The Crystal Structure of the β-Form of Nickel(II) Dithiosemicarbazide Sulphate

RITA GRØNBÆK HAZELL

Department of Inorganic Chemistry, University of Aarhus, Aarhus C, Denmark

The β-form of nickel dithiosemicarbazide sulphate is monoclinic with space group $A2/a$ and cell dimensions $a=13.29$ Å, $b=6.74$ Å, $c=25.41$ Å, and $\beta=106.9°$. The structure was determined from the three-dimensional Patterson function and by direct methods.

The data were measured on an automatic diffractometer, and refinement was carried out to an R-value of 5.0 %. The structure contains two independent sets of complex ions, one of trans-planar, the other of cis-planar configuration. The Ni—S bond is significantly shorter in the cis complex than in the trans complex.

Crystallographic proof of the stereoisomerism of planar nickel complexes has not so far been given, and only a few complexes of this type have been prepared in different crystalline forms.

Jensen[1] prepared $Ni(CH_5N_3S)_2SO_4$ in two different crystalline forms, which he considered cis-trans isomers. Single crystals of each of the two forms may be obtained without much difficulty, and this system was therefore considered suitable for a crystallographic investigation of cis-trans isomerism.

The so called α-form was found to be a trihydrate.[2] The complex ion has trans-planar configuration; the water is not coordinated to the nickel atom.

In a preliminary account[3] it was shown that the β-compound contains two independent sets of complex-ions, one of cis- and another of trans-planar configuration.

The structure of the β-form has been redetermined with improved precision from three-dimensional counter-data for reliable comparison of bond lengths in the isomeric molecules. The Ni—S bond of the cis complex is significantly shorter than that of the trans complex.

EXPERIMENTAL

Preparation. The compound was prepared from thiosemicarbazide and $NiSO_4,7H_2O$. In order to obtain crystals sufficiently large for an X-ray investigation the following procedure was adopted: Two small conical flasks, one containing $NiSO_4,7H_2O$ and the other thiosemicarbazide were immersed in a 2 l beaker of water which was kept at a

Table 1. Final atomic parameters.

a. Coordinates in fractions of the unit cell (standard deviations $\times 10^5$ in parentheses). For the hydrogen atoms the standard deviations $\times 10^4$ are given. Isotropic temperature factors, u, and their standard deviations, both in $Å^2 \times 10^{-4}$ are also given for these atoms.

	x	σx	y	σy	z	σz	u	σu
Ni_{cis}	0.25000	(0)	−0.10674	(8)	0.00000	(0)		
Ni_{tr}	0.00000	(0)	0.25000	(0)	0.25000	(0)		
S_{cis}	0.36508	(7)	0.11636	(11)	0.03495	(4)		
S_{tr}	0.07873	(7)	0.01611	(13)	0.21889	(4)		
C_{cis}	0.47258	(26)	−0.03829	(46)	0.05793	(13)		
C_{tr}	−0.03070	(25)	−0.12696	(47)	0.19129	(13)		
N_{1cis}	0.35619	(20)	−0.30706	(37)	0.02589	(12)		
N_{2cis}	0.45926	(22)	−0.23364	(38)	0.05214	(13)		
N_{3cis}	0.56780	(22)	0.03280	(42)	0.08154	(13)		
N_{1tr}	−0.13080	(22)	0.10963	(41)	0.22376	(13)		
N_{2tr}	−0.12372	(22)	−0.06767	(43)	0.19412	(14)		
N_{3tr}	−0.02286	(23)	−0.29712	(43)	0.16724	(13)		
S	0.20275	(7)	0.49234	(13)	0.12757	(4)		
O_1	0.20427	(25)	0.27772	(44)	0.13704	(15)		
O_2	0.11343	(21)	0.53917	(42)	0.07813	(12)		
O_3	0.18887	(26)	0.59678	(65)	0.17549	(14)		
O_4	0.30230	(23)	0.55696	(54)	0.11871	(14)		
H_{11cis}	0.3601	(46)	−0.3967	(104)	−0.0077	(25)	390	(180)
H_{12cis}	0.3358	(33)	−0.3965	(66)	0.0550	(18)	1	(103)
H_{2cis}	0.5258	(47)	−0.3278	(100)	0.0677	(24)	388	(180)
H_{31cis}	0.5669	(41)	0.1632	(86)	0.0820	(22)	218	(142)
H_{32cis}	0.6315	(39)	−0.0718	(85)	0.0940	(21)	203	(139)
H_{11tr}	−0.1752	(53)	0.0700	(125)	0.2539	(30)	693	(244)
H_{12tr}	−0.1770	(56)	0.1772	(141)	0.1979	(30)	805	(278)
H_{2tr}	−0.1821	(52)	−0.1281	(113)	0.1770	(28)	572	(218)
H_{31tr}	0.0399	(49)	−0.3403	(108)	0.1674	(26)	437	(188)
H_{32tr}	−0.0884	(49)	−0.3835	(105)	0.1520	(26)	436	(189)

b. Anisotropic temperature factor parameters, u_{ij}, (standard deviations in parentheses), in $Å^2 \times 10^{-4}$.

	u_{11}	σu_{11}	u_{22}	σu_{22}	u_{33}	σu_{33}	u_{12}	σu_{12}	u_{13}	σu_{13}	u_{23}	σu_{23}
Ni_{cis}	189	(3)	209	(3)	257	(4)	0	(0)	51	(3)	0	(0)
Ni_{tr}	210	(3)	240	(3)	283	(4)	−38	(3)	37	(3)	−19	(3)
S_{cis}	245	(5)	214	(4)	412	(6)	10	(4)	26	(4)	−41	(4)
S_{tr}	230	(5)	340	(5)	449	(6)	−79	(4)	100	(5)	−114	(5)
C_{cis}	234	(19)	262	(15)	270	(19)	1	(15)	42	(15)	−19	(15)
C_{tr}	251	(20)	274	(16)	269	(20)	−53	(15)	45	(16)	−18	(15)
N_{1cis}	204	(16)	211	(13)	345	(19)	− 5	(12)	61	(14)	0	(13)
N_{2cis}	213	(16)	242	(13)	385	(20)	5	(13)	55	(14)	1	(14)
N_{3cis}	240	(18)	293	(15)	431	(21)	−20	(14)	47	(15)	−49	(15)
N_{1tr}	209	(17)	263	(15)	472	(23)	− 5	(13)	17	(15)	−61	(15)
N_{2tr}	239	(18)	291	(15)	476	(23)	−35	(14)	60	(16)	−94	(16)
N_{3tr}	279	(19)	304	(15)	378	(20)	−25	(14)	99	(15)	−45	(15)
S	164	(4)	208	(3)	291	(5)	18	(3)	40	(4)	17	(3)
O_1	333	(17)	238	(13)	672	(25)	−15	(13)	−39	(16)	150	(15)
O_2	243	(14)	287	(13)	335	(17)	− 6	(11)	−20	(12)	60	(12)
O_3	310	(18)	778	(27)	431	(20)	140	(19)	18	(15)	−207	(20)
O_4	237	(16)	514	(18)	512	(21)	−47	(14)	131	(15)	193	(17)

temperature of 90°C; the components mixed by diffusion. After several days a crop of well developed crystals formed in the flask which had originally contained the thiosemicarbazide.

A crystal fragment of dimensions $0.3 \times 0.4 \times 0.2$ mm³ was used for the collection of intensities. Unit cell dimensions were obtained from precession photographs taken with CuKα and with MoKα radiation. Preliminary three-dimensional intensity data were measured from integrated equi-inclination Weissenberg, Rimsky-retigraph-, and precession films.[3]

Later when a linear diffractometer of the Arndt-Phillips type[4] became available a more complete and uniform set of data was collected using Mo-radiation, balanced filters, (SrO,ZrO$_2$), and a pulse height analyser. Reflexions within a hemisphere of radius $\sin\theta/\lambda = 0.72$ were measured. An ALGOL program was written which evaluated intensities, calculated averages, Lp corrections, and standard deviations, and checked for errors. No absorption correction was made ($\mu_{Mo} = 24$ cm^{-1}).

CRYSTAL DATA

Crystal system: monoclinic (b unique).
Unit cell: $a = 13.29 \pm 0.03$ Å, $b = 6.74 \pm 0.01$ Å, $c = 25.41 \pm 0.05$ Å; $\beta = 106.9 \pm 0.3°$
$d_{obs} = 2.06$ g/cm³, $d_{calc} = 2.055$ g/cm³.

8 moles of Ni(CH$_5$N$_3$S)$_2$SO$_4$ per unit cell.
No piezoelectric effect could be detected.
Systematic absences: hkl for $k+l$ odd

$h0l$ for h odd

Possible space groups: Aa and $A2/a$.

Coordinates and temperature factor parameters at the end of the refinement are given in Table 1. Table 2 is a list of observed and calculated structure factors and Table 3 gives distances and angles.

STRUCTURE DETERMINATION

Using the photographic data the structure was first solved from the three-dimensional Patterson function. The assumption that Ni was in a general 8 fold position of $A2/a$ was found incompatible with the Patterson function. The possibility that Ni should be in two 4-fold positions in Aa led to a solution which could be described in $A2/a$ with Ni on two sets of special positions, one on a centre of symmetry, the other on a twofold axis. This implied that one complex ion had the *trans*-planar, the other the *cis*-planar configuration. The sulphur atoms and most of the light atoms could be found from the Patterson map.

To test this unexpected solution "direct methods" were applied. The coincidence method[5] was applied to two sets of reflexions: $0kl + 1kl$, and $0kl + 5kl$; the odd layer lines were chosen because here $F_{hkl} = -F_{\bar{h}kl}$. Both sets gave the same signs for 28 $0kl$ reflexions and also gave the signs of $1kl$ and $5kl$ reflexions. From this initial set of signs a systematic application of the triple product sign relationship led to the determination of the signs of 410 of the strongest reflexions. 386 of these turned out to be correct.

Table 2. Observed and calculated structure factors (10 × absolute).

h	k	l	Fobs	Fcal	
0	0	2	9	-96	
0	0	4	1392	1541	
0	0	6	95	107	
0	0	8	915	923	
0	0	10	339	-367	
0	0	12	177	-214	
0	0	14	81	75	<
0	0	16	1025	1051	
0	0	18	105	-112	
0	0	20	296	-314	
0	0	22	354	363	
0	0	24	1061	1068	
0	0	26	86	30	<
0	0	28	377	381	
0	0	30	101	62	<
0	0	32	679	652	
2	0	-32	222	-126	
2	0	-30	553	-551	
2	0	-28	170	150	
2	0	-26	405	-360	
2	0	-24	266	257	
2	0	-22	1210	-1245	
2	0	-20	720	715	
2	0	-18	97	43	
2	0	-16	58	-15	<
2	0	-14	538	-516	
2	0	-12	306	-311	
2	0	-10	2263	-2370	
2	0	-8	3486	-4360	
2	0	-6	3656	-4833	
2	0	-4	1109	1146	
2	0	-2	1471	-1677	
2	0	0	158	163	
2	0	2	2390	-2580	
2	0	4	2203	2343	
2	0	6	786	-746	
2	0	8	449	-446	
2	0	10	634	-629	
2	0	12	1641	1708	
2	0	14	1077	-1058	
2	0	16	1086	-1133	
2	0	18	967	-965	
2	0	20	149	174	
2	0	22	382	-383	
2	0	24	790	-782	
2	0	26	650	-618	
2	0	28	149	-61	
2	0	30	634	-586	
4	0	-32	208	211	
4	0	-30	195	177	
4	0	-28	419	472	
4	0	-26	824	-802	
4	0	-24	460	453	
4	0	-22	270	-261	
4	0	-20	1459	1507	
4	0	-18	77	-48	<
4	0	-16	2444	2554	
4	0	-14	1245	1264	
4	0	-12	1708	1742	
4	0	-10	152	114	
4	0	-8	229	193	
4	0	-6	1797	1866	
4	0	-4	526	430	
4	0	-2	1303	-1333	
4	0	0	440	390	
4	0	2	319	332	
4	0	4	821	-827	
4	0	6	621	-667	
4	0	8	2940	3112	
4	0	10	707	-713	
4	0	12	1303	1359	
4	0	14	769	-801	
4	0	16	1716	1750	
4	0	18	922	955	
4	0	20	755	778	
4	0	22	187	214	
4	0	24	734	731	
4	0	26	98	45	<
4	0	28	231	-204	
4	0	30	171	-145	
6	0	-32	195	168	
6	0	-30	275	-267	
6	0	-28	356	-355	
6	0	-26	696	-676	
6	0	-24	68	10	<
6	0	-22	1635	-1634	
6	0	-20	667	-667	
6	0	-18	987	-1002	
6	0	-16	849	852	
6	0	-14	2180	-2239	
6	0	-12	65	56	<
6	0	-10	233	-191	
6	0	-8	670	680	
6	0	-6	109	-109	
6	0	-4	1011	-1001	
6	0	-2	83	68	
6	0	0	444	451	
6	0	2	1707	-1695	
6	0	4	157	130	
6	0	6	432	-432	
6	0	8	538	-505	
6	0	10	2840	-2902	
6	0	12	266	-297	
6	0	14	1537	-1558	
6	0	16	170	175	
6	0	18	953	-949	
6	0	20	550	527	
6	0	22	114	5	<
6	0	24	53	-32	<
6	0	26	399	-382	
8	0	-32	174	172	
8	0	-30	576	535	
8	0	-28	673	684	
8	0	-26	405	377	
8	0	-24	98	90	<
8	0	-22	292	286	
8	0	-20	1217	1221	
8	0	-18	602	-593	
8	0	-16	276	273	
8	0	-14	340	-324	
8	0	-12	1752	1774	
8	0	-10	769	-806	
8	0	-8	212	187	
8	0	-6	691	-711	
8	0	-4	2290	2359	
8	0	-2	721	-753	
8	0	0	790	774	
8	0	2	2083	2100	
8	0	4	2207	2235	
8	0	6	781	779	
8	0	8	543	544	
8	0	10	462	452	
8	0	12	681	695	
8	0	14	634	-637	
8	0	16	243	231	
8	0	18	164	-185	
8	0	20	619	615	
8	0	22	492	-480	
8	0	24	328	368	
8	0	26	253	278	
10	0	-32	137	10	
10	0	-30	208	-213	
10	0	-28	303	-309	
10	0	-26	360	-360	
10	0	-24	204	167	
10	0	-22	180	-199	
10	0	-20	535	-549	
10	0	-18	330	-316	
10	0	-16	961	971	
10	0	-14	630	-647	
10	0	-12	285	-251	
10	0	-10	1130	-1139	
10	0	-8	838	835	
10	0	-6	2425	-2496	
10	0	-4	910	-858	
10	0	-2	2293	-2366	
10	0	0	478	494	
10	0	2	837	-852	
10	0	4	1345	-1401	
10	0	6	449	453	
10	0	8	610	615	
10	0	10	278	-288	
10	0	12	182	-160	
10	0	14	147	-151	
10	0	16	246	264	
10	0	18	639	-633	
10	0	20	380	-331	
12	0	-30	221	-165	
12	0	-28	556	527	
12	0	-26	191	-141	
12	0	-24	156	141	
12	0	-22	290	-277	
12	0	-20	365	361	
12	0	-18	522	538	
12	0	-16	138	95	
12	0	-14	455	480	
12	0	-12	1536	1540	
12	0	-10	773	771	
12	0	-8	1087	1106	
12	0	-6	156	-168	
12	0	-4	1602	1656	
12	0	-2	324	-369	
12	0	0	244	-238	
12	0	2	570	-585	
12	0	4	929	960	
12	0	6	204	-236	
12	0	8	105	66	<
12	0	10	58	-24	<
12	0	12	840	843	
12	0	14	193	207	
12	0	16	84	36	<
12	0	18	267	230	
12	0	20	670	674	
14	0	-30	216	-201	
14	0	-28	356	307	
14	0	-26	674	-654	
14	0	-24	58	40	<
14	0	-22	336	-312	
14	0	-20	384	-420	
14	0	-18	1043	-1052	
14	0	-16	641	-646	
14	0	-14	199	-251	
14	0	-12	514	-548	
14	0	-11	149	-591	
14	0	-10	263	-271	
14	0	-9	485	200	
14	0	-8	162	225	
14	0	-6	47	14	<
14	0	-4	250	158	
14	0	-2	853	-875	
14	0	0	545	557	
14	0	2	342	-327	
14	0	4	133	131	<
14	0	6	1148	-1142	
14	0	8	572	559	
14	0	10	700	-690	
14	0	12	486	-475	
16	0	-22	143	-77	
16	0	-20	319	322	
16	0	-18	24	62	<
16	0	-16	445	475	
16	0	-14	368	-345	
16	0	-12	63	31	<
16	0	-10	400	436	
16	0	-8	160	143	
16	0	-6	329	-308	
16	0	-4	186	133	
16	0	-2	218	265	
16	0	0	631	675	
16	0	2	200	-209	
16	0	4	724	765	
16	0	6	316	271	
16	0	8	621	660	
16	0	10	133	-139	<
0	1	1	710	780	
0	1	3	1662	1806	
0	1	5	2837	3313	
0	1	7	1991	-2199	
0	1	9	747	738	
0	1	11	101	68	
0	1	13	719	734	
0	1	15	177	-217	
0	1	17	354	-345	
0	1	19	941	937	
0	1	21	572	580	
0	1	23	97	143	
0	1	25	63	-46	<
0	1	27	741	702	
0	1	29	159	121	
0	1	31	234	202	
1	1	1	56	-36	
1	1	3	1611	1631	
1	1	5	998	-1019	
1	1	7	1519	1573	
1	1	9	633	-627	
1	1	11	1421	1426	
1	1	13	671	677	
1	1	15	751	722	
1	1	17	176	175	
1	1	19	621	581	
1	1	21	485	-475	
1	1	23	240	238	
1	1	25	287	-306	
1	1	27	347	361	
1	1	29	156	-170	
1	1	31	286	318	
2	1	1	1764	1740	
2	1	3	1328	-1271	
2	1	5	1070	-1037	
2	1	7	235	238	
2	1	9	305	363	
2	1	11	1125	-1105	
2	1	13	708	-678	
2	1	15	462	-463	
2	1	17	535	519	
2	1	19	918	-909	
2	1	21	886	-859	
2	1	23	90	-95	<
2	1	25	331	-342	
2	1	27	256	-237	
2	1	29	564	-517	
2	1	31	187	130	
3	1	1	686	-622	
3	1	3	284	277	
3	1	5	2716	-2805	
3	1	7	293	-276	
3	1	9	868	-838	
3	1	11	74	41	<
3	1	13	561	-546	
3	1	15	694	691	
3	1	17	423	-433	
3	1	19	340	322	
3	1	21	440	-439	
3	1	23	163	152	
3	1	25	491	-508	
3	1	27	84	18	<
3	1	29	452	-465	
4	1	1	1373	-1431	
4	1	3	1652	1620	
4	1	5	121	48	
4	1	7	651	638	
4	1	9	327	-348	
4	1	11	954	930	
4	1	13	1289	1292	
4	1	15	344	367	
4	1	17	490	486	
4	1	19	112	101	
4	1	21	1015	1022	
4	1	23	68	60	<
4	1	25	213	-133	
4	1	27	161	131	
4	1	29	129	105	<
5	1	1	49	-54	<
5	1	3	1096	1061	
5	1	5	794	-766	
5	1	7	1100	1103	
5	1	9	992	-983	
5	1	11	397	409	
5	1	13	127	-125	
5	1	15	694	695	
5	1	17	386	-384	
5	1	19	824	842	
5	1	21	56	110	<
5	1	23	521	512	
5	1	25	70	69	<
5	1	27	350	331	
6	1	1	1070	-988	
6	1	3	320	338	
6	1	5	1821	-1846	
6	1	7	384	-384	
6	1	9	635	-647	
6	1	11	263	-263	
6	1	13	976	-970	
6	1	15	746	-762	
6	1	17	40	71	<
6	1	19	0	-24	<
6	1	21	98	91	<
6	1	23	212	-253	
6	1	25	299	299	
6	1	27	158	-179	
7	1	1	454	-450	
7	1	3	963	955	
7	1	5	1072	-1072	
7	1	7	265	273	
7	1	9	708	-701	
7	1	11	141	150	
7	1	13	1062	-1077	
7	1	15	96	-71	<
7	1	17	521	-534	
7	1	19	65	-2	<
7	1	21	497	-495	
7	1	23	58	-7	<
7	1	25	281	-327	
8	1	1	1312	1294	
8	1	3	387	-376	
8	1	5	1135	1148	
8	1	7	1463	1469	
8	1	9	100	92	<
8	1	11	86	65	<
8	1	13	569	-592	
8	1	15	426	431	
8	1	17	64	13	<
8	1	19	67	-60	<
8	1	21	326	338	
8	1	23	391	369	
8	1	25	25	76	<
9	1	1	259	-285	
9	1	3	999	1023	
9	1	5	131	-109	
9	1	7	945	932	
9	1	9	112	94	
9	1	11	355	363	
9	1	13	180	163	
9	1	15	676	701	
9	1	17	102	-121	
9	1	19	420	443	
9	1	21	87	-38	<
9	1	23	244	242	
10	1	1	342	-308	
10	1	3	87	116	
10	1	5	781	799	
10	1	7	520	-538	
10	1	9	468	-494	
10	1	11	334	314	
10	1	13	305	-314	
10	1	15	209	-193	
10	1	17	434	-424	
10	1	19	242	207	
10	1	21	284	-268	
10	1	23	452	-398	
11	1	1	804	-804	
11	1	3	232	235	
11	1	5	730	-722	
11	1	7	161	-161	
11	1	9	534	-553	
11	1	11	38	-77	<
11	1	13	393	-414	
11	1	15	90	99	<
11	1	17	300	-286	
11	1	19	362	345	
12	1	1	829	849	
12	1	3	164	-143	
12	1	5	116	-146	
12	1	7	231	248	
12	1	9	440	487	
12	1	11	164	-164	
12	1	13	253	230	
12	1	15	495	512	
12	1	17	480	491	
12	1	19	63	159	<
13	1	1	63	-42	<
13	1	3	791	812	
13	1	5	69	-102	<
13	1	7	375	388	
13	1	9	106	-26	<
13	1	11	168	162	
13	1	13	366	-385	
14	1	1	615	-651	
14	1	3	129	-118	
14	1	5	61	39	<
14	1	7	623	-619	
14	1	9	333	-353	
14	1	11	373	-395	
14	1	13	219	213	
15	1	1	586	-608	
15	1	3	378	346	
15	1	5	144	-146	<
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16	1	1	147	168	
16	1	3	551	568	
16	1	5	35	28	<
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1	1	-25	478	482	
1	1	-23	141	103	
1	1	-21	637	659	
1	1	-19	117	88	
1	1	-17	1072	1109	
1	1	-15	323	-290	
1	1	-13	605	595	
1	1	-11	265	269	
1	1	-9	1819	1879	
1	1	-7	1419	-1505	
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1	1	-3	69	81	
1	1	-1	1104	1137	
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2	1	-27	464	-472	
2	1	-25	259	-271	
2	1	-23	309	285	
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2	1	-17	525	-543	
2	1	-15	789	807	
2	1	-13	995	-992	
2	1	-11	1222	-1275	
2	1	-9	185	-192	
2	1	-7	1982	-2044	
2	1	-5	1156	-1116	
2	1	-3	2873	-3103	
2	1	-1	185	200	
3	1	-31	335	-341	
3	1	-29	141	75	
3	1	-27	516	-541	
3	1	-25	91	-29	<
3	1	-23	599	-598	
3	1	-21	184	174	
3	1	-19	953	-968	
3	1	-17	51	-3	<
3	1	-15	998	-979	
3	1	-13	617	603	
3	1	-11	1643	-1658	
3	1	-9	146	163	
3	1	-7	935	-887	
3	1	-5	763	729	
3	1	-3	892	-780	
3	1	-1	32	-66	
4	1	-31	139	-122	
4	1	-29	100	121	<
4	1	-27	85	12	<
4	1	-25	529	546	
4	1	-23	182	-198	
4	1	-21	335	-344	
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4	1	-17	474	479	
4	1	-15	1315	1369	
4	1	-13	644	625	
4	1	-11	1684	1737	
4	1	-9	111	87	
4	1	-7	351	292	
4	1	-5	483	-480	
4	1	-3	1099	1040	
4	1	-1	1765	1783	
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5	1	-27	0	35	<
5	1	-25	576	562	
5	1	-23	100	-82	<
5	1	-21	788	805	
5	1	-19	351	-336	
5	1	-17	1008	1000	
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6	1	-19	704	-674	
6	1	-17	995	-1004	
6	1	-15	229	207	
6	1	-13	345	-344	
6	1	-11	151	-85	
6	1	-9	1779	-1804	
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6	1	-3	208	216	
6	1	-1	714	-712	
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7	1	-19	302	-325	
7	1	-17	278	296	
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7	1	-13	101	88	
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8	1	-23	94	119	
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8	1	-19	106	-87	
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8	1	-11	243	-230	
8	1	-9	755	716	
8	1	-7	1086	1046	
8	1	-5	284	-288	
8	1	-3	510	533	
8	1	-1	722	711	
9	1	-31	128	-125	<
9	1	-29	210	217	
9	1	-27	153	-167	
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9	1	-23	123	-92	
9	1	-21	546	534	
9	1	-19	85	61	<
9	1	-17	744	750	
9	1	-15	265	234	
9	1	-13	1061	1059	
9	1	-11	616	-598	
9	1	-9	1192	1193	
9	1	-7	526	-533	
9	1	-5	359	356	
9	1	-3	134	-143	
9	1	-1	770	756	
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10	1	-25	356	-394	
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10	1	-19	154	146	
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10	1	-5	653	-635	
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10	1	-1	2130	-2168	
11	1	-31	267	-267	
11	1	-29	125	47	<
11	1	-27	275	-266	
11	1	-25	169	-98	
11	1	-23	544	-541	
11	1	-21	69	-45	<
11	1	-19	593	-601	
11	1	-17	251	254	
11	1	-15	632	-623	
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11	1	-11	529	-534	
11	1	-9	344	338	
11	1	-7	852	-862	
11	1	-5	60	42	<
11	1	-3	466	-488	
11	1	-1	81	-29	<
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12	1	-27	47	56	<
12	1	-25	89	-30	<
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12	1	-21	118	-123	
12	1	-19	89	-67	<
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12	1	-15	464	488	
12	1	-13	759	749	
12	1	-11	0	29	<
12	1	-9	1321	1359	
12	1	-7	512	512	
12	1	-5	61	-22	<
12	1	-3	389	-378	
12	1	-1	187	178	
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13	1	-27	24	-15	<
13	1	-25	287	300	
13	1	-23	125	-85	<
13	1	-21	435	452	
13	1	-19	169	-139	
13	1	-17	326	361	
13	1	-15	134	14	
13	1	-13	537	560	
13	1	-11	223	-221	
13	1	-9	322	361	
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13	1	-3	131	-133	
13	1	-1	748	751	
14	1	-25	48	-68	<
14	1	-23	118	-70	<
14	1	-21	815	-794	
14	1	-19	66	-1	<
14	1	-17	489	-474	
14	1	-15	478	-510	
14	1	-13	203	-214	
14	1	-11	0	1	<
14	1	-9	102	66	<
14	1	-7	714	-720	
14	1	-5	0	48	<
14	1	-3	206	-204	
14	1	-1	431	437	
15	1	-25	43	29	<
15	1	-23	376	-380	
15	1	-21	92	83	<
15	1	-19	278	-277	
15	1	-17	100	74	<
15	1	-15	261	-259	
15	1	-13	32	-10	<
15	1	-11	364	-376	
15	1	-9	114	135	
15	1	-7	633	-630	
15	1	-5	155	-176	
15	1	-3	467	-480	
15	1	-1	116	132	
16	1	-21	301	312	
16	1	-19	280	259	
16	1	-17	336	-320	
16	1	-15	435	465	
16	1	-13	247	274	
16	1	-11	119	69	<
16	1	-9	173	-225	
16	1	-7	134	108	
16	1	-5	526	537	
16	1	-3	150	-66	
16	1	-1	282	280	
0	2	2	330	240	
0	2	4	1123	-1164	
0	2	6	413	-425	
0	2	8	397	-340	
0	2	10	1661	1694	
0	2	12	1098	-1151	
0	2	14	1309	1348	
0	2	16	134	-80	
0	2	18	638	619	
0	2	20	1034	-1017	
0	2	22	654	658	
0	2	24	165	99	
0	2	26	374	360	
0	2	27	342	135	
0	2	28	228	-232	
0	2	29	250	-174	
0	2	30	134	114	
0	2	31	0	197	
0	2	32	141	134	
1	2	-32	0	38	<
1	2	-30	120	165	
1	2	-29	177	122	
1	2	-28	55	36	<
1	2	-27	97	33	<
1	2	-26	201	195	
1	2	-25	194	434	
1	2	-24	543	543	
1	2	-22	421	421	
1	2	-20	1070	1090	
1	2	-18	803	822	
1	2	-16	448	466	
1	2	-14	1580	1655	
1	2	-12	167	185	
1	2	-10	183	161	
1	2	-8	709	731	
1	2	-6	204	-243	
1	2	-4	45	18	
1	2	-2	25	-102	
1	2	0	613	-618	
1	2	2	315	275	
1	2	4	1081	1058	
1	2	6	507	506	
1	2	8	1671	1735	
1	2	10	981	1006	
1	2	12	1510	1579	
1	2	14	927	959	
1	2	16	801	827	
1	2	18	552	581	
1	2	20	81	65	<
1	2	22	375	403	
1	2	24	181	-184	
1	2	26	44	82	<
1	2	28	51	92	<
1	2	30	151	71	
2	2	-32	246	-249	
2	2	-30	107	-113	<
2	2	-28	0	34	<
2	2	-26	216	235	
2	2	-24	462	-469	
2	2	-22	292	-327	
2	2	-20	202	-222	
2	2	-18	455	491	
2	2	-16	968	-1025	
2	2	-14	1363	1444	
2	2	-12	824	-852	
2	2	-10	954	1029	
2	2	-8	1860	-1999	
2	2	-6	666	632	
2	2	-4	311	318	
2	2	-2	1487	1500	
2	2	0	1457	-1442	
2	2	2	491	-477	
2	2	4	452	-344	
2	2	6	488	-500	
2	2	8	732	-724	
2	2	10	454	428	
2	2	12	166	-74	
2	2	14	598	610	
2	2	16	1327	-1388	
2	2	18	102	60	
2	2	20	328	-347	
2	2	22	774	758	
2	2	24	821	-842	
2	2	26	208	188	
2	2	28	0	-70	<
2	2	30	115	97	<
3	2	-32	256	-252	
3	2	-30	293	-303	
3	2	-28	490	-486	
3	2	-26	400	-417	
3	2	-24	580	-585	
3	2	-22	533	-562	
3	2	-20	535	-556	
3	2	-18	230	-255	
3	2	-16	384	-395	
3	2	-14	593	-639	
3	2	-12	103	106	
3	2	-10	115	105	
3	2	-8	507	580	
3	2	-6	809	-786	
3	2	-4	354	-318	
3	2	-2	691	-636	
3	2	0	1367	-1343	
3	2	2	1678	-1620	
3	2	4	2027	-2069	
3	2	6	1214	-1200	
3	2	8	1407	-1434	
3	2	10	1393	-1426	
3	2	12	328	-321	
3	2	14	133	-136	
3	2	16	166	-173	
3	2	18	281	284	
3	2	20	255	-263	
3	2	22	0	-58	<
3	2	24	116	-116	<
3	2	26	318	-327	
3	2	28	175	-165	
4	2	-32	0	-84	<
4	2	-30	458	472	
4	2	-28	0	7	<
4	2	-26	152	-90	
4	2	-24	218	-193	

Table 2. Continued.

Table of observed and calculated structure factors (h, k, l, F_{obs}, F_{cal}) arranged in multiple columns.

Table 2. Continued.

Table 2. Continued.

The table consists of multiple repeated columns of structure-factor data with headings **h k l Fobs Fcal**.

A three-dimensional Fourier synthesis, calculated using the normalized structure factors (E-values) of these 410 reflexions as amplitudes, fully confirmed the interpretation of the Patterson function. All the light atoms except hydrogen atoms were found. The trial structure gave $R=28.9$ %; least squares refinement of coordinates and isotropic temperature factor coefficients lowered the R-value to 12.2 % for 1640 reflexions.

When the diffractometer data became available, refinement was continued by means of a block diagonal least squares program including anisotropic temperature factor parameters. At $R=8.44$ % a difference Fourier map was calculated and small peaks were found where hydrogen atoms were expected. When they were included R dropped to 7.25 %. Further refinement reduced R to 5.0 % for reflexions with $F_o{}^2>2\sigma(F^2)$. The weights used in the least squares refinement were $w=1/(\mu(F))^2$, where $\mu(F)=\sqrt{\overline{F^2+\sigma(F^2)}}-F$; $\sigma(F^2)=\sigma(F^2)_{count}+p\cdot F^2$ where $\sigma(F^2)_{count}$ was the standard deviation estimated from the counting statistics and p a constant (0.02) which was adjusted so as to give a mean value of $w|F_o-F_c|^2$ which varied little with F. This was supposed to account for possible systematic errors in the data, due to, e.g., misalignment, cell constant errors, or extinction.

The scattering factors used are those of *International Tables*,[6] Table B for Ni and Table A for the other atoms. They were approximated by Bassi polynomials.[7]

DISCUSSION

The most remarkable feature of this structure is the presence of both *cis*- and *trans*-isomers in one crystal. This has not so far been observed in any other structure, but shortly after this structure had been solved, three papers appeared describing the co-crystallisation of two forms of the same or nearly, the same complex. The green form of bis(benzyldiphenylphosphine) dibromo nickel(II) has two molecules with tetrahedrally coordinated nickel and one with the *trans* square planar configuration in the unit cell.[8] The yellow modification of bis(meso-stilbenediamine) nickel(II) dichloroacetate contains one molecule of square planar configuration and two of octahedral coordination in the unit cell, the extra ligands being oxygen atoms from the anion.[9] Octamethylcyclotetrasilazane forms eight membered rings and in the crystal two conformations, called "chair" and "cradle", are found, one round a centre of symmetry, the other round a twofold axis.[10]

Table 3 gives the bond lengths and angles. The distances given are both the values directly obtained from the coordinates and those corrected for thermal vibration effects. An analysis of the thermal parameters indicates that the complex ions except for the amide groups vibrate as rigid bodies. The amide groups are assumed to ride on the carbon atoms. The rigid body analysis was performed by Cruickshank's method [11] using a program written by Trueblood. The correction for riding motion was performed according to Busing and Levy [12] using their ORFFE program. For the following discussion it is of little importance which set of numbers is used.

The Ni—S bond lengths found are similar to those found in other planar complexes: 2.16 Å in α-NiThio$_2$SO$_4$,3H$_2$O,[2] 2.155$\pm$0.004 Å in thiosemi-

Table 3. Bond lengths and angles.

The distances obtained after correction for thermal vibration are given after the uncorrected distances. The standard deviations (in parentheses) do not include cell parameter errors.

Distance	cis-Planar ion			trans-Planar ion		
	(Å)	(Å × 10⁻³)	corr. (Å)	(Å)	(Å × 10⁻³)	corr. (Å)
Ni—S	2.145	(1)	2.149	2.165	(1)	2.169
Ni—N₁	1.926	(3)	1.930	1.920	(3)	1.926
N₁—N₂	1.426	(4)	1.428	1.430	(4)	1.431
S—C	1.727	(3)	1.731	1.716	(3)	1.721
C—N₂	1.331	(4)	1.336	1.321	(5)	1.327
C—N₃	1.323	(4)	1.331	1.318	(5)	1.323

Angles in degrees, standard deviation in degrees × 10⁻².

S—Ni—N₁ (5-ring)	89.14	(9)		89.96	(12)
S—Ni—S'	90.95	(4)		180.00	
N₁—Ni—N₁'	91.08	(13)		180.00	
S—Ni—N₁'	175.40	(12)		90.04	(12)
Ni—S—C	97.81	(13)		96.72	(15)
Ni—N₁—N₂	115.17	(18)		113.77	(22)
N₁—N₂—C	118.27	(25)		119.17	(26)
S—C—N₂	119.29	(24)		120.21	(25)
S—C—N₃	121.54	(24)		120.45	(27)
N₂—C—N₃	119.17	(29)		119.34	(29)

The sulphate ion:

Distance	(Å)	(Å × 10⁻³)	corr. (Å)	Angle		
S—O₁	1.466	(3)	1.490	O₁—S—O₂	108.49	(17)
S—O₂	1.490	(3)	1.499	O₁—S—O₃	109.70	(24)
S—O₃	1.464	(4)	1.494	O₁—S—O₄	110.32	(21)
S—O₄	1.471	(4)	1.492	O₂—S—O₃	109.71	(19)
				O₂—S—O₄	109.86	(19)
				O₃—S—O₄	108.74	(21)

carbazidato-nickel,[13] and 2.160±0.008 Å in bis(maleonitriledithiolate) nickelate.[14] In tris(mercaptoethyl)phosphine-nickel [15] one Ni—S bond is 2.158±0.006 Å and two others are 2.216 and 2.228 Å. The latter sulphur atoms are also bonded to another nickel atom, thus forming a four membered ring, for which the Ni—S distances of 2.20—2.25 Å seem characteristic (*e.g.* α-nickel-diethyldithiocarbamate [16] and (Ni(SC₂H₅)₂)₆[17]). In octahedral complexes the Ni—S distances are much longer as could be expected: 2.4—2.5 Å, *e.g.* 2.462±0.004 Å in dichlorotetrakisthiourea nickel.[18]

The Ni—S bond of the *cis*-complex in the present investigation is significantly shorter than that of the *trans*-complex. This could be expected since sulphur exhibits a stronger *trans* effect than an amino group does. It is believed that the observed difference is a reliable quantitative estimate of this effect, since many of the errors which can occur in a structure determination may be assumed to affect similar bonds in the same crystal in much the same way;
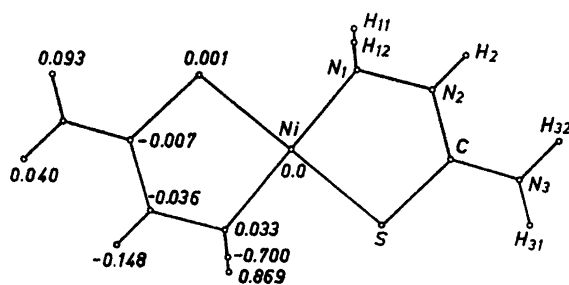
Fig. 1. The *trans*-complex projected on to the best plane through all atoms except hydro-gen: The numbers indicate the distances of the atoms from this plane. The equation of the plane is:

$$0.0835 \ X + 0.4861 \ Y - 0.8699 \ Z = 7.6239.$$

in this connection it may be noticed that corresponding bonds in the two ligands deviate by no more than 1.5 σ. Also any effects of strain or charge distribution within the ligands will be the same for both complexes.

The Ni—N bonds differ in such a way that they confirm the observed *trans* effect, although the standard deviations here are too large to allow a reliable conclusion. Similar Ni—N distances were found in α-NiThio$_2$SO$_4$,3H$_2$O [2] and Ni(CH$_4$SN$_3$) [13] which are both *trans*-planar. Ni—N distances of 1.89—1.94 Å thus seem characteristic of square planar complexes with sp^3-hybridized nitrogen; in complexes with trigonally hybridized nitrogen somewhat shorter Ni—N distances are observed, *e.g.* 1.85 Å in nickel dimethylglyoxime.[19]

The bond angles around Ni are close to 90° and the distances and angles in the organic ligand are the same as those of free thiosemicarbazide [20] suggesting that no strain is introduced by the complex formation. Both complex ions are nearly but not quite planar. In the *trans*-complex (Fig. 1) the space group symmetry requires the coordination to be exactly planar but the three outer atoms of the ligand deviate from the plane. The coordination around the carbon atom is planar, the carbon atom being less than one standard deviation from the plane of its neighbours.
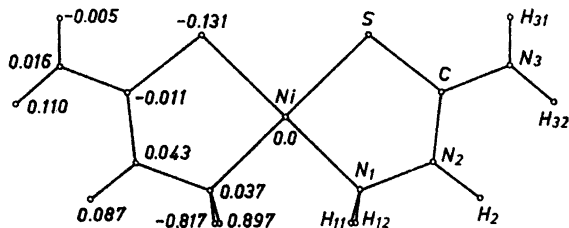

Fig. 2. The *cis*-complex projected on to the best plane through all atoms except hydrogen: The numbers indicate the distances of the atoms from this plane. The equation of the plane is:

$$0.4826 \ X - 0.8759 \ Z = -5.1690.$$

Table 4. Intermolecular distances (in Å) corresponding to possible hydrogen bonds.

	N_{1cis}	N_{2cis}	N_{3cis}	N_{1tr}	N_{2tr}	N_{3tr}
O$_1$			2.859		2.721	
O$_2$	2.974	2.844	2.954			
O$_3$				3.075		2.851
O$_4$	2.810					2.885

In the *cis* complex (Fig. 2) a slight tetrahedral deformation of the coordination plane is observed. Here also the outer part of the ligand plane is tilted somewhat with respect to the Ni—S—N$_1$ plane and the configuration around the carbon atoms is planar.

The packing of the ions is determined by the tendency to hydrogen bond formation. The positions of the hydrogen atoms were determined assuming that N$_1$ is sp^3 hybridized and that the hydrogen atoms at N$_2$ and N$_3$ all lie in the plane of the ligand. These positions were confirmed from the difference-Fourier map. Eight hydrogen atoms are located so that the N—H bonds are close to pointing towards oxygen atoms corresponding to the shortest interionic
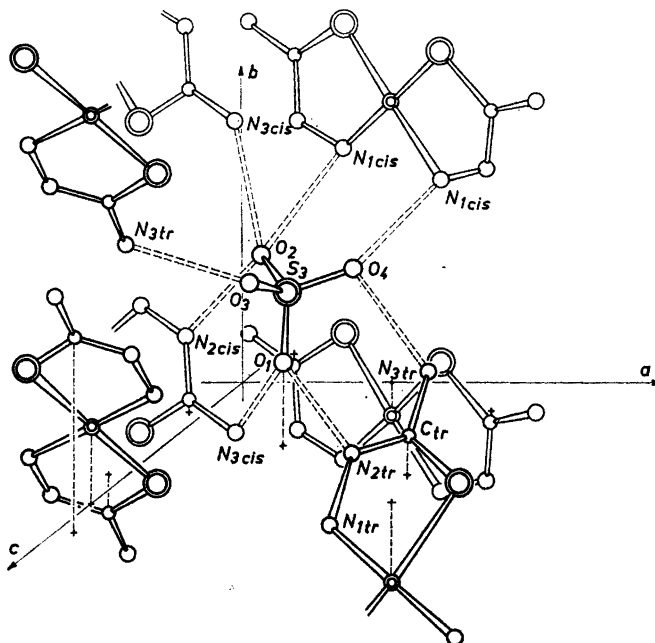

Fig. 3. Clinographic projection of part of the structure showing the hydrogen bonds.

distances found in the structure. The lengths of the hydrogen bonds are given in Table 4. The system of hydrogen bonding is shown in Fig. 3.

The sulphate ion is a practically regular tetrahedron. A rigid body motion does not account too well for the temperature factors found whereas the assumption that oxygen atoms perform a riding motion on sulphur leads to corrected distances which are very similar.

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