Studies on Crystals of Metallic Tris-ethylenediamine-complexes. I. The Crystal Structure of DL-*Tris-ethylenediamine-cobalt (III) Chloride Trihydrate,* $[Co\ en_3]Cl_3\cdot 3H_2O$

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Introduction

No complete structure determination of a complex salt containing the $[Co\ en_3]^{3+}$ ion has yet been reported, although determination of a complex salt containing the $[Ni\ en_3]^{2+}$ ion has been carried out by Watanabé and Atoji[1].

The present work on the familiar crystals of the complex salt $[Co\ en_3]Cl_3\cdot 3H_2O$ was undertaken mainly to determine the shape and size of the complex ion in the course of our studies on metallic tris-ethylenediamine complex compounds. Ter Berg[2] has reported the unit cell dimensions, space group and other crystallographic data of this substance together with several related compounds. In this work his results were indeed verified.

Experimental

Tris-ethylenediamine-cobalt (III) chloride trihydrate was prepared according to the method described by Jörgensen[3]. Jaeger[4] reported that the crystals belong to ditrigonal scalenohedral class with $a:c=1:0.6667$. Crystals grown for this work by slow evaporation of saturated aqueous solution at room temperatures were hexagonal prisma. Cylindrical specimens of about 0.3 mm. in diameter parallel to all principal axes were prepared. All the equatorial reflections were recorded by using Fe K radiation (K_α, $\lambda=1.937$ Å).

The unit cell dimensions were obtained from high order $(hki0)$ and $(h0\bar{h}l)$ reflections on the equatorial lines of oscillation photographs. The results are: $a=11.50\pm0.02$, $c=15.52\pm0.04$ Å, giving the axial ratio $2a:c=1:0.668$, in agreement with that reported by Jaeger.

From the density 1.504 g./cc. obtained by the pyknometer method at 17°C, one finds that the unit cell contains four formula units of $[Co\ en_3]Cl_3\cdot 3H_2O$. Laue symmetry was found to be D_{3d}-$\bar{3}m$. The systematic absences are: $(000l)$ present only with l=even, and $(h0\bar{h}l)$ present only with l=even. Hence the space group is either C_{3v}^3-$P3c1$ or D_{3d}^4-$P\bar{3}c1$. No piezoelectric effect was observed*, so that the space group is probably D_{3d}^4-$P\bar{3}c1$. This space group has 12-fold general positions; accordingly the four cobalt atoms have to be placed in some special positions**.

Usual multiple film technique was used and the intensities of reflections were obtained visually by comparison with a calibrated standard. The usual correction factors were applied by means of the chart given by Cochran[5]. No correction for absorption was made. Observed structure amplitudes were later placed on an absolute scale by comparison with the calculated values.

Determination of the Structure

At the outset of the analysis it was found that reflections $(hki0)$ are generally rather strong when $h-k=3n$ and, moreover, odd-layer lines of oscillation photographs about the c-crystal axis are weaker than even-layer lines. These characteristics of reflections, combined with the results of Patterson projections $P(U, V)$ and $P(U, W)$, suggested that the cobalt atoms are on the 4-fold special positions; $4d$, $1/3$, $2/3$, z, etc. with $z \fallingdotseq 1/8$.

All the large peaks in $P(U, V)$ except those due to Co–Co interatomic vectors were mainly interpreted in terms of Co–Cl and Co–N vectors. The Co–N peaks were readily identified, if an approximate octahedral coordination of six nitrogen atoms of ethylenediamine molecules was assumed. First an electron-density projection $\rho(X, Y)$ was prepared using all the observed $F(hki0)$ values, whose signs were calculated from the arrangement of Co, Cl and N atoms only. The resulting distribution showed heavy cobalt and

TABLE I

FRACTIONAL ATOMIC COORDINATES

atom	x	y	z
Co	1/3	2/3	0.125
Cl	0.097	0.493	0.372
O	0.087	0.225	0.873
C_1	0.180	0.397	0.077
C_2	0.215	0.397	0.173
N_1	0.192	0.525	0.050
N_2	0.333	0.525	0.200

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[1] T. Watanabé and M. Atoji, *Kagaku*, **21**, 301 (1951).

[2] J. Ter Berg, *Diss. Univ. Groningen*, (1937).

[3] S.M. Jörgensen, *J. pr. Ch.*, **2**, 39, 546 (1898).

[4] F.M. Jaeger, *Z. Krist.*, **38**, 546 (1904).

* We are grateful to Mr. Y. Iidaka of the Mineralogical Institute, University of Tokyo, for piezoelectric test of the crystals.

** The unit cell, space group and the assignment of the positions of the cobalt atoms are in agreement with the results obtained by Ter Berg.

[5] W. Cochran, *J. Sci. Instruments*, **25**, 253 (1949).

chlorine atoms clearly resolved, together with faint outlines of the remaining atoms. Successive refinements with $(Fo-Fc)$ syntheses⁶⁾ led to the final projection shown in Fig. 1, which can be interpreted with the aid of Fig. 2. From this electron-density map x- and y-parameters of all the atoms were fixed. The z-parameters of each atom were deduced from $P(U, W)$, taking of complex ions and Cl^- ions into consideration. Successive Fourier syntheses, $\rho(X, Z)$ were carried out and the final electron-density map is shown

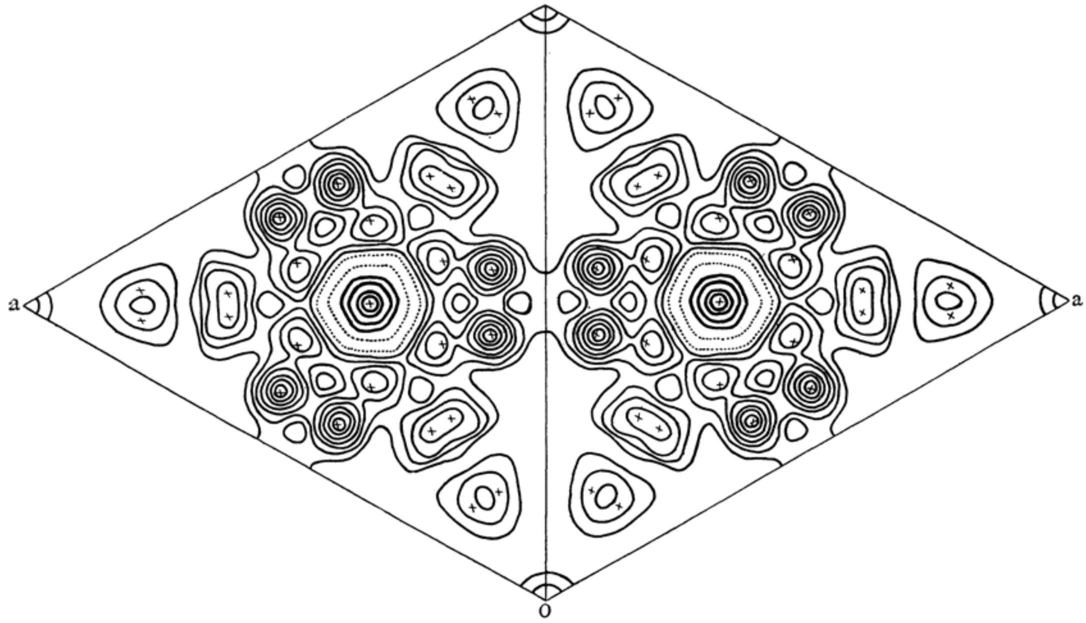

Fig. 1. Electron-density map of [Co en$_3$]Cl$_3$·3H$_2$O projected on (0001) (Contours are drawn at intervals of 4 e. Å^{-2}, the zero contour line being broken. The heavy lines of the Co peak are drawn at intervals of 20 e. Å^{-2}).

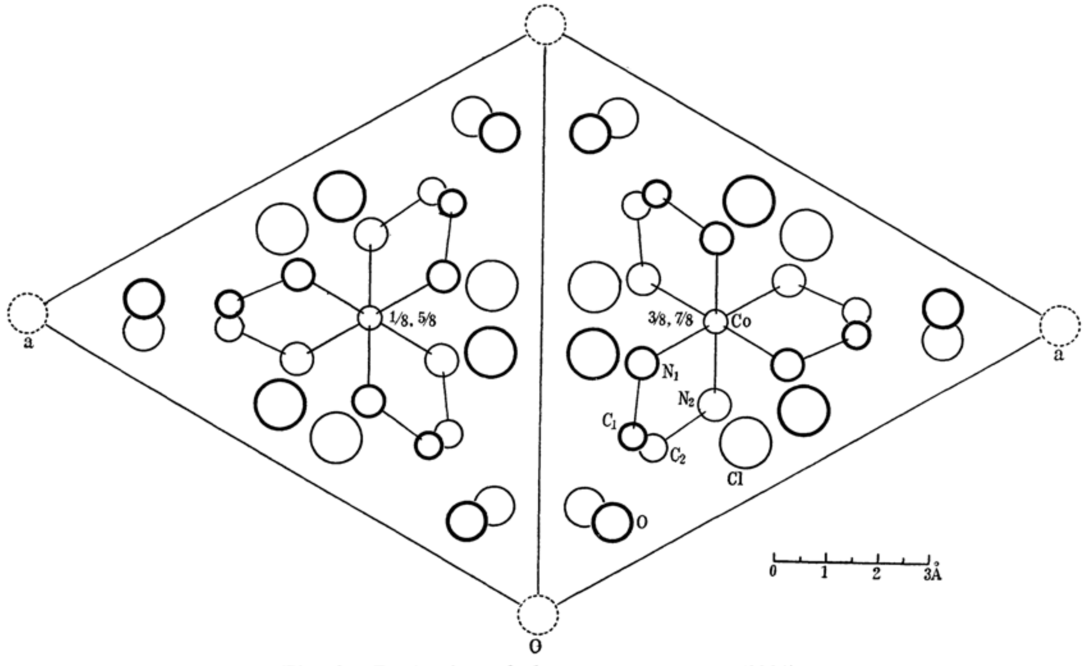

Fig. 2. Projection of the structure upon (0001).

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6) W. Cochran, *Acta Cryst.*, **4**, 408 (1951).

TABLE II

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES

*h*0.0	*Fo*	*Fc*
1	134	−134
2	11	−26
3	51	−55
4	69	−71
5	44	−33
6	66	58
7	84	−93
8	12	1
9	15	20
10	40	42
*h*1.0		
1	84	95
2	17	−28
3	—	−13
4	91	94
5	18	−23
6	35	−34
7	85	74
8	30	−26
9	31	−38
*h*2.0		
2	72	62
3	20	−20
4	56	−52
5	48	33
6	32	−28
7	19	−21
8	50	51
9	—	−11
*h*3.0		
3	105	110
4	50	47
5	49	−53
6	71	51
7	54	−41
8	14	−4
*h*5.0		
4	—	−22
5	10	−8
6	13	−20
7	27	30
*h*5.0		
5	19	15
6	—	2
00.*l*		
2	—	−11
4	315	−313
6	—	18
8	84	103
10	19	−19
12	109	−121
14	25	15

10.*l*	*Fo*	*Fc*
2	104	−104
4	55	35
6	62	−57
8	—	−8
10	24	11
12	40	28
14	12	14
$\bar{2}$	97	102
$\bar{4}$	60	45
$\bar{6}$	70	54
$\bar{8}$	—	−19
$\bar{10}$	17	−6
$\bar{12}$	46	40
$\bar{14}$	25	−19
20.*l*		
2	39	74
4	13	−16
6	82	−77
8	45	34
10	71	72
12	25	−20
14	32	−35
$\bar{2}$	80	−53
$\bar{4}$	8	−13
$\bar{6}$	92	85
$\bar{8}$	52	30
$\bar{10}$	82	−85
$\bar{12}$	20	−16
$\bar{14}$	33	47
30.*l*		
2	177	178
4	25	−14
6	66	−92
8	48	42
10	42	44
12	—	−20
14	29	−34
$\bar{2}$	174	−172
$\bar{4}$	20	2
$\bar{6}$	72	82
$\bar{8}$	54	21
$\bar{10}$	46	−34
$\bar{12}$	—	−7
$\bar{14}$	23	25
40.*l*		
2	27	6
4	84	64
6	40	38
8	32	−45
10	41	−25
12	22	21
14	1	8
$\bar{2}$	17	−4
$\bar{4}$	74	68

40.*l*	*Fo*	*Fc*
$\bar{6}$	41	−44
$\bar{8}$	44	−50
$\bar{10}$	34	32
$\bar{12}$	22	25
$\bar{14}$	1	−13
50.*l*		
2	43	32
4	59	49
6	26	−21
8	60	−68
10	6	20
12	54	52
$\bar{2}$	35	−29
$\bar{4}$	51	46
$\bar{6}$	24	14
$\bar{8}$	60	−68
$\bar{10}$	9	−12
$\bar{12}$	61	50
61.*l*		
2	—	−15
4	13	−6
6	23	1
8	—	−4
12	—	7
14	18	−24
$\bar{2}$	—	17
$\bar{4}$	17	−5
$\bar{6}$	18	−6
$\bar{8}$	—	−5
$\bar{10}$	1	−1
$\bar{12}$	16	−24
70.*l*		
2	129	−125
4	48	52
6	54	51
8	29	−27
10	50	−38
$\bar{2}$	124	127
$\bar{4}$	42	44
$\bar{6}$	41	−57
$\bar{8}$	21	−16
$\bar{10}$	35	45
80.*l*		
2	46	62
4	16	−20
6	8	−8
8	19	25
$\bar{2}$	46	−64
$\bar{4}$	16	−19
$\bar{6}$	—	15
$\bar{8}$	17	24
90.*l*		
2	15	22
4	19	−9
6	11	29
$\bar{2}$	12	22
$\bar{4}$	15	13
$\bar{6}$	11	−25
100.*l*		
2	19	−22
$\bar{2}$	15	19

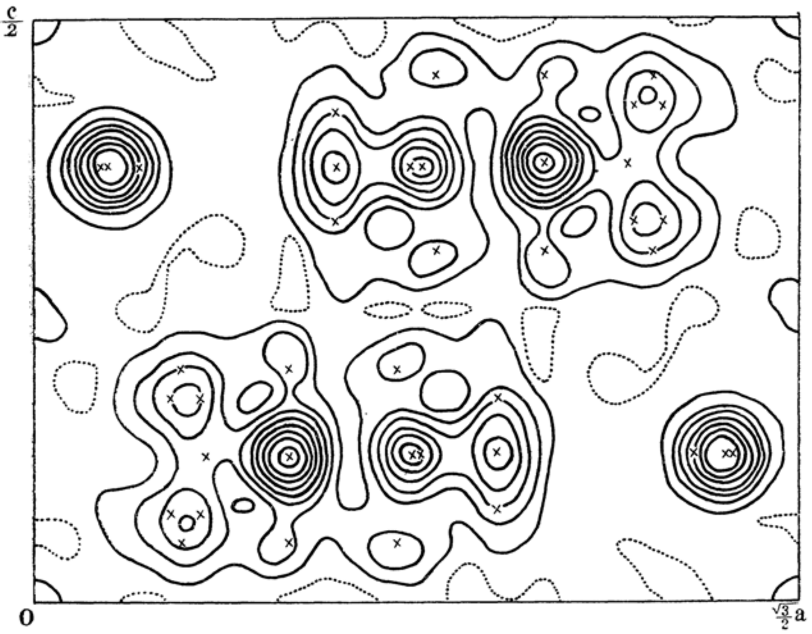

Fig. 3. Electron-density map projected on a plane perpendicular to the a-axis (Contours are drawn in the same manner as Fig. 1.

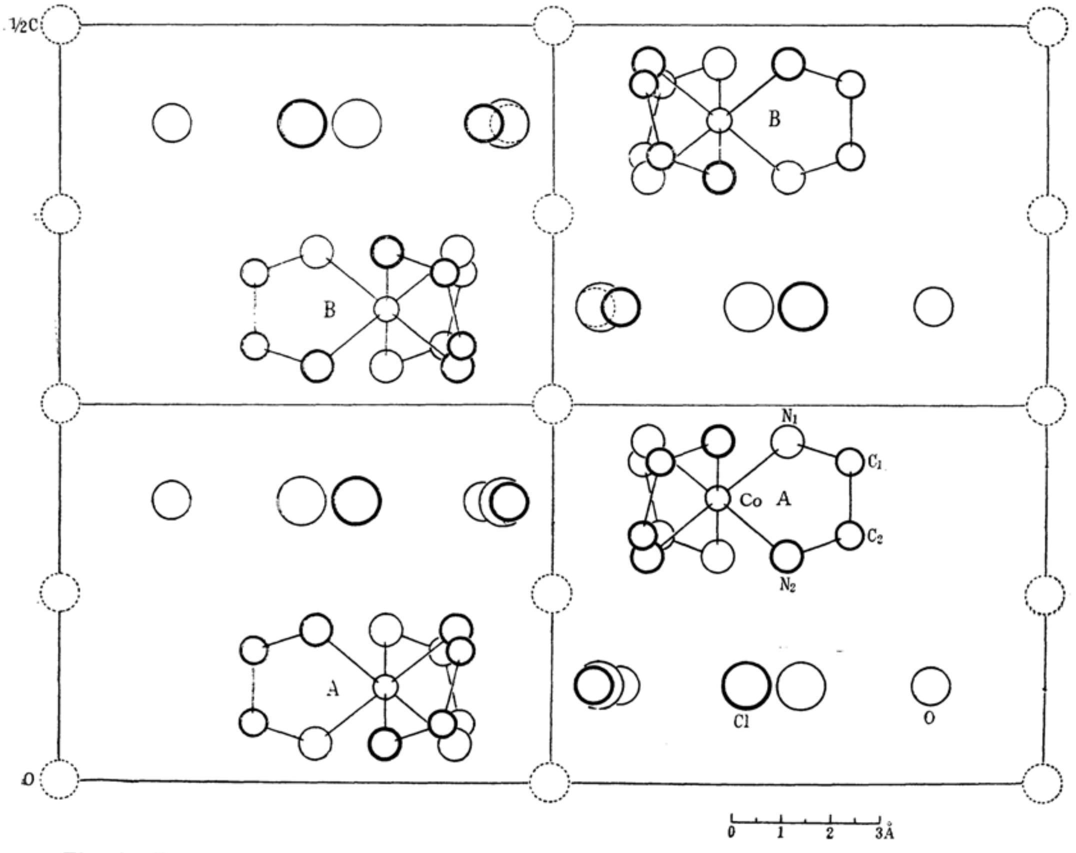

Fig. 4. Projection of the structure upon a plane perpendicular to the a-axis (The figure represents an elevation of the structure shown in Fig. 2, and does not correspond to $\rho(X, Z)$ in Fig.3.)

in Fig. 3. Since the resolution of the atoms on $\rho(X,Z)$ was not very good, the z-parameters deduced from $\rho(X,Z)$ were further refined by the method of least squares. The final set of coordinates thus obtained is shown in Table I, and the observed and calculated structure amplitudes are given in Table II. The atomic scattering factors used for the calculation of the structure factors were those listed in the International Tables. Temperature corrections of the form exp $-B(\sin\theta/\lambda)^2$ were used, where B was given the value 2.5 Å^2 for $(hki0)$ zone and 3.0 Å^2 for $(h0\bar{h}l)$ zone respectively. The values of B and the scale factor were estimated by plotting the values of log Fc/Fo versus $(\sin\theta)^2$ at the final stage. The discrepancy factors $R=\sum||Fo|-|Fc||/\sum|Fo|$, are 0.140 for $(hki0)$ reflections and 0.202 for $(h0\bar{h}l)$ reflections respectively, with a weighted mean value of 0.186, where all the observed reflections up to $\sin\theta=0.98$ are included. The calculated interatomic distances and bond angles are recorded in Table III.

TABLE III

CALCULATED INTERATOMIC DISTANCES AND BOND ANGLES

Co–N_1	2.00 Å	Cl···N_1	3.13 Å
N_2	2.00		3.26
N_1–C_1	1.47	Cl···N_2	3.18
C_1–C_2	1.54		3.41
C_2–N_2	1.47	Cl···O	3.34
		Cl···C_1	3.30
Co–N_1–C_1	105.4°	C_2	3.67
N_1–C_1–C_2	112.6°	O···C_1	3.36
N_2–C_2–C_1	112.6°	C_2	3.12
Co–N_2–C_2	105.4°		

Description of the Structure

The final electron-density map shown in Fig. 3 gives the arrangement of atoms shown in Fig. 4, which represents an elevation of the structure in Fig. 2. The shape and size of a complex ion [Co en$_3$]$^{3+}$ as it exists in the crystal is illustrated in Fig. 5. This figure shows one of the two stereo-isomeric ions, which are present in equal numbers in the structure. The complex ion is required by the space group to have trigonal symmetry. However, within the errors of experiment it possesses the symmetry D_3-32. Six nitrogen atoms of three ethylenediamine molecules form a slightly distorted octahedron around the central cobalt atom. The five-membered ethylenediamine cobalt rings are not planar, that is, the ethylenediamine ligands take so-called "gauche" forms. Arrangement of atoms about C_1-C_2 bond is illustrated in Fig. 6.

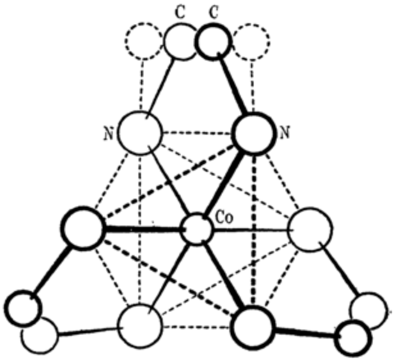

Fig. 5. The complex ion [Co en$_3$]$^{3+}$.

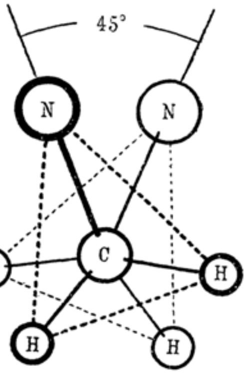

Fig. 6. Arrangement of atoms around C_1–C_2 bond.

The Co–N distances of 2.00 Å as well as the shape and size of the ethylene diamine molecules may be compared with those perviously described by Nakahara and two of us[7] for the complex ion [Co en$_2$Cl$_2$]$^+$.

The gauche configuration of ethylenediamine has a mirror image non-superposable, which we shall denote as *d* and *l*. Then ethylenediamine molecules may enter into combination with a cobalt atom in its *d*- or *l*-form. The possibilities of isomerism are, therefore, greatly increased and the following cases should arise:[8,9]

Dddd, Dddl, Ddll, Dlll,
Llll, Llld, Lldd, Lddd,

where *D* or *L* indicates the configuration of the whole complex ion, i. e. the way in which the three ligands coordinate to a central cobalt atom. Nevertheless, our X-ray evidence showed that the complex ion possesses trigonal symmetry. Thus the representation for the

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[7] A. Nakahara, Y. Saito and H. Kuroya, This Bulletin, 25, 331 (1952).

[8] M. Kobayashi, *J. Chem. Soc. Japan*, 64, 652 (1943).

[9] J. V. Quagliano and S. Mizushima, *J. Am. Chem. Soc.*, 75, 6084 (1953).

complex ion in the crystal should be one of the following sets: (*Dddd, Llll*) and (*Dlll, Lddd*). The projections of the carbon atoms in Fig. 4 will change as indicated by dotted circles, if the other antipode of the ethylenediamine ligands coodinates to the central cobalt atom, keeping the configuration of the whole complex ion as before. However, final electron-density projection $\rho(X, Y)$ excludes this latter possibility, so that only one definite configuration is possible for each stereoisomeric complex ion in the crystal. By no means, should the presence of various stereoisomers in solution be excluded by our *X*-ray evidence. At this stage, however, it is impossible to decide whether the complex ion illustrated in Fig. 4 corresponds to dextro or laevo rotatory. Recently the determination of the absolute configuration of this complex ion has been carried out in our laboratory and a brief account has been published already[10].

The way in which the complex ions form bonds in the structure is best described by referring to Figs. 1 and 4. A complex ion is surrounded by nine Cl ions. Six of them are at the apices of a distorted trigonal prism, being 3.18 Å and 3.26 Å apart form N atoms. The other three form an equilateral triangle, being nearly on the same level as a cobalt atom. These N···Cl distances are 3.13 Å and 3.41 Å. The former distance of 3.13 Å suggests a hydrogen bond of the type N–H···Cl between N_1 and Cl. All these N···Cl distances are in good agreement with those reported by various authors[11,12,13,14,15]. Fig. 4 also indicates the packing of the formula units in the structure. Starting with any complex ion denoted by A, another complex ion denoted by B follows by the operation of the glide plane "*c*" or center of symmetry.

Remarks on the Water of Crystallization

Together with Cl^- ions the complex ions form structure with hollow channels along the *c*-crystal axis, in which water molecules are enclosed. They are on a set of general positions 12 *g*. A water molecule is associated to Cl^- ions with a distance of 3.34 Å. Other environmets of an oxygen atom are as follows: O···C_1=3.36 Å, O···C_2=3.12 Å, O···O=3.90 Å, 4.19 Å and 4.54 Å.

It seems to be an unlikely occurrance that water molecules are held together with such long O···O distances in the hollow channel. On the other hand, it was found that small peaks on electron-density maps, corresponding to the sets of 2-fold positions 2 *a* (000); (00½) and 2 *b* (00¼); (00¾), could by no means be eliminated even at the final stage of refinement. These positions are indicated by dotted circles in Figs. 2 and 4. This fact led us to assume that water molecules are randomly distributed on these positions as well as the above-mentioned general positions. Such a random arrangement of water molecules gives rise to a sequence of oxygen atoms with reasonable distances of 2.96 Å and 3.00 Å in the channel. Calculation of the structure amplitudes based on this model gave a lower value of *R* by about 0.02. From this fact only, one cannot decide whether such random distribution of water molecules is realized or not in the crystal.

It is to be noted here that water content of the crystal varies appreciably according to its history. Careful measurements of the density and analyses of the water of crystallization revealed that the crystal contains about 3.5 mol. of water of crystallization, when freshly prepared, and it gradually loses part of its water of crystallization on standing in the air, and the chemical formula tends to $[\mathrm{Co\ en_3}]\ \mathrm{Cl_3 \cdot 3H_2O}$. These excessive water molecules may be randomly distributed on the sets of special positions 2 *a* and 2 *b*. It was observed that a single crystal can be completely dehydrated by gently heating at 120°C, without bringing about any remarkable change in its appearance except a loss of transparency. A single crystal oscillation photograph was obtained even after complete dehydration, and furthermore, practically no change was found in its cell dimensions. These observations seem to support such a weak bonding of water molecules in the crystal. Further studies on the behaviour of this water of crystallization, including thermal analysis, are now going on. The results will be published soon.

Summary

The crystal structure of $[\mathrm{Co\ en_3}]\mathrm{Cl_3 \cdot 3H_2O}$ has been determined by *X*-ray methods. It is trigonal D_{3d}^4–$P\bar{3}c1$ with four formula units in a cell of dimensions: $a = 11.50 \pm 0.02$, $c = 15.52 \pm 0.04$ Å. The configuration of the two stereoisomeric complex ions $[\mathrm{Co\ en_3}]^{3+}$ is described. The three ethylenediamine molecules in a complex ion assume "gauche" forms; their nitrogen atoms form a slightly distorted

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[10] Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya, *Acta Cryst.*, 8, 729 (1955).

[11] W.P. Binnie and J.M. Robertson, *Acta Cryst.*, 2, 180 (1949).

[12] J.M. Bloomhead, *Acta Cryst.*, 1, 324 (1948).

[13] W. Cochran, *Acta Cryst.*, 4, 81 (1951).

[14] D.C. Phillips, *Acta Cryst.*, 7, 159 (1954).

[15] J. Trommel and J. M. Bijvoet, *Acta Cryst.*, 7, 703 (1954).

octahedron around a central cobalt atom. It is shown that ionic bonds essentially link the complex ions in the structure. The water molecules are weakly associated to chlorine ions. It is found that a single crystal can be completely dehydrated by gently heating at 120°C, without bringing about any remarkable change in its appearance, except a loss of transparency. A single crystal oscillation photograph was obtained even after complete dehydration.

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