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The Crystal and Molecular Structure of 2,2′,2″-Triamino-triethyl-amine-Ni(II)-di-thiocyanate

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The crystal structure of 2,2',2''-triamino-triethylamine-Ni(II)-dithiocyanate (Ni tren $(SCN)_2$) was determined from its three-dimensional Patterson function. Superposition methods were applied using both the nickel atom and the two sulphur atoms as searcher atoms. The structure was refined by a least squares analysis, employing three-dimensional data.

The crystal is built up from Ni tren$(SCN)_2$ units. The four nitrogen atoms from the amine and the two nitrogen atoms from the thiocyanate groups form a distorted octahedron around the nickel atom, the thiocyanate groups being in *cis* positions. A full account is given in the text of axial lengths, atomic coordinates, temperature factors, bond lengths and bond angles, and reliability index.

The polyamine 2,2',2''-triamino-triethylamine, usually abbreviated as "tren", was introduced into complex chemistry in 1925 by Mann and Pope [1], who prepared Pt(II)tren I_2 and Pt(IV)tren Cl_2 Cl. They pointed out that the four nitrogen atoms of the amine could hardly form a planar complex with the divalent platinum atom, and they concluded that the Pt(IV) complex probably was of octahedral configuration with the two chlorine atoms occupying *cis* positions.

In later publications [2,3] Mann and Pope described a number of nickel-tren complexes, especially Ni tren$(SCN)_2$. They were of the opinion that the nickel atom was tetracoordinated in this compound. In Ref.[3] a crystal-morphological investigation, carried out by Notham is mentioned. He found that Ni tren$(SCN)_2$ is orthorhombic, with the axial ratios: $a:b:c = 0.736:1:1.167$. In 1935 Cox and Webster [4] confirmed by an X-ray crystallographic investigation that Ni tren$(SCN)_2$ belongs to the orthorhombic system. The size of the unit cell was given as: $a = 10.79$, $b = 14.69$, $c = 8.59$ presumably KX units. The axial ratios are: $a:b:c = 0.736 : 1 : \frac{1.172}{2}$. The space group was found to be $P2_12_12_1$.

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The density was measured as 1.55 g/cm^3. Hence there are four Ni tren$(SCN)_2$ units in the unit cell. According to the space group these units must be asymmetric.

It was not possible at that time to solve the structure. The authors pointed out that two alternatives were possible: Either a tetrahedral structure or a *cis*-octahedral structure.

In the same year Jaeger and Beintema [5] determined the unit cell and space group of tren$(HCl)_3$. This compound crystallizes in the cubic system with the space group $P2_13$. Consequently it is highly probable that the tren molecule in this crystal has the symmetry C_3 which means that the four nitrogen atoms are at the corners of a tetrahedron.

Some authors, *e.g.* Reihlen [6], have taken the compound Ni tren$(SCN)_2$ as a proof of the existence of tetrahedral nickel complexes. Asmussen [7] concluded from magnetic measurements that Ni tren-complexes were probably of tetrahedral configuration.

At the discussion of the conference on coordination chemistry in Copenhagen in 1953 [8] Ni tren$(SCN)_2$ was mentioned as an example of a tetrahedral nickel-complex. When the investigation reported here was started, no X-ray evidence had ever been reported of any tetrahedral nickel-complex. As the Ni tren$(SCN)_2$ in my opinion would be the most likely of any known nickel-compound to have a tetrahedral structure, I decided to solve its crystal structure in order to get an unambigous answer to an often debated problem.

A preliminary communication was presented at the conference of coordination chemistry, Rome 1957. It appeared in print in 1958 [9].

EXPERIMENTAL

Professor Schwarzenbach, Zürich, and Professor Basolo, Northwestern University, Illinois, kindly supplied me with samples of tren$(HCl)_3$. The nickel complex was prepared in the following way:

0.01 mole tren$(HCl)_3$ was dissolved in water with 0.03 moles of NaOH. The solution was heated until boiling. A hot solution containing 0.01 mole of $Ni(SCN)_2$ was added dropwise. (No systematic experiments were carried out in order to determine the best possible conditions with respect to the concentrations of the solutions, *etc.*) From the hot solution Ni tren$(SCN)_2$ crystallizes at cooling. It is only slightly soluble in cold water. It was purified by recrystallization from water. In the microanalysis laboratory of the Chemistry Department of the University of Copenhagen the following results were found: S 19.86, C 29.30, N 26.85, H 5.40. Calc. for $NiS_2C_8N_6H_{18}$: S 19.97, C 29.92, N 26.18, H 5.65.

Analysis for nickel was carried out by Ole Bostrup: Calc. 18.28, found 18.11.

The crystals are blue and different habits may be observed; both needles and spheroids. A needle-shaped crystal, 0.5 mm long and approximately 0.1 mm × 0.1 mm square, was mounted on a Weissenberg-goniometer and orientated along the needle axis which proved to be the *c*-axis of Cox and Webster [4]. Equi-inclination diagrams were taken using Cu-radiation. $hk0-hk3$ reflexions were registered. Another crystal was orientated along the *b*-axis. It was 0.2 mm long, rather irregularly shaped and it was less than 0.04 mm thick. The reflexions $h0l-h6l$ were registered with Cu-radiation. Multiple film technique was employed. Intensities of X-ray reflexions were estimated visually using an intensity scale constructed by exposing different parts of a film to an X-ray reflexion from the crystal for regularly increasing intervals of time. 711 independent spectra were measured; 1 399 are accessible with Cu-radiation with the cameras employed. The intensities were converted into relative F^2 values, using Cochran's chart [10]. An approximately absolute scale was established using Wilson's [11] statistical

method, which also yields an average temperature factor, found to be equal to 2.3 Å². No correction for absorption was applied. Guinier powder photographs were taken to obtain accurate lattice constants. The space group given by Cox and Webster was confirmed. All numerical crystallographic data are collected below.

THE SOLUTION OF THE STRUCTURE

In the space group $P2_12_12_1(D_2^4)$, No. 19, a general point is fourfold and its symmetry is 1. As there are four units of Ni tren$(SCN)_2$ in the unit cell, each atom must be in a general position. If the origin is taken as halfway between the three pairs of non intersecting screw axes the coordinates of equivalent positions are: x,y,z; $1/2-x, \bar{y}$, $1/2+z$; $1/2+x$, $1/2-y, \bar{z}$; $\bar{x}$, $1/2+y$, $1/2-z$.

The x,y coordinates of the nickel atom were easily found from a Patterson projection along the c-axis, but the positions of the sulphur atoms could not be determined with the same certainty.

The nickel atom is not heavy enough to dominate the phases of a sufficient number of reflexions to permit determination of the structure. Therefore the Patterson-Harker cuts were calculated (Fig. 1, a, b, c) in order to obtain more information about the lighter atoms. The x,y coordinates of the nickel atom found by the Patterson projection were confirmed by the Harker cuts and the z-coordinate was also determined. The determination of the coordinates of the sulphur atoms was, however, not quite straightforward. There are three high peaks in the Patterson function at 0, 1/2, 1/2; 1/2, 1/2, 1/2; and at 1/2, 0, 0. The two first ones are about four times the height expected for an S-S peak, while the peak at 1/2, 0, 0 has exactly the height of an S-S peak. The three peaks might be caused by one or more atoms in one or more of the following non-equivalent positions: 1/4, 1/4, 0; 1/4, 1/4, 1/2; 1/2, 1/4, 0; 1/2, 1/4, 1/2. The Patterson projection is of no use in this special case in distinguishing between the x-coordinates 0.250 and 0.500 by aid of the vectors between these two points and the nickel atom, because the x-coordinate of nickel is 0.375.

It is well known from the work of Buerger [12] that crystal coordinates cannot be determined unambiguosly from Harker cuts. The ambiguities mentioned above are, however, of a rather special type, as they are connected with the fact that the peak at 0, 1/2, 1/2 is common for two Harker cuts and the peak at 1/2, 1/2, 1/2 is common for three Harker cuts.

The general ambiguities which arise in the determination of crystal coordinates from a Harker cut belonging to a twofold screw axis, may be stated in the following way:

Coordinate transformations, such as $x' = x \pm 1/2$; $y' = y$; $y' = y \pm 1/2$; $x' = x$ and $x' = x \pm 1/2$; $y' = y \pm 1/2$ cause no changes in the Patterson function. It causes, however, a fundamental difference, whether different atoms are referred to the same origin or to different origins. For each atom that is recognized in the Harker cut there are four possible choices of origin for its crystal coordinates. Once an origin has been chosen for one atom, all other atoms must be referred to the same origin to give a correct structure.

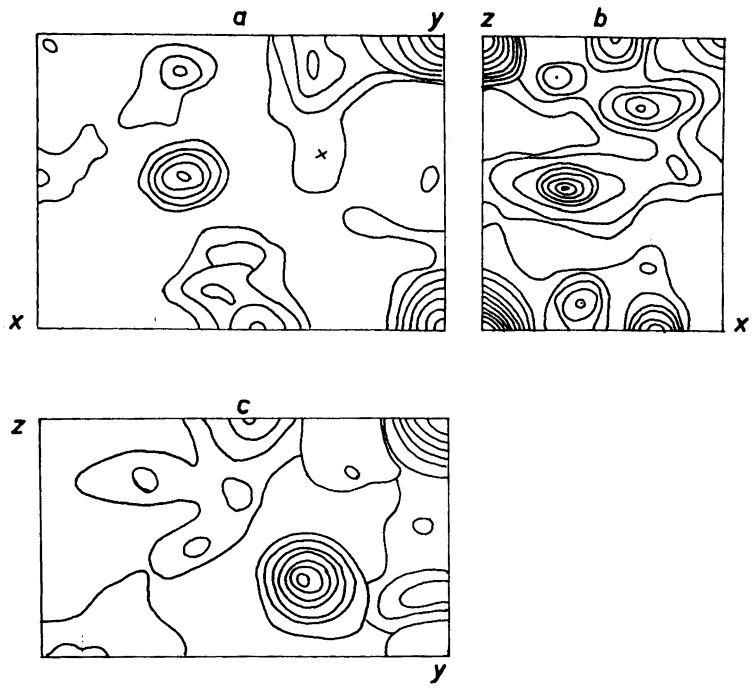

Fig. 1. The three Patterson Harker cuts.

In order to make the correct choice for all atoms it is necessary to have other informations than those obtainable from the Harker cut.

In the present investigation the Harker cuts were severely masked by non-Harker peaks and consequently they gave no information of the positions of the lighter atoms.

The benefit of sharpening the Patterson projection in order to obtain greater resolution was considered to be somewhat doubtful. It was considered to be safer to operate with artificial point atoms on "the other side" of the Fourier transform, and the Harker-Kasper [13] inequalities were applied to the $hk0$ reflexions.

The coordinate transformations stated above influence the signs of certain classes of $hk0$ structure factors. Once an origin is chosen, the signs of these structure factors are determined. On the other hand, a choice of sign for a structure factor determines the origin.

In the projection of $P2_12_12_1$ on a pinacoid it is convenient to take the origin in a screw axis. There are four non-translational equivalent screw axes in a unit cell, and the transformations mentioned above move the origin from one screw axis to another. The structure factors of the types: $h = 2n + 1$; $k = 2n+1$ and $h+k = 2n + 1$, change signs at certain of these transformations, and that means that the sign of one structure factor of each of these two classes of reflexions may be chosen arbitrarily.

The first Harker-Kasper inequality,

$$2|U(hk0)|^2 \leq 1 + U(2h2k0),$$

gave one sign. (840). The inequality,

$$4|U(hk0)|^2 \leq [1 + U(2h00)]\ [1 + U(02k0)],$$

gave a few other signs. These relations only give signs for $h = 2n$, $k = 2n$. With these signs and the two signs which could be chosen abitrarily, a large number of signs was obtained by application of the relations,

$$[U(hk0) \pm U(h'k'0)]^2 \leq [1 \pm U(h+h',\ k+k',\ 0)]\ [1 \pm U(h-h',\ k-k',\ 0)].$$

The nomenclature applied is that of Gillis [14].

In all 66 signs were obtained by these methods. 14 signs were later proved to be wrong.

The Fourier projection calculated with the signs obtained from the inequalities is given in Fig. 2. In the projections shown the origin is taken in a c screw axis. No refinement was obtained, because the projection was not interpreted correctly. It is not very much different from the correct final projection (Fig. 3), and the value of the Harker-Kasper method should be judged from a comparison between these two projections, and not from the fact that the structure was finally solved in another way.

A full three-dimensional Patterson was calculated. The a and b axes were divided in 60ths and the c axis in 30ths. The term $F(000)^2$ obtained by Wilsons method was included in the calculations. If the height of a peak may be taken as proportional to its volume, the height of a single Patterson peak with the scale applied here is given as $H_{ij} = 0.35 \cdot z_i z_j$, where z_i and z_j are the atomic numbers of atoms i and j. On this scale we should expect peaks in the following order: 3 Ni-Ni (218), 8 Ni-S (140), 10 S-S (90), 24 Ni-N (62), 32 Ni-C (52), 48 S-N (39), 64 S-C (34), the rest of the peaks are so low that they disappear in the general background. The Patterson function of $P2_12_12_1$ has the symmetry P_{mmm}. Consequently it is only necessary to compute it within the space defined by $\frac{a}{2}, \frac{b}{2}, \frac{c}{2}$. All peaks must appear within this volume. If the volume of a peak is approximately 1 Å^3, only about 140 spherical peaks could be "packed" into the octant of the Patterson space without overlapping. It is very unlikely that a close "packing" of peaks should ever occur, but even if it were the case, the number of peaks here is so great that overlapping cannot be avoided.

The nickel-nickel vectors had already been recognized in the Harker cuts and the following coordinates were chosen for the nickel atom given in 60ths of the coordinate axes with the origin halfway between the three screw axes: $22\frac{1}{2}$, 25, 5; $\overline{7\frac{1}{2}}$, 5, $\overline{5}$; $7\frac{1}{2}$, $\overline{25}$, $\overline{25}$; $37\frac{1}{2}$, $\overline{5}$, 25.

The structure was solved by what has been called "image seeking" or "super-position" methods. Buerger [15] has given a very profound analysis of

the existing methods of extracting a crystal structure from its vector diagram. The principle of these methods is an extensive use of the symmetry of the Patterson space. If the coordinates of one atom, a, may be fixed, *e.g.* x_a, y_a, z_a, the following vectors to another atom, *e.g.* b, must exist. These are: x_b-x_a, y_b-y_a, z_b-z_a; $1/2 - (x_b + x_a)$, $(y_b + y_a)$, $1/2 + (z_b-z_a)$; $1/2 + (x_b-x_a)$, $1/2 - (y_b + y_a)$ $(z_b + z_a)$; $x_b + x_a$, $1/2 + (y_b-y_a)$, $1/2 - (z_a+z_b)$, with the symmetry of the space group considered here. By shifting the origin of the Patterson function to the four equivalent points of the searcher atom, a, the vectors to the atom, b, are all gathered in the point x_b, y_b, z_b. Different methods may be used to recognize the interatomic vectors. Robertson and Beevers [16] and McLachlan [17] added the numbers of the transcribed Patterson functions, McLachlan [18] and Buerger [15] suggested a multiplication of the vectors, but the closest approach to the electron density is the minimum function of Buerger [15]. Buerger realized that the smallest of symmetry related Patterson peaks would have the greatest chance of being a genuine single peak, and therefore its value should be close to being proportional to the electron density of the crystal. A few examples of the application of the minimum function will be given. Graphical methods were first applied to give a rough idea of the whereabouts of the atoms, but more accurate results were obtained by studying the numerical values of the Patterson function. First the sulphur atoms were sought, using nickel as the searcher atom. One of the positions which could be deduced from the Harker cuts, was confirmed. In 60ths of the coordinate axes its position was found to be 15, $\bar{1}6$, 0 on the basis of the following vectors with their weights given in parentheses,
$7\frac{1}{2}$, 19, 5(191); $22\frac{1}{2}$, 21, 5(146); $7\frac{1}{2}$, 9, 25(170); $22\frac{1}{2}$, 11, 25(196).

The effective atomic number of nickel towards Cu-radiation is 25. The height of a nickel vector is, therefore, according to the relation given above; $H_{ij} = 0.35 \cdot 25 \cdot z_j$.

The minimum of the four peaks given above is 146. The atomic number, z_j, of the atom which yields this vector with the nickel atom is therefore $z \leq \frac{146}{0.35 \cdot 25} = 16.7$. Thus it seems highly probable that the atom found is a sulphur atom. The other sulphur atom was placed in $26\frac{1}{2}$, $8\frac{1}{2}$, $\bar{1}\bar{1}$ on the basis of the following vectors with the nickel atom: 19, $26\frac{1}{2}$, 14(169); 4, $16\frac{1}{2}$, 16(146); 11, $13\frac{1}{2}$, 24(152); 26, $3\frac{1}{2}$, 6(161). Minimum 146, atomic number 16.7. This close correspondence between the atomic numbers of the two sulphur atoms must be purely accidental and is by no means characteristic of the accuracy of the method. The correctness of the coordinates may be checked by the vectors between the two non-symmetry related sulphur atoms, $11\frac{1}{2}$, $24\frac{1}{2}$, 11(103); $18\frac{1}{2}$, $5\frac{1}{2}$, 19(110); $11\frac{1}{2}$, $7\frac{1}{2}$, 19(132); $18\frac{1}{2}$, 22, 11(122). As the minimum here is 103, the atomic number is $z \leq \frac{103}{0.35 \cdot 16} = 18.3$.

It was not possible to determine the positions of the C and N atoms from the nickel vectors alone, as there were more vectors of appropriate height than there were atoms. Because of this, the vectors between the S and the C and N atoms were also employed, and in that way a number of positions suggested by the nickel atom could be ruled out. In Buerger's [15] formulation

it would be: "The image seeking polyhedron comprised of the four nickel atoms and the eight sulphur atoms roved over the Patterson function finding images of itself, whereby the appropriately weighted minimum funtion was mapped out". When applying the minimum function due regard must be taken to the uncertainty of the values of the Patterson function. With the errors inherent in the measurement of intensities, non-convergence of series *etc.* an indeterminacy of about 30 % must be allowed for. This means that atomic numbers as low as 4—4 1/2 must be accepted for C and N atoms, although if more than two or three of the twelve vectors indicated such a low atomic number, the position was not accepted as an atomic site. A few examples will be given of the best and of the worst of the results:

C_1 : 31, 25, $\bar{1}\bar{1}$,

Ni-C vectors: $8\frac{1}{2}$, 0, 16 (106); $21\frac{1}{2}$, 20, 6 (146); $23\frac{1}{2}$, 10, 14 (76); $6\frac{1}{2}$, 30, 24 (61).

$$z \leq \frac{61}{0.35 \cdot 25} = 7.$$

S-C vectors: 16, 9, 41 (73); 14, 11, 41 (55); 14, 39, 11 (53); 16, 41, 11, (80); $5\frac{1}{2}$, $16\frac{1}{2}$, 0 (64); $25\frac{1}{2}$, $3\frac{1}{2}$, 22 (75); $2\frac{1}{2}$, $13\frac{1}{2}$, 8 (45); $27\frac{1}{2}$, $33\frac{1}{2}$ $33\frac{1}{2}$, 30 (80),

$$z \leq \frac{45}{0.35 \cdot 16} = 8.8$$

C_6: 36, 20, 7.

Ni-C vectors: $13\frac{1}{2}$, 5, 2 (75); $16\frac{1}{2}$, 15, 12 (40); $1\frac{1}{2}$, 25, 18 (98); $28\frac{1}{2}$, 15, 28 (146),

$$z \leq \frac{40}{0.35 \cdot 25} = 4.6$$

S-C vectors: 21, 4, 23 (25); 9, 6, 23 (82); 9, 26, 7 (56); 21, 24, 7 (82); $9\frac{1}{2}$, $11\frac{1}{2}$, 18 (80); $20\frac{1}{2}$, $1\frac{1}{2}$, 4 (25); $2\frac{1}{2}$, $18\frac{1}{2}$, 26 (50); $27\frac{1}{2}$, $28\frac{1}{2}$, 12 (95),

$$z \leq \frac{25}{0.35 \cdot 16} = 4.5$$

N_6: $11\frac{1}{2}$, 25, 5.

Ni-N vectors: 11, 0, 0 (256); 19, 20, 10 (188); 26, 30, 20 (115); 4, 10, 30 (148);

$$z \leq \frac{115}{0.35 \cdot 25} = 13.$$

S-N vectors: $3\frac{1}{2}$, 9, 25 (65); $26\frac{1}{2}$, 11, 25 (58); $26\frac{1}{2}$, 21, 5(98); $3\frac{1}{2}$, 19, 5 (82); 15, $16\frac{1}{2}$, 16 (26); 15, $3\frac{1}{2}$, 6 (66); 22, $13\frac{1}{2}$, 24 (120); 15, $26\frac{1}{2}$, 14 (43),

$$z \leq \frac{26}{0.35 \cdot 16} = 5.$$

By a systematic application of this modification of the minimum function, a satisfactory solution of the structure was obtained.

A refinement of the structure was started by difference projections along the *c*-axis. By two successive difference projections the *R*-index decreased from 29 % to 21.7 % without application of a temperature factor. At that

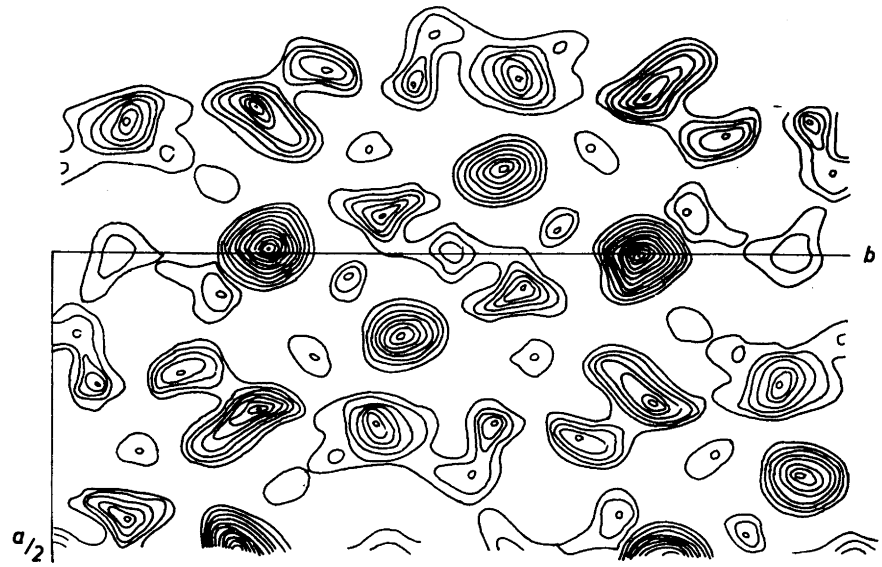

Fig. 2. Fourier projection along the c-axis calculated with signs obtained from Harker-Kasper inequalities.

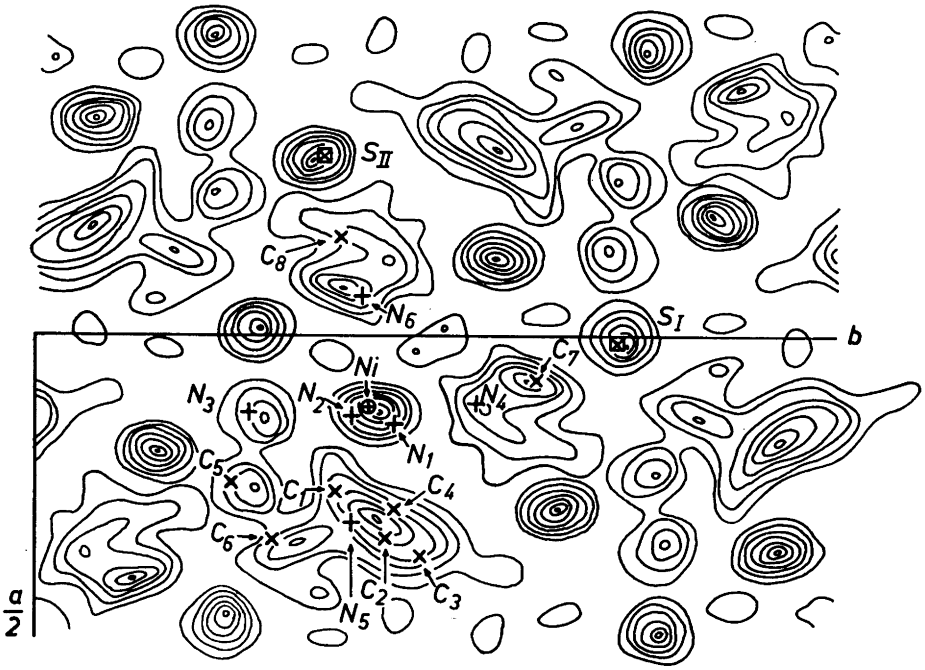

Fig. 3. Final Fourier projection. The atomic positions obtained from the least squares analysis are marked for one molecule.

stage a least squares analysis was carried out using the method of Sayre [19]. Miss Dolores Leagus carried out the work of programming and machine computation.

Two runs were made. One using only 711 observed F values, the other including 181 non observed F values, which were within the $\sin\Theta$ range of the observed F values. The weights of the F values were taken as proportional to their multiplicity (Geller and Abrahams [20], 1958).

The scattering factors used were the following: for Ni the values of Thomas and Umeda [21] corrected for dispersion for Cu-radiation using $\Delta f = -3.1$. For S the values of Tomiie and Stam [22] and for C and N those of Freeman [23].

The final coordinates and temperature factors, as well as the coordinate changes used for the final calculations are stated below. The results are those obtained using observed F values only. The reliability index $R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$ is 13.6 % for these computations. The calculations which included non-observed intensities, gave only slightly different results. The former results were chosen because a re-examination of the Weissenberg-diagrams revealed that 26 observable, although weak intensities were overlooked in the first measurements.

Three strong intensities were evidently affected by extinction, as the calculated F values were 30—40 % higher than the observed values. There are no grave discrepancies between observed and calculated F values. The calculated values of the non-observed intensities are all small, except the ones mentioned above, which could be found on the Weissenberg diagrams. Because of the individual agreements between observed and calculated F values the structure must be essentially correct.

DISCUSSION OF THE STRUCTURE

For convenience all pertinent data of the crystal structure are collected here.

Crystal system: Orthorhombic.

Unit cell from Guinier powder diagrams with Cu$K\alpha$-radiation:

$$a = 10.82_1 \text{ Å}, \qquad b = 14.71_9 \text{ Å}, \qquad c = 8.62_0 \text{ Å}.$$

Space group: $P2_12_12_1$ No. 19, (D_2^4).

Chemical formula: $NiS_2C_8N_6H_{18}$. Four units in the unit cell.

Origin halfway between screw axes. The coordinates and temperature factors obtained are stated below.

Final coordinates and temperature factors, and parameter changes applied for the last least squares calculations.

	x	y	z	B	Δx	Δy	Δz	ΔB
C_8	0.081087	0.385216	0.129809	2.2577	−0.000147	−0.000232	0.000131	−0.1455
C_7	0.326618	0.630510	0.037545	1.3770	0.000197	−0.000196	0.000300	−0.0259
C_6	0.603609	0.305235	0.113750	1.0891	0.000308	0.000082	−0.000466	0.0492
C_5	0.506174	0.246387	0.196275	3.4090	0.000299	0.000324	0.000104	−0.1347
C_4	0.547679	0.453238	0.350924	2.5217	0.000726	−0.000234	0.000249	−0.4579
C_3	0.610642	0.479480	0.196238	2.4667	0.000434	−0.000349	−0.000410	−0.0513
C_2	0.600520	0.439341	0.918240	2.5288	0.000126	0.000631	0.000899	0.0042
C_1	0.518879	0.376199	0.796445	2.2823	0.000398	0.000193	−0.000042	−0.1470
N_6	0.186183	0.410673	0.104150	3.4070	0.000347	0.000842	0.000219	0.0025
N_5	0.566400	0.397124	0.074243	2.5477	0.000130	0.000486	−0.000148	−0.2428
N_4	0.367356	0.557289	0.037369	3.6104	0.000153	0.000034	0.000189	0.1573
N_3	0.381603	0.267628	0.132519	3.0013	−0.000198	−0.000113	0.000187	−0.0831
N_2	0.388276	0.394525	0.837901	3.2958	−0.000287	−0.000158	0.000233	−0.0667
N_1	0.407727	0.450679	0.329351	3.0380	−0.000362	0.000116	−0.000407	−0.1101
S_{II}	0.442430	0.139506	0.818595	2.6136	0.000021	0.000030	−0.000040	−0.0187
S_I	0.242260	0.272368	0.510750	3.5559	−0.000001	−0.000033	−0.000024	0.1195
Ni	0.372013	0.417211	0.085269	1.4411	−0.000009	0.000093	0.000082	−0.0197

Realiability index: $R = \dfrac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} = 13.6\ \%$ for 711 independent measured structure factors.

Bond lengths and bond angles:

N_5-C_2	= 1.527 Å (tren)	$<C_2-N_5-C_3$	= 99°55'
C_2-C_1	= 1.657 Å "	$<C_6-N_5-C_2$	= 120°14'
C_1-N_2	= 1.482 Å "	$<C_6-N_5-C_3$	= 115°28'
N_5-C_3	= 1.675 Å "	$<C_5-C_6-N_5$	= 115°19'
C_3-C_4	= 1.574 Å "	$<N_3-C_5-C_6$	= 108°21'
C_4-N_1	= 1.525 Å "	$<N_1-C_4-C_3$	= 108°48'
N_5-C_6	= 1.452 Å "	$<N_2-C_1-C_2$	= 103°42'
C_6-C_5	= 1.539 Å "	$<C_4-C_3-N_5$	= 102°35'
C_5-N_3	= 1.489 Å "	$<C_1-C_2-N_5$	= 99°59'
N_4-C_7	= 1.164 Å (thiocyanate)	$<N_4-C_7-S_I$	= 170°6'
C_7-S_I	= 1.629 Å "	$<N_6-C_8-S_{II}$	= 172°48'
N_6-C_8	= 1.218 Å "	$<N_1-Ni-N_2$	= 152°29'
C_8-S_{II}	= 1.607 Å "	$<N_5-Ni-N_6$	= 168°51'
$Ni-N_1$	= 2.195 Å	$<N_3-Ni-N_4$	= 178°1'
$Ni-N_2$	= 2.166 Å	$<Ni-N_6-C_8$	= 163°28'
$Ni-N_3$	= 2.242 Å	$<Ni-N_4-C_7$	= 156°21'
$Ni-N_4$	= 2.104 Å		
$Ni-N_5$	= 2.127 Å		
$Ni-N_6$	= 2.020 Å		

The accuracy of this structure determination may be more difficult to assert than its correctness. During the last refinement the R-index only decreased from 13.8 % to 13.6 %. The coordinate changes used for this calculation might be used as a criterion for the underterminacy of the bond lengths. The nickel atom was moved 0.0014 Å for the last refinement, the two sulphur atoms 0.0005 Å, and the light atoms somewhat more. The arithmetic

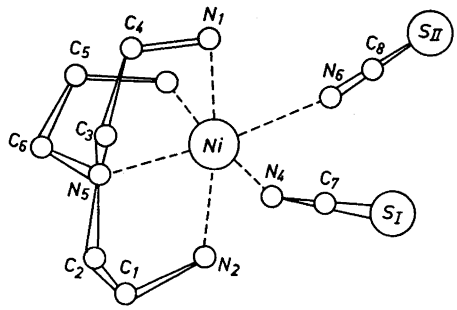

Fig. 4. Parallel projection of the Ni tren molecule.

mean of their displacements is 0.006 Å. Hence one might believe that bond lengths were determined with an accuracy of 0.01 Å.

There are, however, several reasons for viewing this low figure with some scepticism. In the first place, no correction has been applied for either extinction or absorption. Secondly, the effect of 18 hydrogen atoms has been neglected. They are almost bound to affect some of the intensities as they after all carry 10 % of the scattering electrons, although they can hardly ever, all of them, scatter in phase. Thirdly, isotropic temperature factors have been used, although it is certain that the heat oscillations are anisotropic.

A more empirical viewpoint will be taken on the accuracy of the results.

The two thiocyanate groups will be taken as completely equivalent with respect to bond lengths and bond angles. Consequently we shall take the mean values of the two sets of interatomic distances as standard values: N—C = 1.19 ± 0.03 Å, C—S = 1.62 ± 0.01 Å, < N—C—S = 171°.

This means that the N—C distance may be as much as 0.06 Å in error, and the C—S distance 0.02 Å in error. For comparison the following results will be quoted:

Compound	N—C	C—S	<N—C—S	Ni—N—C—S	Ref.
$Nien_2(NCS)_2$	1.20	1.66	175°	2.14	24
$Ni(NH_3)_4(NCS)_2$	1.20	1.61	180°	2.07	25
$Ni[CS(NH_2)_2]_2(NCS)_2$	1.16	1.60	180°	1.99	26
AgSCN	1.186 ± 0.086	1.636 ± 0.029	~180°		27
$C_2H_4(SCN)_2$	1.18	1.63	172°		28
NH_4SCN	1.24 ± 0.02	1.58 ± 0.02	180°		29
$NH_4[Cr(SCN)_4(NH_3)_2]$	1.14 ± 0.03	1.80 ± 0.03	180°		30

The results are all from X-ray investigations.

Beard and Dailey [31] find by microwave spectroscopy on HNCS the following results:

N—C = 1.218 Å, C—S = 1.557 Å, N—H = 1.01 Å, < H—N—C = 136°, assuming that the N—C—S group is linear.

The following conclusion may tentatively be drawn from these figures.

The bond lengths and angles of the thiocyanate group in complexes, in which it is considered as being predominantly ionically bond, falls within the limits: N—C = 1.19 ± 0.03 Å, C—S = 1.63 ± 0.03 Å, < N—C—S = 175±5°. By the complex formation the N—C bond is apparently shortened and the C—S bond is stretched with respect to the bonds of the SCN^- ion of the NH_4SCN lattice. In the Reinecke ion $[Cr(SCN)_4(NH_3)_2]^-$ the N—C bond is the shortest and the C—S bond the longest of any known distances of the thiocyanate group. This is probably connected with the fact that the Reinecke salt exhibits an absorption spectrum of the electron transfer type.

This survey indicates that the indeterminacy of the bond lengths of the thiocyanate group obtained in this paper is probably ± 0.03 Å and at most 0.06 Å.

It is difficult to say whether the bond lengths of the tren molecule are determined with the same accuracy or not.

It is established with certainty that the three N—C—C—N rings are non-planar. In the free tren molecule the three rings are probably equivalent as the molecule has almost certainly the symmetry C_3. With this symmetry it is impossible to fix the four nitrogen atoms at the four corners of an octahedron. The octahedral structure becomes possible when *one* of the rings changes its conformation into one, which is symmetrical with the original one. In Fig. 4 the rings $N_5—C_6—C_5—N_3$ and $N_5—C_2—C_1—N_2$ have identical conformations. One ring can be made to cover the other by rotating the molecule around an axis passing through the N_5 atom, and the nickel atom. But none of these two rings can be made to cover the $N_5—C_3—C_4—N_1$ ring, as this ring in enantiomorphous with the two other ones. Some of the distances of the tren molecule are anomalous. This may be connected with the fact that the molecule is severely strained in the complex. By forming an octahedral complex, only one ring can avoid strain. The distances of the ring $N_5—C_6—C_5—N_3$ are quite normal. In the ring of which the conformation is different from the two other ones, the nitrogen-carbon distance, $N_5—C_3$, is rather high: 1.68 Å. The distance $C_2—C_1$ is also higher than the usual single bond distance. It is at present difficult to say, whether these abnormal distances are really caused by steric strain, or are the results of inadequate measurements, assumptions and computations. By comparison with the accuracy of the determination of the dimensions of the thiocyanate groups, one might be inclined to believe that the apparent effects of the strain are real. By looking through "Interatomic Distances" [32] one finds that C—C distances above 1.60 Å often are reported for strained molecules.

The nickel-nitrogen distances appear to exhibit the following systematics:

Nickel-primary amine nitrogen:	2.20 ± 0.04 Å
Nickel-tertiary amine nitrogen:	2.13 ± 0.04 Å
Nickel-thiocyanate nitrogen:	2.06 ± 0.04 Å

The octahedron of the six nitrogen atoms has no more than triclinic symmetry. The deviations from the regular octahedron are made clear by giving the angles between *trans*-nitrogen atoms and the nickel atom:

$$< N_1NiN_2 = 152°, \quad < N_5NiN_6 = 168°, \quad < N_3NiN_4 = 178°.$$

It is still an open question whether X-ray diffraction methods at present are able to yield determinations of bond lengths of very high precision. Two examples will be quoted which may throw some doubt on the validity of "established" bond lengths. Lynton and Cox [33] and Rowe and Post [34] independently determined the structure of thianthrene and refined the structure by essentially equivalent mathematical methods. Visual estimations of intensities were used in both determinations. Many of the C—C distances of the two determinations agree within 0.01—0.02 Å, but three of the distances deviate with 0.04 Å. In both cases a standard deviation of 0.012 Å is quoted.

The detailed structure of the glycine zwitter ion is another case for discussion. Hahn and Buerger [35] determined the structure of diglycine hydrochloride using Cu-radiation, and measured intensities with a Geiger counter. Marsh [36] redetermined the structure of glycine itself, using Mo-radiation, and visual estimation of intensities. Hahn and Buerger find the following distances for the glycine molecule: N—C = 1.52 ± 0.01 Å, C—C = 1.48 ± 0.01 Å. Marsh reports that N—C = 1.474 Å, and C—C = 1.523 Å. It is as yet an open question whether these discrepancies are real and are caused by the different packing in the different crystals, or whether they are fictitious, and caused by the different ways of measuring intensities or in the different ways of refining the structure. Hahn and Buerger employed isotropic temperature factors, while Marsh used anisotropic B factors.

Because of the non-planarity of the N—C—C—N rings, the Ni tren$(SCN)_2$ molecule is asymmetric and should exist in two enantiomorphous forms. The space group $P2_12_12_1$ permits a separation of left-handed and right-handed crystals simply by handpicking. In that way it should be possible to make optically active solutions of the complex. The non-planar conformation of N—C—C—N rings seems to occur generally in complexes. An interesting consequence of this conformation is the possibility of stereoisomers of *trans*-bis-ethylene-diamine complexes.

At the same time as the structure of Ni tren$(SCN)_2$ was established, Venanzi [37] reported that Powell had proved by X-ray methods that $[(C_6H_5)_3P]_2NiCl_2$ has a tetrahedral structure. In a preliminary publication Gill, Nyholm and Pauling [38] have presented X-ray evidence for a tetrahedral $NiCl_4^{--}$ ion in the compound $[(C_6H_5)_4As]_2NiCl_4$.

It is at present very difficult to say, which factors are decisive for the stereochemistry of nickel complexes.

An investigation has been started on tren$(HCl)_3$ in order to obtain accurate details of the stereochemistry of the non-complexed tren molecule.

While the present paper was in preparation, a note on the structure of Ni tren$(SCN)_2$ by Hall and Woulfe [39] appeared. I have been in correspondence with the authors. The two independent solutions of the structure appear to be essentially in agreement.

When the structure of Hall and Woulfe has been refined, a comparison of the results will be published.

A complete table of observed and calculated F values and a more complete account of the present work will be published in a forthcoming monograph in Danish, with an English summary [40].

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