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The Crystal Structure of *trans*-Bis(ethylenediamine)-Bis(isothiocyanato)nickel(II)

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The crystal structure of $Ni(en)_2(NCS)_2$ has been determined by two-dimensional projections. The compound is monoclinic with space group $P2_1/a$ and cell dimensions $a_0 = 10{\cdot}28$, $b_0 = 8{\cdot}26$, $c_0 = 8{\cdot}88$ Å, and $\beta = 121°3'$. The intensities were obtained from uni-directionally integrated Weissenberg photographs about the three axes, with 40 of the 259 non-extinct reflections too weak to be recorded. The structure was first refined in the projection on (010) to $R = 0{\cdot}10$; the three projections were then refined to an overall R of 0·11 using an overall isotropic temperature factor coefficient of 3·25 $Å^2$.

The arrangement of the ligands about the nickel atom has been shown to be a nearly regular octahedral configuration with nickel-nitrogen distances of 2·10 Å to the *en* molecule and 2·15 Å to the linear NCS group. The *en* molecule has the 'gauche' form with the carbon atoms symmetrically arranged 0·34 Å from the N–Ni–N plane. The measured Ni–NCS valence angle is 140° with N–C and C–S distances of 1·20 and 1·64 Å.

1. Introduction

trans-Bis(ethylenediamine)-bis(isothiocyanato)nickel (II) was first prepared by Werner (1899) as a red-violet precipitate by a metathesis of bis(ethylenediamine)-nickel(II) bromide and potassium thiocyanate. The blue-violet six-sided plates and rose-violet needles obtained from a water recrystallization yielded the identical composition, $Ni(en)_2(NCS)_2.H_2O$. This isomerism was later investigated (Grossman & Schuck, 1906), and, in contradiction to Werner's analysis, the compound was found to be anhydrous. A more recent investigation (Hieber & Levy, 1933) could not confirm the isomerism reported by Werner. Hieber & Levy found the blue form to be $Ni(en)_2(NCS)_2$, and the rose-violet form $Ni(en)_3(NCS)_2$.

The material was observed to be paramagnetic (Rosenbohm, 1919), which led Pauling (1960*a*) to remark that the four atoms attached to nickel are presumably arranged tetrahedrally, but that this has not yet been shown by X-ray examination or by the synthesis of isomers.

Inasmuch as the paramagnetic nickel could correspond to a tetrahedral configuration of $Ni(en)^{2+}$ with unattached thiocyanate ions, or an octahedral configuration with thiocyanate bonded to the nickel, a structure determination was initiated to determine the actual configuration about the nickel.

Preliminary X-ray studies have been made on this compound by Fogle (1954), who found the blue-violet plates to be monoclinic with a probable space group of $P2_1/c(C^5_{2h})$ and parameters of

$$a = 8{\cdot}84,\ b = 8{\cdot}20,\ c = 10{\cdot}24\ \text{Å},$$
$$\beta = 121°\ 4',\ Z = 2,$$

from which the molecule must be centrosymmetric with the nickel atom at a symmetry center. These dimensions correspond to an axial ratio of 1·0780:1:1·2487, which, after suitable transformation of axes to a base-centered lattice, give 1·2448:1:1·8524 and β = 94° 12′ in agreement with the ratio of 1·2371:1:1·8304 and $\beta = 94°$ 14′ reported by Grossman & Schuck (1906).

2. Experimental

Barium thiocyanate was prepared from barium hydroxide and ammonium thiocyanate by the method of Herstein (1950). Nickel thiocyanate was then prepared by the metathesis of nickel sulfate with the barium thiocyanate. Finally, the *trans*-bis(ethylenediamine)-bis(isothiocyanato)nickel(II) was prepared by the addition of a stoichiometric amount of ethylenediamine to an aqueous solution of nickel thiocyanate. An initial red-violet precipitate was redissolved by warming the solution slightly. Evaporation at room temperature yielded only blue-violet six-sided monoclinic plates on {100} on which were also observed {011}, {101}, and {111}.

A selected plate was cleaved parallel to the **b** axis, yielding a needle of cross-section about 0·2 × 0·3 mm, which was used to collect X-ray data for the ($h0l$) net. The cell dimensions were obtained from measurements of rotation and zero level Weissenberg photographs taken about the cleavage (**b**) axis using Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å. Following the Donnay (1943) recommendations, the parameters are:

$$a = 10{\cdot}28,\ b = 8{\cdot}26,\ c = 8{\cdot}88\ \text{Å},\ \beta = 121°\ 3',$$

which are in good agreement with those observed by Fogle (1954).

The observed systematic extinctions from zero to second level Weissenberg photographs about the **b** axis, and zero level **a** axis precession photographs were: $(h0l)$ absent for $h=2n+1$, and $(0k0)$ absent for $k=2n+1$, with no systematic (hkl) extinctions, indicating that the space group is probably $P2_1/a(C_{2h}^5)$. The observed density of 1·561 g.cm^{-3} indicates two molecules per unit cell with a calculated density of 1·570 g.cm^{-3}.

Double-film Weissenberg photographs were taken with several exposure times about the **b** axis for the zero layer using a Nonius integrating camera, with Cu $K\alpha$ radiation. The singly integrated photographs were then photometered using a Moll-type densitometer. The interfilm ratio was determined for each set from the measured values for common reflections and ranged from 3·50 to 5·74 for eight pairs of films, with an average of 4·46. A total of 99 non-extinct reflections were observed, of which 5 had relative intensities 'less-than' 1 in a range of 4900. The intensities were corrected for Lorentz and polarization factors in the usual manner.

The intensities for the $(0kl)$ net were obtained in a similar manner from singly integrated Weissenberg photographs from a crystal mounted parallel to the **a** axis and ground to the shape of a cylinder of 0·23 mm diameter. A total of 87 non-extinct reflections were observed, of which 17 had relative intensities 'less-than' 1 in a range of 3900.

A third crystal, ground parallel to the **a** axis, of 0·33 mm diameter and 0·46 mm long was mounted parallel to the **c** axis (perpendicular to the cylinder axis) for the $(hk0)$ net intensity data. A total of 92 non-extinct reflections were observed, of which 23 had relative intensities 'less-than' 1 in a range of 2900.

3. The structure determination

Although the presence of an atom such as nickel at the origin is able to determine the phase angles in compounds in which the other atoms are all light atoms such as carbon, nitrogen, oxygen, or hydrogen, the presence of the sulfur atom in $Ni(en)_2(NCS)_2$ prevented the simple approach of starting with an $(h0l)$ Fourier synthesis with all phase angles zero.

An electron-density map for the $(h0l)$ projection calculated with all phase angles zero showed the nickel and sulfur peaks in good agreement with those obtained from a Patterson projection, but no satisfactory trial structure could be obtained from a consideration of the other (smaller) peaks. Comparison with the final result showed that this electron-density map was calculated using observed structure factors of which 20 of the 99 terms had erroneous phase angles, accounting for 12% of the ΣF_o in the final results.

Even an electron-density map using phase angles determined by the nickel and sulfur positions was unsatisfactory to determine positions for the light atoms. This calculation, when compared with the final results, had 16 terms with erroneous phase angles, accounting for 11% of the ΣF_o.

The atomic scattering factors used for this and subsequent structure factor calculations were: nickel—interpolation between values of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and Viervoll-Øgrim (1949); sulfur—interpolation between values of Berghuis *et al.* (1955) and Hartree (1935); carbon and nitrogen—Berghuis *et al.* (1955); and hydrogen—McWeeny (1951). No corrections were made for dispersion.

The procedure which led to a satisfactory determination of the structure consisted of the determination of the sulfur position from a Patterson function and the use of a Patterson superposition to obtain possible positions of the light atoms. Successive refinements using electron-density and difference maps were used to determine the x and z parameters with the final value of 0·10 for the discrepancy index, defined as: $R=\Sigma[|F_o|-|F_c|]/\Sigma|F_o|$, for observed non-zero reflections only. The final electron density map for the $(h0l)$ projection is given in Fig. 1.

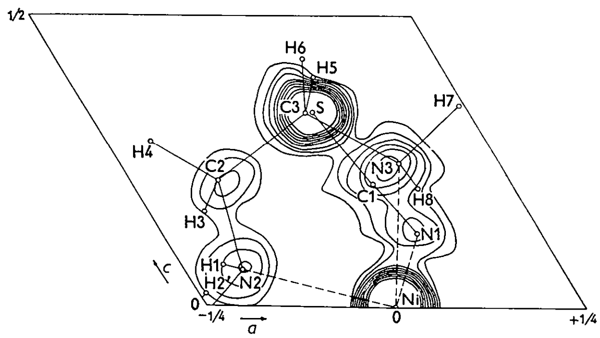

Fig. 1. Final electron-density projection on (010). Contour interval 2 e.Å^{-2} (except at Ni and S centers), lowest contour 4 e.Å^{-2}.

The sulfur position on $(0kl)$ had been determined (Fogle, 1954), but it was not found possible to obtain a satisfactory trial structure from an electron-density map obtained with the phase angles determined from the nickel and sulfur positions and using the z coordinates for the light atoms from the $(h0l)$ projection. It was necessary to make use of the $(0kl)$ and $(hk0)$ projections together to get a trial structure. The final electron-density maps for these projections are given in Figs. 2 and 3.

The three projections were then refined together by successive difference syntheses. The final calculations were made using an overall isotropic temperature factor coefficient of 3·25 Å^2. The hydrogen atom positions for this final set were calculated assuming a tetrahedral configuration about the carbon and nitrogen atoms in the *en*, and C–H and N–H distances of 1·075 and 1·005 Å, respectively. A representation of the structure in the [100] projection is shown in Fig. 4.

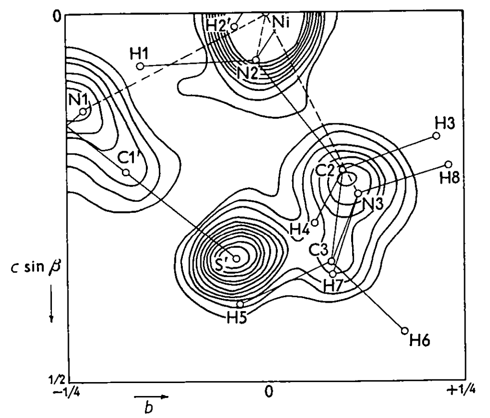

Fig. 2. Final electron-density projection on (100). Contour interval 2 e.Å^{-2} (except at Ni center), lowest contour 4 e.Å^{-2}.

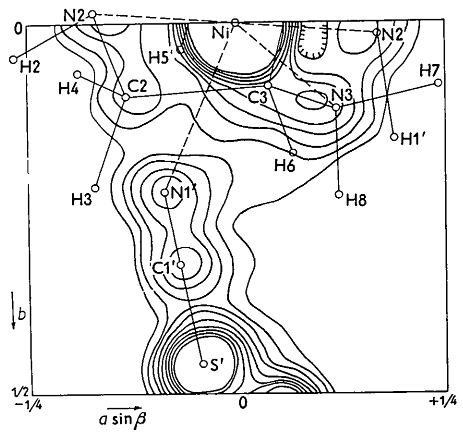

Fig. 3. Final electron-density projection on (001). Contour interval 2 e.Å^{-2} (except at Ni and S centers), lowest contour 4 e.Å^{-2}.

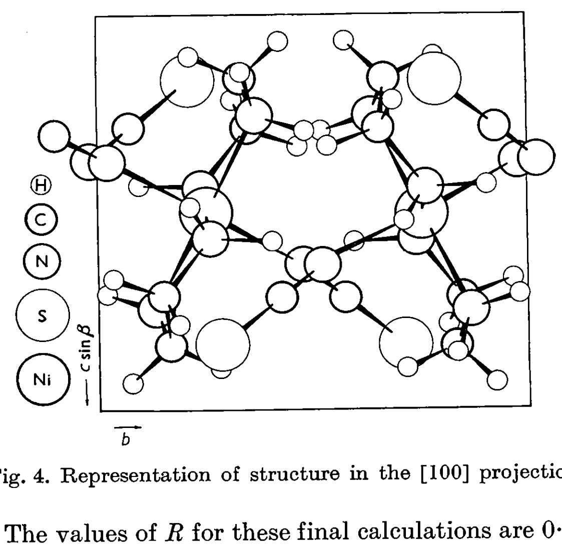

Fig. 4. Representation of structure in the [100] projection.

The values of R for these final calculations are 0·11, 0·12, and 0·087 for the ($hk0$), ($h0l$), and ($0kl$) projections, respectively. The overall value of R for the 259 non-extinct reflections is 0·109. The values of R^* were also calculated, where R^* includes $F_{\min}$ and $F_{\min}-|F_c|$ for those unobserved reflections where F_c calculates greater than $F_{\min}$, the minimum observable intensity. The values of R^* for the three projections are 0·12, 0·12, and 0·095 for the ($hk0$), ($h0l$), and ($0kl$) projections, respectively.

The atomic parameters are listed in Table 1. The notation is consistent with the labeling of the atoms in the electron-density maps. Atoms related through the symmetry center are denoted as S and S′, *etc.*

Table 1. $Ni(en)_2(NCS)_2$

Final atomic coordinates

	x	y	z
Ni	0·0000	0·0000	0·0000
S	0·0427	−0·4607	0·3318
C_1	0·0708	−0·3256	0·2155
C_2	−0·1321	0·0973	0·2148
C_3	0·0365	0·0846	0·3367
N_1	0·0874	−0·2291	0·1265
N_2	−0·1693	−0·0128	0·0639
N_3	0·1204	0·1155	0·2476
H_1	−0·177	−0·127	0·097
H_2	−0·269	0·021	−0·041
H_3	−0·164	0·220	0·170
H_4	−0·190	0·059	0·280
H_5	0·063	−0·035	0·391
H_6	0·071	0·172	0·441
H_7	0·226	0·070	0·318
H_8	0·127	0·235	0·232

The best least-squares temperature factor coefficients were calculated for the three zones, and the values of B obtained were 4·34, 2·54, and 4·18 Å^2 for the ($hk0$), ($h0l$), and ($0kl$) projections. Structure factors calculated with these values of B resulted in values of R of 0·081, 0·099, and 0·092 for the three zones, respectively.

It is evident from the temperature factor coefficients that the mode of vibration in the ($h0l$) projection must be different from that of the other zones. The low value of B for ($h0l$) indicates that there exists anisotropic thermal motion with the maximum amplitude approximately perpendicular to the ac plane. This anisotropy can be seen about the nickel and sulfur atoms in Fig. 2 for the ($hk0$) and in Fig. 3 for the ($0kl$) projection. A difference synthesis for the ($0kl$) projection shows additional anisotropy in the *en*, clearly in atom C_3 and to a lesser degree in the overlapped N_3 and C_2 atoms (Fig. 5).

Structure factors were calculated for the ($hk0$) and ($0kl$) projections correcting for the anisotropy of the nickel and sulfur atoms by the use of a temperature factor coefficient of the form

$$\exp -(A+C\cos^2\Phi)(\sin^2\theta/\lambda^2)$$

where the direction of maximum vibration from the b^* axis, (ε), and the values of A and C are given in Table 2. The size of the asymmetric unit was doubled

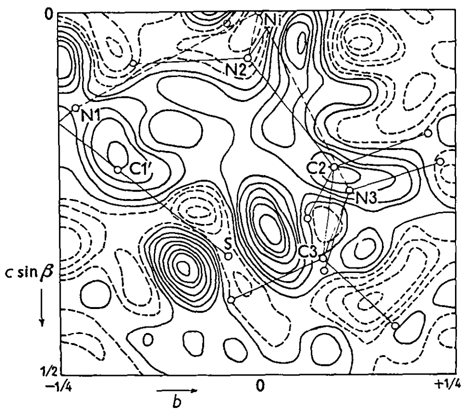

Fig. 5. Difference synthesis projection on (100) with overall temperature factor coefficient of 3·25 Å². Contour interval 0·25 e.Å⁻², negative contours broken.

for the calculations including these anisotropy corrections. All other atoms were calculated with a value of B of 4·25 Å², approximately the average of the least squares B for the (hk0) and (0kl) projections.

Table 2. Ni(en)$_2$(NCS)$_2$

Anisotropy correction coefficients

(hk0) Zone: Ni and S corrections only

Atom	$\varepsilon(mc)$	A	B
Ni	−110	4·00 Å²	0·40 Å²
S	083	3·25	2·00

(0kl) Zone: Ni and S corrections only

Atom	$\varepsilon(mc)$	A	B
Ni	−128	3·60 Å²	0·75 Å²
S	−180	2·50	2·80

The values for R for these calculations were 0·061 for the (hk0) and 0·066 for the (0kl) projections.

The list of observed and calculated structure factors is given in Table 3. The (200) reflection was not included in the calculation of R or in difference syntheses because of the strong secondary extinction observed. The value of F_c was used in place of F_o for this reflection in electron-density maps.

4. Discussion

The arrangement of the ligands about the nickel atom in Ni(en)$_2$(NCS)$_2$ has been shown to have a nearly regular octahedral configuration, rather than the tetrahedral configuration suggested by Pauling (1960a). The four en nitrogen atoms are located at the corners of a rectangle at a mean Ni–N distance of 2·10 Å, and the thiocyanate nitrogen atoms complete the octahedron at a distance of 2·15 Å. The interatomic distances and angles in the molecule are

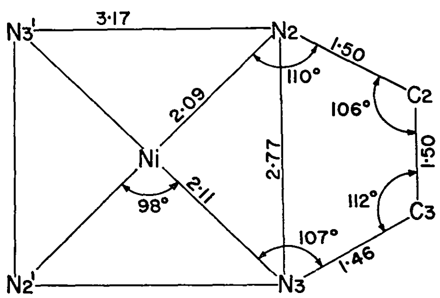

Fig. 6. Interatomic bond lengths and angles in the ethylenediamine ring.

Table 3. *Observed and calculated structure factors*

k	l	F_o	F_c
	h = 0		
0	1	643	646
0	2	347	−265
0	3	643	693
0	4	212	215
0	5	132	135
0	6	313	310
0	7	57	−34
0	8	51	41
0	9	233	200
1	1	42	30
1	2	243	225
1	3	239	206
1	4	27	40
1	5	135	−117
1	6	< 31	−46
1	7	< 32	21
1	8	< 30	−12
1	9	< 23	−7
2	0	1081	994
2	1	212	215
2	2	331	336
2	3	946	924
2	4	241	247
2	5	83	105
2	6	323	302
2	7	< 32	8
2	8	< 29	−9
2	9	117	105
3	1	265	−244
3	2	281	−240
3	3	129	124
3	4	155	166
3	5	105	−88
3	6	< 32	−2
3	7	105	106
3	8	< 27	−4
3	9	34	−31
4	0	494	481
4	1	448	431
4	2	496	490
4	3	390	385
4	4	29	9
4	5	<31	35
4	6	216	220
4	7	132	111
4	8	<25	33
4	9	< 13	56
5	1	200	227
5	2	126	−118
5	3	59	66
5	4	175	184
5	5	110	−106
5	6	56	−50
5	7	< 28	47
5	8	49	−34
6	0	156	166
6	1	241	250
6	2	225	273
6	3	164	182
6	4	203	175
6	5	118	132
6	6	63	67
6	7	75	50
6	8	< 14	19
7	1	259	277
7	2	119	−127
7	3	106	−87
7	4	58	93
7	5	35	−27
7	6	50	62
7	7	51	61
8	0	113	114
8	1	181	189
8	2	125	147
8	3	57	51
8	4	114	112
8	5	38	67
8	6	<18	−2
9	1	83	105
9	2	44	−60
9	3	<25	22
9	4	61	78
9	5	< 15	−52
10	0	54	54
10	1	76	98
10	2	47	66
10	3	< 14	12
	h = 1		
1	0	618	537
2	0	263	−198
3	0	123	136
4	0	101	−73
5	0	53	65
6	0	< 49	−31
7	0	116	131
8	0	79	−80
9	0	194	229
10	0	< 35	−16
	h = 2		
0	0	798	1111
0	1	434	−381
0	2	220	236
0	3	571	640
0	4	27	43
0	5	232	231
0	6	371	363
0	7	51	48
0	8	117	80
1	0	296	254
2	0	608	556
3	0	120	−89
4	0	380	384
5	0	157	159
6	0	136	157
7	0	84	83
8	0	<52	40
9	0	<45	12
10	0	<32	12
	h = 3		
1	0	237	−171
2	0	353	−302
3	0	151	146
4	0	148	−160
5	0	149	140
6	0	72	−83
7	0	103	103
8	0	105	−110
9	0	60	72
10	0	<28	1
	h = 4		
0	0	156	171
0	1	465	−463
0	2	369	401
0	3	352	372
0	4	125	−103
0	5	160	154
0	6	177	172
0	7	< 16	1
1	0	214	206
2	0	483	494
3	0	< 41	28
4	0	313	335
5	0	163	179
6	0	155	185
7	0	153	172
8	0	< 49	22
9	0	71	87
	h = 5		
1	0	251	227
2	0	223	−212
3	0	304	269
4	0	151	−183
5	0	226	215
6	0	111	−128
7	0	127	142
8	0	51	−56
9	0	33	31
	h = 6		
0	0	173	178
0	1	41	−4
0	2	419	404
0	3	193	189
0	4	29	26
0	5	206	163
1	0	75	52
2	0	368	371
3	0	80	90
4	0	151	176
5	0	68	88
6	0	86	131
7	0	89	119
8	0	60	88
	h = 7		
1	0	343	324
2	0	110	−108
3	0	155	158
4	0	137	−143
5	0	123	101
6	0	116	−136
7	0	99	91
8	0	< 29	−43
	h = 8		
0	0	41	o50
0	1	80	81
0	2	243	236
0	3	33	37
0	4	62	41
1	0	< 54	−29
2	0	72	80
3	0	93	87
4	0	< 51	6
5	0	< 47	45
6	0	< 41	23
7	0	< 31	51
	h = 9		
1	0	206	181
2	0	< 50	−37
3	0	83	86
4	0	69	−62
5	0	77	63
6	0	< 28	−50
	h = 10		
0	0	< 32	−14
0	1	91	82
1	0	< 43	−38
2	0	< 41	−23
3	0	< 38	30
4	0	< 32	39
	h = 11		
1	0	< 28	101
	h = −2		
0	1	538	674
0	2	396	−295
0	3	485	548
0	4	147	168
0	5	35	−44
0	6	361	376
0	7	71	102
0	8	35	17
0	9	338	286
0	10	128	110
	h = −4		
0	1	704	823
0	2	436	455
0	3	763	935
0	4	375	436
0	5	50	−34
0	6	527	559
0	7	337	358
0	8	126	−115
0	9	163	129
0	10	192	165
	h = −6		
0	1	522	553
0	2	109	93
0	3	392	416
0	4	433	521
0	5	151	−105
0	6	259	241
0	7	358	365
0	8	154	−146
0	9	31	−18
0	10	202	175
0	11	74	39
	h = −8		
0	1	223	241
0	2	106	−123
0	3	49	27
0	4	472	507
0	5	100	77
0	6	52	20
0	7	356	359
0	8	147	124
0	9	81	44
0	10	166	143
0	11	34	17
	h = −10		
0	1	199	186
0	2	115	82
0	3	45	−7
0	4	337	314
0	5	173	147
0	6	25	−22
0	7	252	262
0	8	197	174
0	9	47	11
0	10	74	77
	h = −12		
0	2	151	135
0	3	25	−34
0	4	63	71
0	5	89	91
0	6	19	−32
0	7	106	102
0	8	92	91
0	9	13	−16

shown in Figs. 6 and 7. No attempt has been made to calculate standard deviations for bond lengths and angles because of the degree of overlap in the projections.

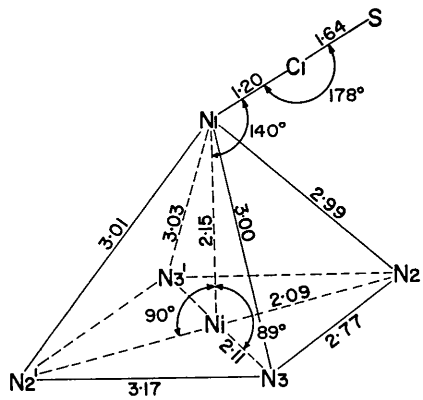

Fig. 7. Interatomic bond lengths and angles in the thiocyanate group and the coordination octahedron.

The nearest intermolecular distances for the $Ni(en)_2(NCS)_2$ molecule centered about (0, 0, 0) are listed in Table 4. Atoms labeled S, N_2, *etc.*, are located at the coordinates given in Table 1, atoms labeled S′, N_2', *etc.*, are related to this set by the symmetry center at (0, 0, 0). The symmetry operation relating the nearest neighbor to the atom at (x, y, z) centered on (0, 0, 0) is also listed.

The mean Ni–N bond length in the *en* ring of 2·10 Å agrees with the Ni–N (*en*) bond lengths in $Ni(en)_3(NO_3)_2$ of 2·12 Å (Swink & Atoji, 1960) and $[Ni(en)(H_2O)_4](NO_3)_2$ of 2·08 Å (Simmons *et al.*, 1961). The sum of the nickel(II) octahedral radius (1·30 Å) and the single bond covalent radius for nitrogen (0·74 Å) gives an octahedral nickel(II)–nitrogen bond length of 2·04 Å (Pauling, 1960*b*), which is in agreement with the measured values for these compounds.

Table 4. $Ni(en)_2(NCS)_2$

Nearest intermolecular neighbors

Atom in molecule at (0, 0, 0)	Nearest neighbor	Distance	Symmetry relation to molecule at (0, 0, 0)
Ni	S	4·80 Å	$x+\frac{1}{2}, \bar{y}-\frac{1}{2}, z$
Ni	C_2	4·65	$x+\frac{1}{2}, \bar{y}+\frac{1}{2}, z$
S	N_2'	3·34	$x-\frac{1}{2}, \bar{y}-\frac{1}{2}, z$
N_1	N_2	3·54	$x+\frac{1}{2}, \bar{y}-\frac{1}{2}, z$
N_2	S′	3·66	$x-\frac{1}{2}, \bar{y}+\frac{1}{2}, z$
N_3	S′	3·61	$x+\frac{1}{2}, \bar{y}+\frac{1}{2}, z+1$
C_1	C_2	3·80	$x+\frac{1}{2}, \bar{y}-\frac{1}{2}, z$
C_2	N_3	3·60	$x-\frac{1}{2}, \bar{y}+\frac{1}{2}, z$
C_3	C_3'	3·63	$x, y, z+1$

The short single-bond C–C distance of 1·50 Å in the *en* group in $Ni(en)_2(NCS)_2$ has also been observed in $[Ni(en)(H_2O)_4](NO_3)_2$ and $Ni(en)_3(NO_3)_2$, while this distance is 1·55 Å in $[Co(en)_2Cl_2]Cl.HCl.2H_2O$ (Nakahara *et al.*, 1952) and 1·54 Å in $Co(en)_3Cl_3.3H_2O$ (Nakatsu *et al.*, 1956).

The spatial configuration of the (*en*) ring is the 'gauche' form which has been observed in many compounds. The carbon atoms in the ring are arranged symmetrically above and below the plane determined by the nickel and nitrogen atoms at a distance of 0·34 Å. The distance observed in $Ni(en)_3(NO_3)_2$ is 0·29 Å and in $[Ni(en)(H_2O)_4](NO_3)_2$ is 0·36 Å. The tris-(*en*) compound, $Co(en)_3Cl_3.3H_2O$ has the carbon atoms arranged symmetrically at a distance of 0·26 Å, which is similar to the tris-(*en*) compound $Ni(en)_3(NO_3)_2$. The observed distance of 0·34 Å in $Co(en)_2Cl_2Cl.HCl.H_2O$ agrees with that observed in $Ni(en)_2(NCS)_2$.

The linear thiocyanate group is bonded through the nitrogen atom at a distance of 2·15 Å. This isothiocyanato bonding has been observed also in compounds of chromium and cobalt in the first long transition period. The valence bond angle at the N atom, however, is not constant in all of the compounds that have been investigated. The ammonium (Saito *et al.*, 1955) and pyridine Reinecke salts (Takeuchi & Saito, 1957) have a linear bond angle, as does $Ni(NH_3)_4(NCS)_2$ (Iukhno & Porai-Koshits, 1957), $Ni(NH_3)_3(NCS)_2$ (Porai-Koshits *et al.*, 1957), and $Ni(tatea)(NCS)_2$ (Hall & Woulfe, 1958).

In the choline Reinecke salt (Takeuchi & Saito, 1957) the valence angle is 156°, and 165° in $Ni(py)_2(NCS)_2$ (Porai-Koshits & Antsyshkina, 1958). In the binuclear $Co(py)_2(NCS)_2$ and $Cu(py)_2(NCS)_2$ (Porai-Koshits & Tishchenko, 1959) the bond through the nitrogen atom of the thiocyanate group has a valence angle of 160°. It is only in the tetrahedrally coordinated $K_2Co(NCS)_4$ (Zhdanov & Zvonkova, 1950), with an angle of 111°, that a valence bond angle more acute than the 140° in $Ni(en)_2(NCS)_2$ is found.

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Studies of some Carbon Compounds of the Transition Metals. IV. The Structure of Butadiene Irontricarbonyl

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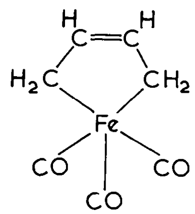
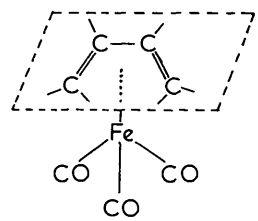
The structure of the complex $C_4H_6Fe(CO)_3$, prepared from butadiene and iron pentacarbonyl, has been determined, at −40 °C, by three-dimensional Fourier methods and refined by least-squares techniques. The compound crystallizes in the orthorhombic system, space group *Pnma*, with four molecules in a unit cell of dimensions $a = 11{\cdot}6$, $b = 11{\cdot}1$, $c = 6{\cdot}2$ Å. The molecule contains the butadiene group in the cisoid form π-bonded to the iron atom to which are also bonded the carbonyl groups in roughly trigonal arrangement. The Fe–C(butadiene) distances are 2·06 and 2·14 Å, whilst the average Fe–C(carbonyl) distance is 1·76 Å. The C–C distances are 1·46 and 1·45 Å and are in agreement with delocalization of the π-electrons.

Introduction

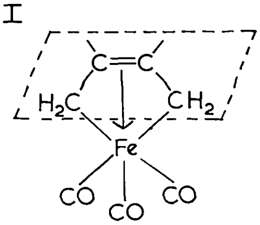
Although Rheilen, Gruhl, Hessling & Pfrengle (1930) first reported the preparation of butadiene irontricarbonyl, it has only recently been reinvestigated (Hallam & Pauson, 1958) and reformulated as a π-complex (II). The earlier structural proposal of Rheilen *et al.* (I) would yield a 34-electron configuration in conflict with the observed diamagnetism and remarkable chemical stability. More recently, Green, Pratt & Wilkinson (1959), mainly on the basis of nuclear magnetic resonance measurements, have considered in addition the structure (III). To determine the exact structural geometry in the hope of being able to infer the type of bonding possible within the molecule, a three-dimensional X-ray analysis was undertaken. A preliminary report of the structure has been published (Mills & Robinson, 1960).



I



II



III

Experimental

A sample of butadiene irontricarbonyl was kindly supplied by Prof. Pauson and approximately 1 cm of the liquid was placed in a Lindemann glass tube (0·2 mm diameter). The sample was cooled by a stream of cold nitrogen whilst mounted inside the low-temperature equipment supplied with the Nonius