The Crystal Structure of Purpureo Salt, [Co(NH$_3$)$_5$Cl]Cl$_2$

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A series of monoacido-pentaammine-cobalt-(III) complexes of the [Co(NH$_3$)$_5$L]X$_2$* type have been extensively investigated with respect to their light absorptions, their substitution reactions, and so on. However, there have been few reports on their crystal structures. In 1935, West determined the crystal structure of the chloro-pentaamine-rhodium(III) chloride, [Rh(NH$_3$)$_5$Cl]Cl$_2$[1] and, furthermore, found, by means of the powder photographic method, that the corresponding cobaltic salt is isotype to this rhodium(III) compound; he did not, however, give any details of the structure of the former.

Therefore, in order to determine exactly the way of packing in the crystalline state, the chloro-pentaammine-cobalt(III) chloride or "purpureo salt," [Co(NH$_3$)$_5$Cl]Cl$_2$, was taken up, and an X-ray analysis of its crystal structure was attempted. It should be noted that this compound is one of the most fundamental of the Werner complexes.

Experimental

Purpureo-cobaltic salt was prepared by Jörgensen's method.[2] The crystals for our X-ray work were grown slowly at room temperature from an aqueous solution as concentrated as possible. They are orthorhombic-bipyramidal, showing a pseudo-regular octahedral shape.

Ni$K\alpha$ radiation (1.659 Å) was used, and a multiple-film technique was employed in taking Weissenberg photographs about the three principal axes. The dimensions of the unit cell, the space group, and other crystallographic data were found to be as follows:

$$a=13.34\pm0.03,\ b=10.33\pm0.03,\ c=6.73\pm0.02\,\text{Å};$$

$$\text{Puma-D}_{2\text{h}}^{16},\ Z=4,$$

$$\rho_{\text{obs}}=1.77\,\text{g. cm}^{-3}\ (25°\text{C}),\quad \rho_{\text{calcd}}=1.79\,\text{g. cm}^{-3}$$

The relative intensities were estimated visually by comparison with a standard scale. The usual correction factors were applied by means of the chart given by Cochran,[3] while no correction for absorption was made.

Determination of the Structure

Possibly, this compound is isostructural with the corresponding rhodium(III) compound, as has already been suggested by West. Therefore, the first trial model, based on the structure of the corresponding rhodium(III) compound, was immediately set up, the bond lengths and bond angles being properly adjusted. The agreement was fairly good between the observed structure amplitudes and those calculated for this model.

Then, all the parameter values were refined by the usual procedure of successive approximations. The final parameters are listed in Table I, while the final electron density projection along the b-axis is shown in Fig. 1. The observed structure factors are compared with the calculated ones in Table II. The atomic scattering factors used for calculating the structure factors were those listed in the International Tables. An overall temperature factor was used in the form of $\exp(-B\sin^2\theta/\lambda^2)$, where B has the value of 2.0 Å^2.

TABLE I. ATOMIC COORDINATES

Atom	x/a	y/b	z/c
Co	0.395	0.250	0.176
Cl(1)	0.528	0.250	−0.033
N$_1$	0.283	0.250	0.353
N$_2$	0.303	0.250	−0.055
N$_3$	0.487	0.250	0.407
N$_4$	0.395	0.059	0.176
N$_5$	0.395	0.441	0.176
Cl(2)	0.148	0.000	0.158

The $R=\sum||F_o|-|F_c||/\sum|F_o|$ reliability factors are 0.104, 0.073 and 0.121 for ($hk0$), ($0kl$) and ($h0l$) respectively. The weighted mean value of R is 0.109 for the observed reflections up to $\sin\theta/\lambda=0.590$.

Description of the Structure

The structure projected upon a plane normal to the b-axis is shown in Fig. 2, which corresponds to Fig. 1. Evidently, the crystal is composed of complex cations, [Co(NH$_3$)$_5$Cl]$^{2+}$, and chloride anions in an arrangement of the CaF$_2$-type; thus, the compound is essentially ionic.

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* L denotes any univalent acid-radical working as a ligand.

1) C. D. West, *Z. Krist.*, **91**, 181 (1935).

2) S. M. Jörgensen, *Z. anorg. Chem.*, **17**, 461 (1898).

3) W. Cochran, *J. Sci. Inst.*, **25**, 253 (1949).

TABLE II. OBSERVED AND CALCULATED STRUCTURE FACTORS

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
2 0 0	10.2	10.1	6 0 3	10.0	8.4	7 0 7	4.6	3.7	10 6 0	24.8	−20.6
4 0 0	28.5	−30.3	7 0 3	16.5	−13.3	2 1 0	26.8	30.1	10 7 0	0	0.7
6 0 0	9.7	6.9	8 0 3	6.1	5.1	2 2 0	22.4	−21.8	10 8 0	2.5	−2.0
8 0 0	19.3	18.1	9 0 3	16.0	16.4	2 3 0	12.7	−13.2	10 9 0	0	−0.6
10 0 0	4.8	5.0	10 0 3	4.9	4.0	2 4 0	6.7	5.3	12 1 0	6.4	6.9
12 0 0	2.3	−3.4	11 0 3	18.9	14.9	2 5 0	24.8	22.8	12 2 0	6.2	6.2
14 0 0	1.9	−3.5	12 0 3	3.0	2.0	2 6 0	17.6	−14.7	12 3 0	0	−3.1
0 2 0	19.1	−18.7	13 0 3	11.0	−10.4	2 7 0	9.3	−10.3	12 4 0	3.1	−2.3
0 4 0	68.0	66.4	14 0 3	2.5	2.1	2 8 0	2.6	2.5	12 5 0	6.1	6.7
0 6 0	18.8	−19.0	1 0 4	23.0	21.2	2 9 0	7.3	8.2	12 6 0	3.9	5.0
0 8 0	30.5	31.2	2 0 4	5.7	6.4	2 10 0	9.3	−8.7	12 7 0	0	−3.0
0 10 0	9.0	−9.2	3 0 4	17.7	17.7	2 11 0	7.7	−7.7	14 1 0	2.2	−0.8
0 12 0	18.3	18.1	4 0 4	13.1	13.9	2 12 0	0	1.8	14 2 0	15.5	14.4
0 0 2	14.1	−13.8	5 0 4	16.2	−16.5	4 1 0	4.8	−2.7	14 3 0	2.3	1.3
0 0 4	15.2	−15.3	6 0 4	3.2	−1.9	4 2 0	32.4	−26.0	14 4 0	1.2	−1.2
0 0 6	20.6	22.0	7 0 4	13.9	−14.1	4 3 0	10.1	7.3	14 5 0	1.4	−0.5
1 0 1	13.5	−13.4	8 0 4	6.1	−6.0	4 4 0	17.8	−17.1	0 1 1	31.8	−30.0
2 0 1	9.1	10.5	9 0 4	1.9	−1.4	4 5 0	1.2	0.4	0 3 1	9.3	13.5
3 0 1	13.9	−12.2	10 0 4	3.4	1.7	4 6 0	11.0	−7.6	0 5 1	23.2	−22.4
4 0 1	25.3	25.2	11 0 4	0	1.6	4 7 0	2.9	2.1	0 7 1	7.9	−8.0
5 0 1	5.9	5.4	12 0 4	2.1	−1.9	4 8 0	8.4	−8.1	0 9 1	8.8	−8.3
6 0 1	0	−1.2	13 0 4	0	1.7	4 9 0	0	−1.2	0 11 1	7.7	7.8
7 0 1	10.8	9.7	1 0 5	11.6	−11.8	4 10 0	6.5	−4.7	0 2 2	21.4	−17.0
8 0 1	28.3	−25.4	2 0 5	4.5	1.8	4 11 0	1.2	0.0	0 4 2	5.1	−6.6
9 0 1	10.6	−8.2	3 0 5	2.7	−2.7	6 1 0	14.9	−15.0	0 6 2	6.2	−5.3
10 0 1	6.8	6.2	4 0 5	4.6	−4.5	6 2 0	14.7	14.4	0 8 2	1.6	−2.4
11 0 1	8.3	−6.2	5 0 5	5.7	6.5	6 3 0	6.9	7.6	0 10 2	3.8	−3.5
12 0 1	25.4	19.1	6 0 5	0	1.3	6 4 0	11.7	8.5	0 1 3	8.5	7.8
13 0 1	15.9	11.7	7 0 5	3.4	1.2	6 5 0	13.9	−13.4	0 3 3	5.7	−5.5
14 0 1	0.9	0.1	8 0 5	21.7	21.8	6 6 0	15.5	14.4	0 5 3	6.7	6.3
15 0 1	7.6	6.4	9 0 5	11.0	−9.2	6 7 0	6.9	7.6	0 7 3	5.1	−4.3
1 0 2	28.3	−28.0	10 0 5	3.8	2.1	6 8 0	9.1	8.2	0 9 3	4.3	3.5
2 0 2	8.2	8.8	11 0 5	4.9	−4.6	6 9 0	5.9	−6.6	0 11 3	3.7	−3.1
3 0 2	34.8	−34.8	12 0 5	7.6	−9.8	6 10 0	9.1	9.0	0 2 4	10.2	−9.0
4 0 2	30.4	30.2	1 0 6	0	−0.5	6 11 0	5.6	6.2	0 4 4	10.7	−11.1
5 0 2	22.8	20.8	2 0 6	0	−0.4	8 1 0	22.8	−23.4	0 6 4	7.3	−5.8
6 0 2	10.1	9.1	3 0 6	5.7	−4.5	8 2 0	1.4	−0.1	0 8 4	7.3	−6.6
7 0 2	10.1	12.2	4 0 6	17.9	−16.5	8 3 0	17.2	16.1	0 10 4	4.5	−4.0
8 0 2	7.6	−8.3	5 0 6	7.6	−6.5	8 4 0	14.5	13.3	0 1 5	18.9	17.7
9 0 2	12.7	−9.5	6 0 6	2.1	−0.7	8 5 0	21.8	−19.9	0 3 5	12.7	−13.1
10 0 2	0	−2.5	7 0 6	0	0.1	8 6 0	2.8	−2.4	0 5 5	15.8	15.2
11 0 2	0	−0.5	8 0 6	5.3	7.4	8 7 0	12.7	12.2	0 7 5	10.4	−10.3
12 0 2	3.8	−2.5	9 0 6	0	−1.6	8 8 0	8.2	7.5	0 9 5	9.0	8.7
13 0 2	5.1	−3.6	10 0 6	2.1	−0.7	8 9 0	11.0	−10.1	0 2 6	5.3	2.5
14 0 2	0	−1.0	1 0 7	4.6	2.4	8 10 0	2.3	−1.5	0 4 6	16.6	17.0
15 0 2	4.2	−2.6	2 0 7	2.7	5.0	10 1 0	2.2	0.4	0 6 6	1.2	−0.4
1 0 3	3.6	−1.6	3 0 7	6.1	−6.9	10 2 0	23.7	−23.0	0 8 6	9.6	10.6
2 0 3	6.3	−6.4	4 0 7	10.1	9.4	10 3 0	1.1	0.9	0 1 7	0	−2.3
3 0 3	6.1	2.6	5 0 7	0	1.3	10 4 0	0	0.8	0 3 7	1.4	−0.4
4 0 3	3.8	5.6	6 0 7	0	−0.6	10 5 0	0	0.5	0 5 7	0	−2.9
5 0 3	26.8	−26.8									

The interatomic distances and bond angles, calculated on the basis of the atomic parameters in Table I, are listed in Table III.

The cobalt atom is surrounded by four nitrogen atoms at the corners of a square ($Co-N_{2\sim5}$, 1.97 Å), with one more nitrogen atom ($Co-N_1$, 1.91 Å) and one chlorine atom ($Co-Cl(1)$, 2.27 Å) just below or above, completing a slightly distorted octahedral coordination. One remarkably shorter distance between Co and $NH_3(1)$, which is in trans-position to Cl, has been found also in the case of $[Co(NH_3)_3(NO_2)_2Cl]$.4) The other Co-N bonds are normal in length, as in $[Co(NH_3)_6]^{3+}$, where the nitrogen atoms are all equidistant from the cobalt atom (Co-N, 2.02 Å or so).

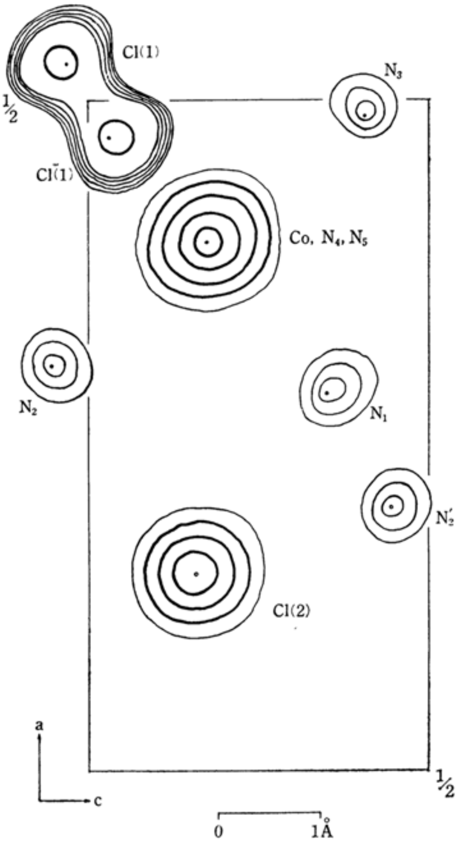

Fig. 1. Contours are drawn at intervals of 2e. $Å^{-2}$, starting at two electron level. Contours above 10 e. $Å^{-2}$ are drawn at 10 e. $Å^{-2}$ with thick lines.

The occurrence of one significantly shorter Co-NH_3 bond is to be noted. This may be because, working as a strongly electronegative ligand, the chlorine atom exerts its influence, if any, most effectively upon a ligand lying in the trans position to it, since to a first approximation the chlorine atom and the ligand can be regarded as bound to one another through the d_{z^2}, p_z and s orbitals of the central cobalt atom.

According to West, there is no distinction between the five Rh-NH_3 bonds involved in $[Rh(NH_3)_5Cl]^{2+}$. This might be shown not to be the case, however, if the structure of this rhodium(III) compound* were more refined.

TABLE III. INTERATOMIC DISTANCES AND BOND ANGLES

Co—Cl(1)	2.27 Å
Co—N_1	1.91
Co—N_2	1.97
Co—N_3	1.98
Co—N_4	1.97
Co—N_5	1.97
Cl(1)···Cl(2)	3.95
N_3···Cl(2)	3.39
N_4···Cl(2)	3.60
N_5···Cl(2)	3.60
N_3'···Cl(2)	3.57
N_4'···Cl(2)	3.35
N_5'···Cl(2)	3.35
N_1'···Cl(2)	3.43
N_2''···Cl(2)	3.61
N_4''···Cl(2)	3.36
N_5''···Cl(2)	3.36
N_1''···Cl(2)	3.41
Cl'''(1)···Cl(2)	4.06
N_2'''···Cl(2)	3.29
N_4'''···Cl(2)	3.59
N_5'''···Cl(2)	3.59
Cl(1)···N_1''	3.61
Cl(1)···N_3'	3.81
Cl(2)···Cl'(2)	4.34
∠N-Co-N	90.0°
Cl(1)-Co-N	90.0
Co—N_4···Cl(2)	101.0
Co—N_5···Cl(2)	101.0
Co—N_3···Cl(2)	107.0
Co—N_3'···Cl(2)	93.8
Co'—N_4'···Cl(2)	100.0
Co'—N_5'···Cl(2)	100.0
Co'—N_1'···Cl(2)	99.1
Co''—N_2''···Cl(2)	93.4
Co''—N_4''···Cl(2)	101.5
Co''—N_5''···Cl(2)	101.5
Co''—N_1''···Cl(2)	93.7
Co'''—N_2'''···Cl(2)	111.5
Co'''—N_4'''···Cl(2)	91.2
Co'''—N_5'''···Cl(2)	91.2

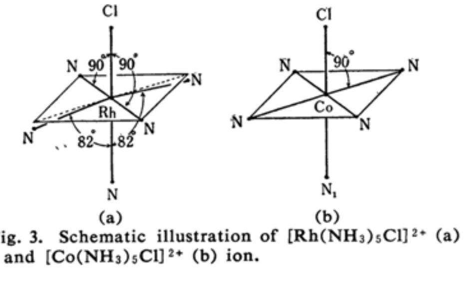

Fig. 3. Schematic illustration of $[Rh(NH_3)_5Cl]^{2+}$ (a) and $[Co(NH_3)_5Cl]^{2+}$ (b) ion.

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4) Y. Tanito, Y. Saito and H. Kuroya, This Bulletin, 26, 420 (1953).

* However, our recalculation based on the atomic coordinates reported by West revealed that the four NH_3-groups are not exactly in a plane normal to the N-Rh-Cl axis (see Fig. 3).

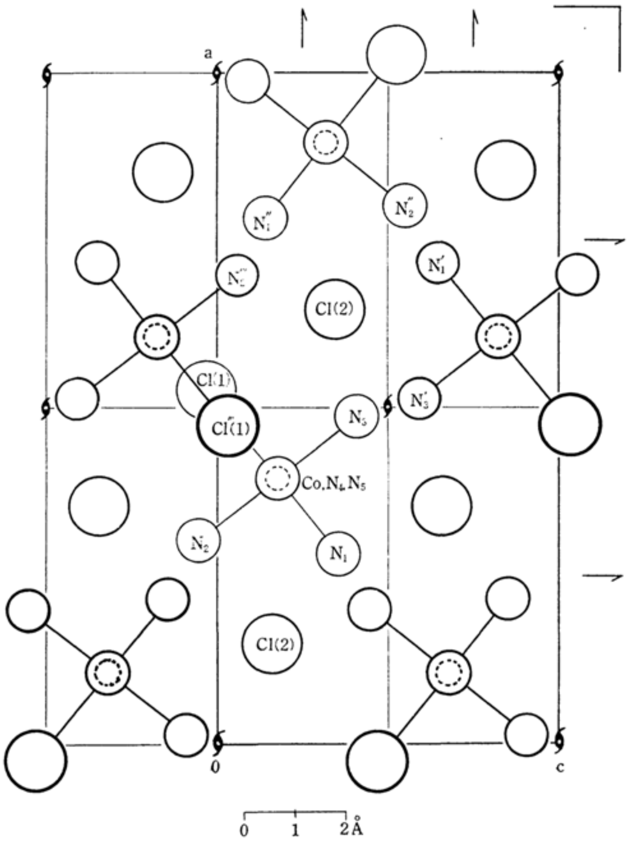

Fig. 2. Projection of the structure along the b-axis.

A chloride anion Cl(2) in the outer atmosphere is surrounded by fourteen NH_3 groups at distances ranging from 3.29 Å to 3.61 Å, as well as by two coordinated chlorine atoms at distances of 3.95 Å and 4.06 Å. Considerations of the distances of $NH_3 \cdots Cl(2)$, the angles of $Co{-}N \cdots Cl(2)$ and the way of packing lead us to the view that the hydrogen bonding is not unfavorable for the following four links of $N{-}H \cdots Cl(2)$:

	N···Cl(2)	∠Co–N···Cl(2)
$N_3{-}H \cdots Cl(2)$	3.39 Å	107.0°
$N_5'{-}H \cdots Cl(2)$	3.35	100.0
$N_4''{-}H \cdots Cl(2)$	3.36	101.5
$N_2'''{-}H \cdots Cl(2)$	3.29	111.5

Summary

The crystal structure of $[Co(NH_3)_5Cl]Cl_2$ has been determined by the two-dimensional Fourier method. The orthorhombic unit cell has dimensions of $a=13.34$, $b=10.33$ and $c=6.73$ Å, and it contains four formula units. The space group is Pnma–D_{2h}^{16}.

The shape and the size of a complex ion were found to be approximately similar to those of the crystal of the corresponding rhodium(III) compound.

One NH_3 group is co-ordinated to the central cobalt atom in the trans position to the chlorine atom; the Co–N(1) distance is 1.91 Å, rather shorter than the four other Co–N distances, 1.97 Å.

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