Structure of Reineckate Complex Ion

By Yoshio Takéuchi and Yoshihiko Saito

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Introduction

In the study of the crystal structure of Reinecke's salt, $NH_4[Cr(NCS)_4(NH_3)_2]\cdot 2/3H_2O$, it was found that the reineckate complex ion $[Cr(NCS)_4(NH_3)_2]^-$ contains linear NCS groups. The bond character of the NCS group is expressed by the structure $N\equiv C-S^-$. The reineckate complex ion with the same bond character was also found in pyridine reineckate, $C_5H_5N[Cr(NCS)_4(NH_3)_2]$. The shape and the size of the complex ion in both crystals are identical within the errors of experiment. However, a modified configuration of the complex ion has been found by the study of Patterson projections of choline reineckate,
$(CH_3)_3N\cdot CH_2\cdot CH_2\cdot OH[Cr(NCS)_4(NH_3)_2]$,
which was prepared from choline chloride and Reinecke's salt solution. In the case of choline reineckate, the bond distances of the complex ion are considerably different from those found in the other two cases and the bond character is no more expressed by the structure $N\equiv C-S^-$ but very close to the structure $N^-=C=S$. Although brief accounts on the crystal structures of these reineckates already appeared separately, because of the importance of understanding the nature of complex ions, a detailed description of the structure of reineckate complex ion will be given in the present paper.

1. The Structure of Reinecke's Salt[1]

(i) Unit Cell and Space Group.— The crystals of Reinecke's salt whose chemical formula had been known as $NH_4[Cr(SCN)_4(NH)_3)_2]H_2O$ crystallize from ethyl alcohol and water in well formed garnet-red rhombic docecahedra combined with a cube (Fig. 1).

Oscillation and Weissenberg photographs taken with copper radiation ($\lambda=1.5418$ Å) gave lattice constant:

$$a=13.25\pm0.02\ \text{Å},$$

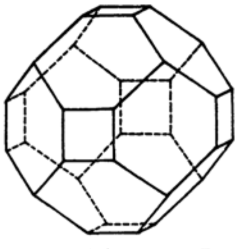

Fig. 1. The crystal habit of Reinecke's salt.

and unit cell contains six formula units. The calculated density 1.496 g./cc. was in good agreement with the observed value 1.503 g./cc. measured by the pycnometer method. The Laue symmetry is O_h-m3m and h,k,l reflexions are systematically absent when $h+k+l$ is odd. Hence, the possible space groups are $O_h^9-I_{m3m}$, $T_d^3-I_{43m}$

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[1] Y. Saito, Y. Takéuchi and R. Pepinsky, *Z. Krist.* **106**, 476, (1955).

or O^5-I_{43}. Taking account of all possibilities of these space groups, the structure analysis was started. However, by the study of Patterson projection, it became obvious that O_h^9 was a distinct possibility.

(ii) Analysis.—The multiple film technique was employed and intensities were recorded for all three dimensional reciprocal spaces which are covered by copper radiation. These intensities were measured visually using an intensity scale prepared with the same specimen as that used for intensity recording.

The following characteristics of reflexions were observed: hkl is strong when $h=4n_1$, $k=4n_2$, $l=4n_3$ or $h=4n_4+2$, $k=4n_5+2$, $1=4n_6+2$, where n_i are integers. These conditions immediately fixed the positions of heavy atoms as follows: 6Cr in the six-fold positions (b) $0\frac{1}{2}\frac{1}{2}$, and 24S in the twenty four-fold positions (h) $0xx$ with $x\simeq0.25$. This arrangement of heavy atoms was in good accord with conclusions drawn from the Patterson projection $P(xy)$. Distribution of peaks in $P(xy)$ also indicated that 24C and 24N atoms from the thiocyanate groups are on 12(e) $x00$. The first Fourier synthesis was calculated using the signs based on chromium and sulphur atoms. In the electron density projection $\rho(xy)$ thus obtained, two peaks were observed between chromium and sulphur. These peaks must be due to nitrogen and carbon atoms. The distances between these peaks approximately corresponded to the usual bond lengths of Cr—N, N—C and C—S. Since it seems reasonable that the majority of the signs of $F(hk0)$ reflexions are determined by the contribution of the complex ion $[Cr(NCS)_4(NH_3)_2]^-$, the further steps of refinement were made by computing $\rho(xy)$ and generalized projection $\rho(xy1)$ using the signs based on the complex ion. The atomic positions found from these refinements are:

	x	y	z
Cr	0	0.5	0.5
N	0.40	0.40	0
C	0.33	0.33	0
S	0.24	0.24	0
NH_3	0.34	0.34	0

If the empirical formula of the Reinecke's salt is correct, there should be six ammonium and six water molecules in the unit cell. However, in the space group I_{m3m} and any of its subgroups, no six-fold positions are available for these atoms. Then, to find out possible positions of these atoms, the contribution of the complex ion F_r was subtracted from observed structure factor F_{hk0} and trial of computing $\sum\sum(F_{hk0}-F_r)\cos 2\pi(hx+ky)$ was made on X-RAC. The result showed well-defined peaks on sets of special positions $2(a)000$ and $8(c)\frac{1}{4}\frac{1}{4}\frac{1}{4}$ (Fig. 2.).

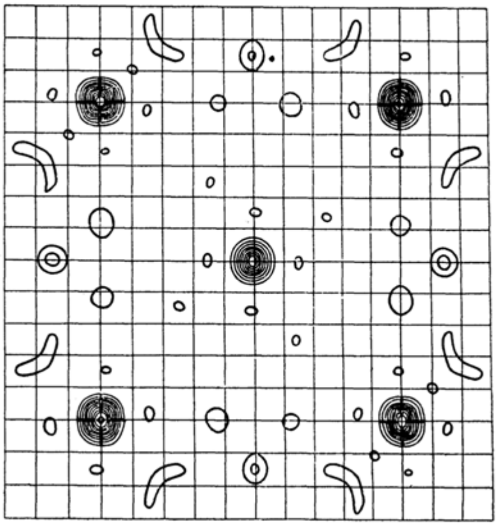

Fig. 2. Residual Fourier projection showing the positions of NH_4 and H_2O groups. Origine is taken at the center of this projection.

In order to obtain the best agreement between observed and calculated structure factors, it was necessary to distribute $6NH_4$ and $4H_2O$ atoms random among these positions. The final refinement of the structure was made by three dimensional Fourier synthesis. The final atomic parameters are:

6Cr:	6(b)	0
24N:	24(h)	$0xx$ with $x=0.395$
24C:	24(h)	$0xx$ with $x=0.334$
24S:	24(h)	$0xx$ with $x=0.238$
$12(NH_3)$:	12(e)	$x00$ with $x=0.338$
$6(NH_4)$ and $2H_2O$:	8(c)	$\frac{1}{4}\frac{1}{4}\frac{1}{4}$
$2H_2O$:	2(a)	000

With these coordinates, structure factors were calculated using the temperature factor of the form $\exp-B(\sin^2\theta/\lambda^2)$, where $B=2.0$ Å^2. The R-factor is 11.6% for $F(hk0)$ and 19.0% for $F(hkl)$ reflexions.

(iii) Description of the Structure.—Fig. 3 shows the structure of Reinecke's salt. Chromium atoms are at six corners of the one-eighth of the unit cell. The rest of the corners and the body-centered position of the cube are occupied by ammonium ions and water molecules randomly. The ammonium ion (and water molecule) at the body-centered position is surrounded by six sulphur atoms octahedrally with the distance of 3.35 Å. The water molecules at the corners of the cube are surrounded by twelve sulphur atoms with the distance of 4.44 Å. Since the bond between ammonium ion and sulphur atoms is ionic from the stand point of atomic distances, it seems reasonable to conclude that the eight-fold position $\left[\frac{1}{4}\frac{1}{4}\frac{1}{4}\right]$ is occupied by six ammonium ions and two water molecules randomly and the two-fold position [000] is occupied by two water molecules. The correct formula of Reinecke's salt is thus $NH_4[Cr(NCS)_4(NH_3)_2]\ \frac{2}{3}\ H_2O$. A similar random distribution of atoms has also been found in the mineral analcite[2].

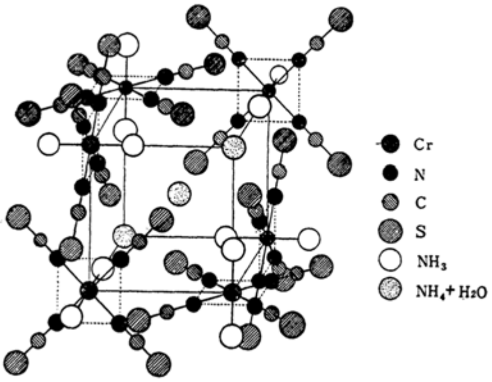

Fig. 3. 1/8 unit cell of Reinecke's salt. $NH_4[Cr(NCS)_4(NH_3)_2]\cdot 2/3\ H_2O$

The square coordination of NCS groups to chromium atoms is shown in Fig. 4 which was obtained from the zero section of the three dimensional Fourier synthesis. The supposed SCN group is actually an iso-thiocyanato group NCS, with N atoms coordinated to chromium. This iso-thiocyanato group is in contrast to $[Hg(SCN)_4][Cu(en)_2]$[3] where the thiocyanato group SCN was found. Four linear NCS groups are arranged along the diagonals of a square around the chromium atom, and NH_3 groups are in the remaining octahedral positions. The symmetry of the complex ion is thus 4/*mmm*. Bond lengths of the complex ions are:

$Cr—NH_3$ …… 2.15±0.03 Å
Cr—N …… 1.97±0.03
N—C …… 1.14±0.03
C—S …… 1.80±0.03

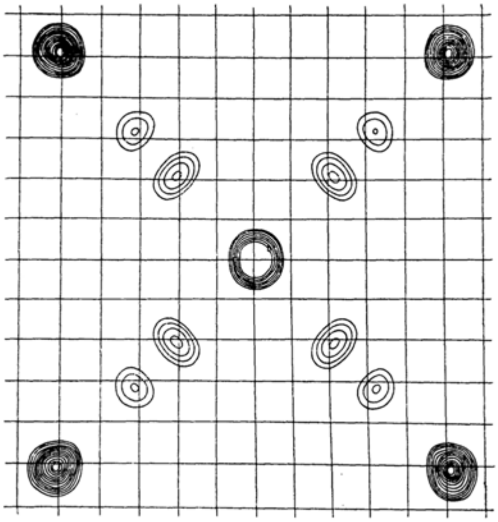

Fig. 4. Three dimensional Fourier section $\rho(xy0)$ of Reinecke's salt with origine at the center.

2. The Structure of Pyridine- and Choline-reineckate

Prior to the discussion on the structure of the complex ion, the crystal structures of pyridine- and choline-reineckate are described. The lattice constants and space groups of these reineckates are given in Table I.

TABLE I
THE LATTICE CONSTANTS AND SPACE GROUPS OF SOME REINECKATES

	Lattice constants				Space group
	a	*b*	*c*	*β*	
Reinecke's salt	13.25 Å				$O_h^9-I_{m3m}$
Pyridine reineckate	15.52	7.64	14.64	102°24′	$C_{2h}^5-A_{2/a}$
Choline reineckate	12.69	22.80	6.75		$D_{2h}^{26}-I_{bma}$

(i) **Pyridine Reineckate**[4].—The crystals of pyridine reineckate were prepared by Christensen's method[5] and recrystallized in hot alchoholic solution. The measured density of the crystals 1.560 g./cc. is in agreement with the calculated

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[2] W. H. Taylor, *Z. Krist.*, **74**, 1 (1930); **99**, 283(1938).
[3] H. Scouloudi, *Acta Cryst.*, **6**, 651 (1953).
[4] Y. Takéuchi and R. Pepinsky, Presented to the Thirteenth Annual Pittsburgh Diffraction Conference, 1955.
[5] O. T. Christensen, *J. Prak. Chem.*, **45**, 364 (1891).

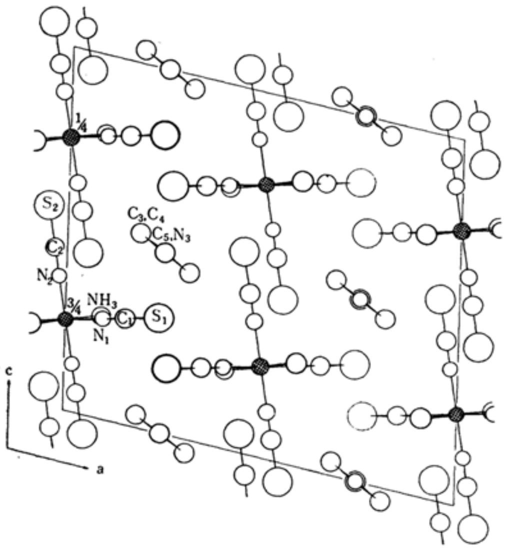

Fig. 5. Projection of the structure of pyridine reineckate aiong *b*-axis.

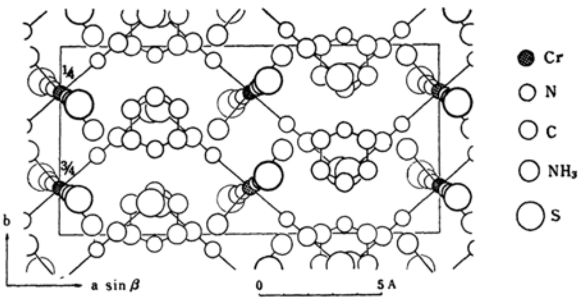

Fig. 6. Projection of the structure of pyridine reineckate along *c*-axis.

density 1.56 g./cc. The crystals obtained were found to be twinned about (101). However, it was possible to separate single crystals and they were used for X-ray work.

The structure was determined by the use of two dimensional Fourier synthesis which resulted in a final agreement factor, $R=\sum(|F_o|-|F_c|)/\sum|F_o|$, of 0.107 for the (010) projection and of 0.112 for the (001) projection. Fig. 5 and Fig. 6 show the projections of the crystal structure of pyridine reineckate on (010) and (001) respectively. Reineckate groups are arranged around a two-fold screw axis, making a frame-like structure and leaving a big hole around the two-fold axis. The pyridine molecule on the twofold axis is located in a region surrounded by twelve sulphur atoms. Four of these sulphur atoms coordinate to the nitrogen atom of the pyridine molecule with two distances of 3.36 Å and two of 3.60 Å. The configuration of sulphur atoms about a pyridine molecule is shown in Fig. 7. The mean values of the bond lengths determined for the reineckate complex ion are Cr–N= 1.95 Å, N–C=1.15 Å and C–S=1.76 Å. These values agree with those found in Reinecke's salt (p. 321). The bond lengths of pyridine molecules and non-bonded distances of atoms are given in Table III.

The estimation of the accuracy of atomic parameters was carried out especially to the atoms of pyridine molecules. Because of the special position, errors of atomic coordinates in a pyridine molecule mainly

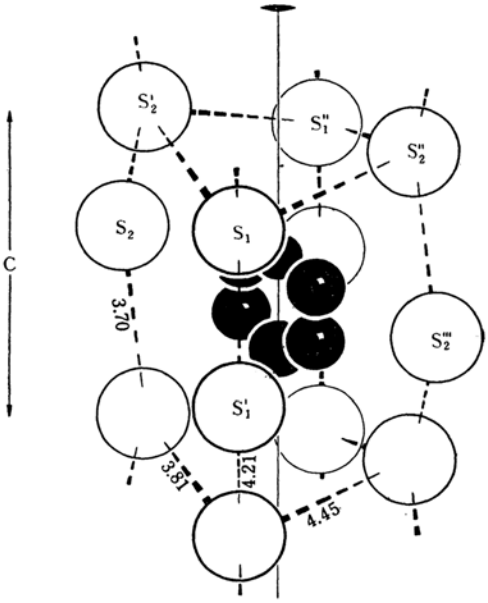

Fig. 7. Configuration of sulphur atoms about a pyridine molecule. Numbers indicate the distances between sulphur atoms in Å.

TABLE II

COORDINATES OF ATOMS IN PYRIDINE REINECKATE

Atom	x/a	y/b	z/c	No. of atoms per cell
Cr	0	3/4	1/4	4
S_1	0.237	0.117	0.306	8
S_2	−0.050	0.831	0.563	8
C_1	0.152	0.021	0.287	8
C_2	−0.035	0.802	0.439	8
N_1	0.095	0.922	0.273	8
N_2	−0.025	0.783	0.365	8
NH_3	0.080	0.536	0.292	8
C_3	0.184	0.489	0.535	8
C_4	0.182	0.671	0.536	8
C_5	1/4	0.746	1/2	4
N_3	1/4	0.420	1/2	4

TABLE III

ATOMIC DISTANCES IN PYRIDINE REINECKATE

Bond lengths of pyridine molecule

$C_3-C_4=1.39$ Å $C_4-C_5=1.40$ Å

$C_3-N_3=1.35$ Å

Nonbond distances

$S_1-S_1'=4.21$ Å $S_1-S_2'=3.80$ Å

$S_2'-S_2=3.70$ $S_1'-S_2''=4.45$

$NH_3-N_3=3.60$ $NH_3-C_3=3.78$

$NH_3-C_3'=3.99$ $NH_3-C_4'=4.11$

$NH_3-C_4=3.90$ $NH_3-C_5=3.84$

$N_3-S_1=3.36$ $N_3-S_2'=3.60$

$C_3'-S_1=3.38$ $C_3'-S_2''=3.47$

$C_4-S_2=3.82$ $C_4-S_1'=4.34$

$C_5-S_1=4.33$

distribute in their y-parameter. The standard deviations $\sigma(y)$ for the positions of carbon and nitrogen atoms were calculated, using Cruickshank's method[6] were found to be 1.9×10^{-2} Å and 1.7×1.0^{-2} Å respectively. Standard deviations $\sigma(x)$ and $\sigma(z)$ for carbon atoms of pyridine molecule were 1.2×1.0^{-2} Å.

(ii) **Choline Reineckate**[7].—Choline reineckate was prepared using a diffusion method with choline chloride and Reinecke's salt solution in silica gel. The colour of the crystal is magenta as are other reineckates. A study of morphology and optical properties showed the crystal to be orthorhombic with holohedral symmetry. The crystal is tabular parallel to (010) and shows (110), (101) forms. There are four formula units of $[C_5H_{13}N(OH)][Cr(NCS)_4(NH_3)_2]$ in the cell giving a calculated specific gravity of 1.48 g./cc. which compares well with the measured value of 1.475 g./cc.

From cell dimension and space group symmetry, it is obvious that the chromium atom is located on a centre of symmetry whose point symmetry is $2/m$. On a Patterson projection $P(uv)$, a fairly well-resolved peak is observed at the point $u=0.175$, $v=0.118$. It has been known that Cr—N—C—S bond is straight and Cr—S distance is 4.9 Å, accordingly the Cr—S vector should appear on the line $y=4.9\times1/\sqrt{2}$ Å (0.153 as decimal fraction of the b-axis). From the packing view point, the estimated Cr—S vector position will be $u_0\simeq0.180$, $v_0\simeq0.153$. (Fig. 8) The relative peak height at (u_0, v_0) seems to be unreasonable as Cr—S vector, while the peak at (u, v) could not be explained from Cr—N—C—S straight configuration. However, it was found that the position (u, v) is better for sulphur location to obtain better agreement between calculated and observed structure factors of several strong reflexions. Then the first Fourier based on signs of $F(hk0)$ calculated from Cr and S at (u, v) position was computed on X—RAC. The result revealed that the Cr—N—C angle is not 180° as has been found in other reineckates but has a value of 158° on the (001) projection.

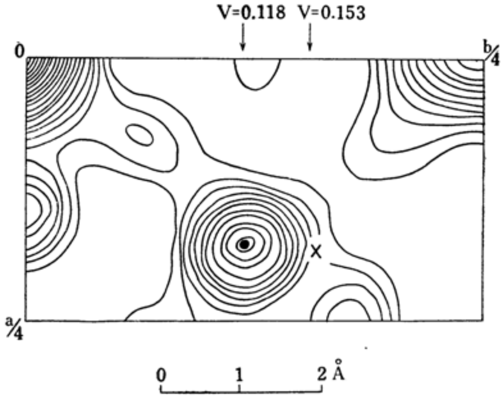

Fig. 8. Patterson projection $P(xy)$ of choline reineckate.

● Cr—S vector position in choline reineckate.

× Cr—S vector position expected from Cr—N—C—S straight configuration.

The structure was refined on the projections (100) and (001). The final refinement was made by computing a three-dimensional Fourier synthesis. The atomic parameters derived from the three-dimensional Fourier are given in Table 4. The R-factor is 11.2% for $F(hk0)$, 13.5% for $F(0kl)$ and 17.0% for $F(hkl)$.

TABLE IV

ATOMIC PARAMETERS FOUND IN CHOLINE REINECKATE

Atom	x/a	y/b	z/c	
Cr	0	0	0	
N	0.058	0.057	0.182	
C	0.107	0.084	0.317	
S	0.173	0.115	0.493	
NH_3	0.139	0	−0.175	
N	0	0.25	0.03	
C_1	0.07	0.28_3	0.16	Choline molecule *
C_2	−0.07	0.28_3	−0.13	
C_3	−0.08	0.25_8	-0.29_1	
OH	0.01_8	0.27	-0.29_3	

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[6] D. W. J. Cruickshank, *Acta Cryst.*, **2**, 154 (1949).

[7] Y. Takéuchi and R. Pepinsky, Presented to the ACA annual meeting (1956).

* This set of coordinates corresponds to the orientation given in Fig. 10.

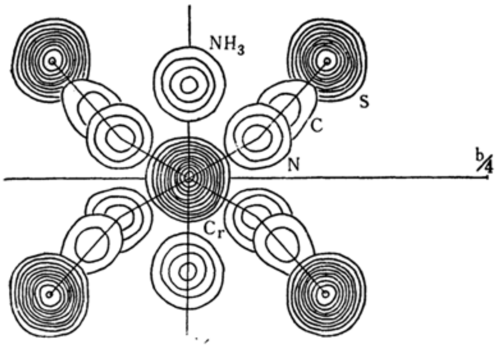


Fig. 9. Composite electron density map of the reineckate group in choline reineckate; view along *c*-axis. Even-contours only drawn for chromium.

Fig. 9 shows the composite electron density map of the complex ion found in choline reineckate. The structure projections on (001) and (100) are given in Fig. 10. The chromium atoms of the complex ions are on the mirror plane and form a layer-like structure parallel to (010). Between these layers, choline molecules are located on the two-fold axis in a region surrounded by four sulphur atoms tetrahedrally. The choline molecule is randomly oriented in four possible positions so that the two fold axis at $\left(0, \frac{1}{4}, z\right)$ has only statistical meaning. The configuration of the choline molecule was found to be close to a "gauche" configuration. Possibly, the weak interaction between the choline and the complex ion results in a significant interaction between the positive nitrogen atom and the hydroxyl group in the same molecule.

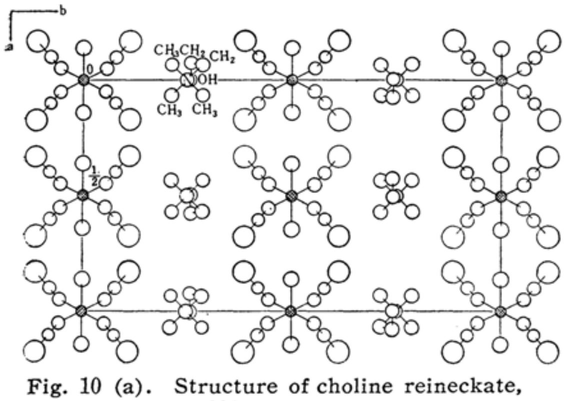


Fig. 10 (a). Structure of choline reineckate, projected on (001).

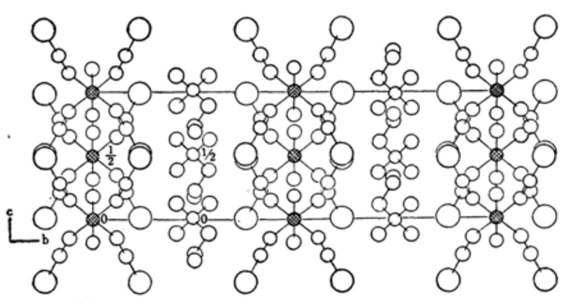


Fig. 10 (b). Structure of choline reineckate, projected on (100). Only one possible orientation is shown for choline molecule.

3. Structure of Reineckate Complex Ion

Fig. 11 shows two different configurations of the reineckate complex ion which we have found by the study of these three reineckates. Bond lengths and bond angles are compared in Table V.

These results suggest that in choline reineckate the contribution of the structure

$$N^{-}=C=S \qquad (1)$$

is dominant, while in ammonium and pyridine reineckates the contribution of the structure

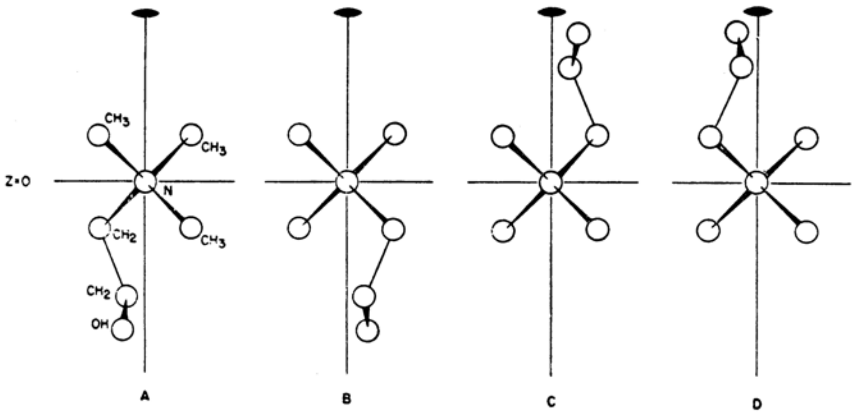
$$N\equiv C-S^{-} \qquad (2)$$

is dominant. These two different cases may be explained as follows.

TABLE V

	Cr-S	N-C	C-S	Cr-NH$_3$	Cr-N-C
Reinecke's salt	1.97	1.14	1.80	2.15	180°
Pyridine reineckate	1.95	1.15	1.76	2.11	180°
Choline reineckate	1.94	1.27	1.64	2.12	155.5°

In the case of ammonium and pyridine reineckates, positively charged nitrogen atoms can approach the sulphur atoms of the reineckate groups closely. The electrons are, accordingly, more shifted towards the sulphur atoms in the NCS groups due to the polarization by the nitrogen atoms. In this case, structure (2) will be more stable than structure (1). On the other hand, in the case of the choline molecule, the nitrogen atom with positive charge is surrounded by carbon atoms tetrahedrally and does not approach the sulphur atoms as closely, and the polarization effect on the NCS groups due to the nitrogen of the choline molecule will be smaller. This would result in the dominant contribution of the structure (1). Actually, the NH_4—S and NH—S distances in ammonium and pyridine reineckates are



Random orientation of choline molecule in choline reineckate.
Four possible orientations are shown.

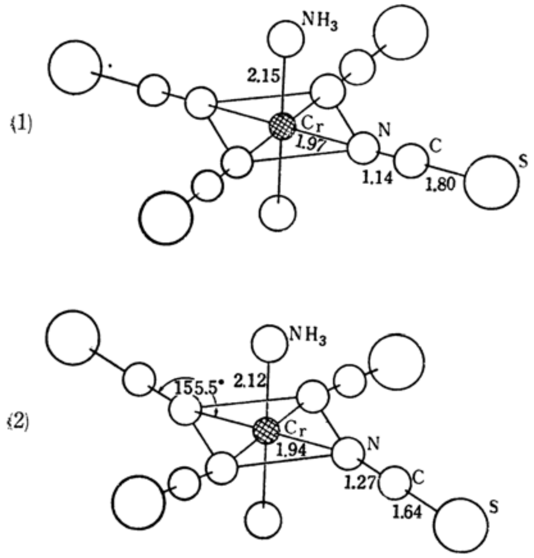


Fig. 11. Configuration of reineckate complex ion found in Reinecke's salt (1) and in choline reineckate (2). Bond distances and bond angle are shown.

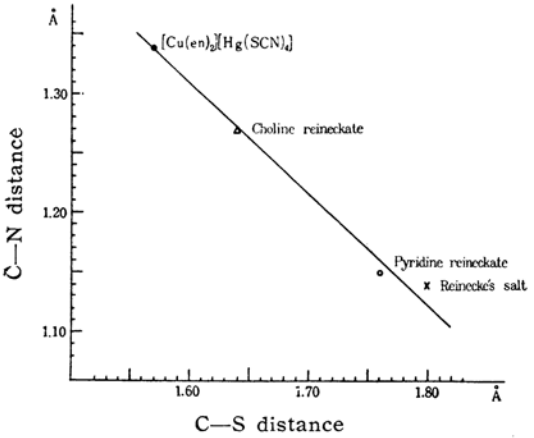


Fig. 12. Relation between the C—N and the C—S distances in various reineckates.

respectively 3.35 Å and 3.36 Å, while in choline reineckate the N—S distance is 4.9 Å. Also, it is interesting to note that in comparison with the other reineckates, the nitrogen atoms of the choline molecule are closer to the nitrogen atoms of the reineckate groups with the distance of about 4.6 Å.

An interesting relation has been found between the C—N and the C—S distances in NCS groups found in various reineckates. If C—N distances are plotted against the C—S distances, a straight line is obtained as illustrated in Fig. 12.

Summary

The crystal structure analyses of Reinecke's salt, pyridine reineckate and choline reineckate established the configuration and bond characters of the reineckate complex ion, $[Cr(NCS)_4(NH_3)_2]^-$.

The bond character of the complex ion in Reinecke's salt and pyridine reineckate corresponds to the structure $N{\equiv}C{-}S^-$, while in choline reineckate the bond character is acounted for by the structure $N^-{=}C{=}S$. This mutation of the bond character is discussed together with crystal structures of these reineckates.

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Mineralogical Institute
Department of Science
The University of Tokyo, Hongo Tokyo

Institute of Polytechnics
Osaka City University, Kita-ku, Osaka