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The Crystal Structures of the *cis* and *trans* Isomer of Nickel(II) Dithiosemicarbazide Dinitrate

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Nickel dithiosemicarbazide dinitrate, $Ni(CH_5N_3S)_2(NO_3)_2$, exists in two forms shown by three-dimensional X-ray crystal structure analyses to be *cis* and *trans* planar, respectively. The *cis* isomer is the one usually obtained whereas the *trans* isomer is unstable if left in the mother liquor. The *cis* complex is monoclinic, $P2_1/a$, with unit cell $a = 17.80$ Å, $b = 9.74$ Å, $c = 7.13$ Å, $\beta = 93.1°$; $Z = 4$; the R-value is 0.073 for 818 significant reflections.

The *trans* complex is triclinic, $P\bar{1}$, with unit cell $a = 7.22$ Å, $b = 6.91$ Å, $c = 6.61$ Å, $\alpha = 93.97°$, $\beta = 93.46°$, $\gamma = 115.03°$, $Z = 1$; the R-value is 0.056 for 1061 significant reflections. Both sets of data were collected on an automatic diffractometer and the structures were refined by the method of least squares. The bond lengths found in the two structures agree with those of related compounds; the Ni–S bond of the *trans* complex is longer than those of the *cis* complex.

In the investigation of several complexes of nickel with thiosemicarbazide (Thio)[1–4] many attempts were made to obtain good crystals of the red $NiThio_2(NO_3)_2$ because this was expected from its colour to be a *cis* planar complex. If aqueous solutions of $Ni(NO_3)_2.6H_2O$ and thiosemicarbazide are mixed and left to evaporate, you get a red crust and blue crystals of the corresponding diaquothiosemicarbazide complex. From mixtures of ethanol and water, tiny red crystals can be obtained, all of very poor quality and nearly all twinned. After many attempts a crystal was found which showed monoclinic symmetry with the angle $\beta = 93.1°$. The reflections show an angular spread of 2 – 3° even for this "good" crystal, but all other crystals investigated showed pseudo orthorhombic twinning across the 001 plane giving reflections of apparent width 10°. All further work was done on this one crystal with dimensions $0.06 \times 0.06 \times 0.07$ mm^3. In the search some different crystals were found in one particular preparation. They exhibit strong red-green dichroism and are triclinic with one molecule per cell and were thus easily shown to be the *trans* isomer. A few days later when more ethanol had evaporated, these crystals had been replaced by other less welldefined compounds, leaving only the one mounted for X-ray work. The dimensions of this crystal are $0.1 \times 0.08 \times 0.18$ mm^3.

DATA COLLECTION

In both cases preliminary investigations were made on rotation, Weissenberg, and precession photographs. The cell dimensions were obtained from the precession films taken with Cu$K\alpha$ ($\lambda = 1.5418$ Å) and Mo$K\alpha$ ($\lambda = 0.7107$ Å) radiation. The intensities were collected using the Arndt-Phillips linear diffractometer [5] with Mo$K\alpha$ radiation. In the case of the *trans* complex, balanced filters were used whereas the data for the *cis* complex were collected using a graphite monochromator. The crystal of the *cis* complex gave very broad peaks with tails so it was decided not to subtract the backgrounds as measured at the edges of the peak but to subtract a function of $\sin\theta$ determined far from the reflections. For both crystals the usual corrections for Lorentz-polarization factors were applied but because of the size of the crystals, absorption correction was considered unimportant at the level of accuracy expected for the data.

STRUCTURE DETERMINATION

The *trans* complex had only one molecule in the triclinic cell, and a Fourier map calculated with all signs positive corresponding to a nickel atom at the origin showed all the atoms. The structure of the *cis* complex was solved from the Patterson function from which the nickel and sulphur atoms were found; a Fourier map then showed all the lighter atoms. Both structures were refined using a block diagonal least squares program written in ALGOL. Anisotropic temperature factor parameters were included in the later stages of the refinement. At the end of the refinement, difference syntheses showed peaks at approximately the positions expected for hydrogen atoms as well as some background noise. Inclusion of the hydrogen atoms caused a slight drop in R-value, although in the case of the *cis* complex not a significant one. The weights used at the end of the refinement were $w = 1/\mu(F)^2$, where $\mu(F) = \sqrt{F^2 - \sigma(F^2)} - |F|$; $\sigma(F^2)$ from the counting statistics did not cover all errors but was modified: $\sigma(F^2) = \sigma(F^2)_{\text{count}} + aF^2$ where a was adjusted so that the mean value of $w\Delta^2$ varied little with the size of F, $a = 0.07$ for the *cis* complex, $a = 0.05$ for the *trans* complex.

Extinction was found to be negligible in both cases. The final R-values were 0.073 for the *cis* complex, 0.056 for the *trans* compound.

CRYSTAL DATA

cis $Ni(CH_5N_3S)_2(NO_3)_2$ (red crystals).
Crystal system: monoclinic (b unique).

$a = 17.80 \pm 0.05$ Å, $b = 9.74 \pm 0.03$ Å, $c = 7.13 \pm 0.02$ Å,
$\beta = 93.1 \pm 0.25°$, $V = 1231$ Å^3, $Z = 4$, $d_{\text{calc}} = 1.97$ g/cm^3.

Systematic absences: $h0l$ for $h = 2n$.
$0k0$ $k = 2n$.

Space group: $P2_1/a$.

Table 1. Final atomic coordinates of the monoclinic *cis* $NiThio_2(NO_3)_2$. Standard deviations $\times 10^4$ in parentheses.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Ni	0.5140	(1)	0.5350	(2)	0.2541	(3)
S_1	0.5219	(3)	0.3182	(4)	0.2039	(6)
S_2	0.3949	(2)	0.5221	(4)	0.2885	(6)
N_{11}	0.6215	(7)	0.5508	(11)	0.2294	(16)
N_{21}	0.6586	(7)	0.4238	(11)	0.1945	(18)
N_{31}	0.6507	(8)	0.1970	(13)	0.1336	(22)
N_{12}	0.5079	(6)	0.7339	(11)	0.3007	(15)
N_{22}	0.4344	(6)	0.7803	(12)	0.3246	(20)
N_{32}	0.3131	(7)	0.7342	(13)	0.3711	(21)
C_1	0.6199	(9)	0.3134	(15)	0.1770	(22)
C_2	0.3792	(8)	0.6919	(15)	0.3300	(19)
N_{01}	0.3374	(8)	0.1299	(15)	0.0101	(21)
N_{02}	0.3514	(7)	0.0902	(13)	0.4889	(23)
O_1	0.3957	(8)	0.0984	(12)	−0.0740	(19)
O_2	0.3007	(7)	0.0409	(11)	0.0798	(20)
O_3	0.3160	(7)	0.2557	(11)	0.0239	(20)
O_4	0.3441	(6)	0.2184	(11)	0.5092	(21)
O_5	0.4149	(6)	0.0447	(11)	0.4662	(18)
O_6	0.2944	(6)	0.0151	(10)	0.5069	(20)
H_{111}	0.6429	(110)	0.6011	(215)	0.3339	(295)
H_{112}	0.6310	(80)	0.6046	(150)	0.1259	(200)
H_{21}	0.7228	(85)	0.4160	(150)	0.1520	(205)
H_{311}	0.7138	(90)	0.2049	(190)	0.1073	(245)
H_{312}	0.6312	(105)	0.1030	(190)	0.1014	(270)
H_{121}	0.5249	(75)	0.8047	(155)	0.1896	(200)
H_{122}	0.5475	(75)	0.7599	(165)	0.4189	(200)
H_{22}	0.4235	(105)	0.8826	(195)	0.3715	(275)
H_{321}	0.3031	(75)	0.8445	(155)	0.4258	(190)
H_{322}	0.2748	(85)	0.6727	(165)	0.3838	(210)

Coordinates and anisotropic temperature factor parameters are given in Tables 1 and 2, a list of observed and calculated structure factors in Table 5. Bond lengths and angles are compared with those of the *trans* complex in Table 7.

trans $Ni(CH_5N_3S)_2(NO_3)_2$ (red-green dichroitic crystals).
Crystal system: triclinic.

$a = 7.22 \pm 0.02$ Å, $b = 6.91 \pm 0.02$ Å, $c = 6.61 \pm 0.01$ Å,
$\alpha = 93.97 \pm 0.1°$, $\beta = 93.46 \pm 0.1°$, $\gamma = 115.03 \pm 0.1°$,
$V = 296$ Å^3, $Z = 1$; $d_{calc} = 1.90$ g/cm^3

Space group: $P\bar{1}$.

Coordinates and anisotropic temperature factor parameters are given in Tables 3 and 4, a list of observed and calculated structure factors in Table 6, and bond lengths and angles in Table 7.

Table 2. Mean square thermal displacements, $u_{ij} \times 10^4$, of the heavier atoms of *cis* $NiThio_2(NO_3)_2$; standard deviations $\times 10^4$ in parentheses.

	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	584	(13)	384	(12)	910	(13)	−84	(10)	125	(11)	−38	(10)
S_1	818	(36)	468	(27)	1010	(31)	−110	(25)	119	(28)	−53	(24)
S_2	677	(32)	506	(27)	906	(29)	−108	(23)	151	(24)	−25	(23)
N_{11}	691	(91)	319	(73)	892	(83)	−52	(64)	114	(69)	−21	(63)
N_{21}	681	(97)	332	(75)	1067	(97)	34	(68)	96	(76)	28	(68)
N_{31}	1238	(136)	320	(81)	1553	(138)	172	(83)	283	(111)	176	(83)
N_{12}	556	(83)	279	(67)	812	(82)	−111	(59)	82	(64)	−54	(60)
N_{22}	462	(83)	519	(90)	1260	(103)	9	(67)	251	(76)	72	(75)
N_{32}	663	(100)	534	(90)	1324	(116)	49	(74)	60	(87)	154	(84)
C_1	903	(131)	387	(93)	915	(105)	94	(89)	139	(98)	−25	(80)
C_2	509	(101)	481	(94)	781	(92)	56	(78)	144	(81)	41	(75)
N_{01}	1082	(129)	766	(109)	1084	(100)	−196	(93)	351	(92)	−187	(82)
N_{01}	639	(104)	465	(89)	1571	(127)	28	(74)	14	(93)	−67	(86)
O_1	1409	(127)	752	(95)	1431	(108)	−402	(87)	512	(95)	−151	(80)
O_2	1203	(111)	519	(79)	1833	(131)	−264	(72)	749	(99)	42	(81)
O_3	1382	(118)	382	(71)	1693	(123)	−88	(71)	461	(95)	12	(74)
O_4	670	(82)	465	(76)	1972	(132)	21	(61)	100	(83)	−29	(78)
O_5	500	(71)	693	(84)	1707	(118)	167	(61)	36	(73)	−223	(79)
O_6	592	(78)	427	(69)	1767	(112)	−29	(58)	135	(76)	36	(70)

All hydrogen atoms have isotropic temperature factors, B, of 5.0 Å^2.

DISCUSSION

Both structures show the features which were expected for them. The red crystals have the complex ion in the *cis*-configuration, the red-green dichroitic ones the *trans*-configuration. The complex ions are similar to the cations in β-$NiThio_2SO_4$.[2] As in this compound the Ni−S bonds in the *cis* complex are shorter than that of the *trans* complex and also of those of the *trans* complex ions in β-$NiThio_2SO_4$ and in α-$NiThio_2SO_4.3H_2O$.[1] The Ni−S bonds in the present *trans* complex are longer than those in the other complexes mentioned; this may be a result of a slight bonding interaction between nickel and two O_3-atoms of the nearest nitrate groups. These oxygen atoms are 3.14 Å away from nickel in directions which give a somewhat distorted octahedron. O_3 is taking part in one weak hydrogen bond and the geometry is such that a lone pair may be pointing towards nickel.

The dimensions of the thiosemicarbazide groups are all similar to those of free thiosemicarbazide [6,7] and of the other complexes investigated in this laboratory,[1–4] at the University of Parma,[8,9] and in Bratislava.[10] The nitrate groups are planar and regular within experimental error.

The structure of the *trans* complex is illustrated in Fig. 1 which is a projection of part of the structure on to the best plane through one complex ion. The *b* axis is approximately perpendicular to this plane. Although all hydrogen atoms take part in some interaction with oxygen atoms only one oxygen atom is in a really favourable position for hydrogen bonding and all the other

Table 3. Final atomic parameters for *trans* $NiThio_2(NO_3)_2$, standard deviations $\times 10^4$ in parentheses. For hydrogen atoms the isotropic temperature factor parameter B (Å^2) is given.

Atom	x	σx	y	σy	z	σz	B	σB
Ni	0.0000	(0)	0.0000	(0)	0.0000	(0)		
S	0.2597	(2)	0.1955	(2)	0.2238	(2)		
N_1	0.1867	(6)	0.0769	(7)	−0.2068	(6)		
N_2	0.3990	(6)	0.1787	(8)	−0.1329	(7)		
N_3	0.6439	(7)	0.3506	(9)	0.1343	(8)		
C	0.4487	(7)	0.2431	(8)	0.0638	(8)		
N	0.1451	(6)	0.7051	(7)	0.3610	(7)		
O_1	0.3223	(6)	0.7486	(8)	0.4360	(7)		
O_2	0.0183	(6)	0.7279	(7)	0.4693	(6)		
O_3	0.0919	(6)	0.6370	(8)	0.1793	(6)		
H_{11}	0.1549	(102)	0.1834	(124)	−0.2684	(120)	3.34	(1.80)
H_{12}	0.1626	(91)	−0.0498	(106)	−0.3075	(101)	1.48	(1.37)
H_2	0.5222	(112)	0.2218	(131)	0.7704	(125)	3.85	(1.94)
H_{31}	0.7485	(90)	0.3712	(98)	0.0529	(96)	0.91	(1.25)
H_{32}	0.6571	(109)	0.3608	(133)	0.2634	(134)	3.94	(2.05)

N−H···O distances are fairly long as shown in Table 8, so compared to the other similar compounds the hydrogen bonding system must be described as weak, a fact that may account for the instability of this compound. One oxygen-sulphur distance of 3.11 Å is shorter than the sum of the van der Waals radii but in the complex the sulphur atom must be slightly positive and a short distance to a negatively charged oxygen atom is therefore not alarming.

Fig. 2 is a projection along the *c* axis of the *cis* compound. The structure is built up of columns along *c* of positive ions stacked with nitrogen on top of sulphur and *vice versa*. The nitrate groups also form columns. A stacking error so that sulphur comes on top of sulphur can easily occur and can be the basis

Table 4. Mean square vibration amplitudes, $u_{ij} \times 10^4$ for the heavier atoms of *trans* $NiThio_2(NO_3)_2$.

	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	154	(4)	261	(5)	267	(4)	52	(3)	30	(4)	−20	(4)
S	211	(6)	431	(8)	296	(6)	84	(6)	44	(6)	−24	(6)
N_1	209	(21)	373	(25)	270	(20)	111	(19)	46	(18)	11	(20)
N_2	187	(20)	435	(27)	333	(22)	99	(19)	56	(19)	4	(22)
N_3	201	(22)	537	(31)	401	(25)	54	(21)	61	(22)	14	(26)
C	181	(23)	261	(25)	300	(24)	47	(20)	26	(21)	41	(23)
N	252	(21)	302	(23)	298	(21)	81	(18)	70	(19)	11	(19)
O_1	240	(20)	659	(30)	417	(22)	138	(20)	8	(19)	29	(23)
O_2	385	(22)	450	(24)	393	(20)	213	(18)	143	(19)	15	(20)
O_3	305	(21)	617	(28)	322	(19)	168	(20)	−31	(19)	−146	(21)

Table 5. Observed and calculated structure factors for *cis* NiThio$_2$(NO$_3$)$_2$.

h	k	l	Fobs	Fcal
4	0	0	482	-514
6	0	0	1462	1425
8	0	0	675	679
10	0	0	779	735
12	0	0	232	235
14	0	0	89	64
2	1	0	129	-130
3	1	0	1413	1393
4	1	0	484	-478
5	1	0	222	221
6	1	0	108	-107
7	1	0	1141	1098
8	1	0	87	67
9	1	0	745	721
10	1	0	135	-144
11	1	0	211	230
14	1	0	135	136
17	1	0	157	141
0	2	0	639	547
1	2	0	1147	-1019
2	2	0	462	387
3	2	0	426	-405
4	2	0	101	66
5	2	0	434	420
6	2	0	318	-346
8	2	0	499	464
10	2	0	635	636
17	2	0	139	103
1	3	0	672	560
2	3	0	811	754
4	3	0	349	340
5	3	0	250	-263
6	3	0	200	199
7	3	0	565	561
10	3	0	243	227
11	3	0	141	137
12	3	0	140	158
15	3	0	152	168
16	3	0	181	199
0	4	0	1640	1437
1	4	0	374	-354
2	4	0	392	354
3	4	0	116	113
4	4	0	424	402
5	4	0	249	245
6	4	0	300	284
7	4	0	354	345
9	4	0	666	652
10	4	0	533	514
11	4	0	448	450
13	4	0	247	240
17	4	0	193	193
1	5	0	823	777
2	5	0	326	340
3	5	0	546	514
4	5	0	119	98
6	5	0	436	413
7	5	0	395	371
8	5	0	285	277
9	5	0	517	475
10	5	0	377	385
11	5	0	158	145
12	5	0	268	257
13	5	0	88	-143
14	5	0	216	227
15	5	0	113	-100
16	5	0	300	292
0	6	0	119	94
1	6	0	234	-224
2	6	0	357	321
4	6	0	217	228
5	6	0	112	125
7	6	0	258	258
8	6	0	208	216
9	6	0	328	332
10	6	0	203	196
15	6	0	175	154
2	7	0	245	-239
5	7	0	248	-244
6	7	0	369	361
0	8	0	229	-219
2	8	0	240	-224
7	8	0	205	207
8	8	0	175	-200
9	8	0	297	295
1	9	0	279	-240
2	9	0	154	167
6	9	0	255	257
7	9	0	201	-225
8	9	0	325	283
4	10	0	175	-188
5	10	0	203	167
-18	0	1	217	228
-16	0	1	423	392
-14	0	1	340	336
-12	0	1	289	268
-10	0	1	816	792
-8	0	1	1265	1232
-6	0	1	689	701
-4	0	1	337	290
4	0	1	170	-158
6	0	1	123	-147
8	0	1	984	-1012
10	0	1	732	-762
12	0	1	353	-362
14	0	1	580	-531
16	0	1	305	-303
18	0	1	213	-166
-17	1	1	241	209
-16	1	1	260	242
-15	1	1	427	398
-14	1	1	218	228
-13	1	1	370	353
-11	1	1	206	208
-10	1	1	386	371
-9	1	1	538	509
-8	1	1	347	338
-7	1	1	818	788
-6	1	1	392	-421
-5	1	1	413	394
-4	1	1	200	186
-2	1	1	129	131
2	1	1	261	275
4	1	1	148	-141
5	1	1	253	-245
7	1	1	905	-894
8	1	1	262	-270
9	1	1	622	-630
10	1	1	134	67
11	1	1	253	-262
12	1	1	175	169
15	1	1	235	-262
17	1	1	370	-336
-18	2	1	225	247
-16	2	1	288	273
-11	2	1	185	201
-10	2	1	131	-91
-9	2	1	256	262
-8	2	1	371	374
-7	2	1	278	263
-6	2	1	483	468
-5	2	1	193	168
-1	2	1	151	146
0	2	1	256	-251
1	2	1	187	166
4	2	1	81	106
6	2	1	187	-192
7	2	1	81	91
8	2	1	343	-336
9	2	1	284	286
10	2	1	225	-231
16	2	1	97	-110
-17	3	1	106	140
-15	3	1	104	156
-10	3	1	96	94
-9	3	1	227	242
-8	3	1	512	500
-7	3	1	222	205
-6	3	1	299	293
-5	3	1	173	-170
-3	3	1	589	-569
-2	3	1	637	591
0	3	1	417	376
2	3	1	485	476
4	3	1	219	193
5	3	1	79	119
7	3	1	371	-394
8	3	1	557	527
9	3	1	177	-164
10	3	1	370	373
-16	4	1	223	221
-14	4	1	160	153
-11	4	1	179	155
-10	4	1	228	162
-9	4	1	538	481
-8	4	1	386	371
-7	4	1	378	385
-6	4	1	341	345
-4	4	1	221	221
-3	4	1	600	572
-2	4	1	482	-474
-1	4	1	1201	1191
0	4	1	532	-538
1	4	1	952	870
2	4	1	358	296
3	4	1	1012	981
5	4	1	518	532
6	4	1	220	-248
7	4	1	229	239
8	4	1	396	-418
9	4	1	425	432
10	4	1	361	-353
11	4	1	209	206
14	4	1	111	-148
-15	5	1	141	151
-11	5	1	208	214
-10	5	1	384	362
-9	5	1	357	311
-8	5	1	608	614
-7	5	1	269	250
-6	5	1	270	253
-5	5	1	513	522
-4	5	1	552	548
-2	5	1	941	907
-1	5	1	147	-102
0	5	1	1077	1040
1	5	1	343	311
2	5	1	843	852
3	5	1	127	-74
4	5	1	355	354
5	5	1	432	-417
6	5	1	514	506
7	5	1	463	-479
8	5	1	471	461
9	5	1	247	-240
10	5	1	392	402
11	5	1	177	-176
12	5	1	174	191
15	5	1	110	-143
-11	6	1	274	279
-9	6	1	494	491
-8	6	1	323	308
-7	6	1	460	440
-6	6	1	473	476
-5	6	1	400	418
-1	6	1	387	367
1	6	1	859	877
2	6	1	271	230
3	6	1	275	272
6	6	1	128	-178
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8	0	2	821	-858
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-8	3	3	246	-264
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-1	8	3	189	-207
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3	8	3	203	-216
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3	10	3	201	-168
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6	0	4	306	264
8	0	4	332	300
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7	1	4	89	99
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7	1	5	112	-105
9	1	5	207	-177
11	1	5	159	-128
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7	3	5	166	-129
9	3	5	132	-138
10	3	5	144	113
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3	4	5	211	198
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6	4	5	82	-83
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8	4	5	138	-141
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10	4	5	107	-119
11	4	5	119	122
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0	5	5	190	186
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4	5	5	219	185
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2	6	5	140	91
3	6	5	168	160
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-1	7	5	114	-98
0	7	5	199	187
1	8	5	184	191
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-6	0	6	131	-156
4	0	6	251	-231
-7	1	6	203	-190
-6	1	6	73	-79
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3	1	6	167	-194
4	1	6	127	-101
5	1	6	92	-70
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-9	2	6	103	45
-8	2	6	218	-211
-6	2	6	234	-217
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2	2	6	256	-248
3	2	6	79	-62
-9	3	6	237	-219
-8	3	6	78	50
-7	3	6	247	-227
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1	3	6	196	-183
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-8	4	6	177	-133
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-6	4	6	213	-162
-5	4	6	127	120
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Table 6. Observed and calculated structure factors for *trans* $NiThio_2(NO_3)_2$.

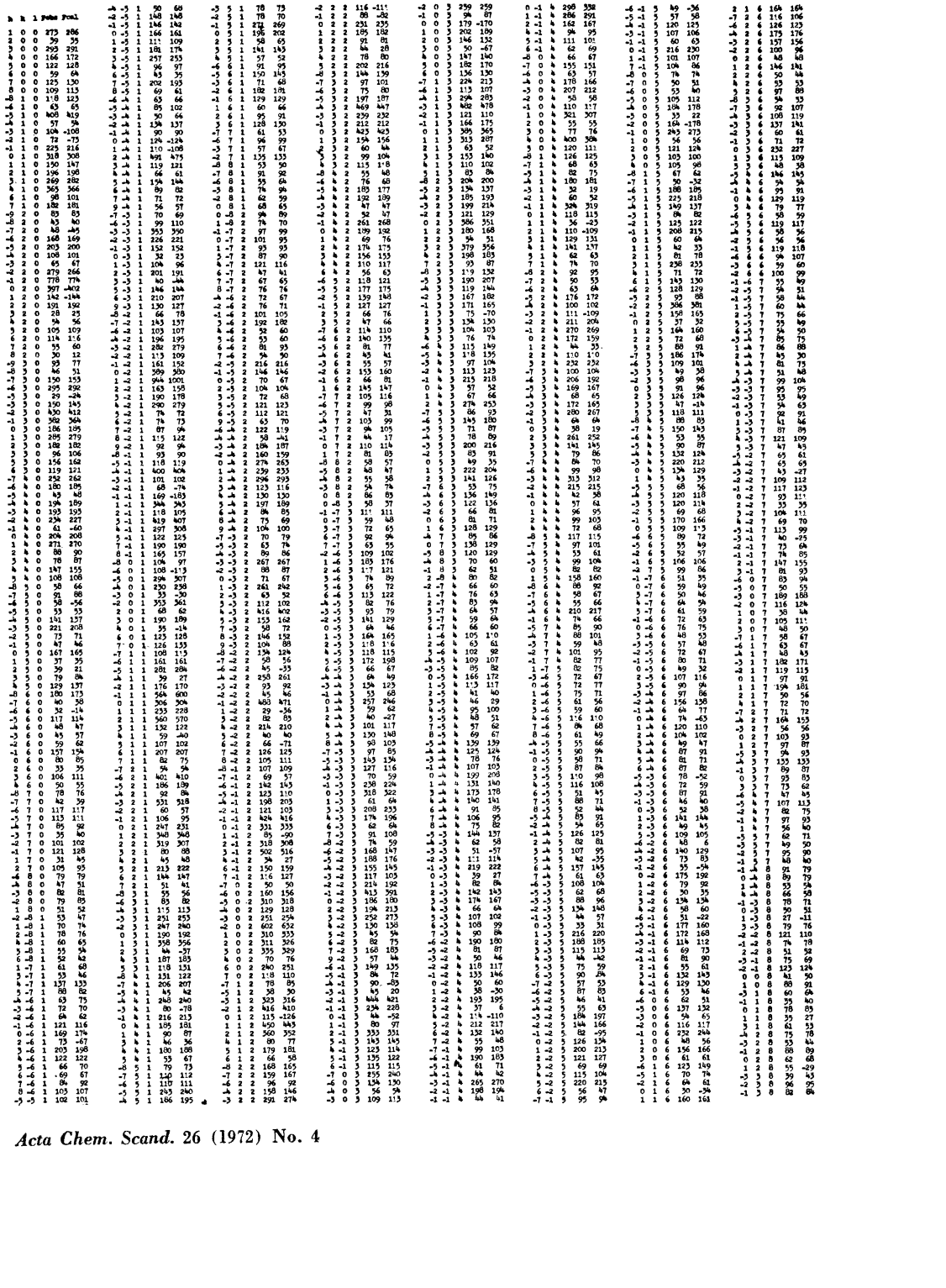

Table 7. Bond lengths and angles in *cis* and *trans* $NiThio_2(NO_3)_2$. For the *cis* complex the values for the two independent halves of the molecule are both given.

Distance	*cis* (1)		*cis* (2)		*trans*	
Ni–S	2.150	(5)	2.150	(5)	2.185	(1)
Ni–N_1	1.945	(11)	1.964	(10)	1.920	(4)
N_1–N_2	1.436	(15)	1.418	(15)	1.426	(6)
N_2–C	1.301	(18)	1.309	(18)	1.321	(7)
C–N_3	1.286	(19)	1.273	(18)	1.320	(6)
S–C	1.771	(16)	1.723	(14)	1.712	(5)
N–O_1	1.259	(20)	1.263	(16)	1.245	(6)
N–O_2	1.196	(18)	1.243	(16)	1.249	(7)
N–O_3	1.292	(17)	1.262	(16)	1.234	(6)

Angle	*cis* (1)		*cis* (2)		*trans*	
S–Ni–N_1 (in ring)	89.41	(0.33)	89.03	(0.32)	88.09	(0.11)
Ni–S–C	97.66	(0.50)	97.97	(0.49)	97.08	(0.16)
S–C–N_3	118.65	(1.20)	120.49	(1.10)	120.44	(0.40)
S–C–N_2	119.76	(1.16)	120.11	(1.53)	119.90	(0.35)
N_2–C–N_3	122.01	(1.44)	119.38	(1.33)	119.62	(0.48)
C–N_2–N_1	119.58	(1.21)	119.88	(1.15)	118.29	(0.44)
N_2–N_1–Ni	114.46	(0.80)	113.48	(0.79)	115.13	(0.30)
O_1–N–O_2	120.94	(1.35)	117.96	(1.16)	120.31	(0.44)
O_1–N–O_3	120.29	(1.34)	118.21	(1.17)	120.49	(0.50)
O_2–N–O_3	118.74	(1.40)	123.62	(1.14)	119.19	(0.45)

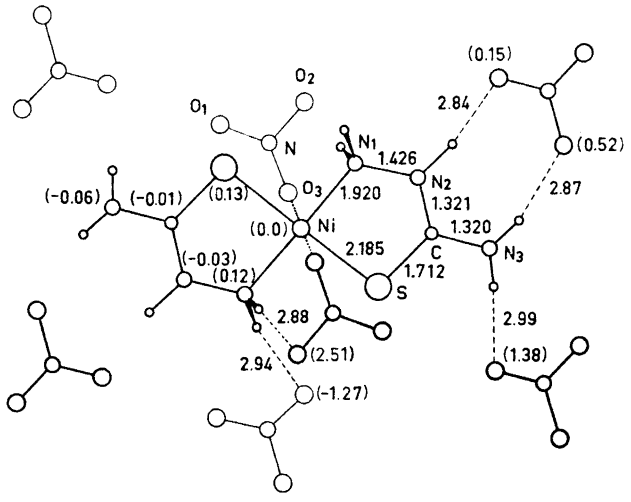

Fig. 1. Part of the structure of *trans* $NiThio_2(NO_3)_2$ projected on to the best plane through a complex ion.

Table 8. Some intermolecular distances in Å in *cis* and *trans* $NiThio_2(NO_3)_2$.

cis (1)		*cis* (2)		*trans*	
$N_{11}-O_3$	2.877	$N_{12}-O_1$	2.918	N_1-O_2	2.884
$N_{11}-O_4$	2.955	$N_{12}-O_4$	2.927	N_1-O_2	2.941
$N_{21}-O_2$	2.718	$N_{12}-O_5$	3.010	N_2-O_1	2.836
$N_{31}-O_1$	3.006	$N_{22}-O_5$	2.794	N_3-O_1	2.988
$N_{31}-O_2$	2.923	$N_{32}-O_4$	2.984	N_3-O_3	2.869
		$N_{32}-O_6$	2.923	N_3-O_3	2.979
		$N_{32}-O_6$	3.042	$S-O_2$	3.110

for the twinning; if these errors occur often you get a disordered structure with broad X-ray reflections as was observed. The structure is held together by hydrogen bonds though three hydrogen atoms point towards the midpoint between two oxygen atoms of a nitrate group rather than towards one particular oxygen atom. The distances in question are listed in Table 8.

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ALGOL programs written by J. Danielsen, J. Nyborg, and the author were used on the GIER computer of Aarhus University.

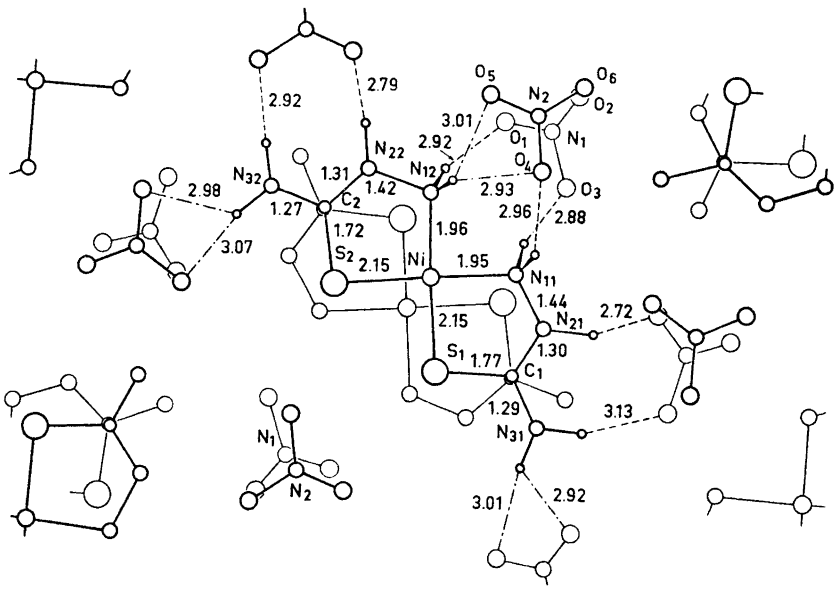

Fig. 2. Projection along the *c*-axis of *cis* $NiThio_2(NO_3)_2$.

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