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The Structure of Nickel(II) Dithiosemicarbazide Sulphate Trihydrate

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Nickel(II) dithiosemicarbazide sulphate can be obtained in different forms. The crystal structure of one of these, a trihydrate, has been solved by X-ray analysis using two dimensional Fourier methods. The complex nickel ion has a *trans*-planar structure. One of the hydrazine nitrogens and the sulphur atom coordinate to the nickel ion. Water molecules do not coordinate to the nickel ion. Atomic coordinates, standard deviations and temperature factors are reported.

A previous note [1] communicated preliminary results from an X-ray investigation of the two forms of nickel(II) dithiosemicarbazide sulphate. These compounds were prepared originally by K. A. Jensen [2] and considered *cis-trans* isomers.

Stereoisomerism of nickel complexes is not established definitely in the literature. The object of this X-ray investigation was the complete structure analysis of the so called α-isomer.

EXPERIMENTAL

Chemistry. α-Nickel(II) dithiosemicarbazide sulphate crystallized as a trihydrate by mixing a 0.1 M solution of $NiSO_4$ with a 0.2 M solution of thiosemicarbazide. Nickel was determined by precipitation with dimethylglyoxime after destruction of the thiosemicarbazide with 30 % H_2O_2. Calc. 15.01, found 15.35.

The crystals exhibit dichroism when viewed in the polarizing microscope. The powdered product looks green.

Water was removed at room temperature by P_2O_5 or by heating to 105°C. The dehydrated products regained water by exposure to atmospheric humidity.

X-Ray powder patterns proved that the anhydrous products obtained in these two ways were identical. The trihydrate was recovered by sorption of water as proved by powder diagrams.

The so called β-isomer precipitated by mixing boiling aqueous solutions of nickel sulphate and of thiosemicarbazide. This product contained no water of crystallization and absorbed no detectable amount of atmospheric humidity.

The X-ray powder pattern of the β-form was different from that of any of the α-compounds, hydrates or anhydrates.

The α-compound may be converted into the β-compound when heated in the presence of its saturated solution as described by Jensen [2]. Conversion in the solid state takes place less easily.

A sample of α-compound which had been heated to 150°C for four days yielded an X-ray powder pattern showing the lines of both the α-compound and the β-compound.

The colour of the sample changed gradually during the four days from green into greyish pink. The proper colour of the pure β-compound was not obtained.

A thermogravimetric analysis of the α-compound yielded the following results: Water was removed between 100 and 140°C. The anhydride was stable between 140°C and 260°C. At 260°C a rather vigourous reaction took place. The loss of weight corresponded to no simple reaction product. Possibly a mixture of NiO and $NiSO_4$ was formed. At 700°C the product was converted to NiO.

X-Ray techniques. Powder patterns were obtained with a 19 cm Bradley-Jay camera using filtered Cr-radiation. The camera was evacuated to a pressure of about 1 mm Hg during the exposure.

The dehydrated products of the α-compounds were placed in sealed Lindemann-glass tubes during the exposure.

A Guinier-de Wolff powder pattern was taken of the trihydrate and of highly purified sodium chloride, the latter being used as a reference for lattice constants measurements.

Integrated and non integrated Weissenberg data were obtained using filtered Cu-radiation. The axis of rotation was *c*. The crystal was about 0.15 × 0.15 × 0.5 mm.

30° Precession photographs were taken using filtered Mo-radiation. The precession axis was *a*.

The intensities of the integrated Weissenberg reflexions were measured photometrically. All other intensities were measured visually. Reflexions from the crystal being investigated were used for the preparation of calibrated intensity scales for the Weissenberg and the precession exposures.

Intensities were corrected for polarization and Lorentz factors using Cochran's chart for Weissenberg data and Waser's chart for precession data. Two sets of relative F^2 values were obtained: $F^2(hk0)$ and $F^2(0kl)$. No absorption correction was applied.

During the refinement of the structure it became evident, that the 100 reflexion was heavily affected by extinction. Therefore the crystal used was dipped in liquid nitrogen and a new set of intensities was collected. The intensity of the 100 reflexion increased by 50 %. All other intensities were constant within the accuracy of measurement.

Some of the Fourier summations were performed on a Hägg-Laurent computer built by Frank [3].

The major part of structure factor and fourier computation was carried out on the electronic digital computer DASK of Regnecentralen, Copenhagen.

DETERMINATION OF THE STRUCTURE

The α-$Ni(CH_5N_3S)_2SO_4,3H_2O$ is monoclinic. The unit cell has the following dimensions:

$$a = 6.98 \text{ Å}$$
$$b = 16.43 \text{ Å}$$
$$c = 6.35 \text{ Å}$$
$$\beta = 99.2°$$

The density is 1.84 g/cm³. Consequently there are two units of $Ni(CH_5N_3S)_2\ SO_4,\ 3H_2O$ per unit cell.

The only systematic extinctions are $0k0$ when k is odd. The possible space groups are $P2_1$ and $P2_1/m$. No piezoelectric effect was detected according to a private communication from professor V. Frank.

In the preliminary publication the space group $P2_1$ was favoured. The structure analysis proved, however, that the proper space group is $P2_1/m$,

which implies that several atoms are placed in special positions. Patterson projections $P(u, v, o)$ and $P(o, v, w)$ were calculated. An interpretation of the $P(u, v, o)$ projection was unsuccesful when based upon the assumption that the space group were $P2_1$.

Then the nickel atom was placed at the origin and the sulphur positions were found at once and it became evident that the correct space group is $P2_1/m$.

The nickel atom and the three sulphur atoms were used as searcher atoms in the interpretation of the Patterson projections. Graphical superposition methods were used to obtain a quick survey of the possible positions of the light atoms and analytical methods were used to obtain more accurate positions. The procedure was equivalent to the use of the Buerger minimum function [4,5] using an M_8 function. The trial structure obtained in this way was essentially correct.

The structure was refined by aid of successive difference fourier projections along the a- and the c-axes.

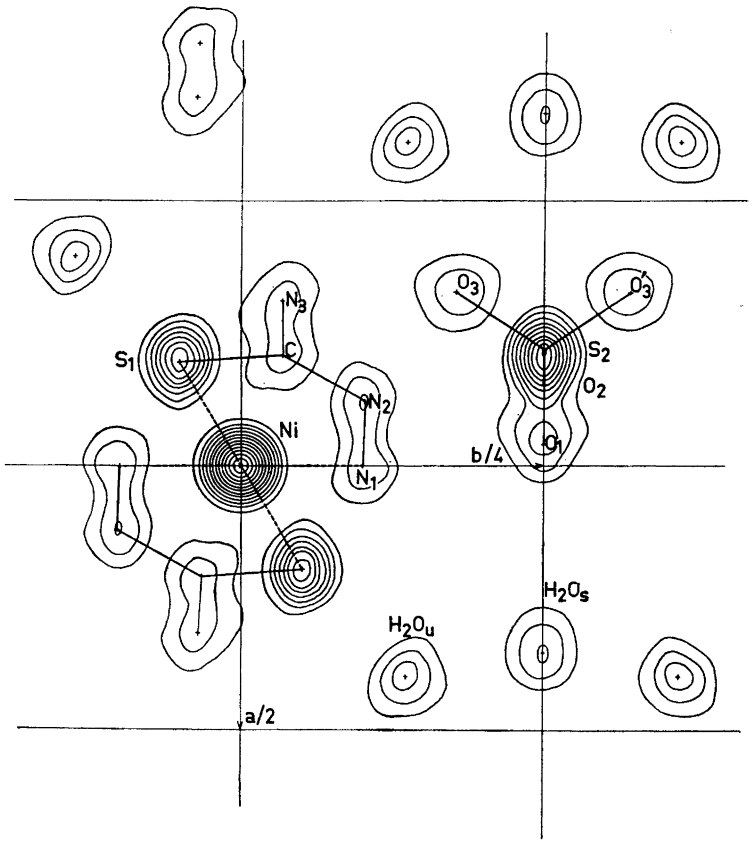

Fig. 1. Fourier projection x,y. Contour lines with equal but arbitrary intervals.

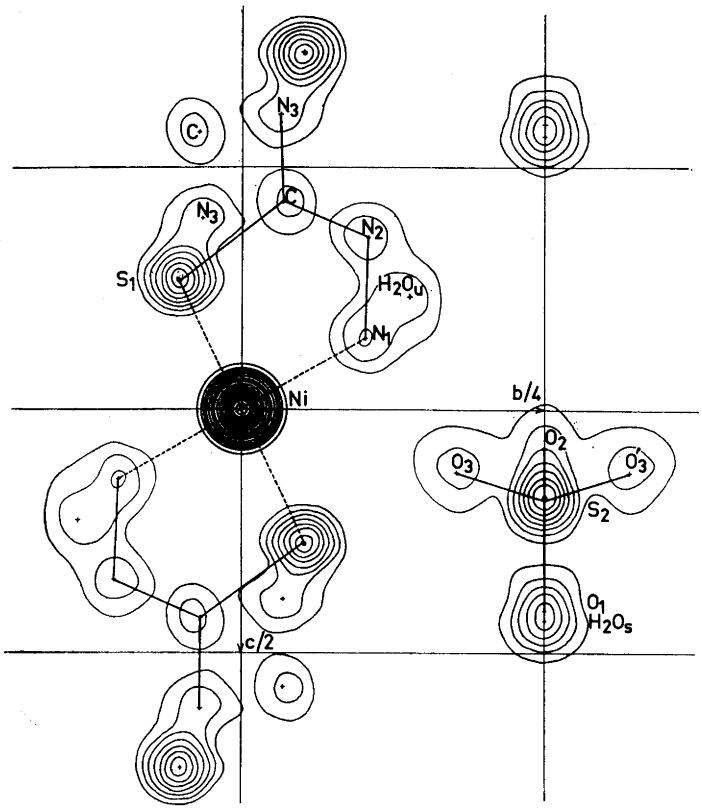

Fig. 2. Fourier projection y,z. Contour lines with equal but arbitrary intervals.

The R-values $\Sigma||F_o|-|F_c||/\Sigma|F_o|$ were reduced from $R(hk0) = 42$ %, $R(0kl) = 26$ % to $R(hk0) = 10.7$ % and $R(0kl) = 10.9$ % through seven successive refinements. Individual isotropic temperature factors were used. The B-factors were refined too from the difference maps using the procedure suggested by Cochran [6].

We now began looking for hydrogen atoms in the difference maps. We actually did find small peaks in positions which could be attributed to the hydrogens of the thiosemicarbazide group assuming the hydrogens to be located according to the usual stereochemical rules. Inclusion of the supposed locations of these hydrogens in the structure factor calculations caused a small decrease in the R-values. We therefore looked for the hydrogen atoms of the water molecules as well and we believe that we have found reasonable positions of these hydrogens too. After two more cycles of refinement we have stopped at the following R-values:

$$R(hk0) = 10.7\ \% \qquad R(0kl) = 10.2\ \%$$

excluding hydrogen atoms and

$$R(hk0) = 9.1\ \% \qquad R(0kl) = 9.3\ \%$$

including hydrogen atoms.

Not observed reflexions are omitted if F_c is well below the lowest observed F-value, else they are included in the R-values and the difference-fourier syntheses with the value $F_{o\ min}/2$.

The two final Fourier projections are shown in Figs. 1 and 2. The following expression [7,8] was used for calculating the atomic scattering factors:

$$f_n(\sin\Theta/\lambda) = A_n\exp[-a_n(\sin\Theta/\lambda)^2] + B_n\exp[-b_n(\sin\Theta/\lambda)^2] + C_n\exp[-c_r(\sin\Theta/\lambda)^2]$$

The parameters used are given in Table 1.

CRYSTAL DATA

All pertinent crystal data are presented below:
Crystal system: Monoclinic.
Unit cell: Mean values from precession, Weissenberg and Guinier diagrams:

$a = 6.98 \pm 0.01$ Å $\quad b = 16.43 \pm 0.01$ Å $\quad c = 6.35 \pm 0.01$ Å
$\beta = 99.2° \pm 0.1°$

Space group: $P2_1/m$, No. 11 (C_{2h}^2); unique axis b.

The coordinates found, their standard deviations and the temperature factors used for $hk0$ (Cu-radiation) and $0kl$ (Mo-radiation), respectively: Table 2.

As no correction for absorption was applied the temperature factors probably include absorption effects. This is a probable explanation of the difference between the two sets of B-factors.

For the standard deviations were used the formulae given by Cruickshank [9] with the second derivative $\partial^2\varrho/\partial r^2$ found by the procedure used by Cochran [10].

The interatomic distances and standard deviations found are given in Table 3. The bond angles found are given in Table 4. The shortest Van der Waals distances are given in Table 5.

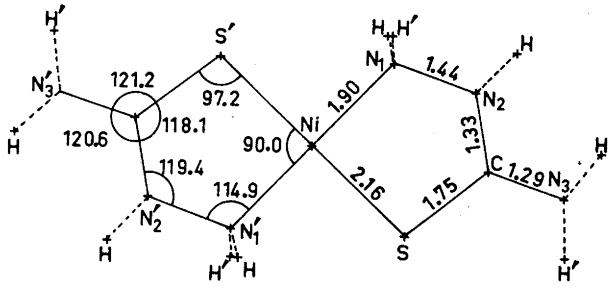

Fig. 3. Bond lengths and bond angles of the nickel(II)dithiosemicarbazide ion.

Table 1.

	A	*B*	*C*	*a*	*b*	*c*	Ref.
Ni_{Cu}	12.76	8.638	2.550	2.637	19.88	0	7
Ni_{Mo}	12.76	8.638	5.650	2.637	19.88	0	
S	7.603	6.354	1.924	1.637	39.98	0	7
C	1.771	1.424	2.779	0.473	9.499	28.008	8
N	1.788	2.606	2.693	0.344	8.670	23.826	8
O	2.113	4.637	1.211	2.867	14.75	0	7
H	0.3882	0.6011	0.0076	7.151	30.18	0	7

Table 2.

Atom	*x/a*	*y/b*	*z/c*	σx Å	σy Å	σz Å	*B*(Cu-radiation) Å²	*B*(Mo-radiation) Å²
Ni	0	0	0	0.004	0.002	0.003	1.4	1.7
S_1	0.1915	0.0515	0.2685	0.006	0.003	0.005	2.0	2.35
N_1	0.001	−0.1005	0.147	0.02	0.015	0.015	2.1	2.4
N_2	0.123	−0.1025	0.352	0.03	0.01	0.015	2.2	2.5
N_3	0.311	−0.034	0.619	0.045	0.02	0.02	2.5	2.8
C	0.208	−0.0345	0.432	0.05	0.015	0.02	2.2	2.5
S_2	−0.215	0.250	0.187	0.008	0.004	0.007	1.85	2.2
O_1	−0.041	0.250	0.086	0.025	0.015	0.05	2.7	3.0
O_2	−0.155	0.250	0.417	0.05	0.01	0.02	2.7	3.0
O_3	−0.324	0.1785	0.127	0.02	0.025	0.035	2.95	3.25
O_5	0.342	0.250	0.438	0.02	0.015	0.02	2.8	3.1
O_4	0.396	0.136	0.773	0.015	0.015	0.02	2.8	3.1
H'_{N_1}	0.048	−0.145	0.060				3.7	4.0
H''_{N_1}	−0.130	−0.117	0.175				3.7	4.0
H_{N_2}	0.125	−0.150	0.445				3.7	4.0
H'_{N_3}	0.375	−0.080	0.706				3.7	4.0
H''_{N_3}	0.344	0.013	0.719				3.7	4.0
$H'_{H_2O_5}$	0.210	0.250	0.362				3.7	4.0
$H''_{H_2O_5}$	0.415	0.250	0.322				3.7	4.0
$H'_{H_2O_4}$	0.500	0.150	0.885				3.7	4.0
$H''_{H_2O_4}$	0.380	0.172	0.655				3.7	4.0

Table 3. Interatomic distances and standard deviations (in Å).

$Ni-S_1$	2.16 ± 0.01
$Ni-N_1$	1.90 ± 0.02
N_1-N_2	1.44 ± 0.04
N_2-C	1.33 ± 0.05
$C-N_3$	1.29 ± 0.05
S_1-C	1.75 ± 0.03
S_2-O_1	1.46 ± 0.05
S_2-O_2	1.45 ± 0.03
S_2-O_3	1.42 ± 0.04
O_1-O_2	2.36
O_1-O_3	2.35
O_2-O_3	2.34
O_3-O_4	2.35

The hydrogen atoms have been placed so that distances N—H are 1.00 Å and O—H 0.96 Å, and so that the valency angles are close to commonly accepted values.

Table 4. The bond angles found are:

S_1-Ni-N_1:	89.97°
$Ni-S_1-C$:	97.23°
$Ni-N_1-N_2$:	114.88°
N_1-N_2-C:	119.42°
N_2-C-N_3:	120.56°
N_2-C-S:	118.07°
N_3-C-S:	121.18°
$O_1-S_2-O_2$:	108.35°
$O_1-S_2-O_3$:	109.26°
$O_2-S_2-O_3$:	109.02°
$O_3'-S_2-O_3$:	111.85°

Table 5. The shortest Van der Waals distances are (in Å):

$H_2O_u-N_1$:	2.95
$H_2O_u-N_3$:	2.99
$H_2O_u-O_3$:	2.82
$H_2O_u-H_2O_s$:	2.82
$H_2O_s-O_1$:	3.20
$H_2O_s-O_2$:	3.45—3.53
$H_2O_s-O_3$:	3.49
N_1-O_1:	2.90
N_2-O_2:	2.82
N_3-O_3:	2.86

DISCUSSION

The nickel(II) dithiosemicarbazide ion has the *trans* configuration and is nearly planar. The deviations from planarity are within the standard deviations.

In this structure the water of crystallization is not coordinated to the nickel atom, the shortest nickel-water distance being 3.98 Å. The bonding $Ni-H_2O$ distance is generally close to 2.0 Å.

Asmussen [11] reported diamagnetism for the anhydrous compound and paramagnetism of $Ni(CH_5N_3S)_2,(NO_3)_2,2H_2O$.

Hare [12] reported that the trihydrate of nickel thiosemicarbazide sulphate is diamagnetic whereas an aqueous solution of the composition:

$C(Ni(NO_3)_2) = 0.1$ m, $C(CH_5N_3S) = 0.2$ m is paramagnetic.

To our knowledge the α-$Ni(CH_5N_3S)_2SO_4$, $3H_2O$ is the only diamagnetic nickel compound containing water.

There is practically no tendency to octahedral coordination around the nickel atom. The N_3-atoms of neighbouring molecules are the next nearest neighbours of the nickel-atom. The $Ni-N_3$ distance is 3.55 Å which is far from bonding distance and is large even for a van der Waals distance.

Fig. 3 shows the bond lengths and bond angles of the complex ion. The Ni—N distance is significantly shorter than the corresponding distance in paramagnetic Ni-complexes (2.0—2.2 Å). It is comparable to the Ni—N distances in other diamagnetic complexes:

1.84 Å in bis-salicylaldiminato-Ni(II), Stewart and Lingafelter [13]

1.86 Å in bis-salicylaldoximato-Ni (II), Merritt *et al.*[14]

Table 6. Calculated and observed structure factors.

h k l	F_c	F_o	*h k l*	F_c	F_o
0 2 0	51.6	46.6	3 9 0	−21.8	−24.3
0 4 0	69.8	61.9	3 10 0	46.6	47.6
0 6 0	−19.3	−21.8	3 12 0	28.4	29.4
0 8 0	51.6	51.4	3 13 0	− 7.3	− 9.4
0 10 0	−33.0	−32.4	3 14 0	15.0	−19.5
0 12 0	20.1	20.8	3 15 0	− 2.7	− 3.4
0 14 0	−29.9	−28.6	3 16 0	2.8	3.2
0 16 0	28.0	26.2	3 17 0	−12.5	−13.5
0 18 0	6.2	10.0	3 19 0	5.4	2.7
0 20 0	30.9	32.7	4 0 0	18.8	21.9
1 0 0	86.3	94.3	4 1 0	12.7	10.8
1 1 0	42.0	39.4	4 2 0	30.8	31.5
1 2 0	57.6	52.5	4 3 0	40.4	40.4
1 3 0	−38.4	−40.7	4 4 0	41.4	41.3
1 4 0	46.0	46.1	4 5 0	3.6	6.7
1 5 0	9.9	9.7	4 6 0	10.9	14.9
1 6 0	−23.6	−23.5	4 7 0	39.3	36.4
1 7 0	−10.3	−18.2	4 8 0	15.7	19.7
1 8 0	35.3	36.9	4 9 0	− 4.9	− 6.0
1 9 0	7.3	10.3	4 10 0	12.3	12.1
1 10 0	26.8	27.7	4 11 0	1.2	5.4
1 11 0	7.2	5.4	4 12 0	17.4	18.6
1 12 0	24.9	27.3	4 13 0	−20.8	−20.4
1 13 0	47.5	46.8	4 14 0	5.0	2.0
1 16 0	12.1	13.2	4 15 0	−10.1	− 9.6
1 17 0	10.7	13.5	4 16 0	9.6	8.0
1 18 0	17.1	18.1	4 17 0	−12.5	−15.1
1 19 0	− 8.0	− 8.1	4 18 0	7.1	6.0
1 20 0	21.7	21.9	5 0 0	59.1	57.4
2 0 0	−27.3	−30.5	5 1 0	4.4	8.8
2 1 0	42.9	40.6	5 2 0	28.7	28.5
2 2 0	17.4	17.5	5 3 0	− 7.2	− 8.2
2 3 0	−30.1	−31.9	5 4 0	28.5	31.6
2 4 0	−26.7	−25.6	5 5 0	16.4	13.7
2 5 0	− 9.4	−13.9	5 6 0	− 5.2	− 5.3
2 6 0	30.8	31.7	5 7 0	− 5.3	− 6.2
2 7 0	−71.1	−71.9	5 8 0	18.1	19.3
2 8 0	48.1	44.3	5 9 0	12.6	11.5
2 9 0	27.0	27.0	5 10 0	−14.9	−12.5
2 10 0	64.1	66.0	5 11 0	− 9.5	−11.6
2 11 0	− 3.9	− 2.0	5 12 0	4.8	6.1
2 12 0	26.3	25.3	5 13 0	− 3.1	− 4.9
2 13 0	18.7	21.9	5 14 0	5.7	2.0
2 14 0	34.2	34.5	5 15 0	− 5.3	− 3.4
2 15 0	5.7	5.9	5 16 0	18.3	18.1
2 17 0	14.0	14.5	6 0 0	41.7	37.0
2 18 0	11.0	11.9	6 1 0	− 2.7	− 2.0
2 19 0	− 8.6	− 9.2	6 2 0	24.0	25.5
3 0 0	31.4	32.2	6 3 0	−29.5	−28.5
3 1 0	−13.5	−16.0	6 4 0	22.0	19.3
3 2 0	7.2	10.5	6 6 0	7.7	8.1
3 3 0	14.5	15.6	6 7 0	−15.9	−15.0
3 4 0	8.8	9.0	6 9 0	6.1	6.2
3 5 0	9.9	10.3	6 10 0	5.8	7.0
3 6 0	51.6	52.1	6 11 0	− 4.8	− 4.9
3 8 0	31.7	34.5	6 12 0	8.3	9.4

Table 6, contd.

h k l	F_c	F_o	*h k l*	F_c	F_o
6 13 0	14.0	10.6	0 9 2	9.1	5.6
7 1 0	3.7	5.4	0 10 2	48.1	43.3
7 2 0	14.6	13.5	0 11 2	6.3	6.1
7 3 0	−11.4	− 9.2	0 12 2	36.0	35.3
7 4 0	− 6.0	− 8.8	0 13 2	−15.3	−12.7
7 5 0	−13.3	−11.9	0 14 2	19.0	20.7
7 6 0	16.2	14.7	0 0 3	15.4	18.8
7 8 0	12.3	13.0	0 1 3	−21.2	−20.7
7 9 0	4.4	6.3	0 2 3	74.4	74.8
7 10 0	28.0	24.6	0 3 3	45.6	45.9
7 11 0	2.9	2.0	0 4 3	30.7	33.1
7 12 0	8.2	9.8	0 5 3	27.3	33.3
8 0 0	− 3.5	− 2.0	0 6 3	33.0	37.4
8 1 0	− 5.2	− 7.5	0 7 3	19.7	19.3
8 3 0	1.4	3.4	0 8 3	7.5	8.1
8 4 0	− 5.0	− 6.1	0 9 3	−10.1	− 6.3
8 5 0	1.7	5.8	0 10 3	16.8	27.6
8 6 0	7.4	8.5	0 13 3	−14.4	−12.5
8 8 0	20.4	17.8	0 14 3	24.3	25.6
			0 15 3	− 9.4	−10.4
0 2 0	58.6	48.1	0 16 3	6.2	7.4
0 4 0	76.7	74.6	0 17 3	−15.7	−13.1
0 6 0	−13.5	−19.1	0 18 3	21.0	19.8
0 8 0	57.2	60.6	0 0 4	17.2	17.2
0 10 0	−27.1	−28.5	0 1 4	9.7	13.2
0 12 0	24.6	26.3	0 2 4	45.1	43.7
0 14 0	−24.1	−24.3	0 3 4	−35.1	−40.3
0 16 0	30.5	33.0	0 4 4	27.6	32.6
0 18 0	9.4	10.1	0 5 4	5.3	8.7
0 20 0	31.2	37.4	0 6 4	23.9	26.5
0 0 1	26.9	27.6	0 7 4	−25.5	−29.6
0 1 1	−34.1	−35.7	0 8 4	9.9	12.7
0 2 1	3.3	6.3	0 9 4	4.6	7.2
0 3 1	52.8	50.9	0 11 4	−10.8	−11.3
0 4 1	10.2	11.4	0 13 4	17.3	17.7
0 5 1	−100.4	−96.5	0 14 4	29.7	27.2
0 6 1	50.2	48.7	0 16 4	21.1	21.1
0 7 1	−41.1	−46.2	0 17 4	9.7	10.1
0 8 1	30.7	32.8	0 18 4	16.4	14.0
0 9 1	−22.0	−28.1	0 0 5	28.6	34.8
0 10 1	39.7	38.5	0 1 5	− 5.1	− 7.2
0 11 1	38.2	37.4	0 2 5	10.4	8.8
0 12 1	37.9	36.1	0 3 5	−17.7	−19.3
0 14 1	24.3	23.6	0 4 5	30.0	35.6
0 15 1	32.9	29.2			
0 16 1	24.4	22.2	0 5 5	−18.7	−17.8
0 18 1	14.5	15.3	0 6 5	13.4	13.1
0 20 1	10.9	11.3	0 7 5	8.9	8.3
0 0 2	−19.7	−25.0	0 8 5	40.0	40.1
0 1 2	−15.0	−11.3	0 9 5	7.4	7.2
0 2 2	13.7	12.5	0 10 5	11.1	11.3
0 3 2	28.3	31.4	0 11 5	3.2	7.2
0 4 2	63.0	59.0	0 12 5	19.6	19.6
0 5 2	15.0	17.1	0 15 5	8.1	7.2
0 6 2	47.2	53.4	0 16 5	10.0	9.4
0 8 2	41.0	40.3	0 0 6	4.0	10.1

Table 6, contd.

h k l	F_c	F_o
0 3 6	9.7	11.3
0 4 6	7.6	8.8
0 6 6	13.0	11.6
0 7 6	8.2	7.2
0 8 6	23.6	26.2
0 9 6	− 5.0	− 6.7
0 10 6	29.6	29.0
0 12 6	22.1	21.4
0 13 6	− 9.2	− 9.4
0 14 6	8.4	7.9
0 0 7	22.8	24.4
0 2 7	21.5	23.4
0 3 7	13.4	14.9
0 4 7	17.1	18.6
0 5 7	5.9	6.1
0 6 7	10.8	8.3
0 7 7	13.4	14.0
0 0 8	13.3	13.7
0 2 8	20.0	26.0
0 3 8	− 6.7	− 6.3

Not observed reflexions:

h k l	F_c
0 17 1	− 2.4
0 19 1	4.9
0 7 2	− 1.9
0 15 2	6.0
0 16 2	4.2
0 17 2	− 5.9
0 18 2	4.5
0 20 2	− 1.6
0 11 3	1.4
0 12 3	1.7
0 19 3	− 0.8
0 10 4	− 4.3
0 15 4	− 3.3
0 13 5	3.7
0 14 5	7.1
0 1 6	5.0
0 2 6	5.5
0 5 6	− 4.6
0 11 6	− 3.3
0 9 7	− 2.9
0 10 7	5.3
0 1 8	− 4.0
1 15 0	0.9
2 16 0	0.8
3 11 0	0.8
3 18 0	1.4
6 5 0	0.9
6 8 0	1.2
6 14 0	− 1.8
7 7 0	− 1.8
8 2 0	1.0
8 7 0	1.0

The Ni—S distance is comparable to the corresponding distance in nickel diethyldithiocarbamate as determined by Shugam and Levina [15]. These Ni—S distances are remarkably short compared to the sum of the radii of the nickel ion and the sulphur atom: 2.4—2.5 Å.

The N_1—N_2 distance is close to the N—N distances of several hydrazine compounds.

The carbon atom may be described as trigonally hybridized. The two C—N and the C—S distances correspond to a bond order of 1.3.

The N_2 atom also seems to be trigonally hybridized. The difference maps indicate the presence of a hydrogen atom in the plane of the complex. Similar considerations may be applied to the N_3 atom, whereas the N_1 atom is probably sp^3 hybridized.

Our bond lengths of the thiosemicarbazide molecule agree with those reported by Cavalca, Nardelli and Branchi [14] for $Zn(CH_5N_3S)Cl_2$. Our Ni—N and Ni—S distances are significantly shorter, by 0.21 Å and 0.13 Å, respectively, than the Zn—N and the Zn—S distances. The difference in ionic radius between Zn^{2+} and Ni^{2+} is 0.10 Å.

Probably the N_3-atom cannot coordinate to the Ni^{2+} ion because bonding orbitals are unavailable in the sp^2 state. The hybridization of sulphur is still

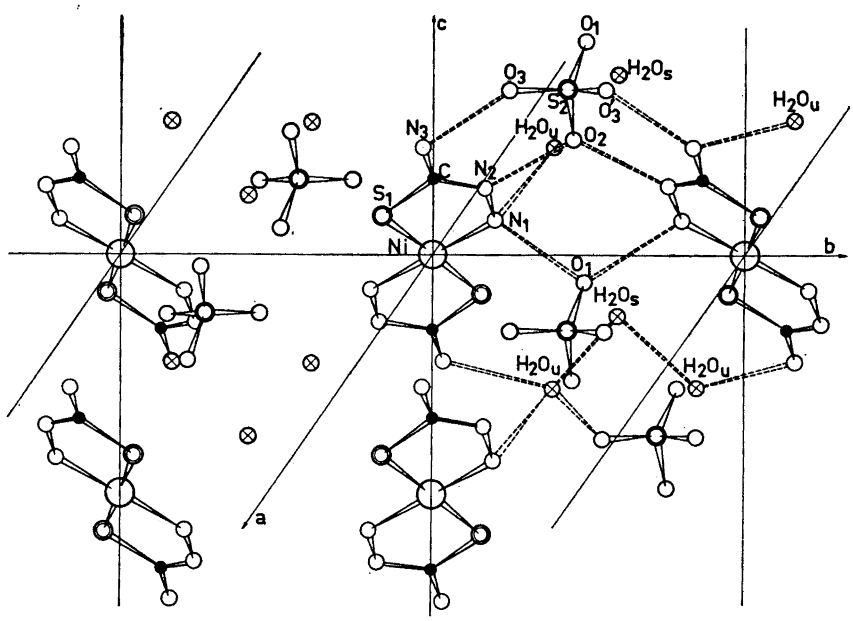

Fig. 4. Parallel projection of selected parts of the structure showing the hydrogen bonding scheme.

undetermined. The bonding between Ni^{2+} and sulphur is rather strong as indicated by the relatively short Ni—S distance.

Bond lengths and bond angles of the sulphate group agree well with accepted values.

The water molecules fit into holes between the complex ions and the sulphate groups. Some of the distances between the water molecules, the sulphate oxygen atoms and the nitrogen atoms indicate weak hydrogen bonding. The interatomic distances in question are 2.8—2.9 Å.

A reasonable hydrogen bonding scheme is shown in Fig. 4 which is a parallel projection of the structure. Some atoms have been omitted to give a clearer picture of details pertinent to the discussion.

One hydrogen of N_1 points towards an oxygen atom of the sulphate group, the other hydrogen towards the oxygen of the H_2O_u molecule. Similar considerations apply to the N_3 atom. The H-atom of the N_2 atom points towards a sulphate oxygen. One hydrogen atom of the H_2O_u molecule points towards a water molecule in the symmetry plane, the other one towards a sulphate oxygen. The hydrogen bonding around the H_2O_u molecule is approximately tetrahedral.

The H-bonding scheme around the water of the symmetry plane is somewhat different. One hydrogen atom is located on the line from the water-oxygen perpendicular to the connecting line between two oxygens of the sulphate group $O_1—O_2$, the other hydrogen approximately points towards the

middle of the line between the other sulphate oxygens $O_3—O_3'$ of the next group in the direction of the x-axis but with some deviation in the direction of a third oxygen (O_2—3.53 Å away).

No hydrogen atoms appear to be located on any of the lines connecting two hydrogen bonded atoms.

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REFERENCES

1. Grønbæk, R. and Rasmussen, S. E. *Acta Chem. Scand.* **14** (1960) 782.
2. Jensen, K. A. and Rancke Madsen, E. *Z. anorg. Chem.* **219** (1934) 243; **221** (1934) 11; **229** (1936) 277.
3. Frank, V. *J. Sci. Instr.* **34** (1957) 210.
4. Buerger, M. J. *Acta Cryst.* **4** (1951) 531.
5. Rasmussen, S. E. *Acta Chem. Scand.* **13** (1959) 2009.
6. Cochran, W. *Acta Cryst.* **4** (1951) 408.
7. Forsyth, J. B. and Wells, M. *Acta Cryst.* **12** (1959) 412.
8. Åsbrink, S., Blomqvist, G. and Westman, S. *Arkiv Kemi* **14** (1959) 545.
9. Cruickshank, D. W. J. *Acta Cryst.* **2** (1949) 154.
10. Cochran, W. *Acta Cryst.* **4** (1951) 81.
11. Asmussen, R. W. *Magnetokemiske undersøgelser* (1944).
12. Hare, C. *Private communication.*
13. Stewart, J. M. and Lingafelter, E. C. *Acta Cryst.* **12** (1959) 842.
14. Merritt, L. L., Guare, C. and Lessor, A. E. *Acta Cryst.* **9** (1956) 253.
15. Shugam, E. A. and Levina, V. M. *Kristallografiya* **5** (1960) 257; Transl. (1960) 239.

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