contact dans les autres directions est de 3,47 Å entre un groupe CH benzénique et l'oxygène cétonique de la molécule translatée de la première.

Nous réservons pour une publication ultérieure la comparaison entre l'indigo, l'oxindigo et le thioindigo.

Nous tenons à remercier ici Mademoiselle C. Stora qui dirige le laboratoire de Chimie Cristallographique du C.N.R.S. où ce travail a été entrepris; le Prof. W. Lüttke de l'Université de Freiburg i. Br. qui a mis à notre disposition un échantillon d'oxindigo; l'Institut Européen de Calcul Scientifique patronné par I.B.M.-France (Place Vendôme, Paris) qui nous a gracieusement accordé le temps machine requis pour les calculs effectués sur ordinateur I.B.M. 704.

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The Crystal and Molecular Structure of *bis*-Thiosemicarbazidato-Nickel(II), (Red Crystals)

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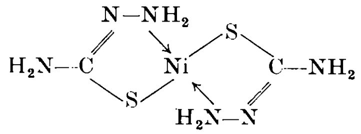
Crystals of red *bis*-thiosemicarbazidato-nickel(II), $Ni(CH_4N_3S)_2$, are monoclinic, $P2_1/c$:

$$a = 7{\cdot}68,\ b = 4{\cdot}32,\ c = 12{\cdot}23\ \text{Å},\ \beta = 93{\cdot}8°,\ Z = 2\ .$$

The structure has been determined by means of three-dimensional Fourier methods and refined by several cycles of Booth's differential synthesis.

The Ni atom coordinates *trans*-planarly two S and two N atoms at the distances: Ni–S = 2·155 ± 0·003, Ni–N = 1·91 ± 0·01 Å. Bond distances indicate the following molecular configuration



The planes of the organic ligands are slightly tilted out of the coordination plane. No Ni–Ni bonding interaction is observed, nor does the Ni atom show any tendency to assume an octahedral coordination.

Introduction

bis-Thiosemicarbazidato-nickel(II), $Ni(CH_4N_3S)_2$, can be obtained as a grey powder by direct mixing of the components in aqueous ammonia solution (Jensen & Rancke-Madsen, 1934) or as small, red-brown crystals by slow action of ammonia gas on the neutral aqueous solution of the components (Nardelli & Boldrini, 1961). The products formed by these two methods have the same chemical formula, but give different X-ray diffraction patterns.

The diamagnetic behaviour of both compounds indicates that the complex molecules are planar. It is probable that in these two forms the same complex molecular entities are present with different packings, as the radial distribution function curves and the colours of their powders are very similar.

A complete X-ray structural analysis was possible only for the red crystals, since crystals of sufficient size for diffraction work could not be obtained from the grey powder.

Experimental

Red crystals of *bis*-thiosemicarbazidato-nickel(II) are very small monoclinic plates showing the three fundamental pinacoids. In polarized light the crystals exhibit pleochroism: observed normal to the plates, the colour is yellow when the electric vector is parallel to the longer edge, [010], and red when perpendicular.

Crystal data were derived from rotating crystal, Weissenberg and precession photographs using [010] as rotation axis; they were improved by powder data (Cu $K\alpha$ radiation monochromatized on a curved quartz plate).

$Ni(CH_4N_3S)_2$, $M = 238{\cdot}94$.
$a = 7{\cdot}68 \pm 0{\cdot}01$, $b = 4{\cdot}32 \pm 0{\cdot}01$, $c = 12{\cdot}23 \pm 0{\cdot}01$ Å, $\beta = 93{\cdot}8 \pm 0{\cdot}1°$.
$V = 404{\cdot}7$ Å^3, $Z = 2$, $D_x = 1{\cdot}96$, $D_o = 1{\cdot}99$ g.cm.$^{-3}$.
$\mu = 79{\cdot}2$ cm.$^{-1}$ (Cu $K\alpha$).
$F(000) = 244$.
Space group: C_{2h}^5–$P2_1/c$ (from systematic absences).

The intensities were determined photometrically on multiple-film integrated and non-integrated equi-inclination Weissenberg photographs (Cu $K\alpha$), taken by rotation around [010]. Discontinuous absorption effects were corrected graphically by Albrecht's (1939) method, the size of the sample being: 0·10 mm. along [100], 0·30 mm. along [010], 0·06 mm. along [001].

Table 1. *Number of observed and possible independent reflections with final R and R′ indices*

	Observed	Possible	R	R'
$h0l$	79	116	9·8%	11·3%
$h1l$	152	231	11·2	14·2
$h2l$	130	208	16·1	20·7
$h3l$	38	169	14·5	30·6
Overall	399	724	12·6	17·0

The numbers of observed and possible independent reflections are given in Table 1. The intensities of only a small number of $h3l$ reflections were measured, as the corresponding photograph was faint in spite of the long exposure used (300 hr. for non-integrated photograph).

The structure amplitudes were derived by the usual formulae, the absolute scale for each layer being established first by Wilson's method, then by correlation with the calculated values.

Structure analysis and refinement

As two molecules are contained in a unit cell, the Ni atom must be located on a symmetry centre. Considering this and the lack of overlapping in the (010) projection, indicated by the short b edge, it was possible to foresee that nearly all the signs of $h0l$ structure factors could be assumed positive. With this assumption, a $\varrho(X, Z)$ projection was calculated which showed all the atoms well resolved. This projection was very similar to the final one; at the end of the refinement only six of the weakest observed $h0l$ structure factors were negative.

For the determination of the y coordinate of the S atom, which dominates the $F(hkl)$ structure factors with $k+l$ odd, a $P_1(U, W)$ first-layer generalized Patterson projection was calculated. The set of coordinates of all atoms was then completed using the cosine, $C_1(X, Z)$, and sine, $S_1(X, Z)$, components of the $\varrho_1(X, Z)$ first-layer generalized projection. At this stage the complete information was available to calculate the three-dimensional distribution of the electron density.

The refinement was accomplished by four cycles of Booth's differential synthesis, two of them with isotropic and two with anisotropic thermal parameters. The refinement was considered at an end when the coordinate shifts were less than one half of the corresponding standard deviations for the light atoms.

Table 3. *Thermal parameters* (Å^2)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	2·42	2·30	2·65	−0·05	−0·14	−0·05
S	2·11	2·23	3·08	−0·14	−0·49	−0·05
N_1	3·64	2·93	3·73	0·26	0·62	0·11
N_2	1·22	1·49	1·57	−0·35	−1·01	0·24
N_3	2·12	2·35	3·58	0·02	−0·46	−0·08
C	1·81	2·21	3·49	0·14	0·19	0·25

The final coordinates with their estimated standard deviations (Cruickshank, 1949) are reported in Table 2. The anisotropic thermal parameters obtained at the end of the refinement by Cruickshank's (1956) method are listed in Table 3. They must be considered only as additional parameters for improving the agreement between the observed and calculated quantities, correlation of the different layers and reflections with $k \geq 4$ being neglected. Observed and calculated structure factors are compared in Table 4, the corresponding R (observed reflections only) and R' values (including

Table 2. *Final atomic coordinates and their e.s.d.'s*

	x/a	y/b	z/c	x' (Å)	y' (Å)	z' (Å)	$\sigma(x)$ (Å)	$\sigma(y)$ (Å) ($\times 10^3$)	$\sigma(z)$ (Å)
Ni	0	0·5000	0·5000	0	2·160	6·115	—	—	—
S	0·2663	0·6587	0·5030	2·041	2·846	6·016	3	5	3
N_1	0·4354	0·9505	0·3362	3·337	4·106	3·890	11	22	10
N_2	0·1409	0·8758	0·3143	1·080	3·784	3·772	10	16	9
N_3	−0·0171	0·7376	0·3679	−0·131	3·186	4·508	11	20	10
C	0·2742	0·8490	0·3775	2·101	3·668	4·477	11	18	11

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

$$\begin{pmatrix} \sin\beta & 0 & 0 \\ 0 & 1 & 0 \\ \cos\beta & 0 & 1 \end{pmatrix}$$

Table 4. *Observed and calculated structure factors*

A minus sign for F_o means 'less than'

l	$\|F_o\|$	F_c
	0 0 1	
2	73	75
4	35	41
6	87	93
8	52	54
10	32	37
12	28	25
14	17	16
	1 0 1	
0	63	60
2	78	76
4	5-	7
6	20	24
8	23	24
10	11	15
12	8-	10
14	6-	3
	$\bar{1}$ 0 1	
2	4-	3
4	47	53
6	34	34
8	37	27
10	23	26
12	8-	6
14	13	14
	2 0 1	
0	16	11
2	28	-14
4	21	-17
6	21	23
8	8-	-1
10	12	-10
12	8-	9
14	6-	0
	$\bar{2}$ 0 1	
2	4-	-1
4	14	-3
6	9	-3
8	7-	6
10	8-	0
12	8-	-2
14	6-	6
	3 0 1	
0	53	53
2	65	64
4	14	17
6	47	42
8	54	53
10	12	10
12	12	16
14	18	20
	$\bar{3}$ 0 1	
2	58	58
4	41	43
6	15	13
8	34	34
10	23	25
12	8-	7
14	6-	9
	4 0 1	
0	76	71
2	57	57
4	58	52
6	40	38
8	50	47
10	24	27
12	10	15
	$\bar{4}$ 0 1	
2	86	82
4	23	27
6	41	43
8	59	57
10	20	19
12	16	16
	5 0 1	
0	21	16
2	8	10
4	11	11
6	8-	3
8	8-	9
10	8-	4
12	5-	-2
	$\bar{5}$ 0 1	
2	14	12
4	8-	6
6	18	21
8	9-	10
10	8-	4
12	7-	10
	6 0 1	
0	8-	5
2	18	-16
4	9	12
6	8-	7
8	8-	-2
10	10	5
	$\bar{6}$ 0 1	
2	17	17
4	8-	-5
6	9-	-2
8	8-	4
10	7-	3
12	5-	2
	7 0 1	
0	48	48
2	19	18
4	20	19
6	37	37
8	20	19
10	12	17
	$\bar{7}$ 0 1	
2	23	27
4	14	15
6	18	23
8	18	16
10	18	15
	8 0 1	
0	27	29
2	28	25
4	18	15
6	19	23
8	11	14
	$\bar{8}$ 0 1	
2	20	18
4	21	21
6	18	18
8	18	17
	9 0 1	
0	6-	0
2	6-	0
4	5-	-4
	$\bar{9}$ 0 1	
2	6-	0
4	6-	5
6	5-	1
	0 1 1	
1	43	50
2	53	-50
3	100	101
4	21	21
5	44	44
6	18	15
7	32	37
8	7-	-2
9	35	38
10	8-	0
11	23	19
12	8-	0
13	19	19
14	7	6
15	13	12
	1 1 1	
0	96	68
1	24	25
2	11	10
3	23	25
4	35	29
5	43	39
6	39	36
7	23	25
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9	14	17
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13	10	11
14	8	8
15	4-	8
	$\bar{1}$ 1 1	
1	67	75
2	50	-50
3	22	33
4	15	-16
5	17	20
6	27	-25
7	38	39
8	26	-19
9	17	17
10	22	-19
11	15	15
12	13	-10
13	17	16
14	6-	-2
15	4-	5
	2 1 1	
0	7	-6
1	18	20
2	29	-22
3	27	25
4	5-	1
5	6-	6
6	6-	1
7	8	8
8	19	-19
9	20	20
10	8-	-3
11	8-	4
12	7-	-1
13	7-	2
14	5-	-6
	$\bar{2}$ 1 1	
1	14	20
2	5	5
3	11	14
4	5-	0
5	13	13
6	6-	3
7	11	14
8	7-	5
9	8-	10
10	8-	-4
11	8-	9
12	7-	1
13	7-	3
14	6-	1
15	4-	3
	3 1 1	
0	44	-35
1	37	36
2	50	-43
3	38	33
4	29	-24
5	56	50
6	7-	-2
7	18	18
8	27	-26
9	21	21
10	20	-20
11	21	25
12	7-	-1
13	8	9
14	4-	-7
	$\bar{3}$ 1 1	
1	64	58
2	24	24
3	18	22
4	11	10
5	29	33
6	31	30
7	36	35
8	27	24
9	11	13
10	8-	4
11	12	13
12	9	9
13	15	12
14	7	8
	4 1 1	
0	6-	3
1	61	55
2	7	6
3	38	34
4	11	7
5	46	39
6	23	19
7	38	35
8	8	10
9	18	18
10	7-	-1
11	14	20
12	8	9
13	14	13
	$\bar{4}$ 1 1	
1	38	38
2	25	-23
3	33	40
4	14	-14
5	47	50
6	13	12
7	20	20
8	11	-7
9	22	22
10	8-	-10
11	25	24
12	7-	3
13	8	10
14	4-	0
	5 1 1	
0	15	15
1	15	17
2	24	20
3	13	9
4	19	17
5	17	15
6	20	14
7	12	15
8	13	14
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10	7-	5
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7	10	11
8	20	-17
9	17	17
10	8-	-8
11	7-	7
12	6-	-5
13	5-	5
	6 1 1	
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1	25	21
2	12	-11
3	8-	8
4	8-	-1
5	8-	1
6	13	-14
7	13	15
8	15	-10
9	6-	5
10	7	-8
11	4-	4
	$\bar{6}$ 1 1	
1	8-	5
2	8-	3
3	8-	7
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5	8-	12
6	8-	9
7	8-	8
8	7-	6
9	7-	7
10	7-	4
11	6-	4
12	4-	0
	7 1 1	
0	17	-17
1	19	18
2	24	-22
3	33	31
4	7-	0
5	19	17
6	7-	-7
7	16	16
8	13	-12
9	16	17
	$\bar{7}$ 1 1	
1	18	17
2	7-	0
3	27	28
4	11	11
5	12	15
6	14	12
7	13	14
8	7-	9
9	13	14
10	5-	4
11	4-	6
	8 1 1	
0	16	12
1	13	13
2	7-	3
3	14	17
4	11	11
5	15	16
6	11	11
7	10	13
	$\bar{8}$ 1 1	
1	21	22
2	12	-11
3	15	18
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5	12	12
6	6-	-5
7	13	14
8	5-	-3
9	4-	9
	9 1 1	
0	5-	7
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2	5-	4
3	5-	5
4	4-	7
	$\bar{9}$ 1 1	
1	5-	8
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3	5-	4
4	5-	-6
5	4-	2
6	4-	-6
	0 2 1	
1	18	27
2	11	16
3	5-	3
4	24	26
5	11	-11
6	17	19
7	8-	10
8	9-	4
9	9-	-1
10	9-	9
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14	6-	4
	1 2 1	
0	8	13
1	19	18
2	44	42
3	49	42
4	47	43
5	31	24
6	23	20
7	22	22
8	19	20
9	10	11
10	16	19
11	10	10
12	9	13
13	15	13
14	7	9
	$\bar{1}$ 2 1	
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2	29	38
3	43	-52
4	43	47
5	24	-19
6	15	16
7	16	-15
8	13	14
9	25	-21
10	21	20
11	12	-7
12	13	12
13	14	-11
14	6-	6
	2 2 1	
0	44	44
1	18	-14
2	42	40
3	8	-8
4	63	47
5	14	-13
6	38	33
7	9-	2
8	16	20
9	9-	-5
10	18	23
11	15	-14
12	15	18
13	7-	1
	$\bar{2}$ 2 1	
1	5-	1
2	41	44
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4	33	39
5	16	14
6	39	37
7	9-	2
8	26	24
9	9-	-3
10	19	18
11	9-	0
12	20	17
13	7-	-2
14	9	11
	3 2 1	
0	10	12
1	40	-35
2	45	37
3	24	-14
4	32	26
5	36	-26
6	10	11
7	33	-24
8	9-	13
9	9-	-2
10	9-	13
11	15	-14
12	7-	9
13	11	-9
	$\bar{3}$ 2 1	
1	15	17
2	16	15
3	27	22
4	37	38
5	33	33
6	20	20
7	9-	8
8	9-	8
9	17	12
10	16	15
11	19	13
12	14	12
13	7-	6
14	4-	6
	4 2 1	
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1	8-	5
2	13	13
3	20	12
4	30	24
5	22	18
6	9-	9
7	9-	-1
8	9-	3
9	9-	9
10	8-	11
11	7-	9
12	6-	8
	$\bar{4}$ 2 1	
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3	8-	2
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11	6-	10
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7	9-	-6
8	9-	10
9	9-	-8
10	10	12
11	13	-13
	6 2 1	
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6	13	13
7	8-	-5
8	13	14
9	7-	-13
10	13	16
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3	14	13
4	22	23
5	10	7
6	19	18
7	10	7
8	17	15
9	8-	1
10	10	10
11	5-	1
	7 2 1	
0	9	8
1	9-	-1
2	9	13
3	9	-11
4	8	11
5	8-	-14
6	7-	5
7	7-	-3
8	5-	4
	$\bar{7}$ 2 1	
1	21	18
2	9-	5
3	15	11
4	13	12
5	9-	5
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7	12	10
8	7-	3
9	6-	4
10	4-	4
	8 2 1	
0	8-	3
1	8-	7
2	7	9
3	9	14
4	6-	9
5	6-	6
6	4-	3
	$\bar{8}$ 2 1	
1	8-	-2
2	8-	6
3	9	-13
4	7	10
5	7-	-6
6	6-	5
7	5-	-3
	9 2 1	
0	7	12
1	4-	2
	$\bar{9}$ 2 1	
1	5-	-5
2	7	9
3	4-	-10
	0 3 1	
1	5-	3
2	7-	-4
3	8-	5
4	9-	9
5	11-	0
6	12-	-6
7	12-	2
8	13-	-1
9	13-	3
10	12-	7
11	11-	2
12	9-	-3
13	6-	3
	1 3 1	
0	6	11
1	28	36
2	8-	8
3	23	24
4	10-	-2
5	25	26
6	12-	-1
7	18	19
8	13-	3
9	13-	13
10	12-	6
11	11-	19
12	9-	-2
	$\bar{1}$ 3 1	
1	14	20
2	8-	10
3	14	16
4	10-	-1
5	31	29
6	17	-15
7	20	16
8	13-	3
9	13	10
10	12-	0
11	11-	9
12	8	-7
13	6-	7
	2 3 1	
0	8-	2
1	43	45
2	9-	2
3	55	49
4	11-	0
5	37	37
6	12-	-5
7	28	34
8	13-	-5
9	12-	21
10	12-	5
11	10-	20
12	8-	-2
	$\bar{2}$ 3 1	
1	26	32
2	9	9
3	48	54
4	11-	1
5	44	43
6	12-	-6
7	23	22
8	13-	2
9	30	27
10	12-	1
11	22	20
12	9-	1
	3 3 1	
0	11-	5
1	11-	10
2	11-	3
3	12-	11
4	12-	-12
5	12-	9
6	13-	2
7	13-	13
8	12-	-2
9	12-	5
10	11-	-3
11	9-	2
	$\bar{3}$ 3 1	
1	15	18
2	14	17
3	17	21
4	12-	-1
5	12-	6
6	13-	-5
7	13-	12
8	13-	7
9	15	14
10	11-	2
11	10-	6
12	8-	0
	4 3 1	
0	12-	-1
1	12-	4
2	12-	12
3	13-	6
4	13-	-5
5	13-	-8
6	13-	-2
7	12-	1
8	12-	7
9	11-	6
10	9-	0
11	6-	-3
	$\bar{4}$ 3 1	
1	12-	-2
2	12-	3
3	12-	-1
4	13-	-6
5	13-	-1
6	13-	2
7	13-	4
8	12-	-3
9	12-	1
10	10-	-2
11	8-	-1
	5 3 1	
0	13-	4
1	18	18
2	13-	8
3	20	32
4	13-	-3
5	13-	24
6	12-	-3
7	11-	11
8	10-	6
9	8-	20
	$\bar{5}$ 3 1	
1	22	23
2	13-	2
3	24	22
4	13-	2
5	19	19
6	13-	-4
7	22	19
8	11-	-5
9	10-	8
10	8-	3
	6 3 1	
0	12-	-5
1	13	21
2	12-	4
3	12-	22
4	12-	-2
5	11-	27
6	10-	-9
7	9-	16
8	7-	4
	$\bar{6}$ 3 1	
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2	12-	3
3	26	23
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7	19	16
8	9-	-1
9	7-	11
	7 3 1	
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1	11-	4
2	10-	-4
3	10-	-2
4	9-	1
5	8-	4
6	6-	-4
	$\bar{7}$ 3 1	
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2	11-	-1
3	11-	2
4	10-	6
5	9-	3
6	8-	-2
7	7-	3
	8 3 1	
0	7-	6
1	7-	8
2	6-	1
	$\bar{8}$ 3 1	
1	7-	-1
2	7-	1
3	6-	-2

Table 5. *Atomic peak heights* (e.Å^{-3}) *and curvatures* (e.Å^{-5})

		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{hk}	A_{hl}	A_{kl}
Ni	obs.	56·10	564·1	343·8	519·2	−10·5	17·1	−4·3
	calc.	57·09	571·8	350·3	526·4	−6·3	14·0	−3·3
S	obs.	34·00	345·1	209·0	321·0	−4·6	3·3	7·2
	calc.	31·98	329·6	200·2	305·8	−2·0	0·1	6·2
N_1	obs.	9·92	93·6	45·2	97·8	−3·2	6·8	0·5
	calc.	9·23	87·9	45·1	92·1	−4·0	7·9	−1·1
N_2	obs.	11·37	110·2	62·7	101·4	0·2	3·2	1·3
	calc.	11·65	113·7	64·4	102·9	1·1	−1·1	−0·1
N_3	obs.	10·73	94·9	49·0	94·0	3·9	−10·7	−1·2
	calc.	9·56	87·3	44·7	85·7	2·6	−8·2	−2·1
C	obs.	9·88	97·2	54·7	88·2	1·6	5·2	−5·4
	calc.	9·15	91·0	50·5	80·2	1·7	3·2	−6·9

$F_o = \frac{1}{2}F_{\text{min.}}$ when $F_c > F_{\text{min.}}$ for unobserved reflections) are shown in Table 1. The e.s.d.'s of the electron density and of its first derivatives are:

$$\sigma(\varrho) = 0{\cdot}39 \text{ e.Å}^{-3};$$
$$\sigma(A_h) = 1{\cdot}06, \quad \sigma(A_k) = 0{\cdot}99, \quad \sigma(A_l) = 0{\cdot}96 \text{ e.Å}^{-4}.$$

The comparison between observed and calculated peak heights and curvatures is given in Table 5.

The atomic scattering factors used were those of Thomas & Umeda (1957) for Ni^{2+}, of Dawson (1960) for S and of Berghuis *et al.* (1955) for O, N and C.

The calculations were performed on an IBM 650 computer using the programmes of Brown, Lingafelter, Stewart & Jensen (1959) for structure factors and Fourier syntheses, and those of Shiono (1957, 1959) for differential synthesis and refinement of thermal parameters.

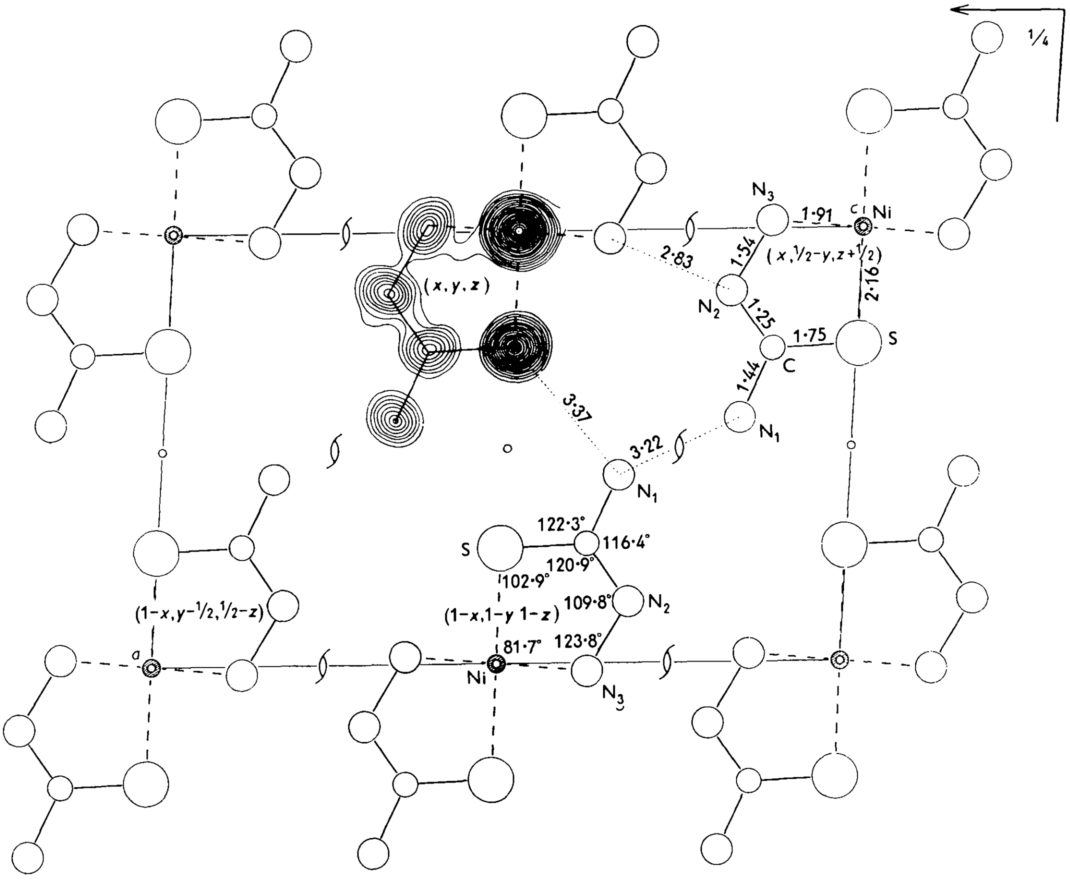


Fig. 1. Projection of the structure on (010). The electron-density contours are from the map calculated with all the signs positive. First line at 3 e.Å^{-2}, 1 e.Å^{-2} intervals for light atoms, arbitrary for Ni and S.

Discussion

Fig. 1 shows the projection of the structure on (010). Each complex molecule is formed by two thiosemicarbazide molecules planarly coordinated by a Ni atom. This could also be inferred from the diamagnetic behaviour ($\chi_M = -79.10^{-6}$ c.g.s.e.m.u.mol.$^{-1}$) and from the crystal data. The coordination occurs in a *trans* form through the sulphur and the hydrazinic nitrogen. Bond distances and angles with their e.s.d. (Ahmed & Cruickshank, 1953; Darlow, 1960) are shown in Table 6.

The Ni–S distance is considerably shorter than the sum of the covalent radii (2·25 Å, Pauling, 1945) but is fairly close to the value (2·18 Å) found in NiS (millerite) by Kolkmeijer & Moesveld (1931). The distances Ni–S in *tetra*-thiourea-nickel(II) chloride (2·45 Å, Cavalca, Nardelli & Braibanti, 1956) and in *bis*-thiourea-nickel(II) thiocyanate (2·51 and 2·57 Å, Nardelli, Braibanti & Fava, 1957) are much longer, but the difference must be related to the different nature of these bonds.

Table 6. *Bond lengths and angles*

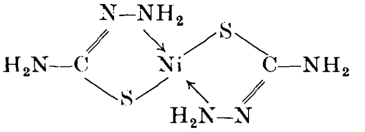
Ni–S	2·155 ± 0·003* Å	N_3–Ni–S	81·7 ± 0·4°
Ni–N_3	1·911 ± 0·014	Ni–S–C	102·9 ± 0·4
S–C	1·746 ± 0·013	S–C–N_2	120·9 ± 1·0
C–N_1	1·436 ± 0·017	C–N_2–N_3	109·8 ± 1·0
C–N_2	1·247 ± 0·015	N_2–N_3–Ni	123·8 ± 0·8
N_2–N_3	1·537 ± 0·017	S–C–N_1	122·3 ± 0·9
		N_2–C–N_1	116·4 ± 1·1

* The e.s.d.'s for the bond lengths do not include the effects of errors in cell parameters. If these effects are accounted for, using the formula of Darlow & Cochran (1961), the starred value must be encreased by 0·001 Å.

The Ni–N_3 distance is a little longer than those reported for other square Ni(II)-complexes: 1·83 Å in phthalocyaninato (Robertson & Woodward, 1937); 1·90 and 1·98 Å in phthalocyaninato analogue (Speakman, 1953); 1·86 Å in *bis*-salicylaldoximato (Merritt, Guare & Lessor, 1956); 1·85 Å in *bis*-dimethylglyoximato (Williams, Wohlauer & Rundle, 1959); 1·84 Å in *bis*-salicylaldiminato (Stewart & Lingafelter, 1959); 1·84 Å in etioporphyrinato (Crute, 1959); 1·90 Å in *bis*-N-methylsalicylaldiminato (Frasson, Panattoni & Sacconi, 1959); 1·88 and 1·83 Å in *bis*-methylethylglyoximato (Frasson & Panattoni, 1960).

The angle on Ni in the chelate ring is close to that found in *bis*-dimethylglyoximato-nickel (83·0°) and in *bis*-methylethylglyoximato-nickel (82°).

The bond distances in the organic molecule indicate a nearly complete localization of a double bond between C and N_2, so the complex can be formulated in the following way:



This was suggested by Jensen (1934) for the grey powder phase, supporting the hypothesis that the difference between red crystals and grey powder concerns only the molecular packing (Nardelli & Boldrini, 1961). The distances C–S and C–N_1 show only a little double-bond character. The N_2–N_3 distance is remarkably longer than that usually accepted (1·48 Å) for the N(sp^2)–N(sp^2) single bond. The cause of this difference may be that, according to the above formula, N_3 is in a sp^3 state.

The angles in the organic ligands are not very different from those found in *mono*-thiosemicarbazide-zinc chloride (Cavalca, Nardelli & Branchi, 1960), except that at N_2, which decreases from 133 to 110°. Unfortunately information on the structure of thiosemicarbazide itself is lacking, but if the angle on N_2 is assumed to be the theoretical sp^2 one the variation observed in the Zn- and in the Ni-complex can be explained by packing considerations. The tendency of the angle on Zn to assume the tetrahedral value

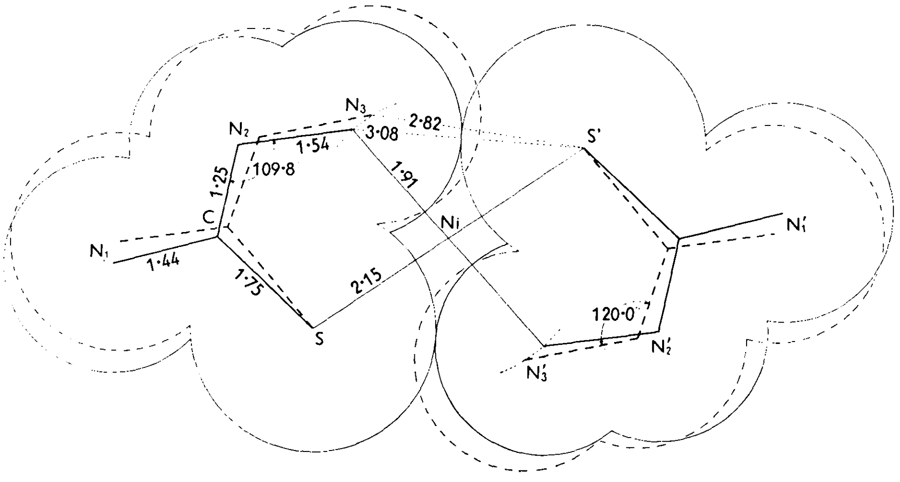


Fig. 2. Deformation of the CN_2N_3 angle caused by the coordination. The molecules supposed undeformed are dotted.

tends to increase it. For the Ni-complex, if it is assumed that no bonding interaction occurs between N_3 and S′ of two adjacent thiosemicarbazide molecules, the angle on N_2 must decrease to maintain the Ni–N_3 and Ni–S distances at the values found and the N_3–S′ contact (3·08 Å) consistent with the sum of the Van der Waals radii ($r_S = 1{\cdot}60$, $r_N = 1{\cdot}5$ Å) (Fig. 2).

The analysis of the planarity of the thiosemicarbazide molecule, shown in Table 7, indicates that the N_1 atom is a little out of the plane of the other atoms, but the distance has little statistical significance. The dihedral angle SCN_1–SCN_2N_3 is 174·8°; this lack of planarity, if real, can be considered as a packing distortion.

Table 7. *Analysis of the planarity of the thiosemicarbazide molecule*

Equation of the plane referred to orthogonal axes:
$m_1x' + m_2y' + m_3z' = d$

Best plane* through	$SN_1N_2N_3C$	SN_2N_3C
m_1	0·1609	0·1792
m_2	−0·8838	−0·8756
m_3	−0·4393	−0·4485
d	−4·8300	−4·8248

Atom	$\sigma_\perp$† (Å)	Δ (Å)	$\Delta/\sigma_\perp$	Δ (Å)	$\Delta/\sigma_\perp$
S	0·004	0	0	0·001	0·25
N_1	0·020	0·029	1·45	0·083	(4·15)
N_2	0·015	0·003	0·20	0·014	0·93
N_3	0·019	0·012	0·63	−0·011	−0·58
C	0·017	−0·040	−2·35	−0·018	−1·06
$\Sigma(\Delta/\sigma_\perp)^2$			8·06		2·39
$\chi^2_{95\%}$			5·99		3·84

* Least squares planes calculated following Schoemaker *et al.* (1959) using a diagonal weight matrix.

† $\sigma_\perp = \{m_1^2\sigma^2(x) + m_2^2\sigma^2(y) + m_3^2\sigma^2(z)\}^{1/2}$.

The whole complex molecule is not planar, as the ligands are slightly tilted with respect to the plane of coordination; the distance of the Ni atom from the plane SCN_2N_3 is 0·19 Å and to this corresponds a dihedral angle NiN_3S–SCN_2N_3 of 172·6°. This distortion is much smaller than that observed in phthalocyaninato–nickel analogue (Speakman, 1953) in which the *iso*-indole residues are tilted out of the coordination plane by 25°.

There is no indication of Ni–Ni bonding as there is in the *bis*-dimethylglyoximato–nickel crystals (Godycki & Rundle, 1953), nor can the coordination around Ni be considered octahedral, as the nearest atom to Ni, outside the bonded S and N_3, is $N_3(x, y-1, z)$ at 3·67 Å, which is much too far to be considered bonded.

The shortest packing distances are listed in Table 8.

Table 8. *Packing distances*†

Ni–$N_3(x, y-1, z)$	3·667 ± 0·019* Å
S–S $(1-x, 1-y, 1-z)$	3·848 ± 0·007*
S–$N_1(1-x, 2-y, 1-z)$	3·372 ± 0·015
S–$N_1(1-x, 1-y, 1-z)$	3·930 ± 0·017*
S–$N_3(x, 1-y, 1-z)$	3·080 ± 0·015
S–$N_3(\bar{x}, 2-y, 1-z)$	3·655 ± 0·016*
S–$N_2(x, \frac{3}{2}-y, \frac{1}{2}+z)$	3·992 ± 0·010
N_3–$N_3(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$	3·627 ± 0·029
N_2–$N_3(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$	2·834 ± 0·018
N_2–$N_3(x, y-\frac{1}{2}, \frac{1}{2}-z)$	3·632 ± 0·021*
N_2–$N_2(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$	3·372 ± 0·025
N_1–$N_1(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3·221 ± 0·033

† When the coordinates are not indicated the atom is at x, y, z.

* See remark for starred value in Table 6.

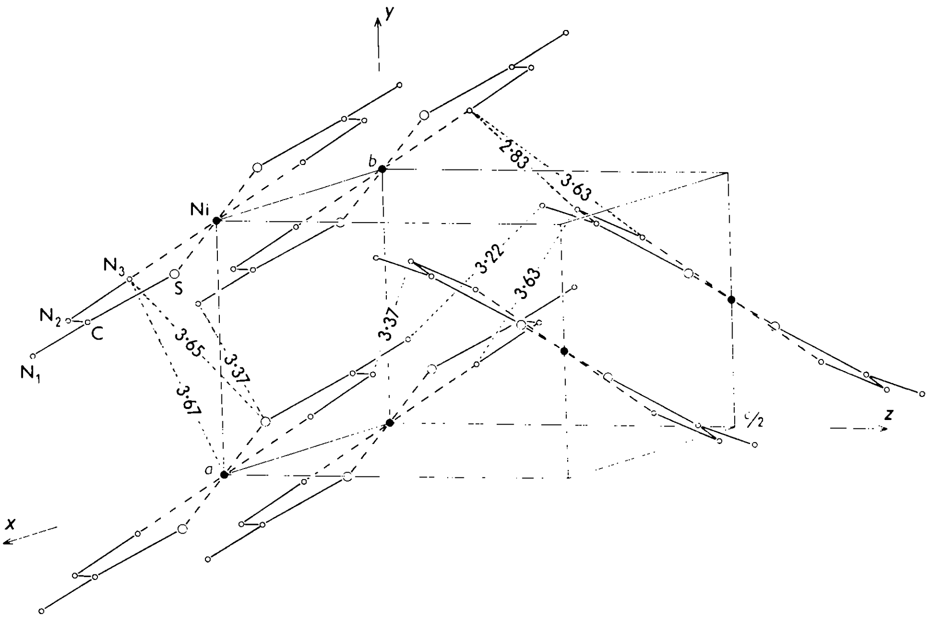


Fig. 3. Clinographic view of the packing of the complex molecules.

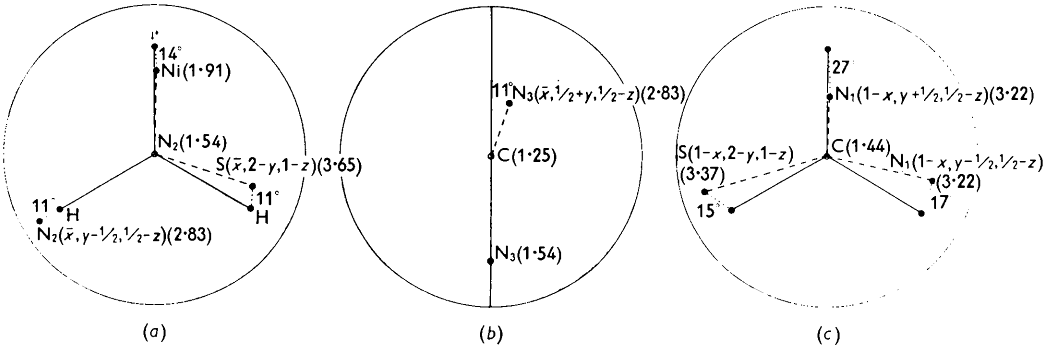


Fig. 4. Stereographic projections of the environments of: (*a*) N_3, (*b*) N_2, (*c*) N_1.

Fig. 3 shows diagrammatically the relative positions of the complex molecules in half a unit cell. The packing is determined chiefly by the N_2–$N_3(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z) = 2{\cdot}83$ Å contact, which can be interpreted as a hydrogen bond; this links together the complex molecules with their Ni atoms lying in planes of $x = \text{const}$. The shortest distance between molecules belonging to two of these adjacent planes is $N_1 - N_1(1-x, \frac{1}{2}+y, \frac{1}{2}-z) = 3{\cdot}22$ Å.

No attempt was made to locate directly the H atoms. Nevertheless, their probable distribution around the N atoms was considered in order to confirm the formula proposed on the basis of observed bond distances. Fig. 4(*a*), which shows the environment of N_3, indicates that this atom is surrounded tetrahedrally by Ni, $S(\bar{x}, 2-y, 1-z)$, N_2, $N_2(\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z)$, so it is in favourable condition to direct the lone pair towards Ni and two H's towards $N_2(\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z)$ (2·83 Å) and $S(\bar{x}, 2-y, 1-z)$ (3·65 Å). The N_2 atom can act as a proton acceptor in hydrogen bonding, the N_3 donor not being far (0·55 Å) from the plane of the organic molecule (Fig. 4(*b*)). The angle formed by N_2–$N_3(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$ and the SCN_2N_3 plane is 11·3°. A tetrahedral environment can be considered for N_1 as well, but there are some differences between the calculated and theoretical angles (Fig. 4(*c*)).

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