

The Structure of 2,2',2''-Triamino-triethylamine-trihydrochloride

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The structure of 2,2',2''-triamino-triethylamine-trihydrochloride ($\text{tren}(\text{HCl})_3$) has been determined from its three-dimensional Patterson function and refined by difference Fourier and least squares analysis. Hydrogen positions have not been refined. The tren molecule has C_3 symmetry. The four nitrogens form a three-sided pyramid. Quadridentate complexes cannot be formed except by conformational changes which disturb the symmetry.

The tetramine 2,2',2''-triaminotriethylamine, usually called tren, acts as a quadridentate ligand in numerous complexes. In Nitren(NCS)₂, the four nitrogen atoms occupy four positions of an octahedral complex¹.

Some authors considered tren-complexes a proof of the existence of tetrahedral coordination compounds. References about earlier literature of tren complexes are given in Ref.¹

The purpose of the investigation reported in this paper was the detailed structure analysis of the non-complexed tren molecule. The trihydrochloride was chosen for convenience as it forms well developed cubic crystals, whereas the pure tren-compound is liquid at room temperature.

Jaeger and Beintema² determined space group and unit cell of $\text{tren}(\text{HCl})_3$ in 1935. Our findings are in full agreement with theirs.

EXPERIMENTAL

The crystals used were kindly supplied by professor G. Schwarzenbach, Zürich. They are optically isotropic, exhibit optical activity and are strongly piezoelectric. The piezoelectricity was determined by V. Frank³.

Equiinclination Weissenberg photographs were taken around the a -axis and around the 110 direction using Cu-radiation. Reflexions $hk0-hk2$ were registered from one crystal (0.15 mm cube) and $hk0-hk6$ from another crystal (0.1 mm cube). The latter crystal also was employed for exposures around the 110 direction. Multiple film technique and multiple time exposure technique were employed. Both integrated and non integrated films were recorded for each layer line.

Intensity scales were constructed for integrated as well as non integrated exposures by exposing different parts of films to an X-ray reflexion from the crystal for regularly

increasing intervals of time. Both integrated and non integrated intensities were measured visually. Integrated intensities having an optical density $D > 0.1$ were measured photo-metrically as well. D was found to be proportional to the intensity until the limit $D \leq 1$.

The different sets of observations overlap to some extent, thus permitting a scaling between them. The agreement is good between the different ways of measuring the intensities as seen from the following typical examples:

$$R = \frac{\sum I_{\text{ph}} - kI_{\text{vis}}}{\sum I_{\text{ph}}} = 6.9 \%, \text{ integrated film, } hk2 \text{ reflexions}$$

$$R = \frac{\sum I_{\text{int}} - kI_{\text{non int}}}{\sum I_{\text{int}}} = 12.3 \%, \text{ } hk2 \text{ reflexions.}$$

Intensities were converted into relative F^2 values, using Cochran's chart⁴. Because of the high symmetry, scaling between different layer lines could be carried out with good accuracy. No absorption correction was employed.

The exposures around the 110 direction served as an extra check on the scaling, and yielded also some reflexions which were not accessible on the films from the rotation around the a -axis. About 370 independent reflexions were measured. Each independent reflexion is an average of about ten measurements. For lattice constant measurements a powder diagram was taken using a 19 cm Bradley-Jay camera and filtered Co-radiation. All numerical data are collected below.

THE SOLUTION OF THE STRUCTURE

From the X-ray diagrams the reflexions $h00$ were found absent for $h = 2n + 1$. This indicates the space group to be $P2_13$. The optical activity and the piezoelectricity are consistent with this space group.

The a -axis is $10.870 \pm 0.001 \text{ \AA}$. The density reported by Jaeger and Beintema is 1.32 g/cm^3 . Consequently there are four units of $\text{N}(\text{CH}_2-\text{CH}_2-\text{NH}_2\text{HCl})_3$ in the unit cell.

The general point in $P2_13$ has twelvefold multiplicity. Points on the threefold axes have fourfold multiplicity.

The tertiary amine-nitrogen is required to be located on the C_3 -axis. The other atoms may be in general positions.

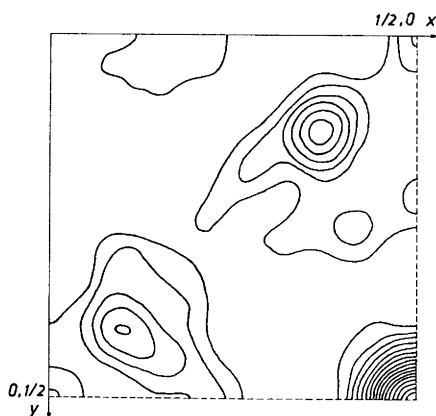


Fig. 1. Harker cut: $x, y, 1/2$. Contour lines at arbitrary, equal intervals except around $1/2, 1/2, 1/2$ where the magnitude of the intervals is doubled.

A Patterson projection, $P(x,y,0)$ did not allow even the chlorine positions to be determined. Later the Harker cut, $P(x,y,1/2)$ was calculated using a Hägg-Laurent computer. The Harker cut is reproduced in Fig. 1.

For lack of computational facilities no Wilson plot⁵ was made to find the absolute scale of the $F^2(hkl)$ values. Instead $F^2(000)$ was arbitrarily given four times the value of the highest $F^2(hkl)$ value.

The heights H_{ij} , of the Patterson peaks were assumed to be:

$$H_{ij} = H(0,0,0) \frac{Z_i \cdot Z_j}{\sum Z_j^2} = 1.46 Z_i \cdot Z_j.$$

In the following discussion of the Patterson function, coordinates are given as sixtieths of the a -axis.

A Cl-Harker vector should have an approximate height of 420. Peaks high enough to contain Cl-Cl vectors exist in (6,24,30) height 514, (22,8,30) height 667, and (30,30,30) height 3347. These peaks must originate from atoms on the C_3 -axis.

The coordinates (12,12,12), (26,26,26) and $(\bar{4},\bar{4},\bar{4})$ yield vectors in (6,24,30) weight 1; (22,8,30) weight 2; and in (30,30,30) weight 8.

At the time we had found the chlorine positions the digital computer DASK in Copenhagen became available to us. Using a programme written by P. Mondrup and F. Larsen of Regnecentralen the full three dimensional Patterson of the structure was computed. The positions found for the Cl-atoms were confirmed.

We then determined the positions of the carbon- and the nitrogen atoms using image seeking methods⁶. The Cl-atoms were used as "searcher atoms" and our procedure was equivalent to the use of an M_{12} function⁶. Analytical, rather than graphical methods were employed.

The structure factors of the $hk0$ reflexions were calculated on the basis of the coordinates found by solving the Patterson function. The R -factor of this trial structure was 31.5%. No temperature factor was applied. Two successive difference Fourier projections decreased the R -factor of the $hk0$ reflexions to 19.3% including an overall isotropic temperature factor of 2.5 Å.

The R -factor of the full three-dimensional set of data was calculated to be 18.6%. The R -factor did not improve significantly through one refinement using three-dimensional difference synthesis.

Further refinement was carried out on an IBM 704 computer using the least squares programme of Vand and Pepinsky. The R -factor decreased to 14.2% after four cycles. Individual isotropic temperature factors were now employed.

The coordinates and temperature factors of the C, N and Cl atoms from the IBM computations were used for a new difference synthesis computed on DASK. The difference synthesis indicated small corrections of coordinates and of B -factors. Spurious peaks were found near positions where hydrogen atoms were expected assuming the usual stereochemical arguments. Extra peaks of similar heights as the alleged hydrogen peaks were found too.

Introduction of 6 hydrogen atoms caused a small decrease in the R -factor. We hope to make additional refinements when a new, highly efficient computer

GIER becomes available to us. We consider it unlikely that additional refinement will change results which are pertinent to the coordination chemistry.

In the R -factor calculations absent reflexions are omitted if F_c is below the lowest observed F -value, otherwise they are included in the R -values and the difference Fourier synthesis with the value $F_{o \text{ min}}/2$. The strong reflexions 220, 310, and 130 were heavily affected by extinction and were not included in the refinement procedures and R -factors.

In the DASK computations the following expression ^{7,8} was used for calculating the atomic scattering factors:

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

The parameters used were:

	A	B	C	a	b	c	Ref.
Cl	7.511	7.487	1.881	1.328	31.76	0	7
C	1.771	1.424	2.779	0.443	9.499	28.008	8
N	1.788	2.606	2.693	0.344	8.670	23.826	8
H	0.3882	0.6011	0.0076	7.151	30.18	0	7

The observed and the calculated structure factors are given in Table 1.

CRYSTAL DATA

The pertinent crystal data are presented below:

Crystal system: cubic

Unit cell: $a = 10.870 \pm 0.001$ Å from Bradley-Jay 19 cm powder camera. Nelson-Riley ⁹ extrapolation employed. $\lambda_{Ka_1} = 1.7889$; $\lambda_{Ka_2} = 1.7928$.

Space group: $P2_13$ from extinctions.

The coordinates found, their standard deviations and the temperature factors used:

Atom	x/a	y/a	z/a	σ_x/a	B
Cl ₁	0.2020	0.2020	0.2020	0.00029	1.93
Cl ₂	0.44025	0.44025	0.44025	0.00035	3.00
Cl ₃	0.9309	0.9309	0.9309	0.00036	3.08
N _{tert}	0.7351	0.7351	0.7351	0.0009	1.20
C ₁	0.6549	0.6515	0.8135	0.0013	2.66
C ₂	0.7183	0.6127	0.9255	0.0012	1.97
N _{prim}	0.7527	0.7158	0.0058	0.0014	3.73
H ₁	0.578	0.695	0.830		5.0
H ₂	0.645	0.570	0.760		5.0
H ₃	0.970	0.675	0.537		5.0
H ₄	0.892	0.809	0.580		5.0
H ₅	0.470	0.680	0.225		5.0
H ₆	0.510	0.813	0.219		5.0

As no correction for absorption was applied the temperature factors probably include absorption effects. For the standard deviations, the formula given by Cruickshank ¹⁰ was used.

Table 1.

<i>h k l</i>	F_c	F_o	<i>h k l</i>	F_c	F_o
2 0 0	23.1	17.8	3 6 0	10.7	10.6
4 0 0	21.6	19.7	4 6 0	4.0	3.7
6 0 0	19.2	18.3	5 6 0	9.1	10.5
8 0 0	21.7	20.3	6 6 0	18.1	16.3
1 1 0	10.3	11.0	7 6 0	9.8	8.8
2 1 0	3.6	5.1	8 6 0	2.5	6.0
4 1 0	5.9	9.2	10 6 0	4.4	5.8
5 1 0	25.2	24.2	1 7 0	4.8	7.9
6 1 0	14.6	15.8	3 7 0	30.9	28.4
8 1 0	10.5	9.8	4 7 0	11.2	10.8
9 1 0	3.7	5.4	5 7 0	2.4	5.8
10 1 0	7.0	7.4	6 7 0	8.2	8.8
11 1 0	9.4	9.2	7 7 0	3.7	4.5
12 1 0	6.4	6.5	8 7 0	8.7	10.8
13 1 0	4.7	4.5	10 7 0	4.8	4.7
14 1 0	6.6	3.7	11 7 0	9.0	9.2
1 2 0	12.9	10.9	2 8 0	10.0	10.6
3 2 0	9.8	10.6	3 8 0	6.7	8.4
4 2 0	18.1	17.2	4 8 0	8.3	9.2
5 2 0	7.3	8.7	6 8 0	7.0	7.8
6 2 0	14.3	15.2	8 8 0	15.0	11.6
7 2 0	3.0	5.7	11 8 0	1.6	3.2
8 2 0	9.7	10.1	1 9 0	13.7	12.9
10 2 0	8.1	9.3	2 9 0	5.7	5.4
11 2 0	1.7	3.0	3 9 0	8.8	10.3
12 2 0	0.5	2.7	4 9 0	3.6	5.5
13 2 0	6.7	6.8	5 9 0	16.1	13.3
2 3 0	14.7	12.7	6 9 0	10.3	9.8
3 3 0	11.9	11.1	8 9 0	5.4	3.9
4 3 0	4.1	6.2	9 9 0	3.9	5.4
5 3 0	18.6	17.4	2 10 0	14.2	12.9
6 3 0	6.7	7.9	3 10 0	3.5	4.5
7 3 0	5.7	6.2	4 10 0	2.8	5.4
8 3 0	3.7	5.1	5 10 0	3.6	4.2
9 3 0	11.0	11.2	6 10 0	2.7	2.8
13 3 0	5.3	5.1	1 11 0	5.1	6.2
1 4 0	6.3	6.4	2 11 0	5.2	5.2
2 4 0	5.8	8.3	3 11 0	2.8	5.1
3 4 0	17.9	18.1	4 11 0	4.6	5.0
4 4 0	19.4	15.2	6 11 0	4.5	4.4
5 4 0	14.6	15.2	2 12 0	5.2	5.7
6 4 0	5.6	5.9	3 12 0	3.6	3.7
7 4 0	12.7	11.9	1 13 0	3.2	3.2
8 4 0	2.8	4.4	2 13 0	2.4	2.0
10 4 0	1.9	4.4	5 13 0	3.1	4.9
11 4 0	5.1	5.1	1 1 1	20.0	15.2
1 5 0	17.5	17.9	2 1 1	4.3	4.2
3 5 0	8.1	8.8	3 1 1	18.5	17.1
4 5 0	2.8	5.4	4 1 1	12.4	13.8
5 5 0	14.7	14.0	5 1 1	2.5	2.0
6 5 0	4.6	4.7	6 1 1	14.4	14.6
7 5 0	1.7	4.2	7 1 1	8.9	10.6
9 5 0	10.4	9.9	9 1 1	8.9	9.8
10 5 0	3.7	6.1	10 1 1	8.2	9.5
1 6 0	13.4	13.1	11 1 1	11.0	10.3
2 6 0	21.4	19.5	12 1 1	4.3	4.6

<i>h k l</i>	<i>F_c</i>	<i>F_o</i>	<i>h k l</i>	<i>F_c</i>	<i>F_o</i>
13 1 1	4.6	4.2	7 7 1	4.2	3.2
2 2 1	6.5	7.3	8 7 1	7.5	8.2
3 2 1	33.5	30.0	9 7 1	3.7	4.1
4 2 1	3.4	2.8	10 7 1	3.1	3.7
5 2 1	17.7	19.2	2 8 1	4.9	6.3
6 2 1	2.3	2.5	3 8 1	8.5	9.5
7 2 1	14.7	15.3	5 8 1	6.2	6.3
8 2 1	5.6	6.9	6 8 1	6.3	7.8
9 2 1	10.0	10.7	7 8 1	5.5	6.9
10 2 1	6.5	7.0	8 8 1	5.2	6.0
11 2 1	6.5	7.0	9 8 1	5.0	4.8
12 2 1	3.9	4.2	10 8 1	4.5	4.1
13 2 1	3.7	4.5	2 9 1	6.2	7.0
2 3 1	25.9	24.0	3 9 1	11.0	10.9
3 3 1	10.1	9.2	4 9 1	10.3	11.0
4 3 1	18.1	20.1	5 9 1	1.5	3.2
5 3 1	9.3	10.0	6 9 1	5.2	5.3
6 3 1	16.5	17.6	7 9 1	6.1	5.8
7 3 1	6.1	8.3	8 9 1	3.6	3.9
8 3 1	20.2	18.9	9 9 1	3.9	5.8
9 3 1	7.5	8.8	10 9 1	4.5	4.4
10 3 1	7.1	7.6	2 2 2	32.1	29.0
11 3 1	8.1	7.8	3 2 2	13.7	13.2
12 3 1	1.7	5.7	4 2 2	13.7	15.2
13 3 1	2.0	2.0	5 2 2	3.8	4.5
2 4 1	13.6	15.3	6 2 2	6.3	8.5
3 4 1	27.1	26.0	7 2 2	8.2	9.2
4 4 1	11.5	11.8	8 2 2	11.8	10.4
5 4 1	20.2	20.6	9 2 2	5.7	6.9
6 4 1	7.8	8.8	10 2 2	6.1	6.9
7 4 1	11.0	12.0	11 2 2	6.8	6.6
8 4 1	6.7	8.6	12 2 2	6.5	5.5
10 4 1	5.7	6.9	13 2 2	3.3	4.2
11 4 1	12.2	11.3	3 3 2	27.0	25.5
12 4 1	6.3	6.3	4 3 2	3.7	5.1
13 4 1	3.7	4.5	5 3 2	19.4	18.2
2 5 1	10.4	12.3	6 3 2	6.9	8.1
3 5 1	3.0	5.1	7 3 2	9.6	10.2
4 5 1	12.0	13.4	8 3 2	3.7	4.2
5 5 1	6.9	7.4	9 3 2	11.2	10.9
6 5 1	11.7	12.7	10 3 2	3.3	5.3
7 5 1	9.3	10.4	11 3 2	7.8	7.6
8 5 1	13.5	13.3	12 3 2	5.5	5.4
10 5 1	7.1	6.7	13 3 2	3.6	3.9
12 5 1	5.5	4.2	3 4 2	7.7	8.7
2 6 1	12.9	12.6	4 4 2	21.1	21.1
3 6 1	13.7	13.9	5 4 2	14.5	14.5
5 6 1	12.2	13.0	6 4 2	15.1	15.0
6 6 1	7.6	8.9	7 4 2	7.1	8.8
7 6 1	6.1	6.2	8 4 2	7.8	8.7
8 6 1	5.5	6.3	9 4 2	2.1	3.2
9 6 1	9.0	9.3	10 4 2	4.9	5.2
10 6 1	7.8	7.6	11 4 2	4.1	3.9
2 7 1	12.1	12.5	12 4 2	3.3	5.0
3 7 1	7.2	9.6	13 4 2	4.3	3.5
4 7 1	6.4	8.7	3 5 2	9.7	11.2
5 7 1	8.2	10.0	5 5 2	7.4	9.3
6 7 1	17.9	16.4	6 5 2	4.5	7.0

<i>h k l</i>	F_c	F_o	<i>h k l</i>	F_c	F_o
7 5 2	11.5	12.1	3 3 3	25.2	23.4
8 5 2	7.0	8.4	4 3 3	10.4	12.0
9 5 2	8.2	8.8	5 3 3	12.4	12.7
10 5 2	3.4	4.1	6 3 3	14.0	13.5
11 5 2	9.6	9.5	7 3 3	7.1	8.9
12 5 2	1.8	2.0	8 3 3	5.7	6.7
3 6 2	9.9	11.2	9 3 3	1.9	5.0
4 6 2	21.3	20.1	10 3 3	4.5	4.5
5 6 2	5.1	5.8	11 3 3	4.8	4.5
6 6 2	4.8	6.7	4 4 3	1.4	3.7
8 6 2	13.2	13.5	5 4 3	16.4	15.6
10 6 2	6.5	6.2	6 4 3	1.9	4.4
11 6 2	3.7	5.2	7 4 3	11.8	13.0
12 6 2	4.9	4.5	8 4 3	9.0	9.4
3 7 2	2.1	4.0	9 4 3	10.5	8.9
4 7 2	3.2	3.0	10 4 3	6.9	6.1
5 7 2	13.9	14.2	11 4 3	5.2	6.1
6 7 2	9.5	10.7	12 4 3	0.8	3.7
7 7 2	8.1	8.9	4 5 3	4.7	5.7
8 7 2	3.6	5.3	5 5 3	9.8	10.3
9 7 2	8.6	8.5	6 5 3	12.4	13.3
10 7 2	3.8	5.7	7 5 3	7.2	10.0
3 8 2	6.1	6.0	8 5 3	7.0	8.8
4 8 2	10.5	10.2	9 5 3	3.9	3.3
5 8 2	3.1	4.5	10 5 3	3.9	5.0
6 8 2	8.6	8.2	11 5 3	1.3	4.5
7 8 2	4.0	4.4	4 6 3	4.9	5.5
8 8 2	2.9	4.1	5 6 3	14.0	13.3
9 8 2	4.9	4.5	6 6 3	4.1	4.9
10 8 2	7.4	5.7	7 6 3	9.1	10.2
11 8 2	1.6	2.0	8 6 3	7.1	7.0
3 9 2	9.3	9.4	9 6 3	7.5	9.8
4 9 2	8.9	9.5	4 7 3	21.0	19.2
5 9 2	8.2	8.2	5 7 3	3.8	7.1
6 9 2	7.0	6.8	6 7 3	2.1	5.3
7 9 2	4.6	4.9	7 7 3	6.8	7.1
9 9 2	1.8	3.2	8 7 3	7.1	7.0
10 9 2	4.6	4.9	9 7 3	2.6	4.7
3 10 2	4.4	5.3	4 8 3	5.5	4.9
4 10 2	4.1	4.2	5 8 3	3.8	5.3
5 10 2	4.3	4.1	6 8 3	6.4	5.2
6 10 2	2.4	3.9	7 8 3	11.1	12.0
7 10 2	3.1	4.4	8 8 3	5.1	6.6
8 10 2	8.5	8.0	9 8 3	4.4	4.0
9 10 2	4.2	4.2	4 9 3	12.9	13.6
3 11 2	6.5	8.1	5 9 3	3.5	5.2
4 11 2	6.2	7.2	6 9 3	5.7	5.2
5 11 2	8.1	9.2	8 9 3	4.0	4.0
6 11 2	4.4	4.6	4 11 3	2.3	6.1
7 11 2	4.6	6.3	4 12 3	4.0	3.7
8 11 2	5.2	4.0	4 4 4	30.6	28.3
3 12 2	6.0	5.4	5 4 4	8.2	8.5
4 12 2	5.1	5.5	6 4 4	3.3	4.5
5 12 2	4.6	4.5	7 4 4	2.3	4.7
6 12 2	4.3	4.7	8 4 4	7.6	10.2
3 13 2	1.6	1.7	9 4 4	6.0	8.7
4 13 2	2.1	1.4	10 4 4	9.8	11.7

<i>h k l</i>	<i>F_c</i>	<i>F_o</i>	<i>h k l</i>	<i>F_c</i>	<i>F_o</i>
11 4 4	3.6	4.1	8 10 4	3.0	3.3
12 4 4	10.2	8.0	5 11 4	5.7	3.7
5 5 4	5.6	9.0	6 11 4	3.4	3.3
6 5 4	5.4	6.7	7 11 4	10.4	7.8
7 5 4	11.4	13.2	5 12 4	3.2	4.1
8 5 4	5.8	5.0	5 5 5	13.1	11.0
9 5 4	7.9	5.0	6 5 5	7.1	7.6
10 5 4	5.5	4.5	7 5 5	9.0	7.8
12 5 4	6.0	4.1	8 5 5	3.4	4.2
5 6 4	3.1	4.7	9 5 5	2.1	4.5
6 6 4	14.7	12.6	7 7 5	3.0	3.2
7 6 4	3.6	5.0	8 8 5	5.2	4.5
8 6 4	6.0	7.1	6 6 6	6.4	5.8
9 6 4	2.7	4.7	7 6 6	1.4	1.0
10 6 4	5.4	6.0	8 6 6	7.1	2.8
5 7 4	6.1	10.1	9 6 6	0.9	1.7
7 7 4	4.0	5.0	10 6 6	3.8	2.5
8 7 4	5.2	4.7	7 7 6	4.8	2.2
9 7 4	2.7	4.4	8 8 6	6.3	4.7
10 7 4	8.5	7.1	7 7 7	5.7	2.8
5 8 4	6.2	7.1	8 7 7	2.7	1.0
6 8 4	7.4	10.1	8 8 7	2.6	1.7
8 8 4	3.8	4.5	8 8 8	7.6	3.6
9 8 4	3.2	4.1			
10 8 4	2.8	3.3			
5 9 4	9.3	5.0			
8 9 4	4.7	5.6			
9 9 4	4.5	5.6			
5 10 4	2.3	4.5			
7 10 4	2.8	3.7			

Reflexions not included in the latest refinements:

3 1 0	47.1	35.7
2 2 0	37.3	28.7
1 3 0	49.8	37.4

The following interatomic distances and standard deviations have been found:

N _{tert} — C ₁	1.52	± 0.02 Å	< C ₁ —N _{tert} —C ₁	= 108.4°
C ₁ — C ₂	1.46	± 0.02 Å	< N _{tert} —C ₁ —C ₂	= 111.6°
C ₂ — N _{prim}	1.47	± 0.02 Å	< C ₁ —C ₂ —N _{prim}	= 112.6°
C ₁ — H ₁	1.00			
C ₁ — H ₂	1.04			
C ₂ — H ₃	1.09			
C ₂ — H ₄	1.11			
N _{prim} — H ₅	1.04			
N _{prim} — H ₆	1.01			

Van der Waal's distances:

N _{tert} — Cl ₁	3.68	C ₁ —C ₂	3.18
N _{prim} — Cl ₁	3.14	N _{prim} —N _{prim}	4.06
N _{prim} — Cl ₂	3.27	Cl ₁ —Cl ₃ along C ₃ -axis	5.10
N _{prim} — Cl ₃	3.22	Cl ₂ —Cl ₃ » »	4.48
C ₁ — Cl ₃	3.86	Cl ₁ —Cl ₃	4.91
C ₂ — Cl ₂	3.75	Cl ₂ —Cl ₃	4.06
C ₂ — Cl ₃	3.69	Cl ₁ —Cl ₂	4.26

DISCUSSION

The bond distances are not exactly equal to generally accepted values for amines, amino acids and other aliphatic carbon compounds. The bond distances C—C and C—N agree with, *e.g.*, those of Hahn and Buerger¹¹ for diglycine-hydrochloride, but we consider it highly probable that additional refinement may change the bond distances a few hundredths of Å. Therefore we abstain from further discussion of bond type *etc.* With computing facilities in the future we hope later to be able to make extended calculations with our data.

Our primary aim was a comparison between coordinated and free tren molecules, and the determination of the shape and size of the polyhedron formed by the four nitrogen atoms of the free molecule.

The N-atoms are situated at the corners of a three sided pyramid. One N—N distance is 4.20 Å the other one 2.95 Å. The center of gravity of the pyramid is 2.4 Å from the three primary amine nitrogens and 1.2 Å from the tertiary amine nitrogen. Most distances between nitrogen atoms and metal atoms in coordination compounds are around 2 Å. It is therefore impossible for the tren molecule to form tetrahedral complexes without distortion. Probably it is easier for the tren molecule to span four corners of an octahedron than spanning the corners of a tetrahedron in formation of a complex compound.

Figs. 2 and 3 are clinographic projections of a tren molecule and of a unit cell of the structure.

The bond lengths of the Nitren(NCS)₂ structure are of low accuracy¹. They deviate 0.1–0.2 Å from the corresponding distances of this investigation. No conclusions can be drawn about small changes in bond lengths at complex formation. However, it is definitely established that the shape of the tren molecule is changed by coordination to the Ni²⁺ ion.

The N—C—C groups are non planar in both compounds. The free molecule has a C₃-axis whereas in the nickel complex the conformation of one

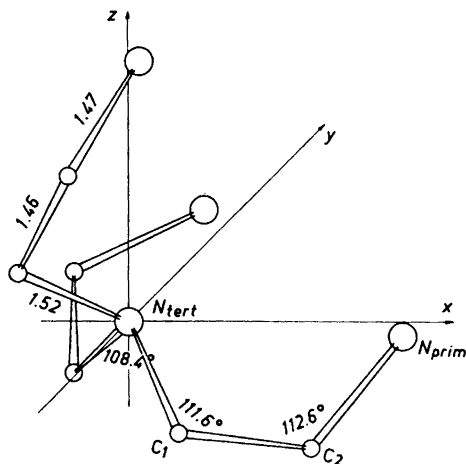


Fig. 2. Clinographic projection of a "tren" molecule.

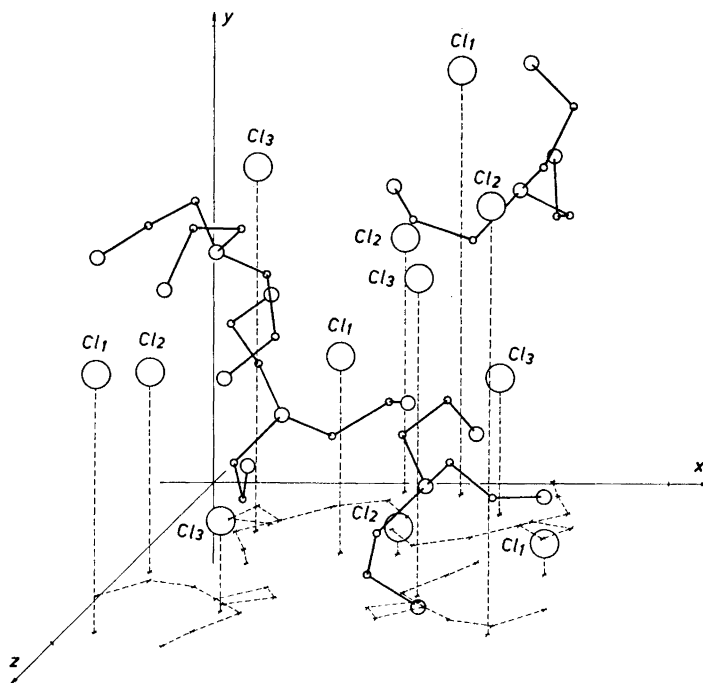


Fig. 3. Clinographic projection of a unit cell. The dotted lines indicate projections of the atoms on the $x-z$ plane.

of the rings is changed, thus destroying the C_3 -symmetry. Some of the consequences of this change may be described by quoting some corresponding interatomic non bonding distances.

	Tren(HCl) ₃	Nitren(NCS) ₂
C_1-C_1	2.47 Å	2.6 Å (mean value)
C_2-C_2	4.23 Å	3.36 Å
		3.94 Å
		4.89 Å
$N_{\text{prim}}-N_{\text{prim}}$	4.20 Å	3.16 Å
		3.20 Å
		4.32 Å
$N_{\text{tert}}-N_{\text{prim}}$	2.95 Å	2.90 Å
		3.05 Å
		2.82 Å

The tren molecule is considerably distorted by coordination to the nickel ion.

No quantitative physical significance should be given to the B -factors, but some qualitative features may be correlated with the structure:

The chlorine atom sandwiched between two other chlorine atoms has the lowest B -factor of the three. The tertiary nitrogen atom has the lowest B -

factor of all atoms of the crystal, and the primary nitrogen has the largest B -factor of the non hydrogenic atoms. Each primary nitrogen atom has three Cl^- neighbours at 3.14–3.22 and 3.27 Å, and each Cl^- ion has three nitrogen neighbours at the same distances. The data do not give any proof of the positions of the hydrogen atoms, especially not the locations of those close to chlorine ions. But chemical evidence and the hardness of the crystal suggest strongly that it be described as built from trenH_3^{3+} ions and Cl^- ions.

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