The Crystal Structure of "Dichrochloride", $[Co(NH_3)_3H_2OCl_2]Cl$

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Introduction

Crystals of dichloro-aquo-triammine-cobalt (III) chloride ("dichrochloride"), $[Co(NH_3)_3H_2OCl_2]Cl$, is well-known for its marked red-blue dichroism. According to Matsuno(1) this modification of $[Co(NH_3)_3H_2OCl_2]Cl$ has trans-configuration with respect to the two chlorine atoms. Stelling(2) has examined the fine structure of K-absorption edge of Cl atoms in this substance and has come to the same conclusion about its configuration.

We have taken up the crystal structure investigation of this complex salt in order to give direct proof of the configuration of the complex ion and also to correlate its structure with its anisotropy in absorption of plane polarized light by crystals.

The Unit Cell and Space Group

The material used in this investigation was prepared according to the method of Meyer, Dirska and Clemens.(3) The crystals for X-ray work have been grown at room temperatures from concentrated solution by adding an equal volume of 6 N hydrochloric acid very slowly through a funnel fitted with a capillary tube. These crystals belong to the hexagonal holohedral class and are usually thin needles, showing faces $(10\bar{1}0)$ and $(10\bar{1}1)$, or rarely tabular in habit with (0001) extended. A crystal rod of less than 0.3 mm. in diameter and another one with no dimension larger than 0.3 mm. were selected for taking oscillation photographs around c- and a-axes. A complete set of oscillation photographs were prepared using Fe K_α radiation ($\lambda = 1.937$ A.), which gave the dimensions:

$$a = 7.37\ \text{A. and } c = 8.75\ \text{A.}^*$$

From the size of the unit cell and the density 1.908 g./cm.^{3},(4) the number of formula units in the unit cell was calculated to be two, the calculated density being 1.891 g./cm.^{3} Oscillation photographs taken about the c-axis with the $[10\bar{1}0]$ as well as $[11\bar{2}0]$ axis at the zero position of oscillation indicated the presence of mirror planes parallel and perpendicular to the c-axis, hence the Laue symmetry was found to be D_{6h}-$6/mmm$. General reflections $(hkil)$ occur in all orders. Reflections $(hh\bar{2}hl)$ are present only with l=even. The space group is therefore one of D_{6h}^4-$C6/mmc$,

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(1) K- Matsuno, *J. Coll. Sci. Imp. Univ. Tokyo* **41**, *Art.* 10, 4, (1921).

(2) O. Stelling, *Ber.* **60**, 652 (1927); Z. Phys. **50**, 520 (1928).

(3) J. Meyer, G, Dirska und F. Clemens, *Z, anorg. Ch.* **139**, 357 (1924). S. M. Jörgensen, *Z. anorg. Ch.* **14**, 418 (1897).

* Even very heavy exposure (50 hrs.) indicated no evidence for larger unit cell size.

(4) E. Birk, *Z. anorg. Ch.*, **158**, 114 (1926).

C_{6v}^4-$6/mc$ or D_{3h}^4-$C\bar{6}2c$.

The Atomic Arrangement

The intensities were estimated visually using the timeexposure calibrated strip, taking into account the shape of specimens in relation to absorption. Structure factors were deduced from these intensity data in the usual way, which are shown in Table 1.

At first an attempt has been made to assign approximate co-ordinates for heavy atoms. In the space group D_{6h}^4, C_{6v}^4 and D_{3h}^4 the general positions are 24 fold, 12 fold and 12 fold respectively. Since there are two formula units, $[Co(NH_3)_3H_2OCl_2]Cl$, in the unit cell, 2Co, 4Cl(1) and 2Cl(2) may either occupy sets of two fold special positions, or alternatively Cl(1) may occupy one set of four fold positions. The intensity of reflection (0004) is the strongest by far compared with the rest, which suggests all the atoms might be nearly in phase for this reflection. In general the reflections (*hkil*) are strong when h-$k=3n$ and $l=2n$. These characteristics for reflections combined with the results of trial calculations of structure amplitudes (*hkil*) at once lead to the following arrangement of heavy atoms based on the space group D_{6h}^4-$C6/mmc$:

2Co in 2(*c*) 1/3 2/3 1/4; etc.
2Cl(2) in 2(*a*) 000; etc.
and 4Cl(1) in 4(*f*) 1/3 2/3 z; etc. with $z \approx 0$.

It is almost evident that the signs of the structure factors for a complete unit would be determined mainly by these atoms. In order to determine the z-parameters of Cl more accurately, the three dimensional Fourier synthesis of the electron density along a line (1/3 2/3 z) was evaluated using all the $F(hkil)$'s, whose signs were known from the arrangement of the heavy atoms. As shown in Fig. 1, this lead us to fix the z-parameter at -0.016.

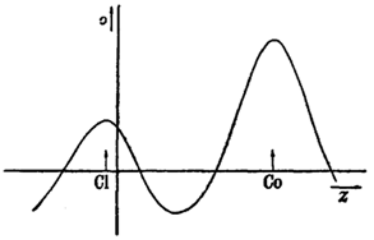

Fig. 1.—$\rho(1/3\ 2/3\ z)$.

It seems reasonable that in this crystal there are complex ions with octahedral co-ordination, —that is, three molecules of ammonia and one water molecule are in the plane of Co atom forming a distorted octahedron together with two Cl (1) atoms up and down the plane, where Co-N and Co-O distances are supposed to be between 1.90~2.00 A. In the space group D_{6h}^4 and its subgroups the proper symmetry of the special position (1/3 2/3 1/4) is ditrigonal or trigonal. Such symmetries cannot be achieved by any regular static arrangement of the complex ions so oriented as the positions of Co and Cl(1) atoms demand. Then we are entitled to assume some kind of statistical arrangement of these octahedral complex ions. The observed intensities are satisfactorily accounted for by means of the space group D_{6h}^4-$C6/mmc$, if the atomic arrangement of N and O atoms are assumed as follows:

6N and 2O in 12 (*j*) $xy\frac{1}{4}$ etc. with
$x_1=0.038$, $y_1=0.451$ and $x_2=0.117$, $y_2=0.372$.

N and O atoms are statistically distributed on these twenty four positions with weights 1/4 and 1/12 respectively.

These parameters were chosen in such a way that the Co-N and Co-O distances bocome 1.96 A. It was not thought worth while to determine these parameter values very accurately as they scatter very poorly compared with other heavy atoms. The electron distribution in the plane of a cobalt atom, $\rho(xy\frac{1}{4})$ was synthesized using all the observed F-values whose sign was calculated from the positions of all the atoms in the unit cell. The result is shown in Fig. 2. The central peak represents a cobalt atom and the only other regions of high electron density lie about the cobalt peak at distances of about 2 A. and are separated by an almost circular minimum. The maxima making up the region surrounding cobalt are twelve in number, though not fully resolved, and are quite a satiafactory representation of statistical orientation of octahedral complex ion with its Cl-Co-Cl axis normal to the plane of section, as shown in Fig. 3. This result is quite consistent with the previous assumption of Co···NH_3 and Co···H_2O distances.

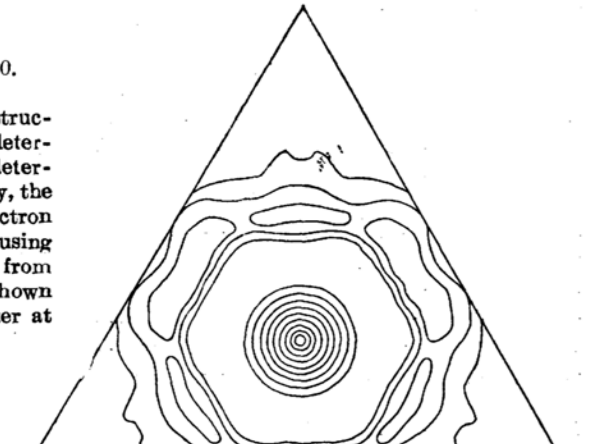

Fig. 2.—Part of the electron distribution, $\rho(xy\frac{1}{4})$. Contours at arbitrary intervals.

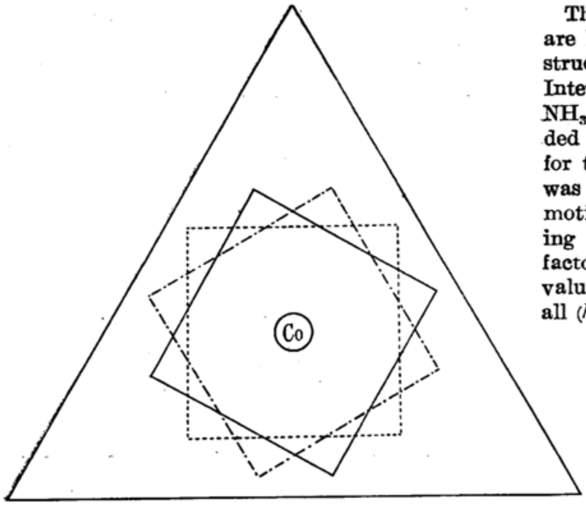

Fig. 3.—Statistical azimuthal orientations of the complex ion. The figure corresponds to Fig. 2.

Table 1
Observed and Calculated *F*-values

hkil	*F*obs.	*F*calc.	*hkil*	*F*obs.	*F*calc.
$10\bar{1}0$	31	−31.2	$30\bar{3}2$	13	12.8
$20\bar{2}0$	10	−6.7	$40\bar{4}2$	15	13.3
$30\bar{3}0$	101	95.0	$50\bar{5}2$	—	6.8
$40\bar{4}0$	18	−14.0	$11\bar{2}2$	54	50.6
$50\bar{5}0$	9	−6.5	$21\bar{3}2$	14	15.7
$60\bar{6}0$	28	36.9	$31\bar{4}2$	15	17.2
$11\bar{2}0$	112	98.0	$41\bar{5}2$	14	17.2
$21\bar{3}0$	16	−18.0	$51\bar{6}2$	—	8.1
$31\bar{4}0$	19	−18.1	$22\bar{4}2$	9	13.6
$41\bar{5}0$	62	56.0	$32\bar{5}2$	8	9.9
$51\bar{6}0$	9	−8.3	$42\bar{6}2$	—	7.2
$22\bar{4}0$	89	82.0	$33\bar{6}2$	9	17.6
$32\bar{5}0$	18	−10.3			
$42\bar{6}0$	8	−7.1	$10\bar{1}3$	39	48.3
$33\bar{6}0$	46	42.7	$20\bar{2}3$	21	−26.5
$43\bar{7}0$	8	−6.8	$30\bar{3}3$	—	−1.1
			$40\bar{4}3$	22	27.9
$10\bar{1}1$	46	−43.7	$50\bar{5}3$	12	−14.4
$20\bar{2}1$	13	14.4	$21\bar{3}3$	29	32.1
$30\bar{3}1$	—	0	$31\bar{4}3$	28	−32.4
$40\bar{4}1$	25	−21.9	$41\bar{5}3$	—	0
$50\bar{5}1$	12	8.8	$51\bar{6}3$	18	16.9
$60\bar{6}1$	—	1.2	$32\bar{5}3$	22	23.6
$21\bar{3}1$	27	−23.8	$42\bar{6}3$	12	−19.1
$31\bar{4}1$	32	26.8			
$41\bar{5}1$	—	0	0004	127	122.2
$51\bar{6}1$	10	−12.3	$30\bar{3}4$	66	68.4
$32\bar{5}1$	17	−17.2	$11\bar{2}4$	65	63.1
$42\bar{6}1$	10	13.9	$41\bar{5}4$	47	44.6
$43\bar{7}1$	12	−10.3	$22\bar{4}4$	67	68.2
			$42\bar{6}4$	30	36.0
0002	18	−23.6			
$10\bar{1}2$	27	28.0	0008	48	48.6
$20\bar{2}2$	5	8.1	$11\bar{2}8$	28	30.3

The observed and calculated structure factors are listed in Table 1. In the calculation of the structure factors the atomic scattering curves in Internationale Tabellen (1935) were employed. For NH_3 and H_2O appropriate corrections for embedded hydrogen atoms were made. A correction for the anomalous dispersion of the cobalt atom was taken into account. The effect of thermal motion was taken into consideration by multiplying the calculated *F*-values by a temperature factor $\exp - B(\sin\theta/\lambda)^2$, where $B = 2.5\,\text{Å}^2$ The value of $R = \sum||Fo|-|Fc||/\sum|Fo|$ was 0.137 for all (*hkil*) reflections.

Description of the Structure

The structure belongs to a new type and the schematic representation is shown in Fig. 4. It is most easily described as NiAs type, consisting of octahedral complex radicals $[Co(NH_3)_3H_2OCl_2]^+$ and Cl^- ions. Interatomic distances are given in the following:

Co…Cl(1) 2.33 Å., Cl(2)…Cl(2) 4.38 Å.,
Cl(1)…Cl(2) 4.28 Å.

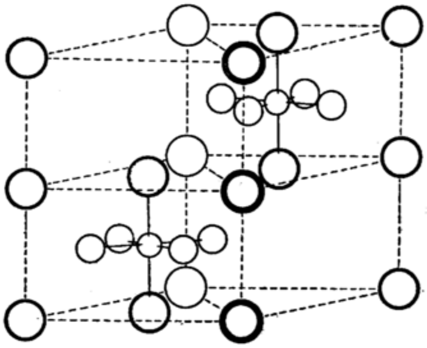

Fig. 4.—Crystal structure of "dichrochloride", $[Co(NH_3)_3H_2OCl_2]Cl$. The small circles represent metal atoms and the medium circles represent NH_3 and H_2O molecules. The largest ones indicate Cl atoms. Each complex ions are shown as taking one of their possible azimuthal orientations.

A complex ion has six Cl^- ions at the apices of a trigonal prism. The proper symmetry of a cobalt atom is $D_{3h}-\bar{6}m2$ and the azimuthal orientations of the octahedral complex radicals are not fixed in space but they are statistically arranged in such a manner that the symmetry becomes D_{3h}; in other words, the octahedral complex ion seems to occupy one of the three equilibrium positions in such a way that one of the four edges of a square consisting of 3N and O atoms becomes parallel to one of the three principal axes, the positions of Co and Cl (1) being fixed. Two chlorine atoms are in trans-coordination, being 2.33 Å. from a cobalt atom. This result is in satisfactory agreement with the value 2.33 Å.

obtained in the case of $[Coen_2Cl_{2(6)}^{(1)}]$ Cl·HCl $2H_2O$.(5)

Some Remarks on the Optical Properties

The crystals of "dichrochloride" have exceptionally marked dichroism. They appear blue when the electric vector is parallel to the *c*-axis, whereas they appear red when the light is polarized perpendicular to the *c*-axis. All the complex ions are arranged in the crystal with the Cl-Co-Cl direction parallel to the *c*-axis. The fact that the crystals appear blue when the light is polarized along the Cl-Co-Cl direction is quite consistent with the results obtained in the case of $[Coen_2Cl_{2(6)}^{(1)}]Cl\cdot HCl\cdot 2H_2O$(5) crystals. Detailed discussion of dichroism of this crystal will be given later, after the quantitative measurement of the absorption spectra with the polarized light has been completed.

Summary

An X-ray diffraction study of crystals of dichloro-aquo-triammine-cobalt (III) chloride eads to a hexagonal unit of structure with $a=7.37$ A. and $c=8.75$ A., containing two formula units in it. The most probable space group is D_{6h}^4-C6/mmc. For an accurate determination of the structure, the method of three dimensional Fourier series was used. The determined structure is most easily described as NiAs type, consisting of $[Co(NH_3)_3H_2OCl_2]^+$ and Cl^- ions. Two chlorine atoms are coordinated to a cobalt atom in trans-positions with respect to each other, each being 2.33 A. from the cobalt atom. The Cl-Co-Cl direction being parallel to the *c*-axis, the octahedral complex ions seem to have statistical azimuthal orientations in the crystal and the apparent symmetry of the complex ion is $D_{3h}-\bar{6}m2$. Such an arrangement of the complex ions in the crystal may well account for the marked red-blue dichroism of the crystals.

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(5) A, Nakahara, Y. Saito and H. Kuroya, This Bulletin, **25**, 331 (1952).