "staggered" forms. The distance N–N in hydrazine is 1·47 Å. The NCS^- group is bound to the metal through the nitrogen atom. The interchain distances N · · · S within layers parallel to (010) are shorter than the distances N · · · S between layers.

The compounds with the general formula

$$[M^{II}(N_2H_4)_2(NCS)_2]\,,$$

where M^{II} = Cd, Zn, Co, Ni, Fe or Mn form monoclinic, isostructural crystals (Ferrari, Braibanti & Lanfredi, 1961). The crystals are always twinned, the twin law being (100).

The crystal structure of the zinc compound has been now investigated.

Experimental

The twinned crystals of bis(hydrazine)zinc isothiocyanate are colorless, very fine needles. Photographs were taken by rotation around [001].

The Buerger symmetry of the Weissenberg photographs is found to be C_{2l} both for the zero-layer photograph and also for the equi-inclination photographs of the upper layers, owing to twinning according to the (100) law. The situation has been illustrated by Trotter (1959).

The unit cell has

$$a = 7{\cdot}141 \pm 0{\cdot}004,\ b = 14{\cdot}756 \pm 0{\cdot}005\,,$$
$$c = 4{\cdot}214 \pm 0{\cdot}005\ \text{Å};\ \beta = 105°\ 30' \pm 8'$$

and contains two stoichiometric units

$$[Zn(N_2H_4)_2(NCS)_2]\,.$$
$$\varrho_o = 1{\cdot}914\ \text{g.cm}^{-3},\ \varrho_c = 1{\cdot}906\ \text{g.cm}^{-3}.$$

One repeat distance (*c* side of the unit cell) in the crystals of bis(hydrazine)zinc isothiocyanate and also of the manganese and cadmium compounds, is constantly 0·08 Å longer than one repeat distance of the corresponding chloride (Ferrari, Braibanti & Bigliardi, 1962) and acetate (Ferrari, Braibanti & Lanfredi, 1963) (Table 1).

Systematic absences allow the assignment of the crystals to the space group $P2_1/a$ (C_{2h}^5).

Integrated spots were obtained by a Weissenberg–Wiebenga apparatus with the multiple film technique. Cu $K\alpha$ radiation (Ni filter) was used throughout. Blackening was estimated visually. Absorption correction as for cylindrical specimens (Bond, 1959) was applied ($\mu R = 0{\cdot}3$). The Lorentz and polarization factors were calculated on an Olivetti Elea 9002 computer. The form factors were calculated by a program prepared by Panattoni, Frasson & Mammi (1960), the Forsyth & Wells (1959) formula being used.

Determination of the structure

Observed intensities were approximately scaled by Wilson's (1942) method. The Patterson synthesis

Table 1. *Comparison between unit cell constants of bis(hydrazine)divalent-metal isothiocyanates, chlorides and acetates*

	$[M^{II}(N_2H_4)_2(NCS)_2]$			$[M^{II}(N_2H_4)_2]Cl_2$			$[M^{II}(N_2H_4)_2](CH_3COO)_2$		
	Cd	Zn	Mn	Cd	Zn	Mn	Cd	Zn	Mn
a (Å)	7·28	7·14	7·21	9·30	8·99	9·08	6·65	6·58	6·63
b (Å)	14·94	14·76	14·82	8·00	7·92	8·01	8·73	8·52	8·60
c (Å)	4·41	4·21	4·37	4·33	4·13	4·29	4·33	4·14	4·28
α	—	—	—	—	—	—	91° 17′	90°	90° 32′
β	106° 26′	105° 30′	105° 59′	106° 10′	105° 32′	105° 30′	90° 58′	90° 25′	90° 39′
γ	—	—	—	—	—	—	97° 52′	96° 52′	96° 42′
Z	2	2	2	2	2	2	1	1	1
Space group	C_{2h}^5–$P2_1/a$			C_{2h}^3–$C2/m$			C_i^1–$P\bar{1}$		

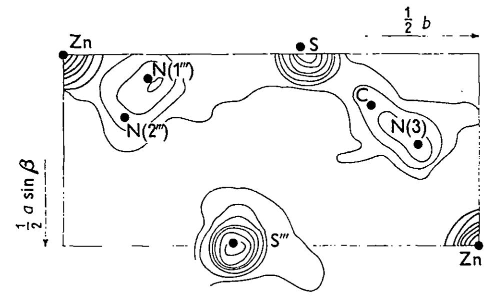

Fig. 1. $\varrho_o(xy)$. Contours every 2 e.Å^{-2} starting from 2 e.Å^{-2}. In Zn-peaks contours are at intervals of 5 e.Å^{-2} starting from 10 e.Å^{-2}.

$P(uv)$ shows outstanding maxima, which were attributed to vectors Zn–S (Beevers & Robertson, 1950). A Fourier synthesis $\varrho_o(xy)$ (Fig. 1) was then calculated and, from this, the location of the other atoms was readily found. Only N atoms of hydrazine molecules overlap appreciably. The residual was at this stage $R_{hk0}=0{\cdot}27$. The atomic z coordinates were approximately derived from the components of the first-layer generalized Patterson projection $_CP_1(uv)$ and $_SP_1(uv)$.

All the coordinates were improved further by the generalized projection components $C_1(xy)$, $S_1(xy)$, $C_2(xy)$, $S_2(xy)$.

Three-dimensional refinement was carried out by calculating the line synthesis $\varrho_o(x_iy_iz)$ at a number of points x_iy_i around the centres of the maxima in the $\varrho_o(xy)$. Finally line electron distributions

Table 2. *Observed reflexions and residuals*

Reflexions	Possible	Observed	Residuals without H contributions	Residuals with H contributions
$hk0$	132	114	0·096	0·092
$hk1$	262	231	0·106	0·103
$hk2$	234	218	0·162	0·158
Total	628	563	0·124	0·121

Table 3. *Comparison between calculated and observed structure factors*

h	k	$10F_c$	$10F_o$
h k 0			
2	0	747	805
4	0	579	629
6	0	373	363
8	0	244	233
1	1	619	616
2	1	251-	292
3	1	331	319
4	1	102	107
5	1	205	219
6	1	95	93
7	1	127	90
8	1	71	49
0	2	478	489
1	2	4	–
2	2	42-	101
3	2	198-	236
4	2	136	135
5	2	58-	61
6	2	55	40
7	2	140-	118
8	2	38	26
1	3	879	947
2	3	468-	495
3	3	560	606
4	3	22-	–
5	3	412	427
6	3	93-	68
7	3	319	283
8	3	61-	50
0	4	199	185
1	4	17	27
2	4	572	607
3	4	120-	116
4	4	516	516
5	4	173	166
6	4	307	269
7	4	4	–
8	4	163	116
1	5	104-	190
2	5	4-	–
3	5	34	11
4	5	92	77
5	5	50	71
6	5	36-	36
7	5	56	55
8	5	15	–
0	6	72	62
1	6	53-	58
2	6	513	539
3	6	112-	102
4	6	280	273
5	6	40	35
6	6	221	191
7	6	76-	61
8	6	138	94
1	7	575	655
2	7	164	175
3	7	667	673
4	7	88	86
5	7	436	408
6	7	33	19
7	7	185	169
8	7	28	27
0	8	133	116
1	8	56	51
2	8	317	312
3	8	167	160
4	8	39	21
5	8	57	34
6	8	65	59
7	8	94	80
1	9	182	176
2	9	23	20
3	9	205	202
4	9	86-	66
5	9	92	65
6	9	0	–
7	9	13-	–
0	10	591	625
1	10	22	17
2	10	578	567
3	10	83	66
4	10	385	368
5	10	155-	149
6	10	241	235
7	10	10	–
1	11	381	385
2	11	42	26
3	11	207	187
4	11	38-	32
5	11	149	151
6	11	83	68
7	11	126	101
0	12	60	31
1	12	51-	48
2	12	32-	38
3	12	18-	35
4	12	61	47
5	12	99-	98
6	12	16	–
1	13	318	380
2	13	7-	–
3	13	193	180
4	13	104-	108
5	13	185	193
6	13	82-	63
0	14	396	392
1	14	44-	111
2	14	206	209
3	14	15-	–
4	14	254	268
5	14	53	56
1	15	21-	37
2	15	14	–
3	15	16	–
4	15	55	35
5	15	45	35
0	16	164	173
1	16	5	–
2	16	51	53
3	16	26-	23
4	16	66	58
1	17	248	269
2	17	39-	28
3	17	242	262
0	18	76	74
1	18	48	38
2	18	106	96
h k 1			
0	0	923	813
2	0	617	595
2-	0	553	551
4	0	697	597
4-	0	410	438
6	0	341	320
6-	0	169	220
8	0	279	178
8-	0	273	283
0	1	266-	283
1	1	157	179
1-	1	120	106
2	1	132-	120
2-	1	185-	234
3	1	518	500
3-	1	464	451
4	1	87-	71
4-	1	264-	271
5	1	226	188
5-	1	161	175
6	1	50-	32
6-	1	265-	275
7	1	95	78
7-	1	180	188
8	1	14-	12
8-	1	180-	175
9-	1	113	113
0	2	180	144
1	2	705	593
1-	2	113-	137
2	2	90	98
2-	2	208	166
3	2	136	117
3-	2	222	274
4	2	204	211
4-	2	265	259
5	2	15-	18
5-	2	87	99
6	2	1-	–
6-	2	102	84
7	2	38-	18
7-	2	63	64
8	2	29	21
8-	2	157	152
0	3	245	260
1	3	727	606
1-	3	845	815
2	3	307	324
2-	3	316	321
3	3	462	438
3-	3	576	589
4	3	96	55
4-	3	181	245
5	3	338	306
5-	3	303	328
6	3	9-	15
6-	3	64	44
7	3	253	257
7-	3	230	259
8-	3	5	20
9-	3	111	87
0	4	539	489
1	4	123	139
1-	4	574-	577
2	4	523	547
2-	4	652	615
3	4	134-	129
3-	4	69-	55
4	4	338	316
4-	4	507	519
5	4	63-	37
5-	4	249-	261
6	4	218	204
6-	4	279	307
7	4	50-	29
7-	4	184-	196
8-	4	77	103
0	5	112-	87
1	5	297	240
1-	5	406	361
2	5	102	109
2-	5	185-	218
3	5	104-	106
3-	5	171	176
4	5	31-	55
4-	5	9-	15
5	5	30-	24
5-	5	243	241
6	5	75-	63
6-	5	22	25
7	5	5	24
7-	5	124	155
8-	5	62-	36
0	6	466	454
1	6	114	109
1-	6	128	115
2	6	440	422
2-	6	496	519
3	6	32	–
3-	6	371	368
4	6	95	104
4-	6	269	287
5	6	113	110
5-	6	195	222
6	6	215	236
6-	6	302	301
7	6	44	19
7-	6	152	178
8-	6	67	55
0	7	159-	152
1	7	630	575
1-	7	552	543
2	7	115-	153
2-	7	172-	200
3	7	428	399
3-	7	375	370
4	7	60-	63
4-	7	57-	43
5	7	378	327
5-	7	437	407
6	7	20-	–
6-	7	20	18
7	7	214	183
7-	7	140	163
8-	7	12-	12
0	8	240	239
1	8	286-	257
1-	8	140-	153
2	8	237	218
2-	8	211	200
3	8	135-	135
3-	8	220-	246
4	8	14-	–
4-	8	35	–
5	8	44-	43
5-	8	109-	124
6	8	152	167
6-	8	214	229
7	8	6	–
7-	8	62-	64
8-	8	99	78
0	9	142	163
1	9	169	167
1-	9	113	129
2	9	33-	25
2-	9	240	286
3	9	153	167
3-	9	92	61
4	9	72	76
4-	9	139	149
5	9	140	159
5-	9	188	168
6	9	92	56
6-	9	101	122
7	9	45	46
7-	9	90	79
8-	9	132	76
0	10	392	375
1	10	11	–
1-	10	193	234
2	10	461	446
2-	10	348	369
3	10	93	86
3-	10	53-	50
4	10	379	349
4-	10	248	298
5	10	10-	22
5-	10	88	107
6	10	281	250
6-	10	197	234
7-	10	70	65
0	11	86-	82
1	11	264	280
1-	11	265	302
2	11	154-	155
2-	11	112-	148
3	11	230	229
3-	11	196	215
4	11	42-	18
4-	11	207-	245
5	11	168	203
5-	11	112	167
6	11	10	–
6-	11	195-	207
7-	11	137	140
0	12	23	–
1	12	8	–
1-	12	159	200
2	12	28	40
2-	12	84	84
3	12	72	90
3-	12	26-	36
4	12	111	130
4-	12	171	182
5	12	9	12
5-	12	3-	22
6	12	41-	50
6-	12	43	34
7-	12	12-	–
0	13	181	173
1	13	238	255
1-	13	293	330
2	13	154	173
2-	13	108	155
3	13	236	245
3-	13	296	319
4	13	59	33
4-	13	106	106
5	13	131	138
5-	13	111	152
6-	13	92	103
0	14	314	321
1	14	86-	97
1-	14	61-	49
2	14	205	230
2-	14	289	322
3	14	48-	–
3-	14	61-	74
4	14	244	230
4-	14	264	293
5	14	7-	–
5-	14	103-	125
6-	14	85	79
0	15	79-	108
1	15	10	–
1-	15	67	84
2	15	11-	–
2-	15	101-	103
3	15	65	65
3-	15	181	169
4	15	40-	47
4-	15	43-	18
5-	15	75	83
0	16	171	185
1	16	108	135
1-	16	10	–
2	16	58	62
2-	16	128	144
3	16*	–	–
3-	16	142	150
4-	16	110	80
0	17*	–	–
1	17	211	201
1-	17	196	210
2	17	26-	–
2-	17	7	–
3-	17	187	182
0	18	83	117
1	18	23-	33
1-	18	173-	148
2-	18	63	50
h k 2			
0	0	659	631
2	0	198	218
2-	0	131	220
4	0	212	212
4-	0	364	466
6	0	218	206
6-	0	174	204
8-	0	96	127
0	1	367-	352
1	1	364	379
1-	1	216	209
2	1	361-	329
2-	1	316-	408
3	1	209	200
3-	1	430	457
4	1	139-	84
4-	1	332-	395
5	1	114	114
5-	1	399	494
6	1	64-	33
6-	1	169-	215
7	1	124	81
7-	1	236	241
8-	1	102-	133
9-	1	65	57
0	2	486	437
1	2	269	254
1-	2	7-	17
2	2	193	182
2-	2	251	261
3	2	51	16
3-	2	23-	40
4	2	147	126
4-	2	456	510
5	2	154	113
5-	2	82	91
6	2	68	68
6-	2	299	271
7	2	50	–
7-	2	200	226
8-	2	198	196
0	3	171	157
1	3	434	430
1-	3	451	583
2	3	36	–
2-	3	210	259
3	3	292	261
3-	3	238	332
4	3	199	171
4-	3	9	–
5	3	225	182
5-	3	137	198
6	3	154	105
6-	3	182	198
7	3	181	114
7-	3	120	133
8-	3	83	105
0	4	294	323
1	4	207-	214
1-	4	337-	394
2	4	418	395
2-	4	340	420
3	4	313-	239
3-	4	275-	354
4	4	332	271
4-	4	243	305
5	4	26-	–
5-	4	264-	318
6	4	152	123
6-	4	130	151
7	4	88-	41
7-	4	43-	58
8-	4	54	51
0	5	15	53
1	5	297	269
1-	5	474	488
2	5	55-	55
2-	5	39-	18
3	5	232	218
3-	5	300	342
4	5	42-	33
4-	5	143-	168
5	5	133	136
5-	5	201	202
6	5	35-	24
6-	5	58	39
7-	5	199	212
8-	5	34-	32
0	6	222	200
1	6	256	204
1-	6	382	442
2	6	365	349
2-	6	465	530
3	6	132	118
3-	6	379	459
4	6	232	206
4-	6	135	159
5	6	181	144
5-	6	152	214
6	6	145	110
6-	6	142	162
7-	6	107	141
8-	6	116	98
0	7	14-	–
1	7	227	237
1-	7	300	332
2	7	24-	18
2-	7	46-	38
3	7	351	305
3-	7	265	342
4	7	107-	97
4-	7	46-	54
5	7	256	201
5-	7	149	199
6	7	91-	70
6-	7	42-	20
7-	7	36	76
8-	7	60-	40
0	8	199	175
1	8	175-	115
1-	8	139-	130
2	8	195	177
2-	8	448	488
3	8	113-	82
3-	8	141-	182
4	8	82	62
4-	8	172	196
5	8	172-	130
5-	8	106-	134
6	8	102	73
6-	8	218	241
7-	8	143-	161
8-	8	188	123
0	9	156	125
1	9	127	101
1-	9	244	197
2	9	176	152
2-	9	220	244
3	9	148	139
3-	9	312	320
4	9	109	90
4-	9	251	278
5	9	101	71
5-	9	282	254
6	9	67	26
6-	9	27	60
7-	9	165	163
0	10	186	185
1	10	64	59
1-	10	48	–
2	10	200	183
2-	10	241	282
3	10	163	95
3-	10	10	31
4	10	165	159
4-	10	185	212
5	10	48-	47
5-	10	125	149
6-	10	133	155
7-	10	13	28
0	11	282-	236
1	11	205	176
1-	11	235	246
2	11	158-	137
2-	11	244-	238
3	11	97	100
3-	11	189	228
4	11	112-	81
4-	11	111-	144
5	11	94	87
5-	11	166	195
6-	11	186-	210
7-	11	136	124
0	12	191	139
1	12	40-	24
1-	12	5-	20
2	12	132	92
2-	12	128	110
3	12	89	70
3-	12	16-	–
4	12	97	87
4-	12	280	274
5	12	7	–
5-	12	45	52
6-	12	186	166
0	13	127	102
1	13	248	235
1-	13	174	182
2	13	165	139
2-	13	71	90
3	13	135	126
3-	13	117	101
4	13	98	51
4-	13	120	144
5-	13	91	78
6-	13	107*	104
0	14	260	238
1	14	141-	131
1-	14	92-	98
2	14	167	159
2-	14	55	82
3	14	88-	61
3-	14	83-	77
4	14	150	119
4-	14	113	152
5-	14	92-	83
0	15	43-	34
1	15	169	147
1-	15	104	107
2	15	68-	51
2-	15	72-	55
3	15	122	79
3-	15	140	140
4-	15	89-	86
5-	15	130	113
0	16	193	137
1	16	156	120
1-	16	152	140
2	16	92	60
2-	16	96	78
3-	16	127	128
4-	16	91	64
0	17	38	63
1	17	112	95
1-	17	93	88
2-	17	72	60

Starred reflexions were not used in the refinement because of their uncertain attribution to the proper individual of the twin.

Table 4. *Atomic coordinates, e.s.d.'s and curvatures*

$\overline{B}=1\cdot9$ Å^2

	x/a	$\sigma(x)$ (Å)	$(-\partial^2\varrho/\partial x^2)$ (e.Å^{-5})	y/b	$\sigma(y)$ (Å)	$(-\partial^2\varrho/\partial y^2)$ (e.Å^{-5})	z/c	$\sigma(z)$ (Å)	$(-\partial^2\varrho/\partial z^2)$ (e.Å^{-5})
Zn	0·5000	—	—	0·5000	—	—	0·0000	—	—
S	−0·0130	0·00370	322·7	0·2940	0·00319	317·3	0·1205	0·00533	117·9
C	0·1295	0·01270	93·9	0·3729	0·00698	144·9	0·0311	0·01614	38·9
N(1)	0·4356	0·01568	76·1	0·6029	0·00834	121·5	0·3257	0·01758	35·8
N(2)	0·3364	0·01030	115·8	0·5740	0·00987	102·6	0·5724	0·01433	43·9
N(3)	0·2335	0·00980	121·7	0·4290	0·00823	123·1	0·0135	0·01626	38·7
H(1)	0·5740	—	—	0·6251	—	—	0·4498	—	—
H(2)	0·3597	—	—	0·6577	—	—	0·1979	—	—
H(3)	0·2646	—	—	0·6300	—	—	0·3685	—	—
H(4)	0·2336	—	—	0·5259	—	—	0·5373	—	—

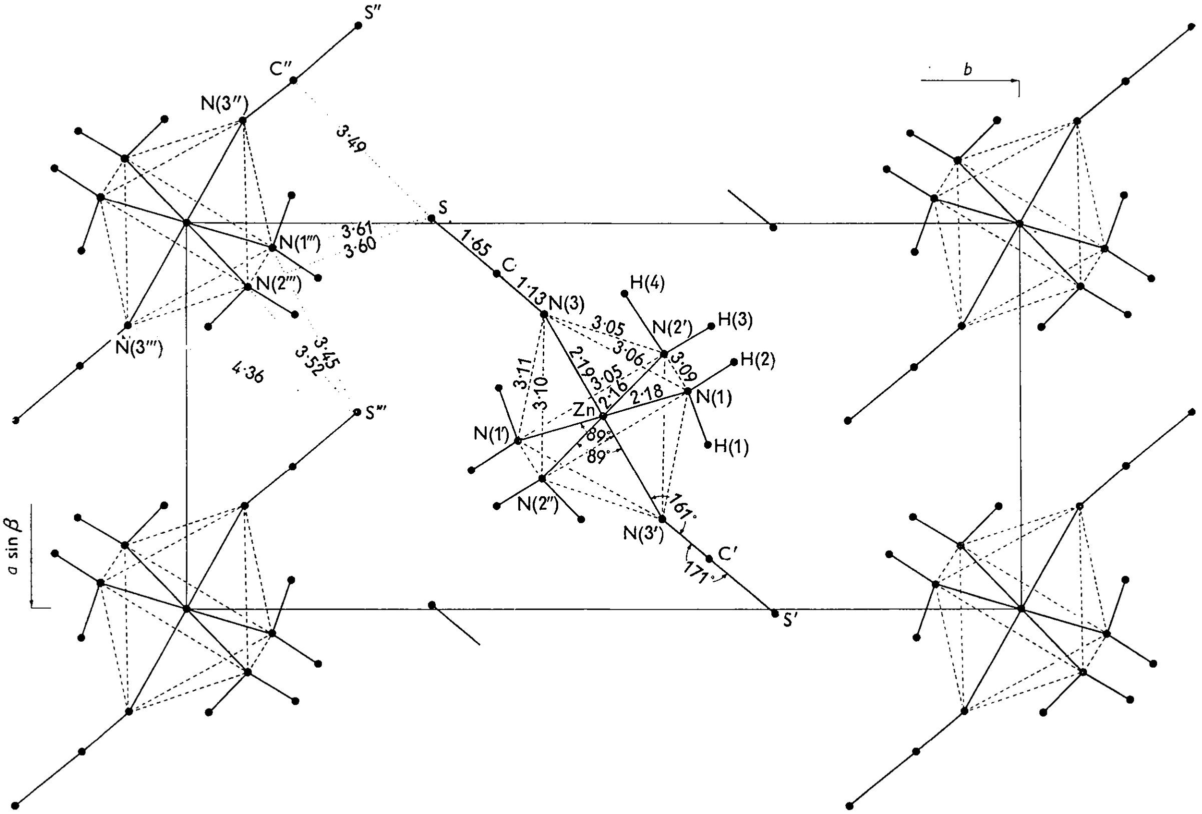

Fig. 2. Diagrammatic projection of the structure on the plane normal to [001]. Broken lines: distances within the complex [Zn(N$_2$H$_4$)$_{4/2}$(NCS)$_2$]. Dotted lines: interchain distances. Full lines: interatomic bonds.

$(\varrho_o-\varrho_c)(x_iy_iz)$ were calculated at the same points and corrections applied.

At the end of the refinement the residuals of Table 2 were obtained. Calculated and observed structure factors are quoted in Table 3. The curvatures (Table 4) of the peaks were calculated at the atomic centres. Standard deviations of the coordinates were calculated by Cruickshank's method (1949). The final atomic coordinates are quoted in Table 4. The coordinates of the hydrogen atoms have been calculated for the 'staggered' form of the hydrazine molecule with the azimuthal angle $\varphi=\pm74°$, as deduced from the positions of the zinc and nitrogen atoms, and from the bond lengths and bond angles N–N = 1·47 Å, N–H = 1·04 Å, N–N–H = 108°, H–N–H = 108°.

Discussion of the structure

The main distances and angles are quoted in Table 5. The e.s.d.'s of the distances have been calculated according to Ahmed & Cruickshank (1953) and those of the angles according to Darlow (1960).

The structure of the compound is diagrammatically represented in Fig. 2 and in Fig. 3. The structure is formed by chains of octahedral complexes [Zn(N$_2$H$_4$)$_{4/2}$(NCS)$_2$] which have the metal at their centre and are bound together by bridges of hydrazine. The chains run throughout the whole crystal parallel to [001]. The metal atom is surrounded by six N atoms; two of them belong to NCS^- groups and four to different hydrazine molecules. The six distances Zn–N are practically equal (2·17 Å), the negative charge of the NCS^- group having no influence. The angles within the octahedron are very near to those of a regular octahedron. The general feature of the structure repeats that of compounds $[M^{II}(N_2H_4)_2]Cl_2$ (Ferrari, Braibanti & Bigliardi, 1963; Ferrari, Braibanti, Bigliardi & Dallavalle, 1963).

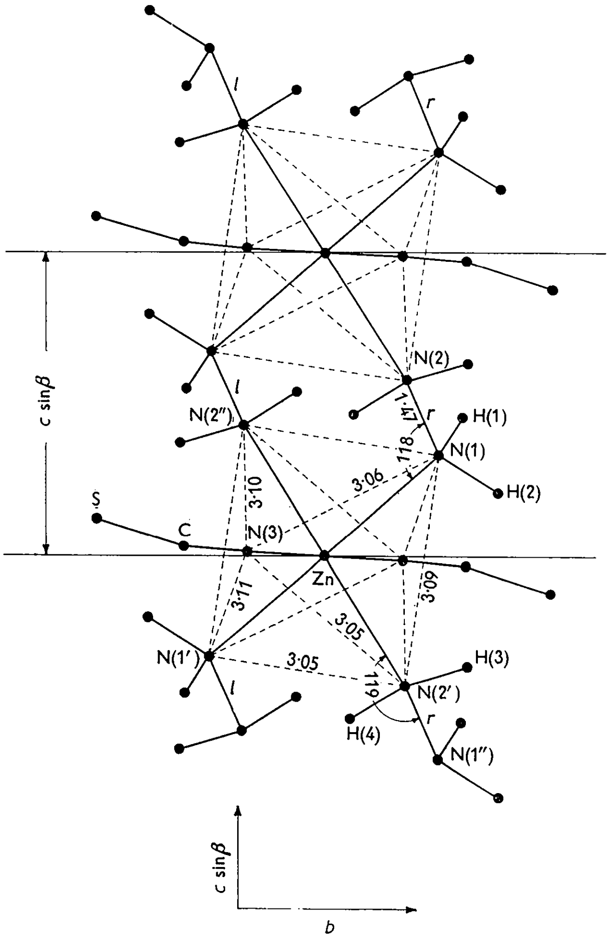

Fig. 3. Diagrammatic projection of one chain on the plane normal to [100] with distances and angles relative to the hydrazine molecules. *l* and *r* indicate the left and right forms of hydrazine.

The hydrazine molecule $H_2N–NH_2$ has practically the same length (N–N = 1·47 Å) as already found in other compounds. Hydrazine is in the 'staggered' form according to the model of Penney & Sutherland (1934) (Fig. 4). The 'staggered' form is confirmed by the rotated disposition of the two halves of the molecule deduced by the azimuthal angle formed by the bonds Zn–N in the projection down the N–N axis. Along the bond directions or very close to them, there must be the lone pairs of the hydrazine nitrogen atoms. The rotation has been calculated to be $\varphi = \pm 74°$ and it is practically the same as that calculated in $[Zn(N_2H_4)_2]Cl_2$ ($\varphi = \pm 74°$) and in $[Mn(N_2H_4)_2]Cl_2$ ($\varphi = \pm 76°$). The angle N–H ⋯ M = 118° is very close to that found in the same compounds (117° in both).

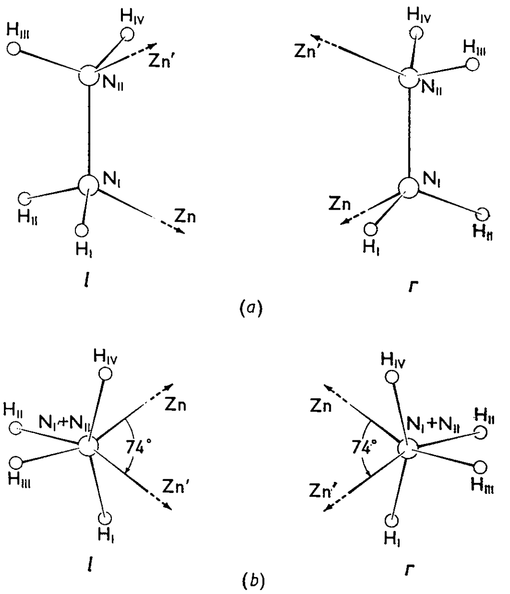

Fig. 4. *l* and *r* enantiomorphous forms of the hydrazine molecule $H_2N–NH_2$. (*a*) Clinographic projection. (*b*) Projection down the N–N axis.

The hydrazine molecules are present in the structure in two enantiomorphous forms (*l* and *r*). A statistical distribution of the two forms *l* and *r* may be present in the solution when the complexes are formed. According to Cuthbert, Brown & Petch (1963), however, free rotation around the bond N–N is possible, at least, in the hydrazonium group $H_2N–NH_3^+$; if this is the case the two forms are 'frozen' at the moment of the formation of the complex chain.

The NCS^- group is in the isothiocyanic form, being bound to the metal through N. It seems to be slightly bent (N–C–S = 171°). Distances in the NCS^- group are S–C = 1·65 Å and N–C = 1·13 Å, in agreement with values in other compounds (Table 6). The S–C distance is longer than the standard double-bond distance, and the N–C distance is approximately equal to that of a normal triple bond. This means that between the two resonating structures

$$\left[|\overline{N}=C=\overline{S}|\right]^{-} \quad \text{and} \quad \left[|\overset{(+)}{N}\equiv C-\overset{(-)}{\underline{\overline{S}}}|\right]^{-}$$

the second makes an important contribution to the bonding of the NCS group.

Sets of chains form layers parallel to (010). The packing distances of the chains within the layers (N ⋯ S = 3·52, 3·45 Å) are shorter than the distances

Table 5. *Main distances and angles*

Distances

$\mathrm{N}(1)(x, y, z)\text{–}\mathrm{N}(2)(x, y, z)$	1·469 ± 0·021 Å
$\mathrm{C}(x, y, z)\text{–}\mathrm{N}(3)(x, y, z)$	1·128 ± 0·014
$\mathrm{S}(x, y, z)\text{–}\mathrm{C}(x, y, z)$	1·655 ± 0·012
$\mathrm{Zn}(x, y, z)\text{–}\mathrm{N}(3)(x, y, z)$	2·186 ± 0·010
$\mathrm{Zn}(x, y, z)\text{–}\mathrm{N}(1)(x, y, z)$	2·177 ± 0·014
$\mathrm{Zn}(x, y, z)\text{–}\mathrm{N}(2')(x, y, \bar{1}+z)$	2·163 ± 0·012
$\mathrm{N}(3)(x, y, z)\text{–}\mathrm{N}(1)(x, y, z)$	3·063 ± 0·015
$\mathrm{N}(3)(x, y, z)\text{–}\mathrm{N}(2')(x, y, \bar{1}+z)$	3·050 ± 0·018
$\mathrm{N}(3)(x, y, z)\text{–}\mathrm{N}(2'')(1-x, 1-y, 1-z)$	3·101 ± 0·015
$\mathrm{N}(1)(x, y, z)\text{–}\mathrm{N}(2')(x, y, \bar{1}+z)$	3·092 ± 0·022
$\mathrm{N}(1')(1-x, 1-y, \bar{z})\text{–}\mathrm{N}(2')(x, y, \bar{1}+z)$	3·046 ± 0·015
$\mathrm{S}(x, y, z)\text{–}\mathrm{N}(1''')(\frac{1}{2}-x, -\frac{1}{2}+y, 1-z)$	3·608 ± 0·013
$\mathrm{S}(x, y, z)\text{–}\mathrm{N}(2''')(\frac{1}{2}-x, -\frac{1}{2}+y, 1-z)$	3·596 ± 0·011
$\mathrm{S}(x, y, z)\text{–}\mathrm{N}(3'')(-\frac{1}{2}+x, \frac{1}{2}-y, z)$	3·725 ± 0·009
$\mathrm{S}(x, y, z)\text{–}\mathrm{C}''(-\frac{1}{2}+x, \frac{1}{2}-y, z)$	3·494 ± 0·011
$\mathrm{S}(x, y, z)-\mathrm{S}''(-\frac{1}{2}+x, \frac{1}{2}-y, z)$	3·799 ± 0·005
$\mathrm{S}'''(\frac{1}{2}+x, \frac{1}{2}-y, z)\text{–}\mathrm{N}(3''')(\frac{1}{2}-x, -\frac{1}{2}+y, 1-z)$	4·360 ± 0·009
$\mathrm{S}'''(\frac{1}{2}+x, \frac{1}{2}-y, z)\text{–}\mathrm{N}(2''')(\frac{1}{2}-x, -\frac{1}{2}+y, 1-z)$	3·521 ± 0·012
$\mathrm{S}'''(\frac{1}{2}+x, \frac{1}{2}-y, z)\text{–}\mathrm{N}(1''')(\frac{1}{2}-x, -\frac{1}{2}+y, 1-z)$	3·453 ± 0·015

Angles

$\mathrm{S}'(1-x, 1-y, \bar{z})\text{–}\hat{\mathrm{C}}'(1-x, 1-y, \bar{z})\text{–}\mathrm{N}(3')(1-x, 1-y, \bar{z})$	170·7° ± 1·6°
$\mathrm{C}'(1-x, 1-y, \bar{z})\text{–}\hat{\mathrm{N}}(3')(1-x, 1-y, \bar{z})\text{–}\mathrm{Zn}(x, y, z)$	161·2° ± 0·9°
$\mathrm{N}(3')(1-x, 1-y, \bar{z})\text{–}\widehat{\mathrm{Zn}}(x, y, z)\text{–}\mathrm{N}(1')(1-x, 1-y, \bar{z})$	89·2° ± 0·5°
$\mathrm{N}(3')(1-x, 1-y, \bar{z})\text{–}\widehat{\mathrm{Zn}}(x, y, z)\text{–}\mathrm{N}(2'')(1-x, 1-y, 1-z)$	89·0° ± 0·4°
$\mathrm{Zn}(x, y, z)\text{–}\hat{\mathrm{N}}(1)(x, y, z)\text{–}\mathrm{N}(2)(x, y, z)$	117·8° ± 0·6°
$\mathrm{Zn}(x, y, z)\text{–}\hat{\mathrm{N}}(2')(x, y, \bar{1}+z)\text{–}\mathrm{N}(1'')(x, y, \bar{1}+z)$	118·9° ± 09 °

Table 6. *Distances and angles in the* NCS *group*

S–C	C–N	N–Ĉ–S	Compound	
1·66 Å	1·13 Å	171°	$[\mathrm{Zn(N_2H_4)_2(NCS)_2}]$	Present work
1·62	1·16	177	$[\mathrm{Cu(en)_2}](\mathrm{NCS})_2$	Brown & Lingafelter (1964)
1·64	1·20	178	$[\mathrm{Ni(en)_2(NCS)_2}]$	Brown & Lingafelter (1963)
1·55	1·19	165	$\mathrm{Cd(C_2H_4.N_2.C{=}S)_2(NCS)_2}$	Cavalca, Nardelli & Fava (1960)
1·66	1·31	167	$\alpha\text{-}[\mathrm{Pt_2(NCS)_2Cl_2(P(C_3H_7)_3)_2}]$	Owston & Rowe (1960)
1·76	1·28	linear	$\mathrm{AgSCN.P}(n\text{-}\mathrm{C_3H_7})_3$	Turco, Panattoni & Frasson (1960)
1·64	1·19	linear	AgSCN	Lindqvist (1957)
1·60	1·24	linear	$\mathrm{NH_4Ag(SCN)_2}$	Lindqvist & Strandberg (1957)
1·71	1·10	linear	$\mathrm{NH_4Ag(SCN)_2}$	Lindqvist & Strandberg (1957)
1·60	1·16	linear	$\mathrm{Ni(NCS)_2.2[SC(NH_2)_2]}$	Nardelli, Braibanti & Fava (1957)
1·64	1·15	linear	$\mathrm{Ni(NH_3)_3(NCS)_2}$	Porai-Koshits, Antzishkina, Dickareva & Jukhnov (1957)
1·70	1·12	linear	$\mathrm{Ni(NH_3)_3(NCS)_2}$	Porai-Koshits *et al.* (1957)
1·61	1·20	linear	$\mathrm{Ni(NH_3)_4(NCS)_2}$	Porai-Koshits *et al.* (1957)
1·69	1·13	linear	$\mathrm{Se(NCS)_2}$	Ohlberg & Vaughan (1954)
1·56	1·21	linear	HNCS	Dousmanis, Sanders, Townes & Zeiger (1953)
1·57	1·34	linear	$[\mathrm{Hg(SCN)_4}][\mathrm{Cu(en)_2}]$	Scouloudi (1953)
1·59	1·23	linear	$\mathrm{K_2[Co(NCS)_4]}$	Zhdanov & Zvonkova (1950)
1·61	1·21	linear	$\mathrm{CH_3.SCN}$	Beard & Dailey (1949)
1·56	1·22	linear	$\mathrm{CH_3.NCS}$	Beard & Dailey (1949)
1·59	1·25	linear	$\mathrm{NH_4NCS}$	Zvonkova & Zhdanov (1949)
1·56	1·22	linear	HNCS	Beard & Dailey (1947)
		Single bond	S – C = 1·81 Å	Pauling (1960)
		Double bond	S = C = 1·607	
		Double bond	C = N = 1·287	
		Triple bond	C ≡ N = 1·157	

between chains of different layers (N ··· S = 3·61, 3·60 Å) (Fig. 5). The distance S ··· C can be interpreted as a van der Waals contact. Interlayer distances N ··· S exclude the possibility of hydrogen bonds. This explains the twinning satisfactorily because the interlayer forces are too weak to oppose adjustment of the twinned chains or layers in an upside-down position. At the twin boundary a glide plane parallel to (100) is substituted for the glide plane parallel to (010) of the regular structure.

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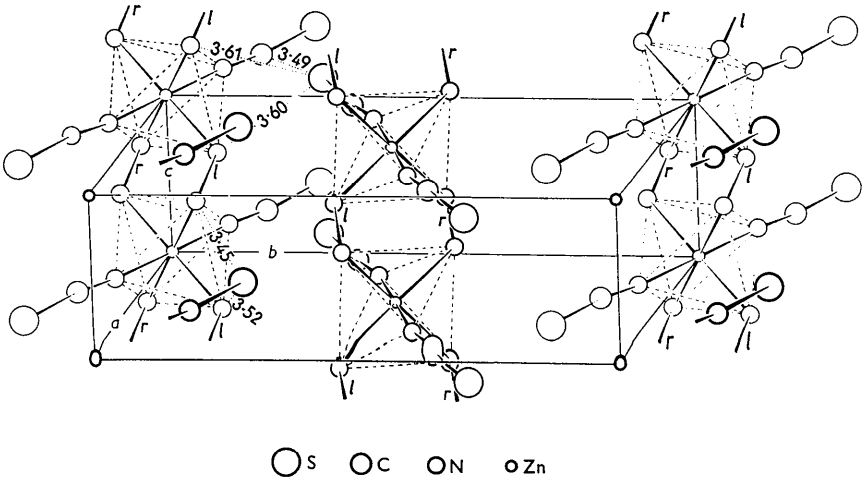

Fig. 5. Packing of chains in the structure. Sets of chains form layers parallel to (010). A large portion of the front chains is omitted for clarity.

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