

## The Crystal Structure of Diaquodithiosemicarbazide Nickel(II) Dinitrate

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Diaquodithiosemicarbazide nickel(II) dinitrate,  $\text{Ni}(\text{CH}_2\text{N}_3\text{S})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2$ , crystallizes in the triclinic crystal system, space group  $P\bar{1}$ , with one molecule per unit cell. The cell dimensions are:  $a=6.48$  Å,  $b=9.325$  Å,  $c=6.22$  Å,  $\alpha=101.17^\circ$ ,  $\beta=110.50^\circ$ ,  $\gamma=89.22^\circ$ . The structure was determined by conventional methods from 3-dimensional counter data and refined to an  $R$ -value of 6.0%. Nickel is *trans* octahedrally coordinated by two water molecules, two sulphur atoms, and two hydrazine nitrogen atoms. The distances in the octahedron are: Ni-S=2.41, Ni-N=2.05, Ni-O=2.11 Å.

The present investigation is part of a series of structure determinations of nickel-thiosemicarbazide complexes. Earlier papers have dealt with  $\alpha$ -nickel dithiosemicarbazide sulphate trihydrate<sup>1</sup> in which nickel has the *trans*-planar coordination and the water molecules are not coordinated, and with  $\beta$ -nickel dithiosemicarbazide sulphate<sup>2</sup> which turned out to contain an ordered arrangement of *cis*-planar and *trans*-planar complex ions.

Nickel dithiosemicarbazide dinitrate dihydrate is a blue, paramagnetic compound<sup>3</sup> and is therefore likely to contain octahedrally coordinated nickel. Its structure was determined in order to compare bond lengths of planar and of octahedral complexes of the same ligand; investigations of tris thiosemicarbazide nickel dinitrate<sup>4</sup> give a comparison with a *cis* octahedral complex.

### EXPERIMENTAL

The crystals were prepared according to Jensen<sup>5</sup> by mixing aqueous solutions of nickel nitrate and of thiosemicarbazide and slow evaporation from a tall beaker.

A crystal of  $0.3 \times 0.3 \times 0.3$  mm<sup>3</sup> was used for the collection of intensity data. The dimensions of the triclinic unit cell were obtained from precession photographs of three projections taken with  $\text{CuK}\alpha$  ( $\lambda=1.5418$  Å) and with  $\text{MoK}\alpha$  ( $\lambda=0.7107$  Å) radiation. The lattice parameters found were:  $a=6.48$  Å,  $b=9.325$  Å,  $c=6.22$  Å,  $\alpha=101.17^\circ$ ,  $\beta=110.50^\circ$ ,  $\gamma=89.22^\circ$ .

This cell has two obtuse angles and one slightly acute; it ought therefore to be transformed to conform with international conventions. A reduced cell has not been used in

the discussion of the structure because a more oblique cell seemed inconvenient. A reduced cell would be:  $a=6.48 \text{ \AA}$ ,  $b=9.325 \text{ \AA}$ ,  $c=7.25 \text{ \AA}$ ,  $\alpha=98.87^\circ$ ,  $\beta=126.45^\circ$ ,  $\gamma=90.78^\circ$ .

Photographic intensity data were measured for the three equator layers. Three-dimensional intensity data were collected on a linear diffractometer of Arndt-Phillips design<sup>6</sup> using balanced filter technique and Mo radiation. 1895 independent reflexions of  $\sin\theta/\lambda < 0.7$  were recorded. In order to safeguard against accidental errors, *e.g.* due to electronic faults, all higher layers were measured twice so that each reflexion is an average of two independent measurements. Data processing and checking was performed by means of an ALGOL program and a GIER computer. No correction for absorption or extinction was applied.

### STRUCTURE DETERMINATION

There is only one molecule per triclinic unit cell. All the three equator layers showed alternating bands of weak and strong reflexions, suggesting that nickel could be placed at the origin of a centrosymmetric cell. The positions of the sulphur atoms were estimated from the separations of the bands, and the signs of the strong reflexions were almost certainly positive. The structure obtained from the Fourier projections calculated with these signs was refined with the three-dimensional data by means of a block diagonal least squares program allowing the refinement of coordinates, and of isotropic and anisotropic temperature factor-parameters. When  $R=7.5\%$  a three-dimensional difference Fourier map was calculated which showed the hydrogen atoms attached to the nitrogen atoms in approximately the positions expected. The difference map showed several peaks around the oxygen atom of the water molecule, and even after further refinement had lowered the  $R$ -value to  $6.2\%$  the situation did not improve much. Some of the bigger peaks were in positions such that they were very unlikely to represent hydrogen atoms. Two small peaks close to the lines to two nitrate oxygens less than  $3 \text{ \AA}$  from the water probably indicate the hydrogen atom positions. The inclusion of these two hydrogens in the structure factor calculation reduced the  $R$ -factor from  $6.2\%$  to  $6.1\%$ .

The final  $R$ -value is  $6.0\%$  calculated with 1733 reflexions. Weak reflexions for which both  $F_o^2$  and  $F_c^2$  are less than twice the standard deviation (from counting statistics) of  $F^2$  are left out of this  $R$ -value and of the least squares totals.

The standard deviations found from counting statistics ( $\sigma F^2_{\text{count}}$ ) were found not to account for all errors. For the weighting of the planes for the least squares refinement the following modification was made:  $\sigma F^2 = \sigma F^2_{\text{count}} + kF^2$  where  $k$  is a constant ( $0.04$ ) which was adjusted so that the average of  $w(F_o - F_c)^2$  was nearly independent of the size of  $F$ . The weight,  $w$ , then is:

$$w = 1/(\sigma F)^2; \sigma F = \sqrt{\sigma F^2 + F^2} - F$$

The scattering curves used were those of table A of *International Tables*<sup>7</sup> for the light atoms, table B for Ni, approximated by Bassi<sup>8</sup> polynomials.

## CRYSTAL DATA

Crystal system: Triclinic.

Unit cell:  $a=6.48\pm 0.01$  Å,  $b=9.325\pm 0.02$  Å,  $c=6.22\pm 0.01$  Å,  
 $\alpha=101.17^\circ\pm 0.2^\circ$ ;  $\beta=110.50^\circ\pm 0.2^\circ$ ,  $\gamma=89.22^\circ\pm 0.2^\circ$ .

$d_{\text{calc}}=1.93$  g/cm<sup>3</sup> for one molecule of Ni(CH<sub>5</sub>N<sub>3</sub>S)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> per unit cell;

No piezoelectric effect could be detected.

Space group:  $P\bar{1}$  (or  $P1$ ).

The final coordinates and temperature factor parameters are given in Table 1. Table 2 gives interatomic distances and angles. Table 3 is a list of observed and calculated structure factors.

Table 1. Final atomic parameters. Coordinates in fractions of the unit cell; standard deviations  $\times 10^4$  in parentheses. For hydrogen, the temperature factor,  $u$ , is given.

	$x$	$\sigma x$	$y$	$\sigma y$	$z$	$\sigma z$	$u \times 10^4$	$\sigma u \times 10^4$
Ni	0.0000	(0)	0.0000	(0)	0.0000	(0)		
S	0.1425	(1)	0.1366	(1)	-0.2138	(1)		
N <sub>1</sub>	0.0425	(5)	0.1972	(3)	0.2290	(5)		
N <sub>2</sub>	0.1220	(5)	0.3171	(3)	0.1649	(5)		
N <sub>3</sub>	0.2599	(6)	0.4184	(3)	-0.0625	(6)		
C	0.1780	(5)	0.2991	(3)	-0.0259	(5)		
O	0.3219	(4)	-0.0458	(3)	0.1980	(5)		
N	0.3348	(4)	0.6798	(3)	0.5098	(5)		
O <sub>1</sub>	0.3756	(5)	0.7897	(3)	0.6673	(5)		
O <sub>2</sub>	0.3992	(6)	0.6760	(3)	0.3405	(6)		
O <sub>3</sub>	0.2239	(6)	0.5746	(3)	0.5174	(5)		
H <sub>11</sub>	0.1433	(87)	0.1753	(54)	0.3923	(91)	515	(152)
H <sub>12</sub>	-0.0957	(76)	0.2283	(47)	0.2489	(83)	327	(134)
H <sub>2</sub>	0.1332	(66)	0.4038	(42)	0.2827	(74)	211	(102)
H <sub>31</sub>	0.2833	(62)	0.5118	(39)	0.0823	(69)	169	(94)
H <sub>32</sub>	0.3427	(86)	0.4103	(52)	-0.1561	(91)	477	(147)
H <sub>01</sub>	0.3616	(89)	-0.1299	(52)	0.2539	(99)	484	(141)
H <sub>02</sub>	0.4229	(178)	-0.0301	(97)	0.2625	(176)	1677	(323)

Table 1 a. Anisotropic temperature factor parameters,  $U_{ij}$ , in Å<sup>2</sup>  $\times 10^{-4}$  with standard deviations.

	$u_{11}$	$\sigma u_{11}$	$u_{22}$	$\sigma u_{22}$	$u_{33}$	$\sigma u_{33}$	$u_{12}$	$\sigma u_{12}$	$u_{13}$	$\sigma u_{13}$	$u_{23}$	$\sigma u_{23}$
Ni	322	(3)	212	(3)	227	(3)	28	(2)	119	(2)	53	(2)
S	455	(5)	294	(5)	251	(4)	-24	(3)	180	(4)	38	(3)
N <sub>1</sub>	612	(18)	289	(15)	297	(15)	-5	(12)	258	(14)	41	(12)
N <sub>2</sub>	520	(16)	227	(14)	350	(16)	15	(11)	216	(13)	24	(11)
N <sub>3</sub>	625	(20)	346	(18)	460	(20)	-70	(14)	229	(17)	121	(14)
C	340	(14)	271	(16)	281	(16)	29	(12)	89	(12)	83	(12)
O	369	(13)	555	(19)	645	(21)	30	(11)	84	(13)	332	(16)
N	398	(14)	317	(15)	373	(16)	67	(11)	153	(12)	94	(12)
O <sub>1</sub>	578	(17)	423	(17)	520	(19)	-76	(12)	125	(15)	-89	(14)
O <sub>2</sub>	809	(22)	524	(20)	602	(21)	136	(15)	486	(19)	155	(16)
O <sub>3</sub>	788	(22)	391	(17)	527	(20)	-115	(14)	312	(18)	25	(14)

Table 2. Interatomic distances and angles. Bond lengths in Å uncorrected and corrected for thermal vibration, standard deviations  $\times 10^3$  in parentheses.

Bond	Uncorrected distance	Corrected distance	e.s.d.	Bond	Uncorrected distance
Ni—S	2.407	2.411	(1)	N <sub>1</sub> —H <sub>11</sub>	1.054
Ni—N <sub>1</sub>	2.052	2.059	(3)	N <sub>1</sub> —H <sub>12</sub>	0.979
Ni—O	2.105	2.123	(2)	N <sub>2</sub> —H <sub>2</sub>	0.965
S—C	1.688	1.694	(3)	N <sub>3</sub> —H <sub>31</sub>	1.094
N <sub>1</sub> —N <sub>2</sub>	1.416	1.417	(5)	N <sub>3</sub> —H <sub>32</sub>	0.913
N <sub>2</sub> —C	1.338	1.344	(5)	O—H <sub>01</sub>	0.916
N <sub>3</sub> —C	1.330	1.349	(5)	O—H <sub>02</sub>	0.899
N—O <sub>1</sub>	1.231	1.254	(4)		
N—O <sub>2</sub>	1.256	1.283	(4)		
N—O <sub>3</sub>	1.241	1.262	(4)		
Short intermolecular distances:					
N <sub>1</sub> —O <sub>1</sub>	2.993			O—O <sub>1</sub>	2.907
N <sub>2</sub> —O <sub>3</sub>	2.829			O—O <sub>2</sub>	2.883
N <sub>3</sub> —O <sub>2</sub>	3.001			N <sub>3</sub> —O <sub>3</sub>	3.070
Angles in degrees, standard deviations $\times 10^3$					
S—Ni—N <sub>1</sub>	83.95	(9)		S—C—N <sub>2</sub>	122.60 (26)
S—Ni—O	90.80	(8)		S—C—N <sub>3</sub>	121.56 (29)
N <sub>1</sub> —Ni—O	88.51	(14)		N <sub>2</sub> —C—N <sub>3</sub>	115.83 (33)
Ni—S—C	96.28	(12)		O <sub>1</sub> —N—O <sub>2</sub>	120.44 (34)
Ni—N <sub>1</sub> —N <sub>2</sub>	115.70	(21)		O <sub>1</sub> —N—O <sub>3</sub>	119.15 (34)
N <sub>1</sub> —N <sub>2</sub> —C	121.35	(29)		O <sub>2</sub> —N—O <sub>3</sub>	120.39 (35)

## DISCUSSION

Nickel is at a centre of symmetry, octahedrally surrounded by two sulphur atoms, two hydrazine nitrogen atoms and two water molecules. The Ni—S distance is in the range 2.4–2.6 Å suggested for Ni—S bonds in octahedral complexes.<sup>9</sup> It is 0.05 Å shorter than the bond of 2.46 Å found in tetrathiourea nickel dichloride.<sup>9</sup> This may be related to the fact that thiosemicarbazide is a considerably stronger complexing agent than is thiourea. The difference between the Ni—S bonds in the present compound and in the *trans* planar complex with the same ligand<sup>2</sup> is 0.24 Å whereas the difference between Pauling's covalent radii<sup>10</sup> is only 0.18 Å and the difference between the Ni—N bonds in the same two complexes is 0.13 Å. This seems to indicate that some additional bonding between nickel and sulphur takes place in the planar complexes, possibly involving the  $d_{xz}$  orbital of the nickel atom. The Ni—N distance is similar to those in dichloro[1.4.8.11]tetraazacyclotetradecanenickel(II),<sup>11</sup> another octahedral complex where  $sp^3$  hybridized nitrogens are *trans* to one another.

The distance from nickel to the water oxygen is similar to the distances in a complex of nickel with an  $\gamma$ -aminobenzaldehyde-condensation product,<sup>12</sup> in which two water molecules are coordinated to nickel *trans* to two nitrogen atoms with Ni—O distances of 2.09 Å and 2.11 Å. The angles around nickel are close to the ideal value of 90° except the angle in the five membered ring

Table 3. List of observed and calculated structure factors (10× absolute scale). The sign < after a reflexion means that it has been left out of the refinements because  $F^2 < 2\sigma F^2$ .

h	k	l	Obs	Calc	h	k	l	Obs	Calc	h	k	l	Obs	Calc	h	k	l	Obs	Calc		
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
0	0	1	210	223	0	0	1	195	188	0	0	2	360	360	0	0	3	360	360	0	0
0	1	0	255	249	0	1	0	403	403	0	1	0	403	403	0	1	0	403	403	0	0
0	2	0	159	17	0	2	0	239	226	0	2	0	239	226	0	2	0	239	226	0	0
0	3	0	258	246	0	3	0	424	420	0	3	0	424	420	0	3	0	424	420	0	0
0	4	0	265	254	0	4	0	466	466	0	4	0	466	466	0	4	0	466	466	0	0
0	5	0	167	155	0	5	0	551	556	0	5	0	551	556	0	5	0	551	556	0	0
0	6	0	103	99	0	6	0	640	644	0	6	0	640	644	0	6	0	640	644	0	0
0	7	0	65	57	0	7	0	727	727	0	7	0	727	727	0	7	0	727	727	0	0
0	8	0	35	32	0	8	0	814	814	0	8	0	814	814	0	8	0	814	814	0	0
0	9	0	20	18	0	9	0	901	901	0	9	0	901	901	0	9	0	901	901	0	0
0	10	0	10	9	0	10	0	988	988	0	10	0	988	988	0	10	0	988	988	0	0
0	11	0	5	5	0	11	0	1075	1075	0	11	0	1075	1075	0	11	0	1075	1075	0	0
0	12	0	2	2	0	12	0	1162	1162	0	12	0	1162	1162	0	12	0	1162	1162	0	0
0	13	0	1	1	0	13	0	1249	1249	0	13	0	1249	1249	0	13	0	1249	1249	0	0
0	14	0	0	0	0	14	0	1336	1336	0	14	0	1336	1336	0	14	0	1336	1336	0	0
0	15	0	0	0	0	15	0	1423	1423	0	15	0	1423	1423	0	15	0	1423	1423	0	0
0	16	0	0	0	0	16	0	1510	1510	0	16	0	1510	1510	0	16	0	1510	1510	0	0
0	17	0	0	0	0	17	0	1597	1597	0	17	0	1597	1597	0	17	0	1597	1597	0	0
0	18	0	0	0	0	18	0	1684	1684	0	18	0	1684	1684	0	18	0	1684	1684	0	0
0	19	0	0	0	0	19	0	1771	1771	0	19	0	1771	1771	0	19	0	1771	1771	0	0
0	20	0	0	0	0	20	0	1858	1858	0	20	0	1858	1858	0	20	0	1858	1858	0	0
0	21	0	0	0	0	21	0	1945	1945	0	21	0	1945	1945	0	21	0	1945	1945	0	0
0	22	0	0	0	0	22	0	2032	2032	0	22	0	2032	2032	0	22	0	2032	2032	0	0
0	23	0	0	0	0	23	0	2119	2119	0	23	0	2119	2119	0	23	0	2119	2119	0	0
0	24	0	0	0	0	24	0	2206	2206	0	24	0	2206	2206	0	24	0	2206	2206	0	0
0	25	0	0	0	0	25	0	2293	2293	0	25	0	2293	2293	0	25	0	2293	2293	0	0
0	26	0	0	0	0	26	0	2380	2380	0	26	0	2380	2380	0	26	0	2380	2380	0	0
0	27	0	0	0	0	27	0	2467	2467	0	27	0	2467	2467	0	27	0	2467	2467	0	0
0	28	0	0	0	0	28	0	2554	2554	0	28	0	2554	2554	0	28	0	2554	2554	0	0
0	29	0	0	0	0	29	0	2641	2641	0	29	0	2641	2641	0	29	0	2641	2641	0	0
0	30	0	0	0	0	30	0	2728	2728	0	30	0	2728	2728	0	30	0	2728	2728	0	0
0	31	0	0	0	0	31	0	2815	2815	0	31	0	2815	2815	0	31	0	2815	2815	0	0
0	32	0	0	0	0	32	0	2902	2902	0	32	0	2902	2902	0	32	0	2902	2902	0	0
0	33	0	0	0	0	33	0	2989	2989	0	33	0	2989	2989	0	33	0	2989	2989	0	0
0	34	0	0	0	0	34	0	3076	3076	0	34	0	3076	3076	0	34	0	3076	3076	0	0
0	35	0	0	0	0	35	0	3163	3163	0	35	0	3163	3163	0	35	0	3163	3163	0	0
0	36	0	0	0	0	36	0	3250	3250	0	36	0	3250	3250	0	36	0	3250	3250	0	0
0	37	0	0	0	0	37	0	3337	3337	0	37	0	3337	3337	0	37	0	3337	3337	0	0
0	38	0	0	0	0	38	0	3424	3424	0	38	0	3424	3424	0	38	0	3424	3424	0	0
0	39	0	0	0	0	39	0	3511	3511	0	39	0	3511	3511	0	39	0	3511	3511	0	0
0	40	0	0	0	0	40	0	3598	3598	0	40	0	3598	3598	0	40	0	3598	3598	0	0
0	41	0	0	0	0	41	0	3685	3685	0	41	0	3685	3685	0	41	0	3685	3685	0	0
0	42	0	0	0	0	42	0	3772	3772	0	42	0	3772	3772	0	42	0	3772	3772	0	0
0	43	0	0	0	0	43	0	3859	3859	0	43	0	3859	3859	0	43	0	3859	3859	0	0
0	44	0	0	0	0	44	0	3946	3946	0	44	0	3946	3946	0	44	0	3946	3946	0	0
0	45	0	0	0	0	45	0	4033	4033	0	45	0	4033	4033	0	45	0	4033	4033	0	0
0	46	0	0	0	0	46	0	4120	4120	0	46	0	4120	4120	0	46	0	4120	4120	0	0
0	47	0	0	0	0	47	0	4207	4207	0	47	0	4207	4207	0	47	0	4207	4207	0	0
0	48	0	0	0	0	48	0	4294	4294	0	48	0	4294	4294	0	48	0	4294	4294	0	0
0	49	0	0	0	0	49	0	4381	4381	0	49	0	4381	4381	0	49	0	4381	4381	0	0
0	50	0	0	0	0	50	0	4468	4468	0	50	0	4468	4468	0	50	0	4468	4468	0	0
0	51	0	0	0	0	51	0	4555	4555	0	51	0	4555	4555	0	51	0	4555	4555	0	0
0	52	0	0	0	0	52	0	4642	4642	0	52	0	4642	4642	0	52	0	4642	4642	0	0
0	53	0	0	0	0	53	0	4729	4729	0	53	0	4729	4729	0	53	0	4729	4729	0	0
0	54	0	0	0	0	54	0	4816	4816	0	54	0	4816	4816	0	54	0	4816	4816	0	0
0	55	0	0	0	0	55	0	4903	4903	0	55	0	4903	4903	0	55	0	4903	4903	0	0
0	56	0	0	0	0	56	0	4990	4990	0	56	0	4990	4990	0	56	0	4990	4990	0	0
0	57	0	0	0	0	57	0	5077	5077	0	57	0	5077	5077	0	57	0	5077	5077	0	0
0	58	0	0	0	0	58	0	5164	5164	0	58	0	5164	5164	0	58	0	5164	5164	0	0
0	59	0	0	0	0	59	0	5251	5251	0	59	0	5251	5251	0	59	0	5251	5251	0	0
0	60	0	0	0	0	60	0	5338	5338	0	60	0	5338	5338	0	60	0	5338	5338	0	0
0	61	0	0	0	0	61	0	5425	5425	0	61	0	5425	5425	0	61	0	5425	5425	0	0
0	62	0	0	0	0	62	0	5512	5512	0	62	0	5512	5512	0	62	0	5512	5512	0	0
0	63	0	0	0	0	63	0	5599	5599	0	63	0	5599	5599	0	63	0	5599	5599	0	0
0	64	0	0	0	0	64	0	5686	5686	0	64	0	5686	5686	0	64	0	5686	5686	0	0
0	65	0	0	0																	



which is only  $84^\circ$ ; similar values have been found in other nickel complexes where five-rings are formed.

The dimensions of the thiosemicarbazide group are nearly the same as those of the free compound and of the ligands in the  $\beta$ -sulphate.<sup>2</sup> The angles in the ring at C, N<sub>1</sub>, and N<sub>2</sub> are a little bigger to allow the ligand to span the larger distances of octahedrally coordinated nickel, but the changes are so small that they can cause little strain.

The thiosemicarbazide group is nearly planar; the carbon atom is only two standard deviations from the plane of S, N<sub>2</sub>, and N<sub>3</sub>; N<sub>1</sub> is 0.07 Å from this plane. The angle between this plane and that of Ni, N<sub>1</sub>, and S is  $1.5^\circ$ . The nitrate group is planar within experimental error, the plane forming an angle of  $11^\circ$  with that of the complex.

All atoms in these planes have their biggest amplitude of vibration across the plane whereas the water molecule vibrates perpendicular to the Ni—O bond. The thermal motion can be described as a rigid body motion of the complex except of the water and of the amide group which are supposed to perform "riding motions" on the nickel and carbon atoms, respectively. In Table 2 the distances calculated using this assumption are included; it does not make much difference to the discussion whether the correction is included or not. The nitrate group does not seem to vibrate as a rigid body so the corrections to the bond lengths are obtained under the assumption of the oxygen atoms performing a "riding motion" on the nitrogen atom. The group is regular within experimental error.

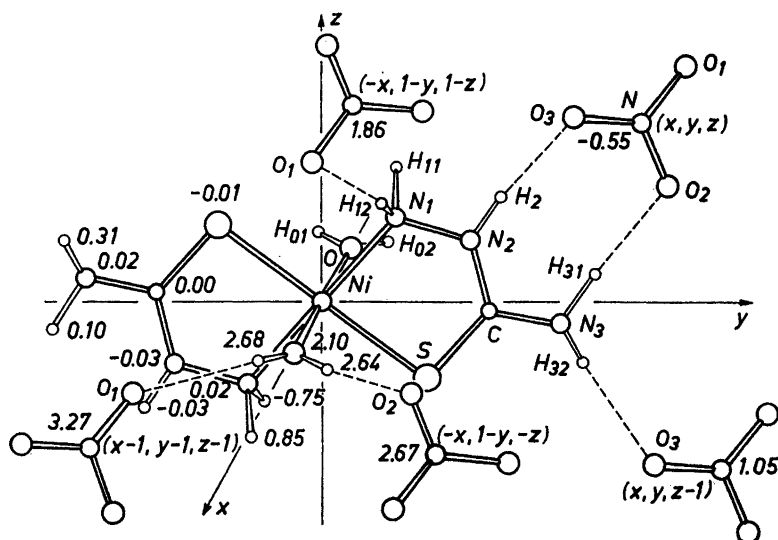


Fig. 1. Clinographic projection of part of the structure on to the best plane through the complex ion. The numbers indicate distances (in Å) from this plane ( $-5.130x + 2.905y - 1.617z = 0$ ). At each nitrate group the relationship to the one given in Table 1 is indicated in parentheses.

A clinographic projection of a part of the structure onto the best plane through the complex is shown in Fig. 1. The short intermolecular distances given in Table 2 correspond to hydrogen bonds. All but one of the hydrogen atoms are involved in hydrogen bonding. The hydrogen bonds are not very strong, but together they probably determine the packing.

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