The Crystal Structure of Trans-dichloro-diethylenediamine-cobalt. (III). Chloride Hydrochloride Dihydrate, $[Coen_2Cl_2]Cl \cdot HCl \cdot 2H_2O$

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Introduction

The crystals of hydrochloride dihydrate of trans-dichloro-diethylendiamine-cobalt (III) chloride, $[Coen_2Cl_2]Cl \cdot HCl \cdot 2H_2O$, are grass green in color, and show an easily perceptible pleochroism which may be mainly attributed to the polarized absorption of light by the trans-dichloro-diethylenediamine-cobalt (III) ion itself. We have investigated the crystal structure of this substance for the purpose of determining the shape and size of the complex ion and also to correlate this structure with the absorption spectra of crystals.

Experimental

The substance was prepared by the method of Werner.[1] The crystals used in this investigation were grown from aqueous solution containing strong hydrochloric acid by slow evaporation at room temperatures. They belong to the monoclinic holohedral class and are tabular on (100), showing faces (011) etc. The crystals show well-formed faces, but when exposed to air they rapidly lose part of the water and hydrogen chloride of crystallization and begin to disintegrate. To prevent this, crystals used for X-ray measurements were coated with vacuum grease. Their dimensions were $0.1 \times 0.15 \times 0.01$ cm.

Oscillation photographs about [010] and [001] were prepared using Fe K_α radiation ($\lambda = 1.937$A.). They gave for the dimensions of the unit cell:

$$a = 10.68 \text{ A.}, \quad b = 7.89 \text{ A.}, \quad c = 9.09 \text{ A.}$$

(1) A. Werner, *Ber.*, **34**, 1733 (1901).

and $\beta = 110°26'$.

From the size of the unit cell and the density, 1.653 g./cm.^{3}, determined at 10°C by the pyknometer method, the number of the formula units in the unit cell was calculated to be $2.01 \approx 2$.

Observed extinctions were $(h0l)$ for l=odd and $(0k0)$ for k=odd, whence the space group is $C_{2h}^5 - P2_1/c$.

The intensities of reflections were estimated by comparison with a time-exposure calibrated strip. They were converted into structure amplitudes in the usual way.

Determination of the Structure

In the space group $C_{2h}^5 - P2_1/c$ the general position is fourfold, and since there are two formula units, $[Coen_2Cl_2]Cl \cdot HCl \cdot 2H_2O$, in the unit cell, it follows that the cobalt atoms must lie in special positions. These special positions are the symmetry centers.

As the first step in the structure determination, Patterson projections on (010) and (001) were made, using the $(h0l)$ and $(hk0)$ data respectively. In the projection upon (010) the peaks close to the origin were readily identified as corresponding to the Co—Cl interatomic distances within the $[Coen_2Cl_2]^+$ complex ion and the Cl—Co—Cl direction was found to be nearly parallel to the c-axis. All other peaks on both projections, $P(xz)$ and $P(xy)$, were easily interpreted in terms of the Co—Co, Co—Cl and Cl—Cl interatomic distances. At this stage, however, it was not possible to find the approximate parameter values of Co and Cl atoms without ambiguity, as there exist various possibilities. In order to decide adequate ones among these, (hkl) reflections were considered. Approximate parameter values for Co and Cl atoms could then be determined uniquely, while those for other lighter atoms remained unfixed.

As the next step, the projections of the electron density upon (010) and (001) were synthesized using the $F(h0l)$'s and $F(hk0)$'s respectively, the signs of which were calculated from the arrangement of the heavy atoms. The projections so obtained showed the heavy cobalt and chlorine atoms quite clearly resolved, together with rather faint outlines of other atoms in the unit cell. Particularly the projection upon (001) showed the ethylenediamine ring very clearly resolved. Using these projections, together with our knowledge about interatomic distances, it was possible to assign approximate coordinates for all other lighter atoms including two molecules of water of crystallization. By the method of successive approximation the final projections including all observed F's were obtained. The results are shown in Figs. 2 and 4, which may be interpreted with the aid of Figs. 1 and 3 respectively. The atomic parameters determined in this way were finally adjusted by small amounts to obtain the best

Table 1

Final Parameters

	x/a	y/b	z/c
Co	0	0	0
Cl (1)	0.036	−0.072	0.260
Cl (2)	0.328	−0.363	0.260
N (1)	0.092	0.219	0.069
N (2)	0.175	−0.107	0.019
C (1)	0.225	0.196	0.056
C (2)	0.278	0.015	0.108
O	0.480	−0.340	0.030

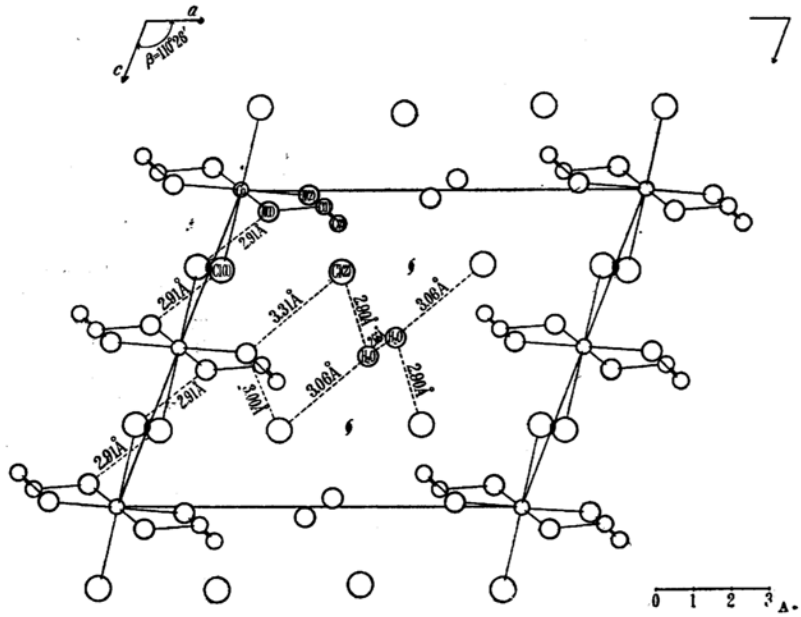

Fig. 1.—Projection of the structure upon the plane (010).

Table 2

Observed and Calculated Structure Factors

hkl	*Fobs.*	*Fcalc.*	*hkl*	*Fobs.*	*Fcalc.*	*hkl*	*Fobs.*	*Ecalc.*
002	3	3	702	9	6	520	6	11
004	29	30	$70\bar{2}$	6	2	530	<1	−3
006	1	−7	704	2	−1	540	1	6
			$70\bar{4}$	<1	5	550	<1	−6
100	22	22	$70\bar{6}$	6	4	560	<1	1
200	14	14	$70\bar{8}$	6	10			
300	25	23				610	<1	0
400	18	18	802	7	9	620	9	8
500	3	2	$80\bar{2}$	9	8	630	7	−6
600	15	16	$80\bar{4}$	<1	−4	640	4	−5
700	2	1	$80\bar{6}$	5	4	650	4	−6
800	<1	−1	$80\bar{8}$	3	−1	660	2	4
900	<1	5						
			902	2	2	710	11	−12
102	1	3	$90\bar{2}$	2	0	720	9	9
102	14	15	$90\bar{4}$	7	7	730	8	−8
104	2	2	$90\bar{6}$	1	−1	740	6	6
$10\bar{4}$	20	21				750	1	1
106	<1	1	$100\bar{2}$	7	6			
$10\bar{6}$	<1	0	$100\bar{4}$	1	1	810	<1	−1
$10\bar{8}$	7	8	$100\bar{6}$	5	3	820	<1	4
						830	3	−1
202	3	3	020	11	12			
$20\bar{2}$	11	11	040	<1	−3	910	2	−3
204	9	9	060	<1	4	920	1	0
$20\bar{4}$	20	18						
206	1	1	110	5	−7	011	19	19
$20\bar{6}$	8	8	120	15	17	012	6	6
$20\bar{8}$	7	4	130	13	−13	013	10	10
			140	15	12	014	<1	−1
302	11	−15	150	4	6	015	7	6
$30\bar{2}$	26	−23	160	6	−4			
304	9	12	170	4	3	021	8	5
$30\bar{4}$	22	19				022	6	0
306	3	−5	210	10	10	023	<1	1
$30\bar{6}$	9	−7	220	12	13	024	10	9
$30\bar{8}$	13	13	230	6	−6			
			240	8	8	031	8	9
402	9	9	250	5	−7	032	<1	−2
$40\bar{2}$	11	9	260	6	−1	033	7	9
404	<1	5	270	3	0			
$40\bar{4}$	13	13				041	8	−12
406	8	7	310	2	−2	042	9	14
$40\bar{6}$	3	−3	320	15	16	043	7	5
$40\bar{8}$	5	6	330	7	−7			
			340	6	3	051	6	7
502	4	4	350	<1	−2	052	<1	2
$50\bar{2}$	12	12	360	4	3	053	4	3
504	4	3	370	2	−2			
$50\bar{4}$	10	10				061	7	−6
$50\bar{6}$	8	9	410	3	−5	062	<1	8
$50\bar{8}$	3	3	420	12	11	063	7	8
			430	7	−8			
602	3	1	440	7	7	071	2	2
$60\bar{2}$	3	−3	450	<1	1			
604	9	11	460	5	6			
$60\bar{4}$	16	17	470	<1	0			
$60\bar{6}$	<1	2						
$60\bar{8}$	9	12	510	8	3			

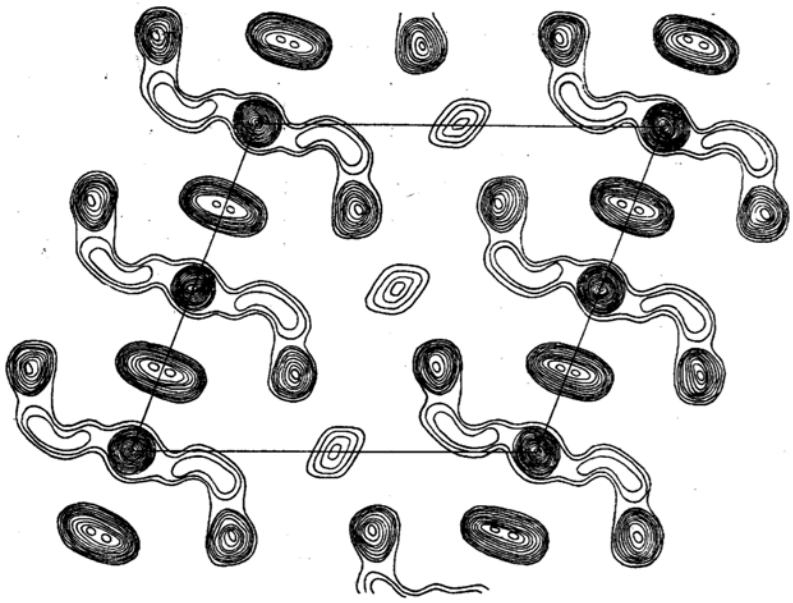

Fig. 2.—A Fourier projection of electron density upon (010). The projection corresponds to Fig. 1. Contours at arbitrary intervals.

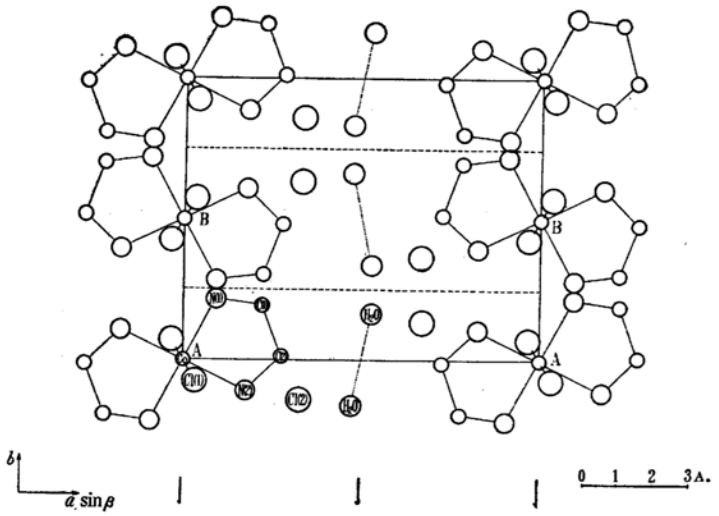

Fig. 3.—Projection of the structure upon a plane normal to the c-axis. Units marked B are derived from those marked A by the operation of a glide plane "c" parallel to (010). Groups $[H_2O...H...H_2O]^+$ are indicated by dotted lines.

agreements between the observed and calculated F's. A list of the final parameters is given in Table 1. In the calculation of the structure factors, the atomic scattering curves in Internationale Tabellen (1935) were employed and corrected for temperature according to the Debye-Waller formula, the constant B being given the value 2.5 A.[2]

The agreement on the whole is quite good and the values of $R=\sum||Fo|-|Fc||/\sum|Fo|$ are 0.194, 0.228 and 0.279 for ($h0l$), ($hk0$) and ($0kl$) respectively. The larger values of R for the ($0kl$) zone may be attributed to the less accurate values due to absorption.

Description of the Structure

Figs. 1 and 3 show the structure projected upon (010) and a plane normal to the c-axis respectively. The interatomic distances and interbond angles calculated from the parameter values are listed in Table 3.

In Fig. 5 is shown a perspective drawing of the $[Coen_2Cl_2]^+$ ion. The cobalt atom lies at the center of symmetry. Two chlorine atoms are co-ordinated at a distance of 2.33 A. to a cobalt atom in trans-positions. The line joining them is perpendicular to the plane in which the four nitrogen atoms of the two ethylenediamine mole-

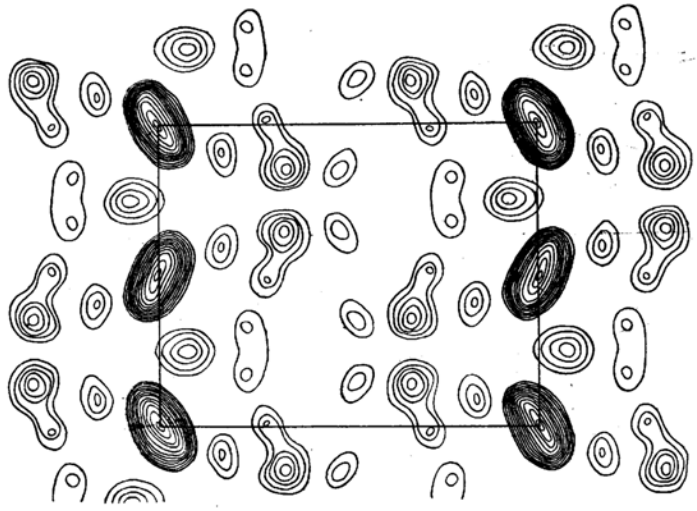

Fig. 4.—A Fourier projection of electron density upon a plane normal to the *c*-axis. The projection corresponds to Fig. 3. Contours at arbitrary intervals.

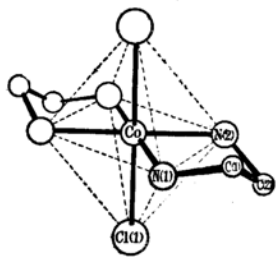

Fig. 5.—A perspective drawing of the complex ion, $[Coen_2Cl_2]^+$.

Table 3

Interatomic distances (in A.) and interbond angles.

Co.....Cl (1)	2.33	Cl (1).....N (1)	2.91
Co.....N (1)	1.98	Cl (1).....Cl (1)	4.01
Co.....N (2)	2.00	Cl (1).....Cl (2)	3.87
N (1)...C (1)	1.48	Cl (2).....H_2O	2.90
N (2)...C (2)	1.47	...H_2O	3.06
C (1)...C (2)	1.55	...N (2)	3.31
$\angle N_1C_1C_2$	110°	...N (2)	3.00
$\angle N_2C_2C_1$	108°	...C (2)	3.25
$\angle CoN_1C_1$	104°	H_2O .....H_2O	2.66
$\angle CoN_2C_2$	105°		

cules were found to lie. Within the errors of experiment these ligand atoms (4 N and 2 Cl) form a distorted octahedron around a cobalt atom. The C—C distance of 1.55 A. as well as the C—N distances, 1.47 A. and 1.48 A., although not very reliable because these atoms were not fully resolved in the projection upon (010), are in good agreement with the well-known values of C—C and C—N distances respectively.

It is interesting to note here that the ethylenediamine molecules are present in the "gauche" forms; there are two kinds of "gauche" molecules in the crystal, the one being the mirror image of the other, and moreover, these two kinds of molecules are co-ordinated to a cobalt atom in such a way that the one is related by the operation of a center of symmetry to the other. Referring to Fig. 1, it is evident that these complex ions are arranged in layers parallel to the plane (100). The Cl—Co—Cl bond direction is inclined to the plane (010) at an angle of 14.5° and the projection of this direction upon (010) makes an angle of 10° with the *c*-axis. The closest distances of approach between the complex ions in the layer are found to be 2.91 A. between Cl(1) atom of one complex ion and N(1) atom of the adjacent. Thus the complex ions are held together in layers by these Cl...N bonds. A projection of a single layer of $[Coen_2Cl_2]^+$ is shown in Fig. 6. Between these layers are arranged the Cl^- ions and H_2O molecules, both occupying general positions. A complex ion has four nearest Cl^- ions. The closest approach of a complex ion and Cl^- ion is between N(2) and Cl^-. The Cl^-...N(2) distances are 3.00 and 3.31 A. which may be compared with the values found in the case of methyl ammonium chloride crystals.[2]

The positions of H cannot in general be determined by the method of X-rays; however, the fact that two molecules of water of crystallization form a pair with O...O distance of 2.66 A. and this pair is surrounded exclusively by Cl^- ions strongly suggests the existence of a group $[H_2O...H...H_2O]^+$. A molecule of H_2O possesses two Cl^- ions at 2.90 A. and 3.06 A., thus every group, $[H_2O...H...H_2O]^+$, is surrounded by four Cl^- ions.

(2) E. W. Hughes and W. N. Lipscomb, *J. Am. Chem. Soc.*, **68**, 1970 (1946).

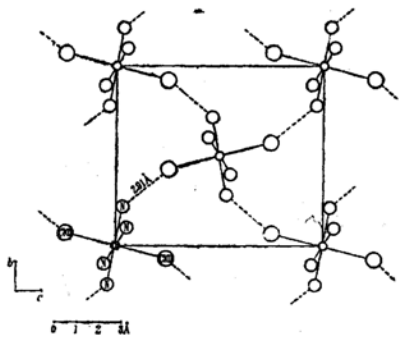

Fig. 6. Projection of a single layer of $[Coen_2Cl_2]^+$ upon the plane (100). Only positions of Co, Cl(1) and N atoms are shown. Cl... N(2) bond directions are indicated by broken lines.

Remarks on the Optical Properties

Thin tabular crystals extended on (100) appear blue when the electric vector is parallel to the *c*-axis, while they appear yellowish green when the light is polarized along the *b*-axis. Such striking dichroism may be reasonable, since there is a large component of the Cl—Co—Cl bond along the *c*-axis. This result cannot be considered to be in full agreement with the conclusion obtained by Yamada and Tsuchida,[3] who have measured microscopically the absorption of the crystals of the praseo-salts.* Detailed discussion will be given in reference to the absorption of the crystals of the "dichrochloride", the crystal structure of which has been determined recently by the present authors;[4] the absorption measurements of the dichrochloride are now in progress.

(3) S. Yamada and R. Tsuchida, This Bulletin, **25**, 127 (1952).

(4) Y. Tanito, Y. Saito and H. Kuroya, This Bulletin, **25**, 328 (1952).

* *a*, *b* and *c*-axes adopted by Yamada and Tsuchida correspond to *c*, *b* and *a*-axes in the present paper respectively.

Summary

The crystal structure of trans-dichlorodiethylenediamine-cobalt (III) chloride hydrochloride has been determined using the rotation method (Fe $K_\alpha\lambda=1.937$ A.). The substance crystallizes in a monoclinic lattice with two formula units in the unit cell, the dimensions of which are $a=10.68$ A., $b=7.89$ A., $c=9.09$ A. with $\beta=110°26'$.

The determined structure seems most easily described as consisting of layers of $[Coen_2Cl_2]^+$ ions parallel to the plane (100) and those of Cl^-, H_2O and H^+. Two chlorine atoms are co-ordinated to a cobalt atom in trans-positions. The line joining them is perpendicular to the plane in which four nitrogen atoms are found to lie. The dimensions of a complex ion are given. The water molecules probably form a group $[H_2O...H...H_2O]^+$ together with a proton, O...O distance being 2.66 A. These groups are located between them. The dichroism of the crystal is discussed on the basis of the determined structure.

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