The Crystal Structure of D*-Tris-ethylenediamine-cobalt(III) Bromide Monohydrate,* D*-*$[Co\,en_3]Br_3\cdot H_2O$*, and the Absolute Configuration of the* D*-Tris-ethylenediamine-cobalt(III) Ion,* D*-*$[Co\,en_3]^{3+}$

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The crystal structure of several complex compounds containing $[Co\,en_3]^{3+}$ ions (en: ethylenediamine, $NH_2-CH_2-CH_2-NH_2$) have been studied to determine the shape and size of the cobalt-ethylenediamine ring[1-3]. The absolute configuration of the complex ion has also been determined[4]. The present work was undertaken to obtain further information on the ion and, at the same time, to confirm the absolute configuration determined for the crystals of D- and L-$2[Co\,en_3]Cl_3\cdot NaCl\cdot 6H_2O$.

Since the $[Co\,en_3]^{3+}$ ion is the most familiar and fundamental one in the coordination chemistry and since it exhibits a typical optical isomerism due to the octahedral configuration, the absolute configuration of the complex ion merits further confirmational study. The stability and ease with which this ion can be obtained further favor its use as an internal reference asymmetric center for the determination of the absolute configuration of other

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

[2] K. Nakatsu, M. Shiro, Y. Saito and H. Kuroya, ibid., **30**, 158 (1957).

[3] H. Kuroya, Y. Saito, A. Nakahara, Y. Komiyama and K. Nakatsu, *J. Inst. Polytech. Osaka City Univ.*, C5, 1 (1956).

[4] Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya, This Bulletin, **30**, 795 (1957); *Acta Cryst.*, **8**, 729 (1955).

optically active compounds[5].

The details of the structure analysis will be given in Part I, while the determination of the absolute structure of the crystal, as well as the absolute configuration of the complex ion, will be described in Part II.

I. The Crystal Structure

Experimental

D-[Co en_3]$Br_3\cdot H_2O$ (which is generally formulated as dihydrate) was prepared by the method described by Werner[6], who concluded that this substance might be dihydrate from the determination of the cobalt as $CoSO_4$. This method of analysis, however, does not seem to be sensitive enough to fix the number of the water of crystallization. The determination of the water of crystallization was made here by direct dehydration. The results are shown in Table I, together with the densities of the crystals. The table supports the monohydrate formula and shows that the results of the chemical analysis are rather dubious; later structure determination verified the monohydrate formula.

TABLE I. DETERMINATION OF THE WATER OF CRYSTALLIZATION

	Calcd. for		Found
	$C_6H_{24}N_6Co\cdot 2H_2O$	$C_6H_{24}N_6Co\cdot H_2O$	
Co	11.42%	11.87%	11.52% for D-crystal[6] 11.62% for L-crystal[6]
H_2O	6.99%	3.62%	3.12%*
Density (g. cm^{-3})	2.06	1.995	1.971(25°C)[7] 2.00(30°C)**

* Dehydrated at 3 mmHg, 110°C, until the sameles reached constant weights. The author is very grateful to Mr. J. Gôda of this Faculty for the use of micro-balance.

** Measured by the flotation method.

The crystals are deep orange in color and appear in ditetragonal bipyramidal form, which agrees with Jaeger's description[7]. The crystallographic and physical data obtained were as follows:

D-Tris-ethylenediamine-cobalt(III) bromide monohydrate, D-[Co en_3]$Br_3\cdot H_2O$, F. W. = 497.1

Crystal system: Tetragonal

Unit cell dimensions: $a=9.95\pm0.03$* and $c=16.73\pm0.05$ Å

Axial ratio $a_0:c_0=1:0.8399$ obtained by morphology[7], $a:c/2=1:0.840_7$ obtained by X-rays

Systematic extinction: $(h\,0\,0)$ present only when $h=2n$, and $(0\,0\,l)$ when $l=4n$

Space group: No. 92, $P4_12_12$-D_4^4 or No. 96, $P4_32_12-D_8^4$, these two are enantiomorphous with each other

Number of the formula units per unit cell: $Z=4$

Volume of the unit cell: 1656 Å^3

Density: Observed 2.00 g. cm^{-3}, 1.971 g. cm^{-3} [7], calculated 1.99_5 g. cm^{-3}

Total number of electrons per unit cell: $F(0\,0\,0)=928$

Linear absorption coefficient for Ni K_α rays ($\lambda=1.651$ Å): $\mu=124.1\ cm^{-1}$

Using Ni K_α radiation, a complete set of relative intensities for $(h\,k\,0)$ and $(0\,k\,l)$ reflections were obtained by the integrated Weissenberg procedure. For the recording of the weak reflections, a non-integrating procedure was used. The specimens used were obtained by cutting the crystals in a cylindrical form, until μr, where r is the radius of the specimen, became smaller than unity. The radii of the specimens were 0.01 cm. for the a-axis rotation and 0.009 cm. for the c-axis rotation; thus the μr were estimated to be 0.8 and 0.7 respectively.

Intensity measurements were carried out by visual comparison with a calibrated scale prepared by using the same specimen. The multiple film technique was used to correlate strong and weak reflections, ranging in relative intensity from about 5×10^4 to unity. The maximum $\sin\theta$ observed was 0.975. Within this limit, 53 reflections were measured out of 58 possible $(h\,k\,0)$ reflections, and 167 out of 186 possible $(0\,k\,l)$ reflections.

The corrections for polarization and Lorentz factors were made by use of Cochran's chart[8], and that for absorption was made by regarding the specimens as cylinders[9].

Determination of the Structure

Since the number of formula units in a unit cell is four, and since there are four fold special positions, $4(a)$, and eight fold general positions, $8(b)$, in the space group[10], it was assumed that 4Co, 4Br (labeled as Br_1) out of 12Br and 4O would lie on $4(a)$, and that the others would lie on $8(b)$ (labeled as Br_2, N_1, N_2, N_3, C_1, C_2 and C_3).

(0 0 1) Projection. — At the outset the Patterson projection $P(UV)$ was evaluated. Although the interpretation of the map was fairly difficult, owing to overlapping of the interatomic vectors, approximate positions of the heavy atoms Co, Br_1 and Br_2 were derived. An electron density projection $\rho(XY)$ was then calculated, assuming the structure factor to have the same phases as the contributions of the heavy atoms. However, none of the atoms, except Br_2, could be resolved owing to the heavy overlapping.

The main problem in interpreting the electron density map thus obtained was to decide where the light atoms should be placed in a composite peak. This was accomplished to

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5) A. McL. Mathieson, ibid., **9**, 317 (1956).

6) A. Werner, *Ber.*, **45**, 128 (1912).

7) F. M. Jaeger, *Akad. Amsterdam Versl.*, **23**, 1293 (1914/1915); *Z. Krist.*, **55**, 207 (1919—1920).

* The a-axis was chosen in such a way that well-formed prismatic faces can be assigned for $(1\,1\,0)$.

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

9) "International Tables for X-Ray Crystallography", Vol. II, The Kynoch Press, England (1959).

10) Ibid., Vol. I (1952).

some extent by the use of partial difference syntheses[11], giving the electron density distribution after subtracting the calculated contributions of those atoms whose parameters were fairly accurately known. The coefficients used in these syntheses were $\Delta F=(F_o-F_c')$, where F_c' included only the contributions of the atoms which were to be subtracted, while the same phase as F_c' was given to F_o. These projections gave more information about the positions of the lighter atoms, and at the same time the necessary changes in the coordinates of heavy atoms were found.

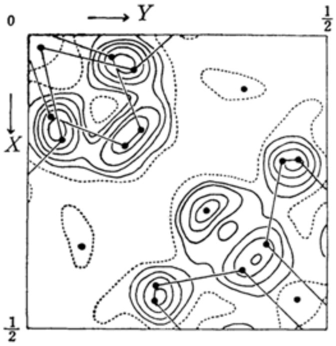

Fig. 1. Electron-density distribution $(\rho_o-\rho_c')$ projected upon (0 0 1) after subtracting the contributions of the cobalt and bromine atoms. Contours are at every 4 e. Å^{-2}, starting at two electron level, whose contours are broken.

Further refinements were made using the ρ_o and ordinary difference syntheses. In some cases difference syntheses using only those reflections with $\sin\theta/\lambda$ larger than 0.35 Å^{-1} were calculated to avoid systematic errors such as the one arising from extinction[12]. A correction for secondary extinction was applied by the method of Pincock et al.[13] Figure 1 shows the result of the partial difference synthesis $(\rho_o-\rho_c')$, where the contributions of heavy atoms were subtracted.

(1 0 0) Projection.—Inspecting $(0\,k\,l)$ reflections, it was found that all the reflections which belong to type $2k+l=4n+2$ were extremely weak intensity compared with the others. The structure factor for this type of reflection can be represented by[10];

$$A=0$$

and

$$B=\sum_j 4f_j \sin 2\pi l z_j(\cos 2\pi k y_j-\cos 2\pi k x_j)$$

where j refers to the jth atom. The values of B will be small only when $\sin 2\pi l z_j$ assumes a small value, because the factor given in parenthesis is not necessarily small, depending on the values of y_j and x_j. This would generally be true for heavier atoms. In order for $\sin 2\pi l z_j$ to become smaller, the z parameters of heavy atoms have to assume 0, 1/4, 1/2 and/or 3/4. Since Co and Br$_1$ lie on $4(a)$ and their z parameters take those values, this condition should be imposed for Br$_2$. If the Br$_2$ atoms take the z parameters given above, then all the heavy atoms lie on plane (0 0 4), giving rise to a layer structure. The extremely strong intensities of $(0\,0\,l)$, especially of (0 0 4), also favored this deduction. A Patterson projection $P(VW)$ showed, however, marked peaks which at first seemed to be inconsistent with these parameters. Later it was found that these peaks were due to the multiple overlapping of the interatomic vectors between heavy and light atoms and those between light atoms. Also for the (1 0 0) projection, the refinement procedures were repeated in a similar way. $(\rho_o-\rho_c')$ is given in Fig. 2.

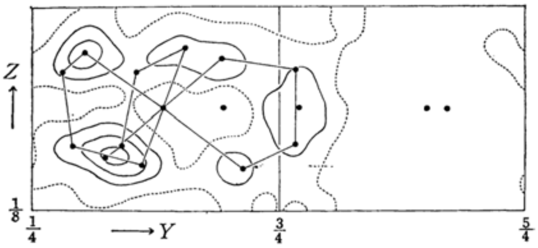

Fig. 2. Electron-density distribution $(\rho_o-\rho_c')$ projected upon (1 0 0). Contours are drawn as same manner as Fig. 1.

TABLE II. ATOMIC COORDINATES

Atom	x/a	y/a	z/c
Co	0.480	0.520	0.250
Br$_1$	0.550	0.550	0.500
O	0.295	0.295	0.500
Br$_2$	0.139	0.590	0.500
C$_1$	0.663	0.313	0.295
C$_2$	0.218	0.433	0.205
C$_3$	0.217	0.463	0.295
N$_1$	0.532	0.360	0.319
N$_2$	0.362	0.395	0.190
N$_3$	0.324	0.558	0.322

The final set of atomic coordinates listed in Table II, and the observed and calculated structure factors are given in Table III. In the structure factor calculations, the atomic scattering factors were taken from Thomas and Umeda[14] for cobalt and bromine, and from

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[11] S. Ooi, Y. Komiyama, Y. Saito and H. Kuroya, This Bulletin, **32**, 263 (1959); P. G. Owton, J. M. Partridge and J. M. Rowe, *Acta Cryst.*, **13**, 246 (1960).

[12] F. Jellinek, ibid., **11**, 677 (1958).

[13] P. R. Pincock, C. A. Taylor and H. Lipson, ibid., **9**, 173 (1956).

[14] L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

TABLE III. OBSERVED AND CALCULATED STRUCTURE FACTORS

h	k	l	$F_o/4$	$F_c/4$	h	k	l	$F_o/4$	$F_c/4$	h	k	l	$F_o/4$	$F_c/4$	h	k	l	$F_o/4$	$F_c/4$
2	0	0	44.2	43.8	0	0	8	41.8	48.8	0	6	14	< 1.0	− 0.5	0	3	14	6.6	7.7
4	0	0	21.0	−18.8	0	0	12	46.0	−44.0	0	6	16	< 0.6	1.4	0	3	16	< 0.9	− 0.1
6	0	0	2.4	− 1.0	0	0	16	32.0	32.5	0	7	1	4.8	1.9	0	3	18	4.8	− 4.3
8	0	0	3.3	− 2.1	0	1	1	5.3	− 5.1	0	7	3	4.5	0.1	0	4	1	33.2	−34.4
10	0	0	< 1.7	− 5.1	0	1	3	4.5	4.8	0	7	5	3.9	− 2.8	0	4	3	24.0	−21.1
1	1	0	32.8	34.3	0	1	5	1.1	1.0	0	7	7	2.5	0.6	0	4	5	31.6	33.2
3	1	0	40.9	40.3	0	1	7	7.0	− 4.0	0	7	9	4.3	3.1	0	4	7	24.4	22.5
5	1	0	27.8	24.4	0	1	9	2.5	− 1.4	0	7	11	3.9	− 3.4	0	4	9	18.1	−15.5
7	1	0	4.4	− 2.0	0	1	11	5.0	2.6	0	7	13	3.5	− 2.3	0	4	11	18.1	−17.6
9	1	0	8.3	− 9.2	0	1	13	< 1.1	3.0	0	7	15	3.4	3.0	0	4	13	10.7	9.0
11	1	0	3.3	− 1.8	0	1	15	< 1.1	− 0.4	0	8	0	3.3	− 2.1	0	4	15	8.9	7.8
2	2	0	21.6	18.3	0	1	17	< 1.0	− 1.2	0	8	2	2.2	− 1.0	0	4	17	7.9	− 7.8
4	2	0	9.7	7.1	0	1	19	0.9	0.2	0	8	4	1.6	1.0	0	5	2	19.5	−14.9
6	2	0	12.9	11.1	0	2	0	44.2	−43.8	0	8	6	2.4	0.6	0	5	4	3.8	− 0.4
8	2	0	7.1	4.5	0	2	2	1.4	− 1.0	0	8	8	2.1	0.9	0	5	6	19.9	15.4
10	2	0	4.1	− 5.7	0	2	4	36.2	35.7	0	8	10	1.4	0.7	0	5	8	< 1.1	− 3.3
3	3	0	22.4	19.7	0	2	6	2.5	1.5	0	8	12	< 0.8	− 0.7	0	5	10	15.9	−12.6
5	3	0	12.3	− 9.8	0	2	8	30.2	−27.8	0	8	14	0.9	− 0.2	0	5	12	1.1	1.1
7	3	0	2.0	− 1.3	0	2	10	4.8	0.0	0	9	1	13.7	−11.3	0	5	14	10.2	7.1
9	3	0	2.8	− 0.4	0	2	12	25.6	21.1	0	9	3	12.4	12.3	0	5	16	2.4	1.9
11	3	0	4.7	1.7	0	2	14	1.9	− 0.8	0	9	5	12.5	11.6	0	6	1	2.3	− 1.9
4	4	0	30.4	32.4	0	2	16	17.5	−11.8	0	9	7	10.1	−11.0	0	6	3	3.3	− 1.2
6	4	0	12.7	10.8	0	2	18	< 0.8	0.0	0	9	9	9.1	7.6	0	6	5	< 0.9	1.0
8	4	0	< 1.9	− 3.5	0	3	1	35.8	−36.6	0	9	11	5.6	6.6	0	6	7	4.5	− 3.6
10	4	0	2.5	− 2.3	0	3	3	18.3	17.3	0	10	0	1.7	5.1	0	6	9	1.6	1.7
5	5	0	< 2.3	0.4	0	3	5	26.4	26.4	0	10	2	0.9	− 1.4	0	6	11	7.6	3.3
7	5	0	6.0	8.0	0	3	7	9.5	−10.0	0	10	4	3.4	− 3.9	0	6	13	4.6	− 3.9
9	5	0	2.1	1.8	0	3	9	10.6	− 7.6	0	10	6	1.5	0.6	0	6	15	3.9	− 0.5
6	6	0	6.9	− 5.2	0	3	11	10.8	10.1	0	10	8	3.7	2.3	0	6	17	< 0.4	1.5
8	6	0	3.9	− 3.6	0	3	13	7.9	4.7	0	10	10	1.4	1.4	0	7	2	36.2	39.7
10	6	0	6.1	6.6	0	3	15	8.6	− 6.9	0	11	1	3.6	3.1	0	7	4	3.0	− 1.5
7	7	0	8.3	11.0	0	3	17	8.4	− 6.0	0	11	3	3.2	− 3.0	0	7	6	25.8	−29.5
9	7	0	1.3	1.5	0	3	19	3.5	4.1	0	11	5	4.7	− 4.2	0	7	8	< 1.1	0.4
8	8	0	1.9	4.0	0	4	0	21.0	−18.8	0	11	7	2.7	2.4	0	7	10	19.5	21.1
2	1	0	< 0.9	0.3	0	4	2	5.0	− 3.5	0	1	2	13.9	−12.4	0	7	12	< 1.0	0.8
4	1	0	8.9	− 7.4	0	4	4	8.4	11.1	0	1	4	2.2	− 0.5	0	7	14	14.0	−15.5
6	1	0	2.1	0.8	0	4	6	1.8	0.5	0	1	6	31.2	−29.5	0	8	1	5.1	− 7.4
8	1	0	10.4	9.4	0	4	8	3.4	− 6.4	0	1	8	1.2	0.7	0	8	3	4.4	− 7.2
10	1	0	6.3	6.0	0	4	10	3.0	− 2.5	0	1	10	19.6	18.3	0	8	5	2.7	5.6
3	2	0	16.3	16.3	0	4	12	3.3	8.1	0	1	12	< 1.1	0.2	0	8	7	2.5	5.2
5	2	0	26.8	26.1	0	4	14	< 1.1	− 1.3	0	1	14	2.2	− 3.1	0	8	9	3.3	− 4.0
7	5	0	12.1	−10.7	0	4	16	2.4	− 6.5	0	1	16	1.1	− 0.3	0	8	11	< 1.0	− 3.2
9	2	0	16.4	−15.1	0	4	18	1.9	1.4	0	1	18	3.4	2.6	0	8	13	4.0	3.1
11	2	0	< 1.3	0.7	0	5	1	26.4	26.7	0	2	1	42.8	42.9	0	9	2	1.5	− 2.1
4	3	0	2.4	1.3	0	5	3	18.1	−19.5	0	2	3	37.3	35.9	0	9	4	< 1.1	− 0.1
6	3	0	10.3	−11.0	0	5	5	21.1	−24.3	0	2	5	45.1	−45.8	0	9	6	6.2	7.3
8	3	0	14.4	13.8	0	5	7	17.9	20.4	0	2	7	34.7	35.9	0	9	8	< 1.0	− 0.4
10	3	0	3.9	1.4	0	5	9	14.0	13.1	0	2	9	36.6	35.3	0	9	10	6.2	− 6.6
5	4	0	25.6	25.8	0	5	11	14.9	−15.9	0	2	11	28.2	30.3	0	9	12	0.8	0.3
7	4	0	12.5	13.3	0	5	13	11.6	−11.0	0	2	13	20.9	−20.6	0	10	1	0.9	1.4
9	4	0	1.7	− 2.5	0	5	15	7.4	7.9	0	2	15	17.4	−17.4	0	10	3	0.9	1.8
11	4	0	2.3	− 2.0	0	5	17	9.9	8.6	0	2	17	10.8	10.7	0	10	5	2.8	3.5
6	5	0	4.7	5.0	0	6	0	2.4	1.0	0	2	19	8.1	7.4	0	10	7	2.8	− 3.8
8	5	0	2.4	− 1.3	0	6	2	1.4	0.1	0	3	2	16.5	−18.3	0	10	9	1.2	1.9
10	5	0	5.7	− 4.3	0	6	4	4.3	− 4.9	0	3	4	2.4	1.3	0	11	2	4.9	− 4.8
7	6	0	7.7	7.3	0	6	6	2.9	− 1.6	0	3	6	5.0	7.4	0	11	4	2.8	2.3
9	6	0	3.5	3.9	0	6	8	5.0	5.5	0	3	8	< 0.8	0.5	0	11	6	3.3	3.7
8	7	0	7.7	− 3.9	0	6	10	1.9	1.0	0	3	10	4.5	− 7.1					
0	0	4	(75.4)*	−118.1	0	6	12	1.5	− 2.3	0	3	12	1.5	− 1.1					

* Extremely large effect of extinction is expected.

Berguis et al.[15] for carbon, nitrogen and oxygen. The correction to be applied to the real part of the atomic structure factor due to the dispersion[16] caused by K-electrons, $\Delta f_K'$, was taken into account for cobalt and bromine. This amounts to -3.5 for cobalt and -1.5 for bromine for Ni K_α rays. No correction was made for the dispersion caused by L-electrons. The isotropic and overall temperature correction was applied in the usual manner. The temperature factor, B, was found to be 3.4Å^2 for $(h\,k\,0)$ and 3.2Å^2 for $(0\,k\,l)$ reflections.

The final reliability indices, $R=\sum\|F_o|-|F_c\|/\sum|F_o|$, are 0.128 for $(h\,k\,0)$ and 0.148 for $(0\,k\,l)$ reflections, without the contribution of hydrogen atoms, non-observed reflections being excluded. In the calculation of R, $(0\,0\,l)$ reflections were omitted, because these reflections would be influenced critically by such an effect as extinction.

Description and Discussion of the Structure

The arrangement of the atoms in the unit cell is shown in Figs. 3, 4 and 5, with some interatomic distances. The most striking feature is that the heavy cobalt and bromine atoms and water molecules are in layers, the layers being $c/4$ apart.

Adopting the absolute configuration of the dextrorotatory complex ion determined previously[4], we can deduce that the present crystal belongs to the space group $P4_32_12$-D_4^8. This choice of space group from the enantiomorphous pair was verified by the anomalous dispersion experiment for the present crystal, as will be shown later.

Since the cobalt atoms lie on the special positions 4(a), having point symmetry 2, the complex ion is required to have a digonal symmetry. This would be compared with the

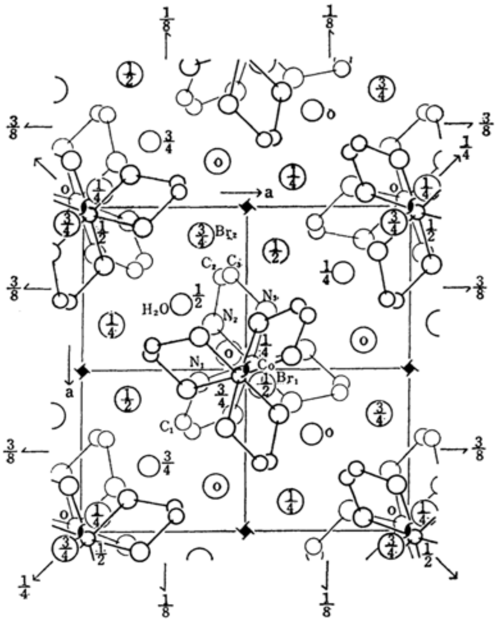

Fig. 3. Projection of the structure upon (0 0 1). The figures in or near the atoms show the z-coordinates of the atoms respectively.

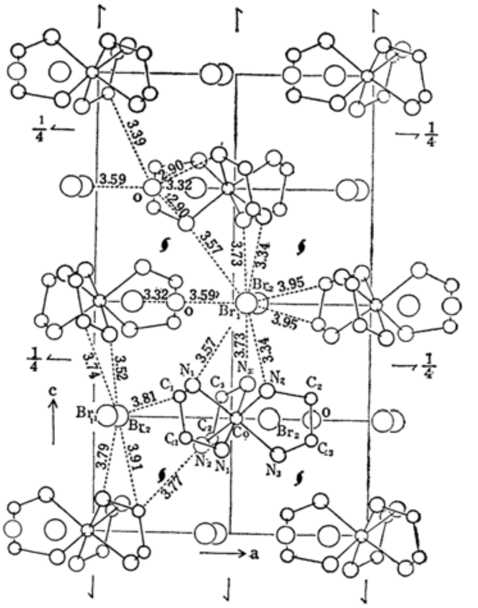

Fig. 4. Projection of the structure upon (1 0 0).

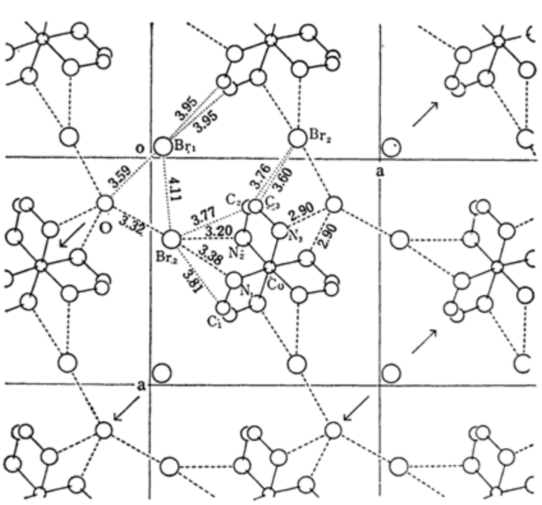

Fig. 5. Atomic arrangements within one layer around $Z=(1/4)C$. The broken lines show the linkages constructing the layer.

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[15] J. Berguis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillabry and A. L. Veenendaal, *Acta Cryst.*, 8, 478 (1955).

[16] R. W. James, "The Optical Principles of the Diffraction of X-Rays", G. Bell & Sons, London (1948), Appendix.

cases of DL-$[Co\,en]Cl_3\cdot 3H_2O$[1] and D- and L-$2[Co\,en_3]Cl_3\cdot NaCl\cdot 6H_2O$[2], where the cobalt atoms lie on the three-fold symmetry axis because of the requirement of the space group. The ethylenediamine molecules take a nearly "gauche" form, and the six nitrogen atoms form a slightly distorted octahedron around the central cobalt atom. There are four possibilities of the configuration of the three cobalt-ethylenediamine rings. To employ the symbols used by Corey and Bailar[17], they are k k k, k′ k k, k k′ k′ and k′ k′ k′*. The relevant combination in the present case is k k k, designated the "lel" form, which is the most stable one according to Corey and Bailar, and which is the same as that existing in the crystals DL-$[Co\,en_3]Cl_3\cdot 3H_2O$, D- and L-$2[Co\,en_3]Cl_3\cdot NaCl\cdot 6H_2O$ and $[Ni\,en_3](NO_3)_2$[18].

The complex ion, therefore, possesses the symmetry D_3-32 within the precision of the experiment. Bond lengths and bond angles within the complex ion are nearly in agreement with those previously found, as is shown in Table IV. The azimuthal angles between the planes determined by the C–C and C–N bonds are found to be 43 and 52° for the two independent ethylenediamine ligands.

TABLE IV. BOND LENGTHS AND BOND ANGLES WITHIN THE COMPLEX ION

$Co-N_1$	2.03 Å	$\angle N_1CoN_1$	87.3°
$Co-N_2$	1.98 Å	$\angle N_1CoN_2$	86.3°, 90.5°
$Co-N_3$	2.00 Å	$\angle N_1CoN_3$	90.4°
C_1-N_1	1.44 Å	$\angle N_2CoN_3$	87.5°, 93.4°
C_2-N_2	1.50 Å	$\angle N_3CoN_3$	93.8°
C_3-N_3	1.49 Å	$\angle N_1C_1C_1$	110.7°
C_1-C_1	1.54 Å	$\angle N_2C_2C_3$	102.0°
C_2-C_3	1.54 Å	$\angle N_3C_3C_2$	114.3°

The complex ions are located at about 0 0 0, 0 0 1/2, 1/2 1/2 1/4 and 1/2 1/2 3/4, and their three-fold axis is nearly in the *c*-direction. This aspect of the complex ions had also been suggested by the study of the dichroism of the crystals[19].

A complex ion is surrounded by $2Br_1$, $2Br_2$ and H_2O in close approach to the N atoms. Among them, the $2Br_1$ lie above and below the complex ion in the *c*-direction and 3.34, 3.57 and 3.73 Å apart from the N_2, N_1 and N_3 atoms respectively. $2Br_2$ and O are in the level of Co and form an isosceles triangle. The $Br_2\cdots N$ distances are 3.20 and 3.38 Å, and the $N\cdots O$ distances are 2.90 Å, probably forming N–H···O type hydrogen bonds. The water molecule is located between the complex ion and the Br_1 lying on the same level. This scheme of the atomic arrangements within a layer can be most easily seen in Fig. 5, where the arrangement of the atoms in one layer around $Z=(1/4)c$ is illustrated. The role of the water molecules is probably to link the positive and negative ions to form a layer.

The layers are related to each other by the operation of the 4_3 axis, and also of the 2_1 axes at $Z=1/8$ or 3/8. No remarkably close contact between two layers, except that one between Br_1 and N_2 has been found.

II. Absolute Structure

"Absolute Structure" vs. "Absolute Configuration"

"Absolute configuration" is usually used to refer to the spatial arrangement of atoms or atomic groups around an asymmetric carbon atom without any ambiguity which otherwise exists between the two antipodes. The crystal which contains only one of the antipodes always lacks a center of symmetry, and if we could determine its crystal structure, including its handedness, we could consequently fix the "absolute configuration" of the antipode involved. On the other hand, there are many crystals which do not contain any optically active group, and yet the handednesses of which present some problems to be solved.

Thus, "absolute structure" means the unambiguous description of the atomic arrangement in a non-centrosymmetric crystal, while "absolute configuration" is to be used when the atomic arrangement within an optically active molecule, ion or atomic group is described in an absolute way. "Absolute structure" rather than "absolute configuration" would be the adequate term for α-quartz[20], sodium chlorate[21], etc. Takéuchi first used the term "absolute structure" in the study of ullmannite[22].

The Problem of Absolute Structure in the Present Case

Since the absolute configuration of D-tartaric acid was determined in 1951 by Bijvoet et al.[23] using the anomalous dispersion effect of X-rays, many attempts have been made to determine the absolute configuration of various com-

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[17] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

* In the Refs. 1 and 3, the symbols D_{ddd}, D_{dll}, D_{ldd} and D_{lll} were used.

[18] L. N. Swink and M. Atoji, *Acta Cryst.*, **13**, 639 (1960).

[19] S. Yamada and R. Tsuchida, This Bulletin, **33**, 98 (1960).

[20] A. de Vries, *Nature*, **181**, 1193 (1958).

[21] G. N. Ramachandran and K. S. Chandrasekaran, *Acta Cryst.*, **10**, 671 (1957).

[22] Y. Takéuchi, *Mineral. J.*, **2**, 90 (1957).

[23] J. M. Bijvoet, A. F. Peerdeman and A. J. van Bommel, *Nature*, **168**, 271 (1951).

pounds in the similar way[24]. The absolute configuration of optically active complex ion D- or L-$[\mathrm{Co\,en_3}]^{3+}$, was determined by Saito, Nakatsu, Shiro and Kuroya[4] from the observation of the Bijvoet inequality, and was examined more quantitatively, using the $P_s(u)$ function, by Saito, Okaya and Pepinsky[25] on the crystals D- and L-$2[\mathrm{Co\,en_3}]\mathrm{Cl_3 \cdot NaCl_3 \cdot 6H_2O}$.

The problem with the present crystal about the absolute structure or absolute configuration is that the crystal has an enantiomorphous pair of space groups which can not be distinguished by the conventional method; this can be done only by the anomalous dispersion technique. If we could substantiate the true space group and therefore, the absolute structure, we could consequently fix the absolute configuration of D- or L-$[\mathrm{Co\,en_3}]^{3+}$.

The phase relation among the reflection pairs which are enantiomorphous with each other and whose intensities are to be compared when the anomalous dispersion takes place, is a rather complicated one, depending on the types of $(h\,k\,l)$ in the present space group. In short, it is possible to classify the types of reflections into two groups:

Group I $h\,k\,l$, $k\,h\,\bar{l}$, $\bar{k}\,h\,l$, $\bar{h}\,k\,\bar{l}$, $\bar{h}\,\bar{k}\,l$,
$\bar{k}\,\bar{h}\,\bar{l}$, $k\,\bar{h}\,l$ and $h\,\bar{k}\,\bar{l}$
Group II $h\,k\,\bar{l}$, $k\,h\,l$, $\bar{k}\,h\,\bar{l}$, $\bar{h}\,k\,l$, $\bar{h}\,\bar{k}\,\bar{l}$,
$\bar{k}\,\bar{h}\,l$, $k\,\bar{h}\,\bar{l}$ and $h\,\bar{k}\,l$

The structure factor for a reflection of a given index which belongs to Group I can find its complex conjugate or its permuted equivalents in the reflections listed in Group II. For example, if $\alpha(h\,k\,l)$ is the phase angle for $(h\,k\,l)$, then $\alpha(h\,k\,\bar{l})=\alpha(k\,h\,l)=\pi-\alpha(h\,k\,l)$*, and $\alpha(k\,h\,\bar{l})=\alpha(h\,k\,l)$. The intensities of all the reflections in groups I and II are mutually equal in the ordinary diffraction experiment. However, when comparing the intensities of pairs of reflections whose indices belong to groups I and II respectively, e.g., $(h\,k\,l)$ and $(h\,k\,\bar{l})$ the failure of Friedel's law due to the anomalous dispersion can be observed and, hence, the absolute structure deduceed. If the reflections considered belong to the same group, then the effect of the anomalous dispersion can not be observed.

Experimental Procedure and Result

Peterson[26] and others[21,27] were successful in measuring the effect of anomalous dispersion, even when the X-rays used are far from the absorption edge of any atom in the crystal. However, it is les difficult to observe the Bijvoet inequality if the radiation whose wavelength is close to the absorption edge is available; the photographic method can be used successfully in this case. Therefore, Cu K_α rays ($\lambda=1.541\,\text{Å}$) where used, because they can excite just the K-electrons of cobalt atoms ($\lambda_K=1.608\,\text{Å}$), and, in addition, a smaller effect

TABLE V. COMPARISON OF THE OBSERVED INEQUALITIES WITH CALCULATED VALUES

h k l	$\lvert F(hkl)\rvert^2$	$\lvert F(hk\bar{l})\rvert^2$	$\Delta\lvert F\rvert^2$ %*	Observed**
2 1 1	416	401	3.7	?
4 1 1	178	123	36.4	>
6 1 1	334	457	−31.1	<
8 1 1	159	171	− 7.3	<
10 1 1	207	221	35.8	>
3 2 1	65	88	−29.9	<
5 2 1	319	240	28.2	>
7 2 1	899	732	20.5	>
9 2 1	80	52	43.8	>
11 2 1	144	223	−42.6	<
4 3 1	398	311	34.5	>
6 3 1	44	88	−66.7	<
8 3 1	281	336	−17.9	<?
10 3 1	679	609	10.9	>
5 4 1	237	272	−13.7	<?
7 4 1	277	230	18.5	>
9 4 1	430	313	31.4	>
11 4 1	195	136	35.5	>
6 5 1	505	433	15.4	>?
8 5 1	326	394	−18.9	<?
10 5 1	312	300	3.9	?
7 6 1	225	337	−39.9	<
9 6 1	302	221	23.6	>
8 7 1	265	215	20.8	>

* $$\Delta|F|^2(\%)=\frac{|F(h\,k\,l)|^2-|F(h\,k\,\bar{l})|^2}{\frac{1}{2}\{|F(h\,k\,l)|^2+|F(h\,k\,\bar{l})|^2\}}\times 100$$

** The inequality sign > or < shows that the observed intensity for $(h\,k\,l)$ is larger or smaller than that for $(h\,k\,\bar{l})$. The sign >? or <? means that the inequality is not so definite as that without the symbol ?. The symbol ? shows that the inequality could not be observed.

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[24] I. Nitta (Editor), "X-Ray Crystallography" (in Japanese), Vol. II, Maruzen, Tokyo (1961), Chap. IV.

[25] Y. Saito, Y. Okaya and R. Pepinsky, *Phys. Rev.*, **100**, 970 (1955); R. Pepinsky, J. M. Robertson and J. C. Speakman (Editors), "Computing Methods and Phase Problem in X-Ray Crystal Analysis", Pergamon Press, Oxford (1961), p. 288.

* In this respect the description in International Tables, Vol. I[10] is not correct. p. 427, 10th and 19th line; p. 430, 6th and 15th line: $-\alpha(h\,k\,l)$ should be $\pi-\alpha(h\,k\,\bar{l})$.

[26] S. W. Peterson, *Nature*, **176**, 395 (1955).

[27] A. W. Hanson and F. R. Ahmed, *Acta Cryst.*, **11**, 724 (1958); J. M. Bijvoet, ibid., **13**, 1100 (1960); G. Kartha, F. R. Ahmed and W. H. Barnes, ibid., **13**, 1038 (1960); A. F. Peerdeman, ibid., **9**, 824 (1956); S. Raman, *Z. Krist.*, **111**, 301 (1959).

due to the *L*-electrons of the bromine atoms ($\lambda_L = 8$ Å) could be expected.

The intensities of $(h\,k\,l)$ and $(h\,k\,\bar{l})$ reflections were compared visually on oscillation photographs taken around the *c*-axis in order to observe the inequalities more conveniently. The specimen used was a small needle about 0.1 mm. in diameter elongated along the *c*-direction. Slight but discernible differences in intensities were found for many pairs of reflections. Large differences were found in some weak reflections. In Table V the observed inequalities are compared with the calculated values. In the calculation of the intensities, the following corrections for atomic scattering amplitude due to anomalous dispersion were used[28] in the form $f = f^0 + \Delta f' + i\Delta f''$, where f^0 is the atomic scattering amplitude for the X-rays far from the absorption edge and $\Delta f'$ and $\Delta f''$ are the corrections for the real and the imaginary parts of the scattering factor respectively :

Atom	$\Delta f'$	$\Delta f''$
Co	-2.2	3.9
Br	-0.9	1.5

The calculated values of the intensities are based on the set of coordinates given in Table II, the space group $P4_32_12$ being assumed. The right-handed coordinate system was used throughout the work.

As a more reliable observation of the effect of dispersion, photometric measurements of intensities for some particular reflections were made. Those reflections were selected which are of moderately low intensity in order to reduce the errors in measurements while reflections of low indices in order to reduce the errors of atomic positions. The results are shown in Table VI, where the observed intensities were measured with a micro-photometer.

The agreement between the observed and calculated inequalities seems to be satisfactory for the present study, and it can be stated with certainty that the atomic positions shown in Table II and Figs. 3 and 4 correspond to the absolute structure of D-[Co en_3]$Br_3 \cdot H_2O$. The absolute configuration of D-[Co en_3]$^{3+}$ deduced from the present study thus substantiates the configuration determined previously[4].

TABLE VI. COMPARISON OF CALCULATED AND OBSERVED $|F|^2$

	Calculated		Observed	
	$\dfrac{\lvert F(h\,k\,l)\rvert^2}{\lvert F(h\,k\,\bar{l})\rvert^2}$	$\Delta\lvert F\rvert^2$ %	$\dfrac{\lvert F(h\,k\,l)\rvert^2}{\lvert F(h\,k\,\bar{l})\rvert^2}$	$\Delta\lvert F\rvert^2$ %*
(611)	0.731	-31.1	0.813	-20.7
(521)	1.33	28.2	1.22	19.6

* See legend of Table V.

Summary

The absolute crystal structure of D-[Co en_3]$\cdot Br_3 \cdot H_2O$ was determined by means of X-rays. The space group is $P4_32_12$-D_4^8, with four formula units in a cell of the dimensions $a = 9.95$ and $c = 16.73$ Å. The complex ion takes the "lel" form designated by Corey and Bailar and is in the same configuration as had been determined previously. The structure can be most easily described as consisting of layers of complex ions, two types of bromine ions and water molecules perpendicular to the *c*-axis. The water molecules link the positive and negative ions to form a layer.

A definition of "absolute structure" and "absolute configuration" was proposed. The absolute structure was determined by means of the X-ray absorption edge technique of Bijvoet. CuK_α rays were used to observe visually the effect of the anomalous dispersion between the reflections $(h\,k\,l)$ and $(h\,k\,\bar{l})$, and quantitative measurements of the effect were attempted for some reflections. The absolute configuration of the complex ion deduced from the absolute structure of the crystal is in agreement with the one previously determined for the crystals D- and L-2[Co en_3]$Cl_3 \cdot NaCl \cdot 6H_2O$.

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[28] C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).