Studies on Crystals of Metallic Tris-ethylenediamine-complexes. II. The Crystal Structure of Sodium D-*Tris-ethylenediamine-cobalt*(*III*) *Chloride Hexahydrate,* 2D-[Co en$_3$]Cl$_3$·NaCl·6H$_2$O

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(Received October 27, 1956)

Introduction

Meisenheimer et al.[1] described a mixed salt having the composition 2[Co en$_3$]Cl$_3$·NaCl·6H$_2$O. It was prepared from an aqueous solution containing racemic [Co en$_3$]Cl$_3$ and NaCl.

Hitherto unrecorded double salt having the same chemical composition has been prepared from a solution containing optically active D-[Co en$_3$]Cl$_3$ and NaCl. This double salt was chosen for confirming the "*gauche*" configuration of the ethylenediamine ligands in the complex ion [Co en$_3$]$^{3+}$, found in crystals of D,L-[Co en$_3$]Cl$_3$·3H$_2$O by X-ray method[2]. Since the *c*-axis is as short as 8.06 Å, it should be possible to obtain a clear projection of a single complex ion with less overlapping of atom.

The determination of the absolute configuration of the optically active complex ion, [Co en$_3$]$^{3+}$ was also made successfully in regard to this compound by using absorption edge technique[3] and a brief account has already been published[4]. In the present paper details of the structure analysis will be described.

Preliminary Investigation

The crystals were grown from a solution of D-[Co en$_3$]Cl$_3$ and NaCl in proportion of 5 : 3 by weight by slow evaporation in a desiccator containing calcium chloride. They form hexagonal prisma, belonging to the hexagonal pyramidal class. Crystals are orange, optically uniaxial and possess optical activity. The form exhibited by the salt is shown in Fig. 1. Assuming the pyramidal planes to be $(10\bar{1}1)$ an axial ratio, $a:c=1:0.704$, was obtained, in agreement with the

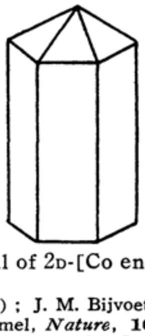

Fig. 1. A crystal of 2D-[Co en$_3$]Cl$_3$·NaCl·6H$_2$O.

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[1] J. Meisenheimer. L. Angermann and H. Holsten. *Ann.*, **438**, 269 (1924).

[2] K. Nakatsu, Y. Saito and H. Kuroya, This Bulletin, **29**, 428, (1956).

[3] J. M. Bijvoet, *Proc. Roy. Soc. Amsterdam*, B **52**, 313 (1949) ; A. F. Peerdemann and A. J. van Bommel, ibid., B **54**, 16 (1951) ; J. M. Bijvoet. A. F. Peerdemann and A. J. van Bommel, *Nature*, **168**, 271 (1951).

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

* Present adress ; Momotani Juntenkan Co., Ltd., Osaka.

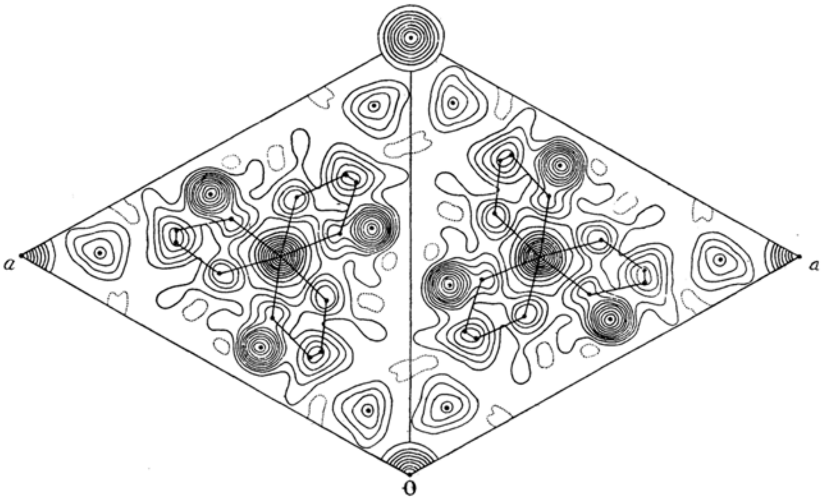

Fig. 2. Electron density projection of 2D-[Co en_3]$Cl_3 \cdot NaCl \cdot 6H_2O$ along the *c*-axis. Contours are drawn at intervals of 4 e. $Å^{-2}$ for peaks at (0, 0), (1/3, 2/3), and (2/3, 1/3), and of 2 e. $Å^{-2}$ for other peaks, zero-electron contour being broken. The atomic positions are indicated by dots, outlines of the complex ions being shown.

value $a : c = 1 : 0.703$ subsequently obtained from diffraction photographs. The density determined by the pyknometer method using organic liquid was 1.559 g./cc. at 20°C.

The results of chemical analysis and the values of specific rotation measured at wave lengths of the Na-D line in aqueous solution are shown below:

Found		Calcd. as $C_{12}H_{48}N_{12}Cl_7Co_2Na \cdot 6H_2O$
Cl	29.0%	29.0%
H_2O	11.8%	12.6%
Specific rotation of		
D-compound		$[\alpha]_D = +138°$
L-compound*		$[\alpha]_D = -133°$.

Determination of the Structure

Laue photographs taken with X-ray beam parallel to the *c*-crystal axis showed hexagonal symmetry. Oscillation photgraphs around the *c*-axis indicated the presence of a symmetry plane perpendicular to the *c*-axis. Hence the Laue symmetry was found to be C_{6h}-$6/m$.

The unit cell dimensions were found from higher order reflections observed on equatorial lines of oscillation photographs. They are

$$a = 11.47 \pm 0.03 \text{ Å} \quad \text{and} \quad c = 8.06 \pm 0.02 \text{ Å}.$$

Iron Kα radiation was used throughout ($\lambda = 1.937$ Å). The unit cell contains one formula unit. The calculated density is 1.552 g./cc., in good agreement with the observed value.

Two cylindrical specimens of about 0.2 mm. in diameter were cut one parallel to each principal axis. All the equatorial reflections were recorded on Weissenberg triple film photographs. The intensities of the observed reflections were estimated by visual comparison procedure and were corrected for Lorentz and polarisation factors using Cochran's chart⁵⁾. No absorption corrections were made. The resulting *F*-values were correlated so that all the observed data were on the same relative intensity scale, and they were later converted into an absolute scale by comparison with the calculated values.

No systematic extinctions were observed, hence the space lattice must be primitive. However, it was found that odd order reflections of (000*l*) are always very weak, contributing only two per cent of total (000*l*) intensity. The corresponding space group should have no center of symmetry, since the crystal is optically active as well as piezoelectric active. The facts indicate that the symmetry is very near but not exactly to that of the space group $P6_3$. Accordingly it was decided to adopt the space group $P6_3$ during the preliminary treatment of the structure. The space group $P6_3$ affords sixfold general positions and two sets of twofold positions. Since there is one formula unit in the unit cell, cobalt atoms must occupy special positions and all other atoms except one sodium and one chlorine atom must occupy sets of general positions leading 21 parameters. In the space group $P6_3$ there exists no singlefold special position for a sodium or a chlorine atom, so they must lie on some position belonging to lower symmetry class.

In attempting to fix the positions of the cobalt and chlorine atoms in the (000*l*) projection, the Patterson function *P*(*UV*) was evaluated. This projection fixed the positions of these atoms with certainty. At the outset of Fourier syntheses only the cobalt and chlorine atoms were used for calculating the signs of the observed structure factors

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* L-compound can be prepared in the same way from L-[Co en_3]Cl_3 and NaCl.

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

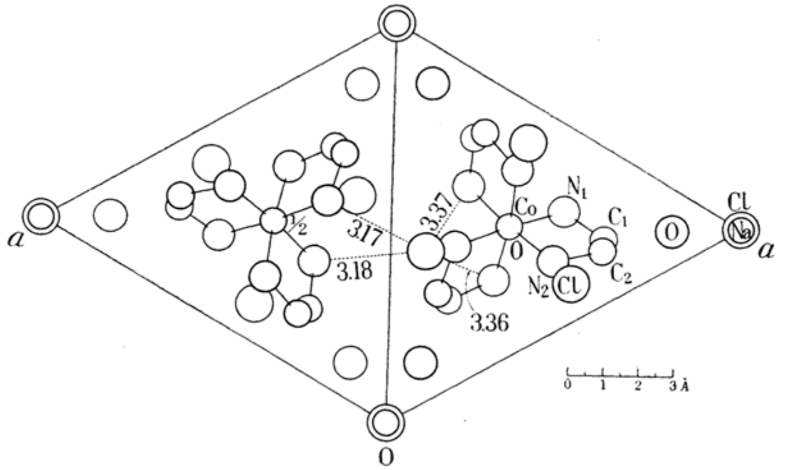


Fig. 3. Projection of the structure along the *c*-axis. Important N···Cl distances are given.

and the series $\rho\ (XY)$ was evaluated. Successive refinements with (F_o-F_c) syntheses were successful and the atoms were mostly resolved. It was found that the odd sodium and chlorine atoms lie on $(00z)$. The projection finally obtained is shown in Fig. 2, which can be interpreted with the aid of Fig. 3. Although some knowledge about the position of hydrogen atoms were obtained from $\{\rho_0(XY)-\rho_c(XY)\}$ as well as $\rho_0\ (XY)$, it does not seem to be significant because the analysis was less accurate.

Since the size and shape of five membered cobalt-ethylenediamine ring and other interatomic distances were known by our previous investigation, z-parameters of all the atoms could be fixed approximately from packing considerations, assuming that all the atoms except Na^+ and Cl^- of NaCl component are arranged according to the symmetry of $P6_3$. The positions of Na^+ and Cl^- were also deduced by packing considerations. They are: $z_{Na}\approx0.77$ and $z_{Cl}\approx0.27$. Thus the assumed structure is based on the space group $P3$. It was easily shown that such an arrangement of atoms may well account for the charactersitic features of Laue and osciallation photographs. The assumed structure was then confirmed by evaluating the Patterson projection $(P)VW$. The real and imaginary parts of $F(0k\bar{k}l)$ were then calculated. The agreement between the observed and calculated values was sufficiently good to start Fourier refinements. $\rho\ (YZ)$ was then evaluated and refinements were repeated as usual. Final projection shown in Fig. 4 lead the structure illustrated in Fig. 5, which corresponds to an elevation of the structure shown in Fig. 3. The z-parameter of oxygen atoms is less reliable because of the poor resolution of the projection $\rho\ (YZ)$. Parameter values thus obtained are listed in Table I. These parameters gave the reliability index $(R=\sum||F_o|-|F_c||/\sum|F_o|)$ of 0.144 and 0.221 for $(hki0)$ and $(0k\bar{k}l)$ respectively.

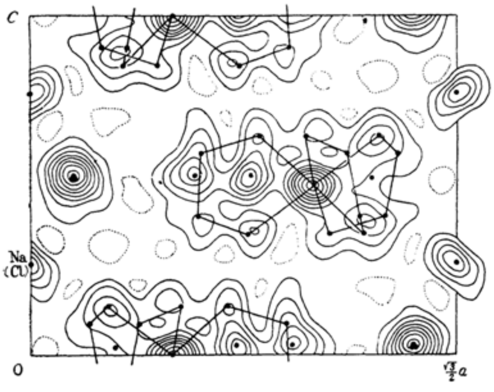


Fig. 4. Electron density projection along the *a*-axis.
Contours are drawn at intervals of 4 e. Å^{-2}, zero-electron contour being broken.

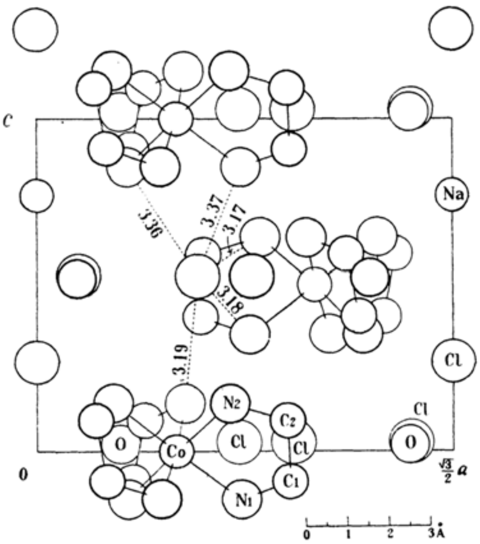


Fig. 5. Projection of the structure along the *a*-axis.

TABLE I

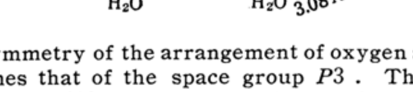
FRACTIONAL ATOMIC COORDINATES

Atom	x	y	z
Co	2/3	1/3	0
N_1	0.783	0.295	0.854
N_2	0.647	0.183	0.146
C_1	0.773	0.167	0.907
C_2	0.742	0.140	0.093
Cl_1	0.617	0.100	0.528
O	0.897	0.098	0.520
Na	0	0	0.770
Cl_2	0	0	0.270

All the atoms except Na and Cl_2 are arranged on the basis of $P6_3$

In the calculation of the structure factors the atomic scattering curves given in International Tables were employed. The structure amplitudes were adjusted in the usual way by multiplication by a temperature factor $\exp -B(\sin\theta/\lambda)^2$. B was evaluated graphically from the slope of a plot of $\log F_0/F_c$ against $(\sin\theta/\lambda)^2$. B was found to be 3.5 Å².

Though it is certain that the structure thus deduced gives a clear picture of the essential features of the structure, the intensities of the odd order reflections of $(000l)$ cannot be satisfactorily explained by the present model. The higher R-value for $(0k\bar{k}l)$ zone compared with that for $(hki0)$ zone may indicate a presence of errors in z-parameters. Namely, the intensities of the odd order reflections of $(000l)$, especially strong intensity of (0003), cannot be quantitatively explained. Calculation of interatomic distances on the basis of the parameters listed in Table I reveals that both Na^+ and Cl^- ions on a line $(00z)$ are surrounded octahedrally by six water molecules at a distance of 2.84 Å. This would be a rather unlikely occurrence. It is well established that Na^+ has a smaller ionic radius than Cl^-. If we change the z-parameters of oxygen atoms slightly and assume a following sequence of Na^+, H_2O and Cl^-:



the symmetry of the arrangement of oxygen atoms becomes that of the space group $P3$. The calculated $F(000l)$ values based on this model indeed gave a better agreement with the observed values, however, the distribution of calculated intensities $I(hkil)$ did not show the presence of a plane of symmetry perpendicular to the c^*-axis in the reciprocal space. This fact is not in conformity with the observed Laue symmetry. In order to account for the observed diffraction symmetry we have to assume a random arrangement of Na^+ and Cl^- ions on $2(a)$ of $P6_3$. But, if we assume complete randomness, then the odd order reflections of $(000l)$ should disappear. However, it may not be impossible to overcome this difficulty, if we assume a kind of polycrystalline twinning. Let us denote as P and Q the two structures where the relative positions in the z-direction of Na^+-$(H_2O)_3$-Cl^--sequence are different with respect to the rest of the structure;

	P	Q	
z_{Na}	z	$\bar{z}$	
z_{Cl}	$z+\frac{1}{2}$	$\bar{z}+\frac{1}{2}$	with $z=0.770$

If these two structures occur in a given single crystal with the same frequency and the size of each crystallites are larger than the coherent region of X-rays, the intensities of $(hkil)$ reflection will be given as sum of contributions from P and Q, for in a polycrystalline twin there will be no phase relation between two structures. So that we have;

$$I(hkil)=L.p\ \ 1/2\{F_P^2(hkil)+F_Q^2(hkil)\} \qquad (1)$$

$$I(hki\bar{l})=L.p\ \ 1/2\{F_P^2(hki\bar{l})+F_Q^2(hki\bar{l})\} \qquad (2)$$

where $L.p$ denotes Lorentz and polarisation factors.

It is possible to show that the difference between $I(hkil)$ and $I(hki\bar{l})$ becomes smaller by considering such a twinned structure, thus resulting better agreement with the observed diffraction symmetry.

On the other hand, the odd order reflections of $(000l)$ can be given as;

$$I(000l)=L.p\,1/2\{F_P^2(000l)+F_Q^2(000l)\}\fallingdotseq 0 \qquad (3)$$

The calculation of intensities based on this model led to improved agreement with the observed values. z-parameters of oxygen atoms were adjusted so as to give the best fit with the observed intensities. This time the value of R reduced to 0.173 for $(0k\bar{k}l)$ zone, giving the weighted mean value of 0.161 for all the observed reflections around the two principal axis. In Table II the parameters of O, Na and Cl atoms are listed.

TABLE II

ATOMIC COORDINATES OF O, Na AND Cl_2 ATOMS IN THE STRUCTURE P AND Q

	Model P			Model Q		
	x	y	z	x	y	z
O_1	0.897	0.098	0.560	0.897	0.098	0.440
O_2	0.098	0.201	0.980	0.098	0.201	0.020
Na	0	0	0.770	0	0	0.230
Cl_2	0	0	0.270	0	0	0.730

Observed and calculated structure amplitudes based on the parameter values shown in Tables I and II are shown in Table III.

With the parameters given in Tables I, and II the interatomic distances and interbond angles tabulated in Table IV were calculated. The accuracy of the determination was estimated using the equation given by Cruickshank⁶⁾. The standard deviation in electron density is $\sigma(\rho)=0.68$

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6) D. W. J. Cruickshank, *Acta Cryst.*, **2**, 65 (1949).

TABLE III

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES

1*k*.0	F_0	F_c	3*k*.0	F_0	F_c	5*k*.0	F_0	F_c	7*k*.0	F_0	F_c
0	31	−35	0	7	4	0	12	17	0	29	−27
1	78	77	1	22	21	1	38	35	1	15	18
2	75	70	2	18	23	2	7	13	2	5	−7
3	10	−21	3	53	50	3	<9	0	3	12	−14
4	81	83	4	42	38	4	10	−10	4	10	0
5	25	−28	5	24	−22	5	12	11	8*k*.0		
6	<9	−3	6	28	24	6	13	−11	0	18	21
7	41	37	7	11	−12	6*k*.0			1	<8	1
8	11	−6	8	11	−13	0	32	30	2	14	15
9	11	−5	4*k*.0			1	3	−1	3	3	6
2*k*.0			0	28	−23	2	8	−4	9*k*.0		
0	7	12	1	30	34	3	47	49	0	10	14
1	40	−43	2	13	−10	4	13	−15	1	5	5
2	35	31	3	27	33	5	13	13	10*k*.0		
3	6	−7	4	21	22				0	18	18
4	7	3	5	10	12						
5	67	58	6	9	13						
6	5	−3	7	12	10						
7	12	−21									
8	46	37									
9	6	2									

0*k*.2	F_o	F_c	F_c(P, Q)*	0*k*.8	F_o	F_c	F_c(P, Q)	0*k*.5	F_o	F_c	F_c(P, Q)
0	138	140	135	0	38	33	27	0	9	2	14
1	35	39	42	1	15	4	9	1	16	9	17
2	17	20	24	0*k*.1				2	32	35	41
3	15	12	15	0	5	6	5	3	17	27	17
4	62	65	63	1	47	58	53	4	20	9	12
5	40	40	40	2	26	36	40	5	10	14	17
6	5	5	7	3	84	78	82	6	7	5	4
7	31	34	33	4	22	12	14	7	23	28	24
8	4	6	8	5	9	6	8	0*k*.7			
9	4	5	4	6	5	8	11	0	5	2	10
0*k*.4				7	60	65	63	1	18	17	21
0	41	71	54	8	19	15	20	2	16	22	18
1	4	12	14	9	17	15	8	3	8	17	9
2	34	29	27	0*k*.3				4	12	12	9
3	41	31	39	0	26	3	24	5	8	8	8
4	20	19	25	1	38	29	32				
5	12	20	21	2	42	43	37				
6	20	14	17	3	31	39	30				
7	10	12	11	4	18	10	12				
8	17	15	13	5	13	12	11				
0*k*.6				6	5	8	11				
0	28	45	38	7	35	34	34				
1	37	21	26	8	5	6	5				
2	8	7	12								
3	11	15	16								
4	14	16	17								
5	29	25	22								
6	14	13	13								

* Calculated on the basis of twinned structure.

e. Å^{-2} on the (0001) projection. The standard deviation $\sigma(x)$ of some atoms are 0.014 Å for Cl_1, 0.031 Å for N_1, 0.048 Å for N_2 and 0.051 Å for O, respectively.

TABLE IV

CALCULATED INTERATOMIC DISTANCES AND BOND ANGLES

Co—N_1	1.98 Å	∠Co—N_1—C_1	109.6°
Co—N_2	2.00	∠Co—N_2—C_2	109.4°
N_1—C_1	1.48	∠N_1—C_1—C_2	109.0°
N_2—C_2	1.47	∠N_2—C_2—C_1	110.2°
C_1—C_2	1.54	∠N_1—Co—N_2	87.4°
Cl_1···N_1	3.18, 3.36, 3.37 Å		
Cl_1···N_2	3.17, 3.19 Å		
Cl_1···C_1	3.43, 3.82, 4.07 Å		
Cl_1···C_2	3.73, 4.06, 3.66 Å		

		Model P	Model Q
O_1···Cl_1	3.22 Å	3.23 Å	3.30 Å
O_2···Cl_1	3.22	3.25	3.22
O_1···C_1	3.38	3.48	3.26
	3.67	3.76	3.56
	3.68	3.41	4.24
O_2···C_1	3.38	3.31	3.38
	3.67	3.58	3.67
	3.68	3.95	3.68
O_1···C_2	3.37	3.17	3.40
	3.83	3.79	3.98
	4.08	4.36	3.56
O_2···C_2	3.37	3.29	3.37
	3.83	3.89	3.83
	4.08	3.81	4.08
Na···O_1 & O_2	2.84	2.62	2.62
Cl_2···O_1 & O_2	2.84	3.08	3.08
O_1···O_1 (O_2···O_2)	3.46	3.46	3.46

Description of the Structure

The arrangements of the atoms in the unit cell can be most clearly seen in the projection on the plane (0001), which is shown in Fig. 3. The size and shape of the complex ion are in good agreement with those previously described by us. The ethlyenediamine molecules take "*gauche*" forms and six nitrogen atoms form a slightly distorted octahedron around the central cobalt atom.

The azimuthal angle between planes containing the C—N bond and the C—C bond is found to be 48°. A complex ion is surrounded by nine Cl^- ions, six being at the corners of a trigonal prism and the other three at the apexes of an equilateral triangle. The closest approach of the complex ions and Cl^- occurs between NH_2 group and Cl^-, suggesting hydrogen bond of type N—H···Cl^-. The Cl^-···N distances are 3.17, 3.18 and 3.19 Å, which are comparable to the values obtained by various authors. The way in which a complex ion forms ionic bonds is very similar to that of racemic [Co en$_3$] $Cl_3 \cdot 3H_2O$.

If we adopt the above mentioned model having a twinned structure, a sodium ion is surrounded nearly octahedrally by six water molecules at a distance of 2.62 Å. forming $[Na(H_2O)_6]^+$ group. The packing of the complex ions and Cl^- ions brings about a structure having hollow tunnels parallel to the *c*-axis, in which the above mentioned sequence of $[Na(H_2O)_6]^+$ and Cl^- ions is held.

This structure was worked out without assuming any other relationship to the racemic [Co en$_3$]$Cl_3 \cdot 3H_2O$, except the initial assumption of the interatomic distances and bond angles. The unit cell dimensions of both substances show interesting relations; namely, both unit cells have nearly the same *a*-axis, and the *c*-axis of the racemic chloride is about twice that of the optically active double salt. Moreover, the above mentioned surroundings of the complex ion $[Co\ en_3]^{3+}$ are very similar in both structures, so that one may expect to find some common building units of which both structures are made up. In an effort along this line we pick out from the two substances, neglecting the minor differences, the groups, having the composition [Co en$_3$]$Cl_3 \cdot 3H_2O$. This group is marked A in Fig. 3 in the previous report. If we double this group by the operation of a digonal screw axis, the structure, having the space group *P*6$_3$, would be obtained. This is the structure of this double salt without NaCl component. In the structure of D, L-[Co en$_3$]$Cl_3 \cdot 3H_2O$, whose corresponding space group is $P\bar{3}cl$, the group [Co en$_3$] $Cl_3 \cdot 3H_2O$ is repeated four times by the operation of a glide plane *c* and *a* center of symmetry. Thus the concept of the polysynthetic structure developed by Ito[7] is applicable to the broad structural principles and is shown to be useful in discussing the structure of related complex compounds as illustrated by the present example. It enables us to describe the complicated structure in a straightforward and simple way.

Summary

The preparation of two mixed salts, 2D-[Co en$_3$]$Cl_3 \cdot NaCl \cdot 6H_2O$ and 2L-[Co en$_3$] $Cl_3 \cdot NaCl \cdot 6H_2O$ is described. The space group is P3, with one formula unit in

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[7] T. Ito, "X-ray Studies on Polymorphism", Maruzen, Tokyo (1950).

a cell of dimensions: $a=11.47\pm0.03$ Å, $c=8.06\pm0.02$ Å. However, the structure has the pseudo space group $P6_3$. By evaluating the functions $\rho(XY)$ and $\rho(YZ)$, projections of the structure on two crystallographic planes were obtained. A kind of twinned structure was proposed to get a better agreement between the observed and calculated intensities. The structure shows very close resemblance to that of D, L-[Co en$_3$]Cl$_3\cdot$3H$_2$O. A sodium ion is octahedrally surrounded by six water molecules, with Na$^+\cdots$O distances of 2.62 Å. The whole structure is ionic consisting of the ions [Co en$_3$]$^{3+}$, [Na(H$_2$O)$_6$]$^+$ and Cl$^-$.

The authors are grateful to Professors I. Nitta and T. Watanabé of the Osaka University for their kind advice and encouragement throughout this work. Helpful discussions were given by Mr. K. Osaki of the Osaka University. Thanks are also due to Mr. Y. Iidaka of the Mineralogical Institute, University of Tokyo for piezoelectric test of the cystals. The authors are indebted to the Ministry of Education for financial assistance.

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