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The Crystal and Molecular Structure of Bis-(2-thioimidazolidine)-nickel(II) Thiocyanate

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The crystal structure of bis-(2-thioimidazolidine)nickel thiocyanate, $Ni[SC(NHCH_2)_2]_2(NCS)_2$, has been determined and refined by three-dimensional Fourier methods (final $R=11{\cdot}6\,\%$). There is one formula unit in the triclinic ($P\bar{1}$) unit cell: $a=5{\cdot}592(21)$, $b=8{\cdot}664(18)$, $c=8{\cdot}686(22)$ Å, $\alpha=113°39'(7')$, $\beta=95°8'(7')$, $\gamma=108°43'(6')$. Each nickel atom is octahedrally surrounded by two sulphur atoms (Ni–S 2·51 Å) from two thioimidazolidine molecules, and by two sulphur atoms (Ni–S 2·54 Å) and two nitrogen atoms (Ni–N 1·99 Å) from four different NCS groups. These nitrogen atoms are *trans* with respect to the plane of the sulphur atoms. The octahedra are linked in zigzag chains by the NCS groups, which form bridges between adjacent nickel atoms. The thioimidazolidine molecule is not strictly planar, the two CH_2 groups being shifted by ~0·1 Å on opposite sides of the plane of the thiourea part of the molecule. The infrared C–S and C–N stretching frequencies of bridged NCS groups in some thioimidazolidine-metal complexes are compared.

Introduction

The structure of bis-(2-thioimidazolidine)-nickel thiocyanate, Ni*etu*$_2$(NCS)$_2$ [*etu* = 2-thioimidazolidine = ethylenethiourea = $SC(NHCH_2)_2$] has been investigated as part of a programme for studying metal complexes of ligands containing sulphur as donor atom. The principal aim of the research was the comparison of this structure with those of the similar thiourea complex, Ni*tu*$_2$(NCS)$_2$ [*tu* = thiourea = $SC(NH_2)_2$] (Nardelli, Fava Gasparri, Giraldi Battistini & Domiano, 1966; hereafter quoted as NFGD) and thioacetamide complex, Ni*tam*$_2$(NCS)$_2$ [*tam* = thioacetamide = $SC(CH_3)NH_2$] (research in progress). All these compounds are polymeric in nature with chains of coordination octahedra, but, while sulphur bridges are present in the thiourea complex, bridging is due to the NCS groups in the other compounds. This comparison is useful in studying the influence of the nature of the ligands on the behaviour of the NCS group: the coordination polyhedron and the number of thiocyanate groups are unchanged in all these compounds.

Experimental

The crystals of Ni*etu*$_2$(NCS)$_2$ used in the present work were those already described by Nardelli & Chierici (1958). Cell constants, remeasured and refined by a least-squares procedure on powder diffractometer data (Cu $K\alpha$, $\lambda=1{\cdot}5418$ Å), are as follows:

$Ni[SC(NHCH_2)_2]_2(NCS)_2$. $M=379{\cdot}1$.
$a=5{\cdot}592\pm0{\cdot}021$, $b=8{\cdot}664\pm0{\cdot}018$, $c=8{\cdot}686\pm0{\cdot}022$ Å,
$\alpha=113°39'\pm7'$, $\beta=95°8'\pm7'$, $\gamma=108°43'\pm6'$.
$V=353{\cdot}4$ Å^3, $Z=1$, $D_x=1{\cdot}781$, $D_m=1{\cdot}77$ g.cm^{-3} (flotation).
$\mu=72{\cdot}8$ cm^{-1} (Cu $K\alpha$).
Space group $P\bar{1}$ (by structure analysis).

Three-dimensional intensity data were recorded in the usual way on multiple-film Weissenberg photographs, using integration and equi-inclination techniques with Cu $K\alpha$ radiation, and the intensities were measured photometrically. Layers 0*kl* to 5*kl* were recorded about the *a* axis. Of the 1631 possible independent reflexions within the Cu $K\alpha$ sphere, 1449 were recorded; of these, 244 were too weak to be estimated. The shape of the spots of non-equatorial layers was taken into account following Phillips (1956) and in the correction for absorption the sample was treated as spherical ($\bar{r}=0{\cdot}025$ cm). The structure factors were derived by the usual formulae, the absolute scale being established for each layer separately first by Wilson's method, then by correlation with the calculated values.

Structure analysis and refinement

The structure was solved directly, assuming all the structure factors to be positive in the first Fourier calculation. This implied the assumption of the space group $P\bar{1}$ with the choice of origin at the Ni atom, which is heavy enough to dominate the majority of the signs. In this way the S atoms were located first and all the other atoms were located in successive calculations.

The refinement was carried out in the $P\bar{1}$ space group by means of Booth's differential syntheses with anisotropic thermal parameters. These parameters were derived from the second derivatives of the electron-density from differential synthesis, following the method of Nardelli & Fava (1960). At the end of this refinement, the ratios $r(x)=\sigma(x)/\varepsilon(x)$ between the e.s.d.'s and the shifts of the coordinates were as shown in Table 1 and the agreement indices (R, for observed reflexions only; R' assuming $F_o=\frac{1}{2}F_{\min}$ when $F_c>F_{\min}$ for unobserved reflexions; multiplicities not considered) were: $R=11{\cdot}6\%$, $R'=13{\cdot}0\%$.

An attempt to refine the structure in the $P1$ space group did not improve the R index and did not give interatomic distances significantly different from those obtained after the centrosymmetrical refinement.

The final coordinates with e.s.d.'s (Cruickshank, 1949) are given in Table 1; observed and calculated peak heights and curvatures, with the e.s.d.'s of electron-density and second derivatives, are reported in Table 2. As a consequence of the scaling by layers, the thermal parameters B_{ij} listed in Table 1 must be considered simply as additional parameters introduced to reduce the residuals. The F_c values reported in Table 3 are calculated with the final parameters of Table 1 using the scattering factors of Thomas & Umeda (1957) for Ni^{2+}, of Dawson (1960) for S and of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for N and C.

The standard deviations, quoted in the next section, are calculated from the formulae of Ahmed & Cruickshank (1953) for bond lengths and of Darlow (1960) for angles, the effects of errors in cell parameters being accounted for following Darlow & Cochran (1961).

Discussion

The coordination around each nickel atom is octahedral: the nickel is coordinated to two S(1) atoms from two thioimidazolidine molecules, and to two S(2) and two N(1) atoms from four different NCS groups. The octahedra are linked in zigzag chains, running parallel to [100], by NCS groups which form bridges between the nickel atoms as shown in Fig. 1. This structure, which occurs also in the Mn- and Co-etu_2 thiocyanates (Nardelli & Chierici, 1958), is quite similar to that of the corresponding cadmium and lead complexes (Cavalca, Nardelli & Fava, 1960) although these last are not isostructural with the previous ones.

Distances in the coordination polyhedron are in fairly good agreement with those found in the octahedra of bisthiourea-nickel(II) thiocyanate (NFGD) (the e.s.d.'s quoted in parentheses are in units of the last place):

Nietu_2(NCS)$_2$	Nitu_2(NCS)$_2$
Ni–S(1) 2·507(8) Å	Ni–S 2·531(6) Å
Ni–S(2′) 2·544(14)	2·564(9)
Ni–N(1) 1·992(23)	Ni–N 1·992(7)

Table 1. *Final atomic fractional coordinates* (× 10⁴), *thermal parameters* (× 10 Å²) *with e.s.d.'s and ratios (e.s.d.)/(coordinate shift)*

	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	$B_{11}(\sigma)$	$B_{22}(\sigma)$	$B_{33}(\sigma)$	$B_{23}(\sigma)$	$B_{13}(\sigma)$	$B_{12}(\sigma)$	$\|r(x)\|$	$\|r(y)\|$	$\|r(z)\|$
Ni	0	0	0	50 (2)	35 (3)	37 (3)	14 (3)	16 (3)	17 (3)	∞	∞	∞
S(1)	2574 (8)	2267 (5)	3053 (5)	42 (2)	33 (2)	25 (2)	5 (2)	13 (2)	6 (2)	17	28	∞
S(2)	6542 (8)	−2221 (6)	662 (6)	41 (2)	27 (2)	30 (2)	13 (2)	14 (2)	14 (2)	87	5	28
N(1)	2226 (29)	−1385 (22)	32 (21)	37 (5)	22 (7)	36 (8)	13 (9)	14 (9)	10 (8)	37	7	43
N(2)	1820 (37)	4011 (19)	6151 (23)	64 (8)	35 (7)	27 (8)	2 (9)	21 (10)	1 (9)	16	∞	12
N(3)	−1484 (34)	1515 (21)	4463 (22)	57 (7)	48 (9)	28 (9)	9 (11)	20 (11)	7 (11)	∞	7	57
C(1)	−2303 (45)	2124 (27)	6057 (26)	61 (9)	37 (9)	24 (9)	4 (11)	21 (12)	11 (12)	58	35	15
C(2)	−123 (44)	4007 (26)	7204 (26)	63 (11)	37 (10)	30 (10)	12 (12)	22 (13)	21 (14)	76	16	67
C(3)	880 (32)	2608 (21)	4605 (19)	50 (6)	22 (7)	22 (7)	6 (8)	6 (9)	8 (9)	27	11	198
C(4)	4016 (33)	−1731 (23)	278 (22)	47 (7)	17 (6)	24 (7)	4 (8)	15 (9)	9 (8)	7	27	33

Table 2. *Atomic peak heights* (e.Å⁻³), *curvatures* (e.Å⁻⁵) *and e.s.d.'s*

		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{kl}	A_{hl}	A_{hk}
Ni	obs.	49·3	386	486	489	175	67	126
	calc.	51·0	387	485	489	175	66	126
S(1)	obs.	28·2	218	244	297	82	53	45
	calc.	28·7	220	244	296	82	53	45
S(2)	obs.	31·1	250	327	326	124	44	83
	calc.	31·5	251	325	324	122	44	82
N(1)	obs.	9·1	75	96	82	32	6	28
	calc.	9·4	76	95	81	32	7	28
N(2)	obs.	7·9	48	52	66	12	18	5
	calc.	7·9	48	52	65	12	18	5
N(3)	obs.	7·4	51	54	63	14	13	8
	calc.	7·8	51	56	65	18	12	8
C(1)	obs.	6·3	38	52	62	18	9	9
	calc.	6·6	39	52	62	18	9	10
C(2)	obs.	7·5	46	65	69	24	12	13
	calc.	7·5	46	65	69	24	12	13
C(3)	obs.	8·7	55	82	85	32	7	17
	calc.	9·1	55	82	85	32	7	17
C(4)	obs.	7·9	57	79	84	23	19	9
	calc.	8·1	57	78	84	22	19	9
	e.s.d.	0·3	2	2	3	2	2	1

Table 3. *Observed and calculated structure factors*

A minus sign for F_o means 'less than'

h	k	l	$\lvert 10F_o\rvert$	$10F_c$
1	0	0	254	318
2	0	0	192	-182
3	0	0	171	188
4	0	0	98	93
5	0	0	68	54
0	1	0	271	379
1	1	0	220	-165
1	$\bar{1}$	0	195	400
2	1	0	154	201
2	$\bar{1}$	0	70	-103
3	1	0	140	153
3	$\bar{1}$	0	68	71
4	1	0	51	-45
4	$\bar{1}$	0	218	195
5	1	0	48	41
5	$\bar{1}$	0	45	34
0	2	0	336	-456
1	2	0	412	440
1	$\bar{2}$	0	137	137
2	2	0	363	461
2	$\bar{2}$	0	245	303
3	2	0	15-	1
3	$\bar{2}$	0	9-	14
4	2	0	21	-21
4	$\bar{2}$	0	196	184
5	2	0	46	44
5	$\bar{2}$	0	75	67
0	3	0	239	-191
1	3	0	373	461
1	$\bar{3}$	0	50	-16
2	3	0	137	149
2	$\bar{3}$	0	320	495
3	3	0	17-	19
3	$\bar{3}$	0	140	137
4	3	0	110	102
4	$\bar{3}$	0	6-	-10
5	3	0	24	21
5	$\bar{3}$	0	41	37
0	4	0	258	267
1	4	0	112	111
1	$\bar{4}$	0	68	-34
2	4	0	45	-51
2	$\bar{4}$	0	110	132
3	4	0	93	90
3	$\bar{4}$	0	267	314
4	4	0	77	69
4	$\bar{4}$	0	7-	7
5	4	0	3-	-15
5	$\bar{4}$	0	28	25
0	5	0	325	375
1	5	0	150	-146
1	$\bar{5}$	0	291	339
2	5	0	15-	8
2	$\bar{5}$	0	29	-27
3	5	0	95	99
3	$\bar{5}$	0	172	183
4	5	0	19	17
4	$\bar{5}$	0	109	106
5	$\bar{5}$	0	64	57
0	6	0	43-	-27
1	6	0	95	-87
1	$\bar{6}$	0	212	235
2	6	0	119	128
2	$\bar{6}$	0	67	68
3	6	0	39	40
3	$\bar{6}$	0	55	-45
4	$\bar{6}$	0	84	79
5	$\bar{6}$	0	47	41
0	7	0	42-	-22
1	7	0	187	180
1	$\bar{7}$	0	23-	44
2	7	0	80	72
2	$\bar{7}$	0	177	181
3	$\bar{7}$	0	53	-40
4	$\bar{7}$	0	54	55
5	$\bar{7}$	0	70	68
0	8	0	109	92
1	8	0	130	131
1	$\bar{8}$	0	21-	-28
2	$\bar{8}$	0	117	109
3	$\bar{8}$	0	76	71
4	$\bar{8}$	0	26	24
5	$\bar{8}$	0	44	46
0	9	0	83	78
1	$\bar{9}$	0	16-	0
2	$\bar{9}$	0	45	-40
3	$\bar{9}$	0	111	109
4	$\bar{9}$	0	45	51
5	$\bar{9}$	0	11	13
2	$\overline{10}$	0	22	-31
3	$\overline{10}$	0	44	49
4	$\overline{10}$	0	46	50
0	0	1	170	225
1	0	1	206	-288
1	0	$\bar{1}$	9-	-15
2	0	1	132	152
2	0	$\bar{1}$	241	216
3	0	1	307	365
3	0	$\bar{1}$	166	173
4	0	1	8-	-1
4	0	$\bar{1}$	21	21
5	0	1	28	-21
5	0	$\bar{1}$	145	160
0	1	1	249	364
0	1	$\bar{1}$	320	449
1	1	1	46	72
1	$\bar{1}$	1	178	166
1	1	$\bar{1}$	235	255
1	$\bar{1}$	$\bar{1}$	243	270
2	1	1	241	313
2	$\bar{1}$	1	163	-140
2	1	$\bar{1}$	167	151
2	$\bar{1}$	$\bar{1}$	184	162
3	1	1	121	122
3	$\bar{1}$	1	150	156
3	1	$\bar{1}$	26	19
3	$\bar{1}$	$\bar{1}$	201	194
4	1	1	49	-42
4	$\bar{1}$	1	225	213
4	1	$\bar{1}$	91	84
4	$\bar{1}$	$\bar{1}$	31	39
5	1	1	117	114
5	$\bar{1}$	1	66	-51
5	1	$\bar{1}$	114	121
5	$\bar{1}$	$\bar{1}$	23	15
0	2	1	29-	5
0	2	$\bar{1}$	331	343
1	2	1	273	333
1	$\bar{2}$	1	558	871
1	2	$\bar{1}$	318	273
1	$\bar{2}$	$\bar{1}$	126	161
2	2	1	106	127
2	$\bar{2}$	1	280	302
2	2	$\bar{1}$	12-	8
2	$\bar{2}$	$\bar{1}$	180	182
3	2	1	115	-106
3	$\bar{2}$	1	151	-108
3	2	$\bar{1}$	70	70
3	$\bar{2}$	$\bar{1}$	208	197
4	2	1	58	53
4	$\bar{2}$	1	215	205
4	2	$\bar{1}$	152	153
4	$\bar{2}$	$\bar{1}$	173	183
5	2	1	87	85
5	$\bar{2}$	1	88	64
5	2	$\bar{1}$	7-	0
5	$\bar{2}$	$\bar{1}$	93	-106
0	3	1	205	209
0	3	$\bar{1}$	187	-143
1	3	1	357	422
1	$\bar{3}$	1	104	104
1	3	$\bar{1}$	224	229
1	$\bar{3}$	$\bar{1}$	176	195
2	3	1	33	-34
2	$\bar{3}$	1	319	387
2	3	$\bar{1}$	77	88
2	$\bar{3}$	$\bar{1}$	205	220
3	3	1	45	-43
3	$\bar{3}$	1	11-	21
3	3	$\bar{1}$	88	80
3	$\bar{3}$	$\bar{1}$	126	130
4	3	1	106	105
4	$\bar{3}$	1	6-	-6
4	3	$\bar{1}$	9	11
4	$\bar{3}$	$\bar{1}$	257	240
5	3	1	4-	-3
5	$\bar{3}$	1	136	123
5	3	$\bar{1}$	53	-50
5	$\bar{3}$	$\bar{1}$	69	60
0	4	1	101	108
0	4	$\bar{1}$	220	200
1	4	1	23-	-11
1	$\bar{4}$	1	79	-68
1	4	$\bar{1}$	242	231
1	$\bar{4}$	$\bar{1}$	165	169
2	4	1	15-	-7
2	$\bar{4}$	1	159	182
2	4	$\bar{1}$	177	179
2	$\bar{4}$	$\bar{1}$	191	197
3	4	1	124	136
3	$\bar{4}$	1	258	295
3	4	$\bar{1}$	68	61
3	$\bar{4}$	$\bar{1}$	32	29
4	4	1	42	41
4	$\bar{4}$	1	85	-80
4	4	$\bar{1}$	27	-27
4	$\bar{4}$	$\bar{1}$	53	-47
5	$\bar{4}$	1	61	51
5	4	$\bar{1}$	32	32
5	$\bar{4}$	$\bar{1}$	145	137
0	5	1	82	79
0	5	$\bar{1}$	202	192
1	5	1	60	-55
1	$\bar{5}$	1	76	81
1	5	$\bar{1}$	23-	21
1	$\bar{5}$	$\bar{1}$	102	112
2	5	1	177	185
2	$\bar{5}$	1	43	-33
2	5	$\bar{1}$	154	162
2	$\bar{5}$	$\bar{1}$	89	99
3	5	1	112	114
3	$\bar{5}$	1	215	243
3	5	$\bar{1}$	61	57
3	$\bar{5}$	$\bar{1}$	151	136
4	5	1	42	-39
4	$\bar{5}$	1	51	43
4	5	$\bar{1}$	23	21
4	$\bar{5}$	$\bar{1}$	97	-82
5	$\bar{5}$	1	62	-55
5	$\bar{5}$	$\bar{1}$	73	70
0	6	1	133	123
0	$\bar{6}$	1	126	126
1	6	1	65	57
1	$\bar{6}$	1	213	249
1	6	$\bar{1}$	23-	4
1	$\bar{6}$	$\bar{1}$	157	150
2	6	1	111	106
2	$\bar{6}$	1	15-	13
2	6	$\bar{1}$	49	43
2	$\bar{6}$	$\bar{1}$	52	47
3	6	1	9-	-14
3	$\bar{6}$	1	30	-16
3	6	$\bar{1}$	34	27
3	$\bar{6}$	$\bar{1}$	126	109
4	$\bar{6}$	1	177	192
4	$\bar{6}$	$\bar{1}$	86	76
5	$\bar{6}$	1	45	46
5	$\bar{6}$	$\bar{1}$	8-	-4
0	7	1	40-	31
0	7	$\bar{1}$	43-	27
1	7	1	68	72
1	$\bar{7}$	1	163	171
1	7	$\bar{1}$	39	35
1	$\bar{7}$	$\bar{1}$	35	34
2	7	1	31	-31
2	$\bar{7}$	1	183	204
2	7	$\bar{1}$	31	-29
2	$\bar{7}$	$\bar{1}$	41	51
3	$\bar{7}$	1	81	-79
3	7	$\bar{1}$	52	48
3	$\bar{7}$	$\bar{1}$	17-	20
4	$\bar{7}$	1	106	100
4	$\bar{7}$	$\bar{1}$	156	161
5	$\bar{7}$	1	116	134
5	$\bar{7}$	$\bar{1}$	29	25
0	8	1	67	50
0	8	$\bar{1}$	38-	9
1	8	1	69	69
1	$\bar{8}$	1	71	-61
1	8	$\bar{1}$	86	83
1	$\bar{8}$	$\bar{1}$	19-	10
2	$\bar{8}$	1	107	107
2	8	$\bar{1}$	7-	5
2	$\bar{8}$	$\bar{1}$	79	68
3	$\bar{8}$	1	56	53
3	$\bar{8}$	$\bar{1}$	14-	0
4	$\bar{8}$	1	30	-24
4	$\bar{8}$	$\bar{1}$	88	90
5	$\bar{8}$	1	60	59
5	$\bar{8}$	$\bar{1}$	82	92
0	9	$\bar{1}$	111	92
1	$\bar{9}$	1	17-	5
1	9	$\bar{1}$	65	69
1	$\bar{9}$	$\bar{1}$	31	31
2	9	1	12-	-8
2	$\bar{9}$	$\bar{1}$	48	43
3	$\bar{9}$	1	143	147
3	$\bar{9}$	$\bar{1}$	42	39
4	$\bar{9}$	1	16	13
4	$\bar{9}$	$\bar{1}$	29	-32
5	$\bar{9}$	1	31	-27
5	$\bar{9}$	$\bar{1}$	16	24
1	$\overline{10}$	1	69	70
2	$\overline{10}$	1	25	-24
3	$\overline{10}$	1	67	67
4	$\overline{10}$	1	58	63
0	0	2	325	508
1	0	2	219	328
1	0	$\bar{2}$	173	-119
2	0	2	12-	-1
2	0	$\bar{2}$	385	343
3	0	2	28	31
3	0	$\bar{2}$	170	196
4	0	2	8-	15
4	0	$\bar{2}$	167	-163
5	0	2	61	48
5	0	$\bar{2}$	48	49
0	1	2	406	656
0	1	$\bar{2}$	158	132
1	1	2	295	323
1	$\bar{1}$	2	234	268
1	1	$\bar{2}$	457	469
1	$\bar{1}$	$\bar{2}$	149	-129
2	1	2	79	95
2	$\bar{1}$	2	170	182
2	1	$\bar{2}$	371	338
2	$\bar{1}$	$\bar{2}$	39	20
3	1	2	34	30
3	$\bar{1}$	2	111	118
3	1	$\bar{2}$	103	-94
3	$\bar{1}$	$\bar{2}$	463	468
4	1	2	28	-24
4	$\bar{1}$	2	155	143
4	1	$\bar{2}$	25	26
4	$\bar{1}$	$\bar{2}$	140	133
5	1	2	77	66
5	$\bar{1}$	2	18	5
5	1	$\bar{2}$	152	168
5	$\bar{1}$	$\bar{2}$	43	-39
0	2	2	221	256
0	2	$\bar{2}$	251	-240
1	2	2	47	69
1	$\bar{2}$	2	383	-370
1	2	$\bar{2}$	596	709
1	$\bar{2}$	$\bar{2}$	328	347
2	2	2	83	84
2	$\bar{2}$	2	125	113
2	2	$\bar{2}$	99	111
2	$\bar{2}$	$\bar{2}$	234	-156
3	2	2	54	55
3	$\bar{2}$	2	148	140
3	2	$\bar{2}$	56	-49
3	$\bar{2}$	$\bar{2}$	12-	11
4	2	2	49	45
4	$\bar{2}$	2	194	173
4	2	$\bar{2}$	182	187
4	$\bar{2}$	$\bar{2}$	298	299
5	2	2	35	31
5	$\bar{2}$	2	8-	5
5	2	$\bar{2}$	49	51
5	$\bar{2}$	$\bar{2}$	22	15
0	3	2	226	-223
0	3	$\bar{2}$	297	296
1	3	2	72	73
1	$\bar{3}$	2	68	62
1	3	$\bar{2}$	285	296
1	$\bar{3}$	$\bar{2}$	288	284
2	3	2	151	158
2	$\bar{3}$	2	164	173
2	3	$\bar{2}$	45	-32
2	$\bar{3}$	$\bar{2}$	242	219
3	3	2	96	97
3	$\bar{3}$	2	148	139
3	3	$\bar{2}$	179	174
3	$\bar{3}$	$\bar{2}$	179	-139
4	3	2	57	54
4	$\bar{3}$	2	57	52
4	3	$\bar{2}$	130	128
4	$\bar{3}$	$\bar{2}$	157	146
5	3	2	77	67
5	3	$\bar{2}$	49	-48
5	$\bar{3}$	$\bar{2}$	117	111
0	4	2	42-	6
0	4	$\bar{2}$	204	199
1	4	2	223	238
1	$\bar{4}$	2	384	439
1	4	$\bar{2}$	255	-234
1	$\bar{4}$	$\bar{2}$	54	50
2	4	2	120	120
2	$\bar{4}$	2	251	276
2	4	$\bar{2}$	163	160
2	$\bar{4}$	$\bar{2}$	373	352
3	4	2	41	37
3	$\bar{4}$	2	216	203
3	4	$\bar{2}$	222	245
3	$\bar{4}$	$\bar{2}$	154	139
4	4	2	15	11
4	$\bar{4}$	2	56	-43
4	4	$\bar{2}$	17	-20
4	$\bar{4}$	$\bar{2}$	49	-42
5	$\bar{4}$	2	60	49
5	4	$\bar{2}$	21	-23
5	$\bar{4}$	$\bar{2}$	122	118
0	5	2	158	143
0	5	$\bar{2}$	38-	22
1	5	2	23-	23
1	$\bar{5}$	2	253	256
1	5	$\bar{2}$	119	-97
1	$\bar{5}$	$\bar{2}$	46	-36
2	5	2	12-	-8
2	$\bar{5}$	2	77	87
2	5	$\bar{2}$	201	210
2	$\bar{5}$	$\bar{2}$	143	126
3	5	2	10-	4
3	$\bar{5}$	2	102	97
3	5	$\bar{2}$	17-	3
3	$\bar{5}$	$\bar{2}$	279	300
4	5	2	33	30
4	5	$\bar{2}$	58	-54
4	$\bar{5}$	$\bar{2}$	79	-67
5	$\bar{5}$	2	18	12
5	$\bar{5}$	$\bar{2}$	16	-10
0	6	2	178	153
0	6	$\bar{2}$	101	94
1	6	2	47	-45
1	$\bar{6}$	2	124	136
1	6	$\bar{2}$	194	190
1	$\bar{6}$	$\bar{2}$	119	97
2	6	2	25	22
2	$\bar{6}$	2	111	119
2	6	$\bar{2}$	62	56
2	$\bar{6}$	$\bar{2}$	69	-53
3	$\bar{6}$	2	15-	4
3	6	$\bar{2}$	52	-48
3	$\bar{6}$	$\bar{2}$	163	159
4	$\bar{6}$	2	110	113
4	6	$\bar{2}$	60	64
4	$\bar{6}$	$\bar{2}$	134	131
5	$\bar{6}$	2	45	36
5	6	$\bar{2}$	7-	2
0	7	2	69	59
0	7	$\bar{2}$	136	130
1	7	2	15-	-5
1	$\bar{7}$	2	24-	-30
1	7	$\bar{2}$	157	194
1	$\bar{7}$	$\bar{2}$	200	162
2	$\bar{7}$	2	77	77
2	7	$\bar{2}$	60	-56
2	$\bar{7}$	$\bar{2}$	16	11
3	$\bar{7}$	2	17-	-14
3	7	$\bar{2}$	32	30
3	$\bar{7}$	$\bar{2}$	127	-116
4	$\bar{7}$	2	76	74
4	$\bar{7}$	$\bar{2}$	107	111
5	$\bar{7}$	2	69	67
5	$\bar{7}$	$\bar{2}$	54	60
0	8	2	29	-19
0	8	$\bar{2}$	142	137
1	$\bar{8}$	2	49	49
1	8	$\bar{2}$	42	36
1	$\bar{8}$	$\bar{2}$	50	49
2	$\bar{8}$	2	50	54
2	8	$\bar{2}$	26	-29
2	$\bar{8}$	$\bar{2}$	127	129
3	$\bar{8}$	$\bar{2}$	54	-54
4	$\bar{8}$	2	31	34
4	$\bar{8}$	$\bar{2}$	20	26
5	$\bar{8}$	2	63	66
5	$\bar{8}$	$\bar{2}$	60	72
0	9	$\bar{2}$	32-	3
1	$\bar{9}$	2	87	79
1	9	$\bar{2}$	32	-36
2	$\bar{9}$	2	12-	13
2	$\bar{9}$	$\bar{2}$	59	60
3	$\bar{9}$	2	103	105
3	$\bar{9}$	$\bar{2}$	89	95
4	$\bar{9}$	2	34	33
4	$\bar{9}$	$\bar{2}$	9	8
5	$\bar{9}$	2	6-	-1
0	10	$\bar{2}$	20	-28
1	$\overline{10}$	2	32	34
2	$\overline{10}$	2	9-	-3
3	$\overline{10}$	2	35	39
4	$\overline{10}$	2	38	40
5	$\overline{10}$	2	11	-21
0	0	3	408	588
1	0	3	239	310
1	0	$\bar{3}$	212	-182
2	0	3	117	-124
2	0	$\bar{3}$	62	-2
3	0	3	78	79
3	0	$\bar{3}$	221	211
4	0	3	130	129
4	0	$\bar{3}$	133	130
5	0	3	7	12
5	0	$\bar{3}$	133	139
0	1	3	366	452
0	1	$\bar{3}$	98	-72
1	1	3	165	-159
1	$\bar{1}$	3	322	425
1	1	$\bar{3}$	235	203
1	$\bar{1}$	$\bar{3}$	28	41
2	1	3	65	-56
2	$\bar{1}$	3	168	197
2	1	$\bar{3}$	429	392
2	$\bar{1}$	$\bar{3}$	194	-136
3	1	3	177	207
3	$\bar{1}$	3	78	-72
3	1	$\bar{3}$	120	112
3	$\bar{1}$	$\bar{3}$	159	140
4	1	3	46	39
4	$\bar{1}$	3	105	101
4	1	$\bar{3}$	38	34
4	$\bar{1}$	$\bar{3}$	124	113
5	1	3	13	13
5	$\bar{1}$	3	39	26
5	1	$\bar{3}$	49	49
5	$\bar{1}$	$\bar{3}$	88	82
0	2	3	49	42
0	2	$\bar{3}$	147	-116
1	2	3	63	58
1	$\bar{2}$	3	154	158
1	2	$\bar{3}$	425	573
1	$\bar{2}$	$\bar{3}$	280	296
2	2	3	242	276
2	$\bar{2}$	3	304	425
2	2	$\bar{3}$	142	135
2	$\bar{2}$	$\bar{3}$	212	185
3	2	3	91	96
3	$\bar{2}$	3	14-	1
3	2	$\bar{3}$	130	-101
3	$\bar{2}$	$\bar{3}$	183	163
4	2	3	44	-44
4	$\bar{2}$	3	13	-7
4	2	$\bar{3}$	9	4
4	$\bar{2}$	$\bar{3}$	176	166
5	$\bar{2}$	3	64	51
5	2	$\bar{3}$	17	8
5	$\bar{2}$	$\bar{3}$	7-	4
0	3	3	179	-162
0	3	$\bar{3}$	249	243
1	3	3	220	209
1	$\bar{3}$	3	134	-71
1	3	$\bar{3}$	339	355
1	$\bar{3}$	$\bar{3}$	225	208
2	3	3	130	132
2	$\bar{3}$	3	229	245
2	3	$\bar{3}$	31	24
2	$\bar{3}$	$\bar{3}$	404	346
3	3	3	88	-84
3	$\bar{3}$	3	276	278
3	3	$\bar{3}$	88	84
3	$\bar{3}$	$\bar{3}$	59	49
4	3	3	5-	-4
4	$\bar{3}$	3	17	-10
4	3	$\bar{3}$	101	89
4	$\bar{3}$	$\bar{3}$	66	52
5	3	3	43	30
5	3	$\bar{3}$	27	23
5	$\bar{3}$	$\bar{3}$	40	-32
0	4	3	43-	4
0	4	$\bar{3}$	362	362
1	4	3	191	166
1	$\bar{4}$	3	19-	-10
1	4	$\bar{3}$	20-	-1
1	$\bar{4}$	$\bar{3}$	23-	8
2	$\bar{4}$	3	231	-236
2	4	$\bar{3}$	111	99
2	$\bar{4}$	$\bar{3}$	258	243
3	4	3	11-	-14
3	$\bar{4}$	3	202	193
3	4	$\bar{3}$	143	134
3	$\bar{4}$	$\bar{3}$	163	145
4	$\bar{4}$	3	82	69
4	4	$\bar{3}$	40	35
4	$\bar{4}$	$\bar{3}$	36	32
5	$\bar{4}$	3	8-	-6
5	4	$\bar{3}$	14	17
5	$\bar{4}$	$\bar{3}$	52	50
0	5	3	275	256
0	5	$\bar{3}$	165	164
1	5	3	21-	24
1	$\bar{5}$	3	376	413
1	5	$\bar{3}$	109	-94
1	$\bar{5}$	$\bar{3}$	60	48
2	5	3	11-	-26
2	$\bar{5}$	3	14-	30
2	5	$\bar{3}$	204	202
2	$\bar{5}$	$\bar{3}$	67	-59
3	$\bar{5}$	3	15-	10
3	5	$\bar{3}$	118	110
3	$\bar{5}$	$\bar{3}$	96	84
4	$\bar{5}$	3	119	116
4	5	$\bar{3}$	24	25
4	$\bar{5}$	$\bar{3}$	18	20
5	$\bar{5}$	3	40	30
5	5	$\bar{3}$	3-	19
5	$\bar{5}$	$\bar{3}$	97	102
0	6	3	136	127
0	6	$\bar{3}$	136	-113
1	6	3	91	-83
1	$\bar{6}$	3	202	185
1	6	$\bar{3}$	94	81
1	$\bar{6}$	$\bar{3}$	161	151
2	6	3	43	47
2	$\bar{6}$	3	258	299
2	6	$\bar{3}$	129	136
2	$\bar{6}$	$\bar{3}$	39	-35
3	$\bar{6}$	3	40	-37
3	6	$\bar{3}$	34	30
3	$\bar{6}$	$\bar{3}$	30	26
4	$\bar{6}$	3	64	59
4	6	$\bar{3}$	15	13
4	$\bar{6}$	$\bar{3}$	16	20
5	$\bar{6}$	3	81	75
5	$\bar{6}$	$\bar{3}$	39	46
0	7	3	32	-24
0	7	$\bar{3}$	43-	40
1	7	3	30	29
1	$\bar{7}$	3	78	-61
1	7	$\bar{3}$	167	162
1	$\bar{7}$	$\bar{3}$	94	78
2	$\bar{7}$	3	176	193
2	7	$\bar{3}$	62	-61
2	$\bar{7}$	$\bar{3}$	104	98
3	$\bar{7}$	3	45	47
3	$\bar{7}$	$\bar{3}$	51	45
4	$\bar{7}$	3	8-	2
4	$\bar{7}$	$\bar{3}$	92	96
5	$\bar{7}$	3	76	73
5	$\bar{7}$	$\bar{3}$	28	30
0	8	$\bar{3}$	189	185
1	$\bar{8}$	3	23-	-5
1	8	$\bar{3}$	73	72
1	$\bar{8}$	$\bar{3}$	28	-24
2	$\bar{8}$	3	15-	-15
2	8	$\bar{3}$	41	-40
2	$\bar{8}$	$\bar{3}$	76	81
3	$\bar{8}$	3	122	133
3	$\bar{8}$	$\bar{3}$	10	6
4	$\bar{8}$	3	33	34
4	$\bar{8}$	$\bar{3}$	50	53
5	$\bar{8}$	3	14	11
5	$\bar{8}$	$\bar{3}$	3-	23
0	9	$\bar{3}$	103	94
1	$\bar{9}$	3	109	103
1	9	$\bar{3}$	15-	-5
2	$\bar{9}$	3	87	-90
3	$\bar{9}$	3	64	63
4	$\bar{9}$	3	72	69
5	$\bar{9}$	3	29	-26
0	10	$\bar{3}$	22	-24
1	$\overline{10}$	3	108	104
2	$\overline{10}$	3	55	53
3	$\overline{10}$	3	16	15
4	$\overline{10}$	3	59	57
5	$\overline{10}$	3	3-	14
0	0	4	197	232
1	0	4	72	85
1	0	$\bar{4}$	254	260
2	0	4	15-	31
2	0	$\bar{4}$	381	322
3	0	4	133	152
3	0	$\bar{4}$	70	23
4	0	4	79	81
4	0	$\bar{4}$	21	21
5	0	4	27	-27
5	0	$\bar{4}$	141	160
0	1	4	263	280
0	1	$\bar{4}$	114	120
1	1	4	75	78
1	$\bar{1}$	4	100	105
1	1	$\bar{4}$	221	242
1	$\bar{1}$	$\bar{4}$	110	98
2	1	4	94	93
2	$\bar{1}$	4	55	-52
2	1	$\bar{4}$	97	-67
2	$\bar{1}$	$\bar{4}$	266	245
3	1	4	84	86
3	$\bar{1}$	4	35	-31
3	1	$\bar{4}$	24	-20
3	$\bar{1}$	$\bar{4}$	129	113
4	1	4	63	-65
4	$\bar{1}$	4	159	168
4	1	$\bar{4}$	176	195
4	$\bar{1}$	$\bar{4}$	123	-104
5	1	4	3-	8
5	$\bar{1}$	4	38	30
5	1	$\bar{4}$	43	44
5	$\bar{1}$	$\bar{4}$	94	102
0	2	4	133	119
0	2	$\bar{4}$	33-	42
1	2	4	87	71
1	$\bar{2}$	4	173	163
1	2	$\bar{4}$	197	210
1	$\bar{2}$	$\bar{4}$	93	63
2	2	4	86	80
2	$\bar{2}$	4	194	211
2	2	$\bar{4}$	36	31
2	$\bar{2}$	$\bar{4}$	96	82
3	2	4	14-	-17
3	$\bar{2}$	4	23	-14
3	2	$\bar{4}$	253	262
3	$\bar{2}$	$\bar{4}$	243	217
4	2	4	27	-29
4	$\bar{2}$	4	67	63
4	2	$\bar{4}$	173	192
4	$\bar{2}$	$\bar{4}$	74	67
5	$\bar{2}$	4	91	80
5	2	$\bar{4}$	49	-50
5	$\bar{2}$	$\bar{4}$	51	-48
0	3	4	74	56
0	3	$\bar{4}$	78	70
1	3	4	209	205
1	$\bar{3}$	4	19-	9
1	3	$\bar{4}$	183	175
1	$\bar{3}$	$\bar{4}$	38	43
2	3	4	86	76
2	$\bar{3}$	4	184	208
2	3	$\bar{4}$	234	228
2	$\bar{3}$	$\bar{4}$	90	-62
3	3	4	12-	-13
3	$\bar{3}$	4	164	164
3	3	$\bar{4}$	157	149
3	$\bar{3}$	$\bar{4}$	126	110
4	$\bar{3}$	4	80	-70
4	3	$\bar{4}$	61	-58
4	$\bar{3}$	$\bar{4}$	268	282
5	$\bar{3}$	4	30	22
5	3	$\bar{4}$	7-	-2
5	$\bar{3}$	$\bar{4}$	26	-25
0	4	4	43-	33
0	4	$\bar{4}$	173	155
1	4	4	87	84
1	$\bar{4}$	4	205	181
1	4	$\bar{4}$	49-	0
1	$\bar{4}$	$\bar{4}$	139	121
2	4	4	11-	2
2	$\bar{4}$	4	122	130
2	4	$\bar{4}$	195	183
2	$\bar{4}$	$\bar{4}$	75	54
3	4	4	30	31
3	$\bar{4}$	4	246	252
3	4	$\bar{4}$	38	-25
3	$\bar{4}$	$\bar{4}$	86	-68
4	$\bar{4}$	4	9-	-5
4	4	$\bar{4}$	51	-47
4	$\bar{4}$	$\bar{4}$	100	96
5	$\bar{4}$	4	52	-40
5	4	$\bar{4}$	88	90
5	$\bar{4}$	$\bar{4}$	78	81
0	5	4	38-	9
0	5	$\bar{4}$	126	108
1	5	4	17-	-23
1	$\bar{5}$	4	226	215
1	5	$\bar{4}$	36	40
1	$\bar{5}$	$\bar{4}$	109	103
2	5	4	49	47

Table 3 (*cont.*)

h	k	l	$\|10F_o\|$	$10F_c$
2	$\bar5$	4	14-	40
2	5	$\bar4$	125	117
2	$\bar5$	$\bar4$	251	233
3	$\bar5$	4	68	68
3	5	$\bar4$	17-	11
3	$\bar5$	$\bar4$	119	108
4	$\bar5$	4	135	127
4	5	$\bar4$	82	79
4	$\bar5$	$\bar4$	58	-54
5	$\bar5$	4	2-	5
5	5	$\bar4$	32	51
5	$\bar5$	$\bar4$	102	118
0	6	4	58	45
0	6	$\bar4$	141	118
1	6	4	21	-25
1	$\bar6$	4	156	136
1	6	$\bar4$	116	96
1	$\bar6$	$\bar4$	26	18
2	$\bar6$	4	63	58
2	6	$\bar4$	43	-40
2	$\bar6$	$\bar4$	65	60
3	$\bar6$	4	139	-145
3	6	$\bar4$	66	62
3	$\bar6$	$\bar4$	133	127
4	$\bar6$	4	80	73
4	6	$\bar4$	74	83
4	$\bar6$	$\bar4$	43	-44
5	$\bar6$	4	95	69
5	$\bar6$	$\bar4$	26	28
0	7	$\bar4$	138	124
1	$\bar7$	4	73	65
1	7	$\bar4$	124	108
1	$\bar7$	$\bar4$	41	33
2	$\bar7$	4	153	171
2	7	$\bar4$	14-	0
2	$\bar7$	$\bar4$	24	-24
3	$\bar7$	4	17-	18
3	7	$\bar4$	100	102
3	$\bar7$	$\bar4$	40	42
4	$\bar7$	4	8-	-2
4	$\bar7$	$\bar4$	59	73
5	$\bar7$	4	85	87
5	$\bar7$	$\bar4$	13	-21
0	8	$\bar4$	75	66
1	$\bar8$	4	23-	-16
1	8	$\bar4$	68	61
2	$\bar8$	4	14-	25
2	8	$\bar4$	55	49
3	$\bar8$	4	136	150
3	8	$\bar4$	5-	8
4	$\bar8$	4	17	16
5	$\bar8$	$\bar4$	6-	-4
0	9	$\bar4$	35-	17
1	$\bar9$	4	56	55
1	9	$\bar4$	16-	17
2	$\bar9$	4	43	-40
2	9	$\bar4$	52	49
3	$\bar9$	4	98	100
4	$\bar9$	4	78	76
5	$\bar9$	$\bar4$	32	-32
0	10	$\bar4$	24-	3
1	$\overline{10}$	4	73	64
1	10	$\bar4$	2-	25
2	$\overline{10}$	4	32	26
3	$\overline{10}$	4	11-	-2
4	$\overline{10}$	4	51	56
5	$\overline{10}$	4	3-	12
2	$\overline{11}$	4	59	77
3	$\overline{11}$	4	11	-13
0	0	5	43	29
1	0	5	169	186
1	0	$\bar5$	49	39
2	0	5	45	43
2	0	$\bar5$	246	228
3	0	5	37	-37
3	0	$\bar5$	25	-14
4	0	5	21	23
4	0	$\bar5$	21	-15
5	0	$\bar5$	135	154
0	1	5	200	181
0	1	$\bar5$	38-	54
1	1	5	209	209
1	$\bar1$	5	67	56
1	1	$\bar5$	448	511
1	$\bar1$	$\bar5$	322	-281
2	1	5	15-	22
2	$\bar1$	5	170	194
2	1	$\bar5$	79	77
2	$\bar1$	$\bar5$	173	151
3	1	5	42	45
3	$\bar1$	5	40	39
3	1	$\bar5$	161	-147
3	$\bar1$	$\bar5$	347	360
4	1	5	25	27
4	$\bar1$	5	39	36
4	1	$\bar5$	121	126
4	$\bar1$	$\bar5$	35	35
5	$\bar1$	5	5-	-6
5	1	$\bar5$	99	107
5	$\bar1$	$\bar5$	49	44
0	2	5	247	232
0	2	$\bar5$	237	250
1	2	5	39	42

h	k	l	$\|10F_o\|$	$10F_c$
1	$\bar2$	5	112	-91
1	2	$\bar5$	420	480
1	$\bar2$	$\bar5$	39	-34
2	2	5	14-	15
2	$\bar2$	5	84	94
2	2	$\bar5$	76	-55
2	$\bar2$	$\bar5$	150	-121
3	2	5	51	59
3	$\bar2$	5	122	122
3	2	$\bar5$	15-	25
3	$\bar2$	$\bar5$	212	189
4	2	5	1-	11
4	$\bar2$	5	56	53
4	2	$\bar5$	110	112
4	$\bar2$	$\bar5$	139	131
5	$\bar2$	5	21	20
5	2	$\bar5$	26	-20
5	$\bar2$	$\bar5$	49	-47
0	3	5	43-	19
0	3	$\bar5$	223	217
1	3	5	83	-63
1	$\bar3$	5	128	109
1	3	$\bar5$	146	-117
1	$\bar3$	$\bar5$	365	351
2	3	5	52	57
2	$\bar3$	5	42	-35
2	3	$\bar5$	46	33
2	$\bar3$	$\bar5$	133	117
3	3	5	37	46
3	$\bar3$	5	92	89
3	3	$\bar5$	213	223
3	$\bar3$	$\bar5$	17-	-12
4	$\bar3$	5	19	20
4	3	$\bar5$	17	14
4	$\bar3$	$\bar5$	152	155
5	$\bar3$	5	42	32
5	3	$\bar5$	36	-38
5	$\bar3$	$\bar5$	7-	8
0	4	5	128	-110
0	4	$\bar5$	36-	17
1	4	5	63	48
1	$\bar4$	5	273	273
1	4	$\bar5$	146	-115
1	$\bar4$	$\bar5$	179	162
2	4	5	67	62
2	$\bar4$	5	50	52
2	4	$\bar5$	376	388
2	$\bar4$	$\bar5$	234	209
3	$\bar4$	5	63	66
3	4	$\bar5$	153	196
3	$\bar4$	$\bar5$	42	-40
4	$\bar4$	5	42	28
4	4	$\bar5$	31	-30
4	$\bar4$	$\bar5$	50	46
5	$\bar4$	5	22	15
5	4	$\bar5$	24	28
5	$\bar4$	$\bar5$	73	83
0	5	5	32-	26
0	5	$\bar5$	42-	34
1	5	5	86	54
1	$\bar5$	5	160	139
1	5	$\bar5$	150	137
1	$\bar5$	$\bar5$	58	-47
2	$\bar5$	5	137	140
2	5	$\bar5$	178	177
2	$\bar5$	$\bar5$	101	94
3	$\bar5$	5	17-	3
3	5	$\bar5$	70	-60
3	$\bar5$	$\bar5$	59	64
4	$\bar5$	5	39	35
4	5	$\bar5$	15	21
4	$\bar5$	$\bar5$	69	-72
5	$\bar5$	5	13	8
5	5	$\bar5$	42	61
5	$\bar5$	$\bar5$	46	57
0	6	5	129	129
0	6	$\bar5$	99	89
1	$\bar6$	5	23-	4
1	6	$\bar5$	215	187
1	$\bar6$	$\bar5$	27	-27
2	$\bar6$	5	188	199
2	6	$\bar5$	97	-90
2	$\bar6$	$\bar5$	19	-15
3	$\bar6$	5	57	57
3	6	$\bar5$	14-	-7
3	$\bar6$	$\bar5$	140	151
4	$\bar6$	5	58	54
4	6	$\bar5$	89	98
4	$\bar6$	$\bar5$	7	10
5	$\bar6$	5	59	48
5	6	$\bar5$	4-	8
0	7	$\bar5$	169	153
1	$\bar7$	5	23-	-12
1	7	$\bar5$	63	65
2	$\bar7$	5	29	31
2	7	$\bar5$	84	-84
2	$\bar7$	$\bar5$	43	-46
3	$\bar7$	5	66	62
3	7	$\bar5$	99	94
3	$\bar7$	$\bar5$	6-	12
4	$\bar7$	5	34	31
5	$\bar7$	$\bar5$	52	50
0	8	$\bar5$	106	101

h	k	l	$\|10F_o\|$	$10F_c$
1	$\bar8$	5	120	117
1	8	$\bar5$	52	-43
2	$\bar8$	5	53	-48
2	8	$\bar5$	52	46
3	$\bar8$	5	37	38
4	$\bar8$	5	21	22
5	$\bar8$	5	6-	1
0	9	$\bar5$	35-	-7
1	$\bar9$	5	119	123
1	9	$\bar5$	43	40
2	$\bar9$	5	29	27
2	9	$\bar5$	113	117
3	$\bar9$	5	47	46
4	$\bar9$	5	54	54
5	$\bar9$	5	12	-12
0	10	$\bar5$	24-	-22
1	$\overline{10}$	5	16-	-1
2	$\overline{10}$	5	55	60
3	$\overline{10}$	5	20	22
4	$\overline{10}$	5	32	32
2	$\overline{11}$	5	67	55
0	0	6	61	51
1	0	6	193	192
1	0	$\bar6$	23-	-26
2	0	6	14-	16
2	0	$\bar6$	99	98
3	0	6	26	-24
3	0	$\bar6$	95	83
4	0	6	53	75
4	0	$\bar6$	75	70
5	0	$\bar6$	29	25
0	1	6	326	328
0	1	$\bar6$	165	-146
1	1	6	52	47
1	$\bar1$	6	68	68
1	1	$\bar6$	217	204
1	$\bar1$	$\bar6$	104	92
2	1	6	113	-105
2	$\bar1$	6	159	183
2	1	$\bar6$	190	196
2	$\bar1$	$\bar6$	56	58
3	1	6	39	52
3	$\bar1$	6	25	-28
3	1	$\bar6$	132	134
3	$\bar1$	$\bar6$	45	37
4	$\bar1$	6	26	30
4	1	$\bar6$	74	73
4	$\bar1$	$\bar6$	39	37
5	1	$\bar6$	7-	-10
5	$\bar1$	$\bar6$	98	110
0	2	6	136	154
0	2	$\bar6$	42-	24
1	2	6	53	-49
1	$\bar2$	6	82	-72
1	2	$\bar6$	202	206
1	$\bar2$	$\bar6$	135	123
2	2	6	39	27
2	$\bar2$	6	125	142
2	2	$\bar6$	15-	5
2	$\bar2$	$\bar6$	83	73
3	2	6	53	73
3	$\bar2$	6	66	72
3	2	$\bar6$	61	59
3	$\bar2$	$\bar6$	110	99
4	$\bar2$	6	43	-47
4	2	$\bar6$	60	57
4	$\bar2$	$\bar6$	57	56
5	$\bar2$	6	3-	7
5	2	$\bar6$	31	34
5	$\bar2$	$\bar6$	60	65
0	3	6	47	-65
0	3	$\bar6$	294	281
1	3	6	60	48
1	$\bar3$	6	56	53
1	3	$\bar6$	112	104
1	$\bar3$	$\bar6$	52	40
2	3	6	99	102
2	$\bar3$	6	14-	7
2	3	$\bar6$	77	69
2	$\bar3$	$\bar6$	23	26
3	$\bar3$	6	171	194
3	3	$\bar6$	62	67
3	$\bar3$	$\bar6$	33	31
4	$\bar3$	6	20	21
4	3	$\bar6$	39	47
4	$\bar3$	$\bar6$	49	51
5	$\bar3$	6	31	-25
5	3	$\bar6$	54	63
5	$\bar3$	$\bar6$	19	-22
0	4	6	65	-53
0	4	$\bar6$	204	189
1	4	6	119	118
1	$\bar4$	6	227	229
1	4	$\bar6$	59	-45
1	$\bar4$	$\bar6$	39	39
2	$\bar4$	6	59	-59
2	4	$\bar6$	100	99
2	$\bar4$	$\bar6$	117	115
3	$\bar4$	6	49	54
3	4	$\bar6$	17-	4
3	$\bar4$	$\bar6$	63	61
4	$\bar4$	6	83	56
4	4	$\bar6$	23	24

h	k	l	$\|10F_o\|$	$10F_c$
4	$\bar4$	$\bar6$	50	61
5	$\bar4$	6	6-	-3
5	4	$\bar6$	12	47
5	$\bar4$	$\bar6$	22	-21
0	5	6	48	49
0	5	$\bar6$	90	-71
1	5	6	195	184
1	5	$\bar6$	24-	-2
1	$\bar5$	$\bar6$	15-	9
2	$\bar5$	6	126	125
2	5	$\bar6$	137	124
2	$\bar5$	$\bar6$	35	33
3	$\bar5$	6	82	-80
3	5	$\bar6$	65	62
3	$\bar5$	$\bar6$	45	44
4	$\bar5$	6	40	40
4	5	$\bar6$	38	37
4	$\bar5$	$\bar6$	39	39
5	$\bar5$	6	63	52
5	5	$\bar6$	2-	-5
5	$\bar5$	$\bar6$	32	50
0	6	$\bar6$	43-	26
1	$\bar6$	6	24-	-4
1	6	$\bar6$	202	198
2	$\bar6$	6	183	195
2	6	$\bar6$	80	76
2	$\bar6$	$\bar6$	12	10
3	$\bar6$	6	17-	-13
3	6	$\bar6$	90	83
3	$\bar6$	$\bar6$	32	33
4	$\bar6$	6	24	-25
4	6	$\bar6$	22	21
5	$\bar6$	6	66	59
0	7	$\bar6$	183	161
1	$\bar7$	6	45	-36
1	7	$\bar6$	105	94
2	$\bar7$	6	31	32
2	7	$\bar6$	62	-54
3	$\bar7$	6	93	96
3	7	$\bar6$	34	34
4	$\bar7$	6	7-	-6
5	$\bar7$	6	5-	7
0	8	$\bar6$	129	115
1	$\bar8$	6	90	81
1	8	$\bar6$	20-	-3
2	$\bar8$	6	66	-64
2	8	$\bar6$	9-	18
3	$\bar8$	6	93	107
4	$\bar8$	6	42	57
5	$\bar8$	6	14	-12
0	9	$\bar6$	33-	-15
1	$\bar9$	6	102	99
1	9	$\bar6$	15-	7
2	$\bar9$	6	12-	-17
2	9	$\bar6$	70	64
3	$\bar9$	6	13-	-5
4	$\bar9$	6	66	67
5	$\bar9$	6	3-	5
0	10	$\bar6$	35	-31
1	$\overline{10}$	6	26	22
2	$\overline{10}$	6	84	93
3	$\overline{10}$	6	15	-11
4	$\overline{10}$	6	7	-6
0	0	7	129	107
1	0	7	60	51
1	0	$\bar7$	247	218
2	0	7	12-	11
2	0	$\bar7$	53	53
3	0	7	10-	5
3	0	$\bar7$	37	-30
4	0	$\bar7$	135	151
5	0	$\bar7$	81	97
0	1	7	42-	-26
0	1	$\bar7$	205	192
1	1	7	35	35
1	$\bar1$	7	86	85
1	1	$\bar7$	114	113
1	$\bar1$	$\bar7$	52	-54
2	1	7	50	42
2	$\bar1$	7	14-	26
2	1	$\bar7$	170	-153
2	$\bar1$	$\bar7$	161	136
3	$\bar1$	7	28	-37
3	1	$\bar7$	52	42
3	$\bar1$	$\bar7$	17-	-5
4	$\bar1$	7	19	33
4	1	$\bar7$	131	151
4	$\bar1$	$\bar7$	21	-20
5	1	$\bar7$	33	-36
5	$\bar1$	$\bar7$	123	144
0	2	7	64	53
0	2	$\bar7$	58	77
1	2	7	53	52
1	$\bar2$	7	50	39
1	2	$\bar7$	52	52
1	$\bar2$	$\bar7$	55	-49
2	2	7	55	50
2	$\bar2$	7	73	75
2	2	$\bar7$	54	70
2	$\bar2$	$\bar7$	140	135
3	$\bar2$	7	39	51
3	2	$\bar7$	170	166
3	$\bar2$	$\bar7$	140	135

h	k	l	$\|10F_o\|$	$10F_c$
4	$\bar2$	7	5-	3
4	2	$\bar7$	27	-30
4	$\bar2$	$\bar7$	57	-59
5	2	$\bar7$	47	-54
5	$\bar2$	$\bar7$	28	35
0	3	7	74	56
0	3	$\bar7$	70	8
1	3	7	43	43
1	$\bar3$	7	23-	24
1	3	$\bar7$	42	54
1	$\bar3$	$\bar7$	19-	21
2	$\bar3$	7	15-	26
2	3	$\bar7$	252	296
2	$\bar3$	$\bar7$	35	4
3	$\bar3$	7	52	101
3	3	$\bar7$	62	61
3	$\bar3$	$\bar7$	143	151
4	$\bar3$	7	6-	-5
4	3	$\bar7$	53	-50
4	$\bar3$	$\bar7$	81	91
5	3	$\bar7$	62	73
5	$\bar3$	$\bar7$	62	-53
0	4	7	32	31
0	4	$\bar7$	43-	-28
1	4	7	82	71
1	$\bar4$	7	45	38
1	$\bar4$	$\bar7$	112	104
2	$\bar4$	7	15-	25
2	4	$\bar7$	121	177
2	$\bar4$	$\bar7$	9-	-31
3	$\bar4$	7	45	51
3	4	$\bar7$	24	-21
3	$\bar4$	$\bar7$	11-	-3
4	$\bar4$	7	17	26
4	4	$\bar7$	42	51
4	$\bar4$	$\bar7$	113	149
5	$\bar4$	7	3-	-22
5	4	$\bar7$	71	75
5	$\bar4$	$\bar7$	3-	0
0	5	$\bar7$	131	106
1	$\bar5$	7	124	111
1	5	$\bar7$	120	117
2	$\bar5$	7	101	101
2	5	$\bar7$	14-	-11
2	$\bar5$	$\bar7$	76	65
3	$\bar5$	7	15-	-3
3	5	$\bar7$	45	45
3	$\bar5$	$\bar7$	25	-25
4	$\bar5$	7	49	57
4	5	$\bar7$	108	118
5	$\bar5$	7	31	27
0	6	$\bar7$	139	118
1	$\bar6$	7	56	53
1	6	$\bar7$	23-	9
2	$\bar6$	7	90	94
2	6	$\bar7$	120	-116
3	$\bar6$	7	15-	-14
3	6	$\bar7$	99	100
4	$\bar6$	7	6-	6
4	6	$\bar7$	51	51
5	$\bar6$	7	54	54
0	7	$\bar7$	83	69
1	$\bar7$	7	23-	23
1	7	$\bar7$	21-	10
2	$\bar7$	7	14-	29
2	7	$\bar7$	50	45
3	$\bar7$	7	51	58
3	7	$\bar7$	74	74
4	$\bar7$	7	6-	-6
5	$\bar7$	7	15	16
0	8	$\bar7$	51	47
1	$\bar8$	7	62	67
1	8	$\bar7$	83	75
2	$\bar8$	7	12-	-26
2	8	$\bar7$	106	105
3	$\bar8$	7	55	53
4	$\bar8$	7	30	35
5	$\bar8$	7	2-	-24
0	9	$\bar7$	30-	1
1	$\bar9$	7	65	57
1	9	$\bar7$	57	53
2	$\bar9$	7	11-	14
3	$\bar9$	7	13	15
4	$\bar9$	7	52	53
0	10	$\bar7$	24	20
1	$\overline{10}$	7	13-	3
2	$\overline{10}$	7	59	61
3	$\overline{10}$	7	10	13
0	0	8	80	-62
1	0	8	19-	20
1	0	$\bar8$	171	149
2	0	8	89	85
2	0	$\bar8$	76	62
3	0	$\bar8$	61	-57
4	0	$\bar8$	39	52
5	0	$\bar8$	61	52
0	1	8	53	43
0	1	$\bar8$	42-	-13
1	1	8	126	115
1	$\bar1$	8	134	-113
1	1	$\bar8$	215	196
1	$\bar1$	$\bar8$	36	-30
2	1	8	5-	11

h	k	l	$\|10F_o\|$	$10F_c$
2	$\bar1$	8	65	61
2	1	$\bar8$	58	-46
2	$\bar1$	$\bar8$	179	173
3	1	$\bar8$	15-	10
3	$\bar1$	8	20	50
3	$\bar1$	$\bar8$	92	90
4	1	$\bar8$	93	105
4	$\bar1$	$\bar8$	24	-26
5	1	$\bar8$	25	27
5	$\bar1$	$\bar8$	19	29
0	2	8	157	126
0	2	$\bar8$	228	207
1	2	8	65	60
1	$\bar2$	8	27-	30
1	2	$\bar8$	79	74
1	$\bar2$	$\bar8$	109	-97
2	$\bar2$	8	12-	-21
2	2	$\bar8$	14-	-12
2	$\bar2$	$\bar8$	11-	13
3	2	8	32	56
3	$\bar2$	8	130	131
3	2	$\bar8$	134	147
4	$\bar2$	8	53	63
4	$\bar2$	$\bar8$	23	30
5	$\bar2$	8	4-	7
5	$\bar2$	$\bar8$	3-	-6
0	3	8	91	86
1	$\bar3$	8	194	195
1	3	$\bar8$	150	-150
1	$\bar3$	$\bar8$	91	86
2	3	8	115	95
2	$\bar3$	8	15	-17
3	$\bar3$	8	12-	17
3	3	$\bar8$	90	92
3	$\bar3$	$\bar8$	31	33
4	3	$\bar8$	3-	15
4	$\bar3$	8	20	-18
4	$\bar3$	$\bar8$	57	71
5	3	$\bar8$	4-	9
0	4	8	70	-54
1	$\bar4$	8	138	127
1	4	$\bar8$	46	42
2	$\bar4$	8	50	80
2	4	$\bar8$	195	196
3	$\bar4$	8	13-	1
3	4	$\bar8$	25	-24
4	$\bar4$	8	14	24
4	4	$\bar8$	18	-20
0	5	$\bar8$	43-	3
1	$\bar5$	8	57	-43
1	5	$\bar8$	191	190
2	$\bar5$	8	94	101
2	5	$\bar8$	29	30
3	$\bar5$	8	13-	1
3	5	$\bar8$	21	-21
4	$\bar5$	8	4-	0
4	5	$\bar8$	58	60
0	6	$\bar8$	150	127
1	$\bar6$	8	63	-58
1	6	$\bar8$	112	97
2	$\bar6$	8	39	37
2	6	$\bar8$	67	-59
3	$\bar6$	8	31	41
3	6	$\bar8$	91	88
4	$\bar6$	8	5-	-2
0	7	$\bar8$	158	139
1	$\bar7$	8	113	97
1	7	$\bar8$	31	-26
2	$\bar7$	8	12-	-18
2	7	$\bar8$	11	10
3	$\bar7$	8	38	50
3	7	$\bar8$	84	85
4	$\bar7$	8	22	33
0	8	$\bar8$	35	-29
1	$\bar8$	8	113	110
1	8	$\bar8$	54	-43
2	$\bar8$	8	11-	-9
2	8	$\bar8$	67	57
3	$\bar8$	8	11-	8
4	$\bar8$	8	21	41
0	9	$\bar8$	40	-37
1	$\bar9$	8	16	20
1	9	$\bar8$	57	61
2	$\bar9$	8	48	47
3	$\bar9$	8	9-	2
1	$\overline{10}$	8	31	-33
2	$\overline{10}$	8	50	53
3	$\overline{10}$	8	3-	24
0	0	9	29-	-11
1	0	9	63	63
1	0	$\bar9$	39	32
2	0	$\bar9$	21	25
3	0	$\bar9$	69	74
4	0	$\bar9$	31	42
0	1	9	90	73
0	1	$\bar9$	41	36
1	$\bar1$	9	30	20
1	1	$\bar9$	147	129
1	$\bar1$	$\bar9$	15-	12
2	$\bar1$	9	62	77
2	1	$\bar9$	56	49
2	$\bar1$	$\bar9$	9-	7
3	1	$\bar9$	59	61

h	k	l	$\|10F_o\|$	$10F_c$
3	$\bar1$	$\bar9$	10-	8
4	1	$\bar9$	16	-18
4	$\bar1$	$\bar9$	65	85
0	2	$\bar9$	67	56
1	$\bar2$	9	43	-35
1	2	$\bar9$	57	53
1	$\bar2$	$\bar9$	9-	6
2	$\bar2$	9	8-	2
2	2	$\bar9$	38	34
2	$\bar2$	$\bar9$	7-	23
3	2	$\bar9$	13-	13
3	$\bar2$	$\bar9$	6-	-19
4	2	$\bar9$	5-	5
0	3	$\bar9$	74	53
1	$\bar3$	9	19-	16
1	3	$\bar9$	20-	25
2	$\bar3$	9	59	-61
2	3	$\bar9$	110	101
3	$\bar3$	9	19	47
3	3	$\bar9$	12-	2
4	3	$\bar9$	36	42
0	4	$\bar9$	36-	27
1	$\bar4$	9	123	118
1	4	$\bar9$	20-	22
2	$\bar4$	9	39	36
2	4	$\bar9$	86	84
3	$\bar4$	9	9-	-26
3	4	$\bar9$	52	48
4	4	$\bar9$	58	72
0	5	$\bar9$	36-	-26
1	$\bar5$	9	49	43
1	5	$\bar9$	20-	12
2	$\bar5$	9	120	126
2	5	$\bar9$	12-	9
3	$\bar5$	9	9-	-16
3	5	$\bar9$	69	73
0	6	$\bar9$	91	78
1	$\bar6$	9	19-	-15
1	6	$\bar9$	65	58
2	$\bar6$	9	65	62
2	6	$\bar9$	16	-15
3	$\bar6$	9	23	46
3	6	$\bar9$	49	47
0	7	$\bar9$	106	88
1	$\bar7$	9	17-	21
1	7	$\bar9$	31	22
2	$\bar7$	9	49	-54
2	7	$\bar9$	8-	7
3	$\bar7$	9	21	39
0	8	$\bar9$	38	28
1	$\bar8$	9	84	78
1	8	$\bar9$	42	38
2	$\bar8$	9	32	-31
3	$\bar8$	9	7-	2
0	9	$\bar9$	21-	-11
1	$\bar9$	9	43	42
2	$\bar9$	9	55	56
1	0	$\overline{10}$	72	81
2	0	$\overline{10}$	82	-85
0	1	$\overline{10}$	78	67
1	1	$\overline{10}$	13-	4
2	1	$\overline{10}$	50	-53
3	1	$\overline{10}$	102	112
0	2	$\overline{10}$	25-	11
1	$\bar2$	10	50	43
1	2	$\overline{10}$	19	-18
2	2	$\overline{10}$	122	116
3	2	$\overline{10}$	45	46
0	3	$\overline{10}$	29-	-2
1	$\bar3$	10	72	66
1	3	$\overline{10}$	58	50
2	$\bar3$	10	4-	35
2	3	$\overline{10}$	139	140
3	3	$\overline{10}$	51	-59
0	4	$\overline{10}$	30-	-5
1	$\bar4$	10	15-	-4
1	4	$\overline{10}$	59	64
2	$\bar4$	10	26	25
2	4	$\overline{10}$	9-	5
3	4	$\overline{10}$	19	-23
0	5	$\overline{10}$	106	85
1	$\bar5$	10	15-	-10
1	5	$\overline{10}$	60	57
2	$\bar5$	10	21	19
2	5	$\overline{10}$	52	-48
3	5	$\overline{10}$	86	83
0	6	$\overline{10}$	91	73
1	$\bar6$	10	45	36
1	6	$\overline{10}$	15-	-13
2	$\bar6$	10	21	20
2	6	$\overline{10}$	15	15
0	7	$\overline{10}$	25-	-12
1	$\bar7$	10	57	49
1	7	$\overline{10}$	12-	-7
2	$\bar7$	10	7-	5
0	8	$\overline{10}$	19-	-14
1	$\bar8$	10	39	38
0	3	$\overline{11}$	9-	-32
1	3	$\overline{11}$	27	-32
0	4	$\overline{11}$	16-	-22
1	4	$\overline{11}$	80	75
0	5	$\overline{11}$	56	55
1	5	$\overline{11}$	63	62

and only relatively small distortions are observed for the angles:

N(1)–Ni–S(1) 87·3(0·5)°
S(1) –Ni–S(2′) 98·6(0·2)
N(1)–Ni–S(2′) 88·0(0·5)

The distances Ni–S for the two kinds of coordinated sulphur atom are not significantly different [$t_0=(l_1-l_2)\times(\sigma_1^2+\sigma_2^2)^{-\frac{1}{2}}=2{\cdot}3$, significance test of Cruickshank & Robertson, 1953]. All these Ni–S distances are lower than the value (2·62 Å) found by Porai-Koshits (1959) in $Ni(NH_3)_3(NCS)_2$, but are significantly greater than either the sum of Pauling's covalent radii (2·43 Å) or the value (2·46 Å) found in $Ni[SC(NH_2)_2]_4Cl_2$ by Lopez-Castro & Truter (1963). As already observed (Cavalca, Nardelli & Fava, 1962; Lopez-Castro & Truter, 1963) these distances are much longer than those present in 4-coordinated diamagnetic nickel complexes which lie in the range 2·1–2·3 Å, *e.g.* 2·16 Å in bisthiosemicarbazidato-nickel (Cavalca, Nardelli & Fava, 1962), 2·16 Å in α-*trans*-bisthiosemicarbazide-nickel sulphate (Grønbæk & Rasmussen, 1962), 2·15 and 2·16 Å in the *cis* and *trans* configurations respectively of β-bisthiosemicarbazide-nickel sulphate (Grønbæk, 1963), 2·23 and 2·24 Å in nickel xanthate (Franzini, 1963), 2·21 and 2·20 Å in α-nickel bis(*N*,*N*-diethyldithiocarbamate) (Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965), 2·20 and 2·21 Å in nickel bis(*N*,*N*-propyldithiocarbamate) (Peyronel & Pignedoli, 1966).

The Ni–N distances in both thiourea and thioimidazolidine compounds are amongst the lowest observed in octahedral nickel(II) complexes. This is seen from the values quoted in Table 4, in which distances for planar and tetrahedral complexes are also reported, for comparison.

It seems remarkable that in the octahedra of both thiourea and thioimidazolidine-nickel complexes, discussed in the present paper, the nitrogen atoms are *trans* with respect to the plane of the sulphur atoms; the octahedra are deformed to form flattened, nearly tetragonal bipyramids. The same occurs in bisthioacetamide-nickel(II) thiocyanate, in which the Ni atom is octahedrally surrounded by four S atoms from two thioacetamide molecules and two NCS groups, and by two N atoms from two NCS groups. In this compound too the NCS groups are in a bridging position and the nitrogen atoms are *trans* with respect to the plane of sulphur atoms, but the organic molecules are both on adjacent corners of the coordination polyhedron. The flattened bipyramid, therefore, seems to be the most stable arrangement for Ni^{2+} with the particular ligands involved, and is realized in different ways with different behaviour of NCS, probably in consequence of packing interactions concerning the organic molecules.

Distances and angles in the thioimidazolidine molecule are not significantly different from those found in the cadmium complex and in thioimidazolidine itself (Table 5).

The thioimidazolidine molecule is not strictly planar and the distortion is of a different kind and is much greater than that observed when it is uncomplexed: in this case the S atom is 0·030 Å from the plane of the other atoms (Wheatley, 1953). In the nickel complex the planarity is observed only for the thiourea

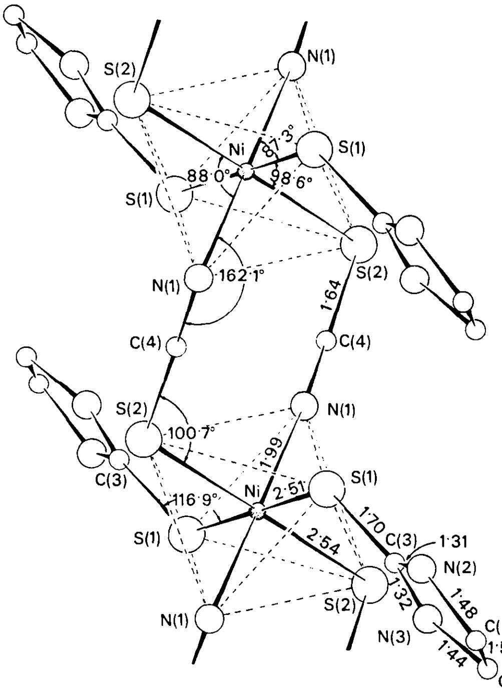


Fig. 1. Clinographic projection of a chain of coordination polyhedra.

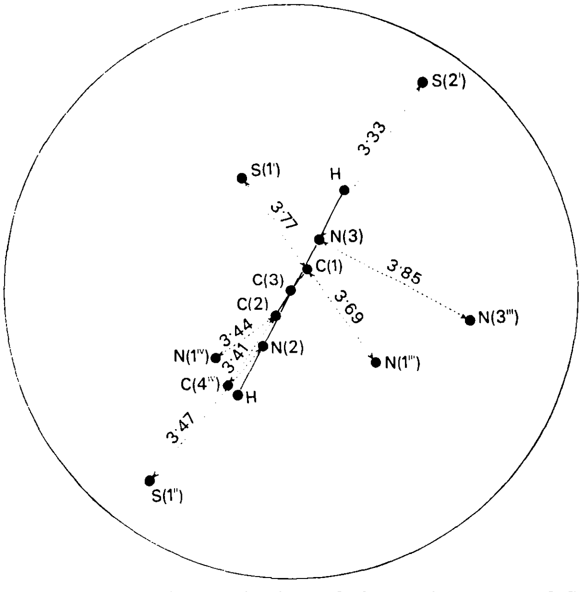


Fig. 2. Stereographic projection of the environment of S(1) viewed along S(1)–C(3) and showing the distortion of the ethylenic part of the molecule. The contacts are indicated with dotted lines; distances are in Å.

Table 4. Ni–N *distances* (Å) *in* Ni(II) *complexes*

Octahedral complexes

Bis-2-thioimidazolidine-Ni thiocyanate	1·99	Present paper
Bisthiourea-Ni thiocyanate	1·99	Nardelli, Fava Gasparri, Giraldi Battistini & Domiano (1966)
Nitritobisethylenediamine-Ni tetrafluoroborate	2·10, 2·12 (en)	Drew, Goodgame, Hitchman & Rogers (1965)
Dinitrito-(*N,N,N′,N′*-tetramethylethylenediamine)Ni	2·09	Drew & Rogers (1965)
Bishistidino-Ni monohydrate	2·09, 2·11	Frazer, Long, Candlin & Harding (1965)
β-Alanine-Ni dihydrate	2·10	Jose, Pant & Biswas (1964)
Bis-*meso*-stilbenediamine-Ni dichloroacetate(blue form)	2·05	Nyburg & Wood (1964)
Trans-bisethylenediamine-Ni dithiocyanate	2·10 (amine), 2·15 (NCS)	Brown & Lingafelter (1963)
Bisethylenediamine-nitrito-Ni perchlorate	2·13, 2·17	Llewellyn & Waters (1962)
Bisethylenediamine-Ni chloride and bromide	2·0	Antsyshkina & Porai-Koshits (1962)
Trisethylenediamine-Ni nitrate	2·12	Swink & Atoji (1960)
Dihydrogenethylenediaminetetra-acetato-aquonickelate	2·08, 2·13	Smith & Hoard (1959)
Triamino-Ni dithiocyanate	2·06 (NCS), 2·07 (NH$_3$)	Porai-Koshits (1959)
(2,2′,2″-Triaminotriethylamine)-Ni dithiocyanate	2·13, 2·17, 2·19, 2·34 (*tren*) 2·02, 2·10 (NCS)	Rasmussen (1959)
Amino-Ni cyanide (hydrated)	2·10 (NH$_3$), 2·11 (NC)	Rayner & Powell (1958)
Tetrapyridine-Ni dithiocyanate	2·03 (py), 2·12 (NCS)	Antsyshkina & Porai-Koshits (1958)
Tetrapyridine-Ni chloride	2·00	Porai-Koshits (1954)

Planar complexes

Dichloro-1,4,8,11-tetra-azacyclotetradecane-Ni	2·05, 2·07	Bosnic, Mason, Pauling, Robertson & Tobe (1965)
Tetraphenylporphine-Ni	1·96	Fleischer, Miller & Webb (1964)
Bis-*meso*-stilbenediamine-Ni dichloroacetate(yellow form)	1·89	Nyburg & Wood (1964)
Bisthiosemicarbazidato-Ni (red form)	1·91	Cavalca, Nardelli & Fava (1962)
Bisthiosemicarbazide-Ni sulphate (*α* form, *trans*)	1·90	Grønbæk & Rasmussen (1962)
Bisthiosemicarbazide-Ni sulphate (*β* form, *cis* and *trans*)	1·94	Grønbæk (1963)
Bismethylethylglyoximato-Ni	1·83, 1·88	Frasson & Panattoni (1960)
Bisdimethylglyoximato-Ni	1·85	Williams, Wohlauer & Rundle (1959)
Bissalicylaldiminato-Ni	1·84	Stewart & Lingafelter (1959)
Bis-(*N*-methylsalicylaldiminato)-Ni	1·90	Frasson, Panattoni & Sacconi (1959)
Bissalicylaldoximato-Ni	1·86	Merritt, Guare & Lessor (1956)
Phthalocyaninato analogue	1·90, 1·98	Speakman (1953)

Tetrahedral complexes

Bis-(*N*-isopropylsalicylaldiminato)-Ni	1·95, 1·99	Fox, Orioli, Lingafelter & Sacconi (1964)

Table 5. *Interatomic distances and angles in the 2-thiomidazolidine molecule and the nickel and cadmium thiocyanate complexes*

	Nietu_2(NCS)$_2$ Present study	Cdetu_2(NCS)$_2$ Cavalca, Nardelli & Fava (1960)	*etu* Wheatley (1953)	
S(1) –C(3)	1·70 (2) Å	1·74 (3) Å	1·708 Å	$\sigma=0{\cdot}01$ Å
C(3)–N(2)	1·31 (2)	1·32 (6)	1·315	
C(3)–N(3)	1·32 (3)	1·30 (6)	1·328	
N(2)–C(2)	1·48 (3)	1·47 (4)	1·480	
N(3)–C(1)	1·44 (3)	1·48 (4)	1·461	
C(1)–C(2)	1·53 (3)	1·57 (7)	1·536	
S(1) –C(3)–N(2)	123·4°(1·5°)	125·9°(2·4°)	123·5°	$\sigma=1{\cdot}5°$
S(1) –C(3)–N(3)	126·1 (1·4)	125·0 (2·3)	126·2	
N(2)–C(3)–N(3)	110·4 (1·7)	109·1 (3·2)	110·2	
C(3)–N(2)–C(2)	111·8 (1·7)	114·2 (3·3)	112·8	
C(3)–N(3)–C(1)	112·6 (1·8)	114·4 (3·2)	112·3	
N(3)–C(1)–C(2)	102·8 (1·9)	101·4 (2·9)	103·0	
N(2)–C(2)–C(1)	101·4 (1·7)	100·9 (3·0)	101·8	

part, the least-squares equation of this part being $0{\cdot}3039x'-0{\cdot}8911y'+0{\cdot}3371z'=0{\cdot}6484$*.

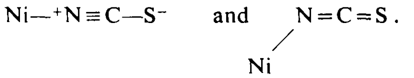
The C(1) and C(2) atoms are out of this plane by −0·09 and +0·08 Å respectively. This distortion can be accounted for by the contacts involving the NH and CH_2 groups, as can be seen from the stereographic projection of Fig. 2, in which the poles of the nearest atoms to a thioimidazolidine molecule are represented. The two NH groups are involved in hydrogen bonding with S atoms: the two distances N(3)···S(2′), 3·33(2) Å and N(2)···S(1″), 3·47(2) Å are consistent with the mean value of 3·40 Å suggested by Wallwork (1962) and fulfil the angular criterion for hydrogen bonding (Donohue, 1952; Fuller, 1959) (S(2′)–N(3)–H, 14·3° and S(1″)–N(2)–H, 13·2°; the hydrogen atoms are in calculated positions). On the other hand the two CH_2 groups show the following van der Waals contacts: C(1)···S(1′), 3·77(3) Å; C(1)···N(1‴), 3·69(3) Å and C(2)···N(1^{iv}), 3·44(3) Å; C(2)···C(4^{iv}), 3·41(3) Å. These are consistent with the sums of the van der Waals radii.

The molecules of thioimidazolidine are tilted with respect to the plane of sulphur atoms surrounding a nickel atom (Fig. 3) and the dihedral angle formed by this plane and that of S(1)C(3)N(2)N(3) is 72·9°, which is near to the corresponding angle (79·8°) in Nitu_2(NCS)$_2$. This is a consequence of the lack of collinearity of the Ni–S(1) and S(1)–C(3) bonds: the angle Ni–S(1)–C(3) is 116·9°(0·6°), which is larger than the tetrahedral value for bonds involving sulphur. The resonance structure with a single S–C bond is most important (~80%), but the packing requirements already quoted can be responsible for the distortion.

Bond distances in NCS and the angle Ni–NCS are not significantly different from those found in Nitu_2(NCS)$_2$:

	Nietu_2(NCS)$_2$	Nitu_2(NCS)$_2$
N(1)–C(4)	1·16(3)	1·169(14) Å
C(4)–S(2)	1·64(2)	1·635(13)
Ni–N(1)–C(4)	162·1(1·7)°	162·2(1·0)°

These N–C distances and Ni–NCS angles fit the curve calculated by Hazell (1963); this is in agreement with a description of the coordinated thiocyanate group in terms of the resonance structures



$$\mathrm{Ni{-}^{+}N{\equiv}C{-}S^{-}} \quad \text{and} \quad \underset{\mathrm{Ni}}{\mathrm{N}}\mathrm{{=}C{=}S}\,.$$

On the contrary, the S–C distance is shorter than that predicted from the curve S–C against Ni–NCS, as calculated by the same author; this fact, which is observed generally, suggests that other configurations, in addition to the one given previously, should be considered.

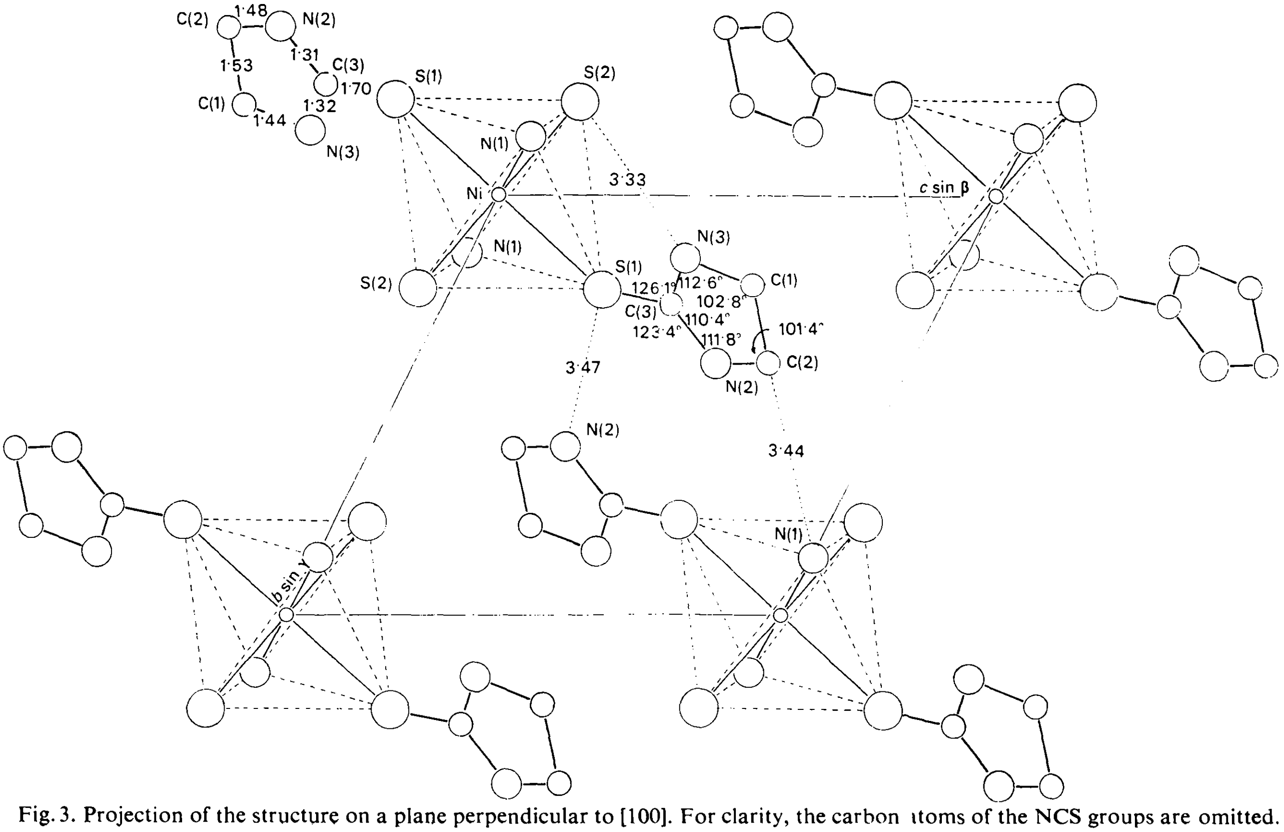


Fig. 3. Projection of the structure on a plane perpendicular to [100]. For clarity, the carbon atoms of the NCS groups are omitted.

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* Transformation matrix from triclinic x,y,z to orthogonal x',y',z' coordinates:

$$\begin{pmatrix} \sin\gamma & 0 & -\sin\alpha\ \cos\beta^* \\ \cos\gamma & 1 & \cos\alpha \\ 0 & 0 & \sin\alpha\ \sin\beta^* \end{pmatrix}.$$

The Ni–SCN, 100·7°(0·7°), angle is near to those generally observed in bridged thiocyanate complexes, *e.g.* 102° in $[Hg(SCN)_4][Cuen_2]$ (Scouloudi, 1953), 104° in AgSCN (Lindqvist, 1957), 109° in $Cdetu_2(NCS)_2$ (Cavalca, Nardelli & Fava, 1960), 110° in $NH_4Ag(SCN)_2$ (Lindqvist & Strandberg, 1957). The lack of collinearity in the NCS group [N(1)–C(4)–S(2) = 178·6°(1·2°)] is not significant.

The other packing distances (Fig. 4) less than 4 Å are given in Table 6.

Infrared spectra

In recent years there has been some interest in correlating the infrared spectra of the NCS group with its behaviour in metal complexes. Therefore, it seemed

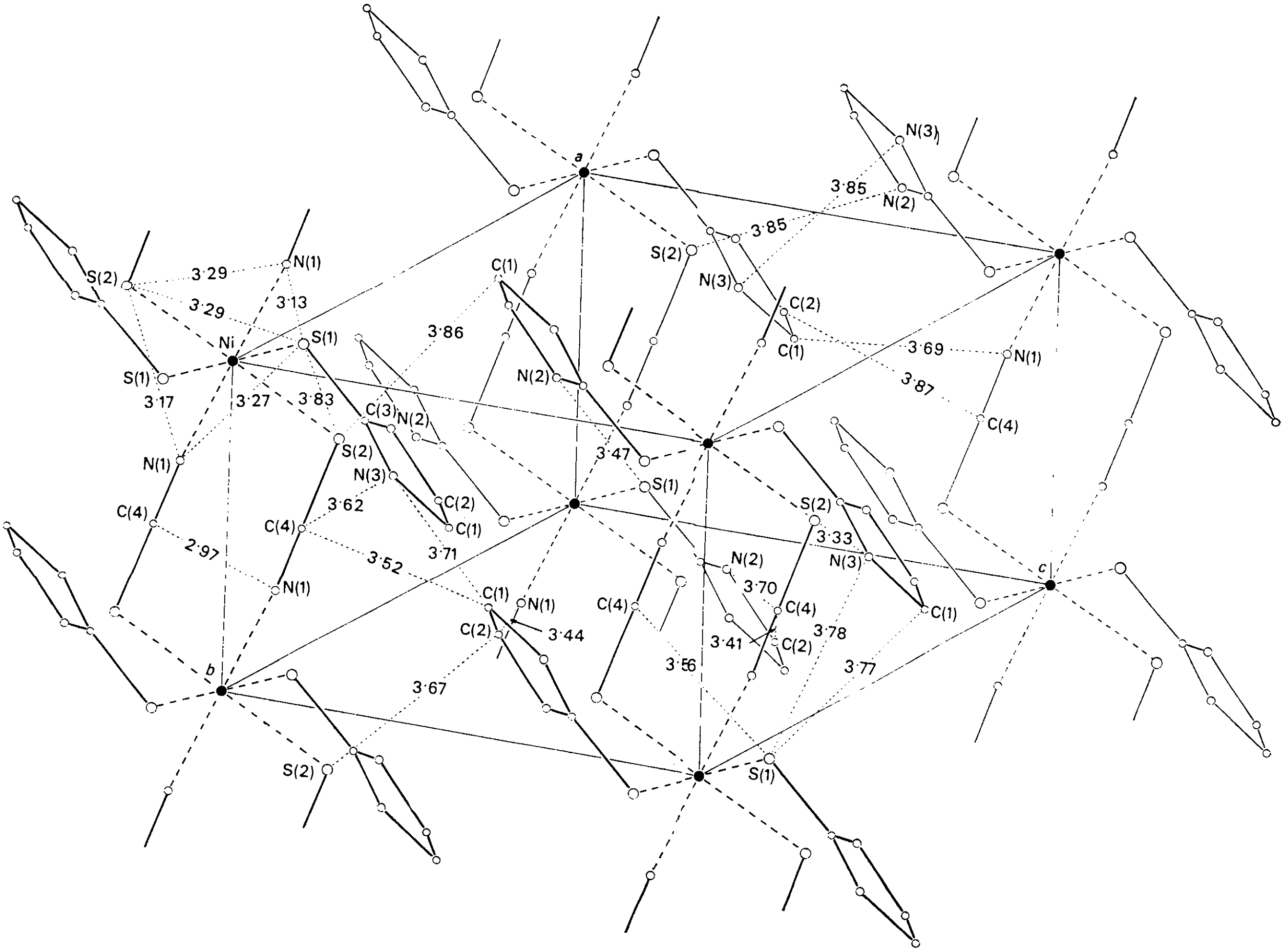

Fig. 4. Packing in the unit cell.

Table 6. *Interatomic distances less than* 4 Å *in* $Ni[SC(NHCH_2)_2]_2(NCS)_2$

′ $x-1, y, z$
″ $1-x, 1-y, 1-z$
‴ $\bar{x}, \bar{y}, 1-z$
iv $x, y+1, z+1$
v $\bar{x}, \bar{y}, \bar{z}$
vi $1-x, \bar{y}, \bar{z}$
vii $x+1, y, z$
viii $\bar{x}, 1-y, 1-z$
ix $1-x, \bar{y}, 1-z$
x $\bar{x}-1, \bar{y}, 1-z$

$N(1)\cdots C(4^{vi})$	2·97 (3)	$S(2)\cdots C(2^{ix})$	3·67 (3)	$S(2)\cdots C(1''')$	3·86 (3)
$S(1)\cdots N(1)$	3·13 (2)	$N(2)\cdots C(4^{iv})$	3·70 (3)	$C(2)\cdots C(4''')$	3·87 (3)
$S(2)\cdots N(1^{vii})$	3·17 (3)	$N(3)\cdots C(1^{x})$	3·71 (4)	$S(2)\cdots C(4^{vi})$	3·92 (4)
$S(1)\cdots N(1^{v})$	3·27 (2)	$N(3)\cdots S(1')$	3·78 (3)	$N(1)\cdots S(2^{iv})$	3·92 (2)
$S(1)\cdots S(2^{vi})$	3·29 (1)	$N(1)\cdots C(3^{v})$	3·81 (2)	$C(2)\cdots N(1''')$	3·93 (3)
$S(2)\cdots N(1^{vi})$	3·29 (3)	$S(1)\cdots S(2')$	3·83 (2)	$N(1)\cdots C(3^{viii})$	3·94 (3)
$C(4)\cdots C(1''')$	3·52 (3)	$N(1)\cdots N(3^{v})$	3·84 (3)	$S(2)\cdots C(3^{vii})$	3·95 (2)
$S(1)\cdots C(4^{vi})$	3·56 (2)	$S(2)\cdots N(2^{ix})$	3·85 (3)	$S(1)\cdots C(2^{viii})$	3·96 (4)
$N(3)\cdots C(4')$	3·62 (3)	$N(3)\cdots N(3''')$	3·85 (3)	$N(2)\cdots N(1^{iv})$	3·98 (3)

worth while to examine the infrared spectra of the compound described in this paper and of those closely related to it. The frequencies corresponding to the symmetric (ν_1), and antisymmetric (ν_3) vibrational modes of NCS group are shown in Table 7, in which the same frequencies for KSCN (Jones, 1958) are also reported for comparison. These spectra were measured with a Perkin–Elmer model 125 spectrophotometer in Nujol suspensions. While the ν_1 band is weak, the ν_3 band is always strong and frequently shows a multiplicity which is not indicated in Table 7 and is of no interest for the following discussion.

Table 7. *Infrared frequencies* (cm^{-1}) *of the thiocyanate group in related metal complexes*

Compound	C–N stretching (NCS antisymmetric) ν_3	C–S stretching (NCS symmetric) ν_1
Mn*etu*$_2$(NCS)$_2$	2103	780
Co*etu*$_2$(NCS)$_2$	2113	787
Ni*etu*$_2$(NCS)$_2$	2128	777
Cd*etu*$_2$(NCS)$_2$	2064	763
Pb*etu*$_2$(NCS)$_2$	2059	742
Ni*tam*$_2$(NCS)$_2$	2113	782
Ni*tu*$_2$(NCS)$_2$	2088	812
KNCS	2053	749

There is a small but sensible increase of the ν_3 frequency in the order Mn < Co < Ni for the isostructural Mn, Co and Ni *etu* complexes which give very similar spectra. In the same order a decrease in ν_1 would be expected, but this is only observed in going from the Co to the Ni complex.

For all the complexes examined, except the Cd and Pb compounds, the rule is verified that the C≡N stretching frequency in a bridging is higher than in a terminal thiocyanate group (Chatt & Duncanson, 1956; Mitchell & Williams, 1960). The values for the ν_1 frequency are intermediate between the ranges observed for thiocyanates (690–720 cm^{-1}) and isothiocyanates (780–860 cm^{-1}) (Pecile, Giacometti & Turco, 1960; Lewis, Nyholm & Smith, 1961). The frequencies for Ni*tam*$_2$(NCS)$_2$ are in quite good agreement with the bridge structure present in that compound.

The two frequencies ν_3 and ν_1 in the isostructural Cd and Pb complexes, in which NCS bridges are present, are rather near to those of KSCN, and this is in agreement with a prevailing ionic character of the NCS group in these two compounds. This is also indicated by the rather high values of the distances M–S and M–N in the Cd compound (Cd–S, 2·73; Cd–N, 2·53 Å).

All the calculations were performed on the Olivetti Elea 6001/S computer of the Centro di Calcolo Elettronico della Università di Parma with the programs of Nardelli, Musatti, Domiano & Andreetti (1964, 1965). This work was done with the financial support of the Consiglio Nazionale delle Ricerche (Roma). The authors are indebted to Dr E. Pauluzzi (SNAM Progetti) who kindly recorded and interpreted the infrared spectra.

References

AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.

ANTSYSHKINA, A. S. & PORAI-KOSHITS, M. A. (1958). *Krystallografija* (Amer. transl.) **3**, 684.

ANTSYSHKINA, A. S. & PORAI-KOSHITS, M. A. (1962). *Doklady Akad. Nauk SSSR*, **143**, 105.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BONAMICO, M., DESSY, G., MARIANI, C., VACIAGO, A., ZAMBONELLI, L. (1965). *Acta Cryst.* **19**, 619.

BOSNICH, B., MASON, R., PAULING, P. J., ROBERTSON, G. B. & TOBE, M. L. (1965). *Chem. Comm.* p. 97.

BROWN, B. W. & LINGAFELTER, F. C. (1963). *Acta Cryst.* **16**, 753.

CAVALCA, L., NARDELLI, M. & FAVA, G. (1960). *Acta Cryst.* **13**, 125.

CAVALCA, L., NARDELLI, M. & FAVA, G. (1962). *Acta Cryst.* **15**, 1139.

CHATT, J. & DUNCANSON, L. A. (1956). *Nature, Lond.* **178**, 997.

CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.

CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 698.

DARLOW, S. F. (1960). *Acta Cryst.* **13**, 683.

DARLOW, S. F. & COCHRAN, W. (1961). *Acta Cryst.* **14**, 1250.

DAWSON, B. (1960). *Acta Cryst.* **13**, 403.

DONOHUE, J. (1952). *J. Phys. Chem.* **56**, 502.

DREW, M. G. B., GOODGAME, D. M. L., HITCHMAN, M. A. & ROGERS, D. (1965). *Chem. Comm.* p. 477.

DREW, M. G. B. & ROGERS, D. (1965). *Chem. Comm.* p. 476.

FLEISCHER, E. B., MILLER, C. K. & WEBB, L. E. (1964). *J. Amer. Chem. Soc.* **86**, 2342.

FOX, M. R., ORIOLI, P. L., LINGAFELTER, E. C. & SACCONI, L. (1964). *Acta Cryst.* **17**, 1159.

FRANZINI, M. (1963). *Z. Kristallogr.* **118**, 393.

FRASSON, E. & PANATTONI, C. (1960). *Acta Cryst.* **13**, 893.

FRASSON, E., PANATTONI, C. & SACCONI, L. (1959). *J. Phys. Chem.* **63**, 1908.

FRAZER, K. A., LONG, H. A., CANDLIN, R., HARDING, M. M. (1965). *Chem. Comm.* p. 344.

FULLER, W. (1959). *J. Phys. Chem.* **63**, 1705.

GRØNBÆK, R. (1963). *Acta Cryst.* **16**, A65, and private communication.

GRØNBÆK, R. & RASMUSSEN, S. E. (1962). *Acta Chem. Scand.* **16**, 2325.

HAZELL, A. C. (1963). *J. Chem. Soc.* p. 5745.

JONES, L. H. (1958). *J. Chem. Phys.* **28**, 1234.

JOSE, P., PANT, L. M. & BISWAS, A. B. (1964). *Acta Cryst.* **17**, 24.

LEWIS, J., NYHOLM, R. S. & SMITH, P. W. (1961). *J. Chem. Soc.* p. 4590.

LINDQVIST, I. (1957). *Acta Cryst.* **10**, 29.

LINDQVIST, I. & STRANDBERG, B. (1957). *Acta Cryst.* **10**, 173.

LLEWELLYN, F. J. & WATERS, J. M. (1962). *J. Chem. Soc.* p. 3845.

LOPEZ-CASTRO, A. & TRUTER, M. R. (1963). *J. Chem. Soc.* p. 1309.

MERRITT, JR., L. L., GUARE, C. & LESSOR, JR., A. E. (1956). *Acta Cryst.* **9**, 253.
MITCHELL, P. C. H. & WILLIAMS, R. J. P. (1960). *J. Chem. Soc.* p. 1912.
NARDELLI, M. & CHIERICI, I. (1958). *Gazz. chim. ital.* **88**, 248.
NARDELLI, M. & FAVA, G. (1960). *Ric. Sci.* **30**, 898.
NARDELLI, M., FAVA GASPARRI, G., GIRALDI BATTISTINI, G. & DOMIANO, P. (1966). *Acta Cryst.* **20**, 349.
NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDREETTI, G. (1964). *Ric. Sci.* **34**, II-A, 711.
NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDREETTI, G. (1965). *Ric. Sci.* **35**, II-A, 469, 477 & 807.
NYBURG, S. C. & WOOD, J. S. (1964). *Inorg. Chem.* **3**, 468.
PECILE, C., GIACOMETTI, G. & TURCO, A. (1960). *Rend. Accad. Lincei,* VIII, **28**, 189.
PEYRONEL, G. & PIGNEDOLI, A. (1966). Private communication.
PHILLIPS, D. C. (1956). *Acta Cryst.* **9**, 819.
PORAI-KOSHITS, M. A. (1954). *Trudy Inst. Krist. Akad. Nauk SSSR,* **10**, 117.
PORAI-KOSHITS, M. A. (1959). *Zh. Neorg. Khim.* **4**, 730.
RASMUSSEN, S. E. (1959). *Acta Chem. Scand.* **13**, 2009.
RAYNER, J. H. & POWELL, H. M. (1958). *J. Amer. Chem. Soc.* **80**, 3412.
SCOULOUDI, H. (1953). *Acta Cryst.* **6**, 651.
SMITH, G. S. & HOARD, J. L. (1959). *J. Amer. Chem. Soc.* **81**, 556.
SPEAKMAN, J. C. (1953). *Acta Cryst.* **6**, 784.
STEWART, J. M. & LINGAFELTER, E. C. (1959). *Acta Cryst.* **12**, 842.
SWINK, L. N. & ATOJI, M. (1960). *Acta Cryst.* **13**, 639.
THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.
WALLWORK, S. C. (1962). *Acta Cryst.* **15**, 758.
WHEATLEY, P. (1953). *Acta Cryst.* **6**, 369.
WILLIAMS, D. E., WOHLAUER, G. & RUNDLE, R. E. (1959). *J. Amer. Chem. Soc.* **81**, 755.

Acta Cryst. (1966). **21**, 919

The Crystal Structure of Zinc Ethylxanthate

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Zinc ethylxanthate, $Zn(SSCOC_2H_5)_2$, is monoclinic with $a = 18{\cdot}278 \pm 0{\cdot}014$, $b = 5{\cdot}700 \pm 0{\cdot}003$, $c = 11{\cdot}381 \pm 0{\cdot}012$ Å; $\beta = 101{\cdot}47° \pm 0{\cdot}10°$, and space group $P2_1/c$. The unit cell contains four formula units. A three-dimensional X-ray structure analysis has shown that each zinc atom is tetrahedrally coordinated to four sulphur atoms belonging to different xanthate groups at distances 2·362, 2·337, 2·364 and 2·369 Å, all approximately within ±0·010 Å. The bonds are directed to the corners of a slightly distorted tetrahedron. Each xanthate group, in turn, bridges two zinc atoms with its dithiocarbonic end in the *y*- or *z*-axis direction to complete a two-dimensional network consisting of the zinc atoms and $-\mathrm{S}-\overset{|}{\mathrm{C}}-\mathrm{S}-$ atom groups. Zn–S–C bond angles are 104·9, 105·1, 105·5 and 114·8°, all ±1·0°. The xanthate group is almost planar. The ethyl group, bonded with the dithiocarbonic carbon atom through an oxygen atom, protrudes on both sides of the network in the ±*x*-axis direction. The methyl ends of the ethyl groups belonging to successive sheets of the two-dimensional network come into van der Waals contact through twofold screw axes.

Introduction

In the technical process of froth flotation, sulphide minerals are separated from the gangue minerals or from each other by their difference in wettability by water. With the galena(PbS)–zincblende(ZnS) system, for instance, their separation is made possible by soaking the powders in aqueous ethylxanthate solution. Galena reacts readily with the solution to develop a hydrophobic property on its surface, while zincblende remains hydrophilic in the same solution. In order to make the zincblende surface sufficiently hydrophobic for the purpose, a pretreatment of its particles with a dilute aqueous solution containing Cu^{2+} ion is necessary before the reaction with xanthate solution. Cu^{2+} ions in the solution activate the zincblende surface, while Zn^{2+} ions do not.

In these reactions it is supposed that a small amount of heavy metal cations, either dissolved from the mineral surfaces or added purposely to the solution, reacts with xanthate anions to produce molecular or crystalline aggregates of the heavy metal xanthate at the mineral surface. The above mentioned behavior of galena and activated zincblende in the xanthate solution suggests that the formation of a molecular or crystalline aggregate of lead and copper xanthates at mineral surfaces is effective for endowing galena and zincblende surfaces respectively with the hydrophobic property, while the formation of similar aggregates of zinc xanthate has no such effect on zincblende surfaces. In order to elucidate these differences from the viewpoint of the molecular and crystalline structure of heavy metal xanthates, it was decided to determine the crystal structure of zinc ethylxanthate, $Zn(SSCOC_2H_5)_2$,