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The Crystal Structure of $(+)_{589}$-Dicyanobis(ethylenediamine)cobalt(III) Chloride Monohydrate

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The crystal structure of $(+)_{589}$-$[Co(CN)_2en_2]Cl \cdot H_2O$ has been determined from three-dimensional X-ray photographic data. The crystals are monoclinic, with the lattice constants of $a=8.15(1)$, $b=11.69(2)$, $c=6.61(1)$Å, and $\beta=107.1(2)$°, and with the space group of $P2_1$, containing two formula units in the cell. The structure was solved by a conventional Fourier technique and was refined by the least-squares method to an R factor of 0.114. The absolute configuration of the complex ion can be denoted as $\Lambda(\lambda\lambda)$; this is in accordance with the assignment made by Mason *et al.* The complex ion has an approximately two-fold axis, and both of the ethylenediamine chelate rings are of the *ob*-conformation.

The absolute configurations of the several bisethylenediamine cobalt(III) complexes with C_2-symmetry have been studied on the basis of the optical properties, such as CD or ORD spectra.[1-4] However, since no X-ray diffraction study had been made on the bisdiamine complexes, we carried out the direct determination of the absolute structure of $(+)_{589}$-$[Co(CN)_2en_2]Cl \cdot H_2O$ by the X-ray method. The preliminary results of this work have been reported previously.[5,6] In this paper, the complete crystal structure, as refined by the use of the three-dimensional reflection data, will be described.

Experimental

The plate-like, yellow crysatls of $(+)_{589}$-$[Co(CN)_2en_2]Cl \cdot H_2O$ were kindly supplied by Ohkawa and Fujita.[7] Lattice constants were determined by the least-squares refinement of the twenty-eight θ values from the $h0l$ and $hk0$ Weissenberg photographs, on which aluminum-powder diffraction lines were superimposed for calibration.

The observed systematic absences ($0k0$, $k=2n+1$) indicate two possible space groups, $P2_1$ and $P2_1/m$; however, the latter can be excluded, because the compound is optically active, including only the dextrorotatory enantiomer of the complex ions. The crystal data are shown in Table 1.

Table 1. Crystallographic data

Monoclinic
$a=8.15(0.01)$Å
$b=11.69(0.02)$Å
$c=6.61(0.01)$Å
$\beta=107.1(0.2)$°
Space group $P2_1$
$Z=2$ ($D_m=1.56$, $D_c=1.57\ \mathrm{g \cdot cm^{-3}}$)
$\mu=51.3\ \mathrm{cm^{-1}}$ (for Ni$K\alpha$, $\lambda=1.6591$ Å)

Multiple-film, equi-inclination Weissenberg photographs, $h0l$ through $h6l$, and $hk0$ through $hk3$, were taken with Ni$K\alpha$ radiation. The intensities were estimated by visual comparison with the calibrated intensity scale and were corrected for the Lp factor and spot-shape.[8] Since the crystal specimens used were sufficiently small ($\sim 0.10 \times 0.03 \times 0.4$ mm), the absorption correction was not applied. A total of 860 independent reflections were collected. However, 163 of these were too weak to be measured and so their intensities were assumed to be zero.

Determination of the Crystal Structure

At the early stages of this work, the electronic computer available to us was OKITAC 5090D, with which it was difficult to deal with the three-dimensional data; hence, we started on the structure analysis

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[5] K. Matsumoto, S. Ooi, and H. Kuroya, Presented at the 14th Symposium of Coordination Chemistry, Chemical Society of Japan, Nov. 1964, Fukuoka.

[6] K. Matsumoto, Y. Kushi, S. Ooi, and H. Kuroya, This Bulletin, **40**, 2988 (1967).

[7] K. Ohkawa, J. Fujita, and Y. Shimura, *ibid.*, **38**, 66 (1965).

[8] D. C. Philips, *Acta Crystallogr.*, **7**, 746 (1954).

by the two-dimensional method. The positions of the cobalt and chlorine atoms were found from the Patterson functions, $P(UW)$ and $P(UV)$. The remaining atroms were difficult to locate on the Fourier map $\rho(xz)$ phased by the heavy atoms, because of the poor resolution of the atomic peaks. Subsequently, the minimum function, $M(xy)$, was synthesized graphically[9] utilizing the coordinates of the Co and Cl atoms. The x and y coordinates of all the non-hydrogen atoms but the oxygen atom of the water molecule were found on the $M(xy)$ by the use of the scaled model of the complex ion. The oxygen atom could be located on the subsequent Fourier map, $\rho(xy)$. The crystal structure was refined to an R factor of 0.13 for the $hk0$ data by a diagonal least-squares method. At this stage, the z coordinate of each atom was readily obtained from the $\rho(xz)$. The R value for $h0l$ data was reduced to 0.14 by successive difference syntheses.

Further refinements were made by the block-diagonal least-squares method using the three-dimensional reflection data. The weighting scheme employed was as follows:

$$w=0.4 \text{ for } F_o<5.3$$

$$w=1.0 \text{ for } 5.3\leq F_o\leq 40.0$$

$$w=40.0/F_o \text{ for } F_o>40.0$$

The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[10] The real part of the anomalous dispersion correction for Co was taken into account.[11] After four cycles of the refinement with an individual isotropic temperature factor, the R value was reduced to 0.114 for the 697 non-zero reflections. A subsequent refinement in which the Co and Cl atoms were allowed to vibrate anisotropically could improve neither the R factor nor the e.s.d.'s of the parameters. A difference Fourier map calculated at this point confirmed the crystal structure, but did not show peaks corresponding to any of the hydrogen atoms. The final atomic coordinates and temperature factors are listed in Table 2; a complete list of the observed and calculated structure factors is preserved by the Chemical Society of Japan.[12]

TABLE 2. THE FINAL ATOMIC COORDINATES, TEMPERATURE FACTORS AND THEIR e.s.d.s.

Atom	x	y	z	B
Co	0.0632(6)	0.0000	0.1346(7)	2.38(7)
Cl	−0.2253(9)	0.1815(8)	0.5424(12)	3.4(1)
N_1	0.135(3)	0.087(2)	0.407(3)	2.4(4)
N_2	0.278(3)	−0.081(2)	0.247(4)	2.8(5)
N_3	−0.155(3)	0.086(2)	0.036(4)	3.5(5)
N_4	−0.063(3)	−0.110(2)	0.256(4)	2.6(4)
N_5	0.262(4)	0.179(3)	−0.037(4)	4.3(6)
N_6	−0.026(4)	−0.146(3)	−0.262(5)	4.6(6)
C_1	0.296(4)	0.035(3)	0.548(5)	4.6(7)
C_2	0.400(4)	−0.013(3)	0.419(5)	3.9(6)
C_3	−0.298(4)	0.009(3)	0.038(4)	3.4(5)
C_4	−0.243(4)	−0.064(3)	0.233(5)	3.7(6)
C_5	0.180(4)	0.108(3)	0.018(5)	3.0(5)
C_6	0.007(4)	−0.085(3)	−0.113(4)	2.6(5)
O	0.415(3)	−0.202(2)	−0.084(4)	4.8(5)

In order to determine the absolute configuration of the complex ion, the oscillation photographs were taken around the b axis with Cu$K\alpha$ radiation. The right-handed coordinate system was carefully used in the indexing of photographs throughout the present work. Some Bijvoet pairs are shown in Table 3, together with the observed inequality relationships. In the table, the intensities of the reflections, as calculated on the basis of the atomic coordinates in Table 2, are also listed. A comparison of the observed inequality relationships with the calculated ones indicates that the set of the atomic coordinates shown in Table 2 corresponds exactly to the absolute structure of the crystal.

TABLE 3. CALCULATED AND OBSERVED INTENSITIES

$h\ k\ l$	$F_c^2(hkl)$	obsd.	$h\ \bar{k}\ l$	$F_c^2(h\bar{k}l)$
2 1 2	49	<	$2\ \bar{1}\ 2$	178
2 1 5	140	<	$2\ \bar{1}\ 5$	307
2 1 1	1857	>	$2\ \bar{1}\ 1$	1062
3 1 1	615	<	$3\ \bar{1}\ 1$	1267
4 1 1	71	<	$4\ \bar{1}\ 1$	238
4 1 5	178	>	$4\ \bar{1}\ 5$	115
$6\ 1\ \bar{4}$	406	<	$6\ \bar{1}\ \bar{4}$	502
$6\ 1\ \bar{5}$	317	>	$6\ \bar{1}\ \bar{5}$	186
$6\ 1\ \bar{7}$	16	<	$6\ \bar{1}\ \bar{7}$	31
$7\ 1\ \bar{5}$	393	>	$7\ \bar{1}\ \bar{5}$	263
$7\ 1\ \bar{6}$	46	<	$7\ \bar{1}\ \bar{6}$	89

Result and Discussion

The absolute crystal structures viewed along the c and b axes are shown in Figs. 1 and 2 respectively. The crystal is composed of $(+)_{589}$-$[Co(CN)_2en_2]^+$, Cl^- and H_2O, which are held together mainly by ionic forces. In order to find the hydrogen bonds, the positions of the hydrogen atoms in the NH_2 groups were calculated on the assumption that the N-H bond length is 1.03 Å.[13] The data for the N-H···B hydrogen bonds (B=N, O, and Cl) are summarized in Table 4a. In the chelate ring involving N_1 and N_2, all the hydrogen atoms linked to the nitrogen atoms participate in the hydrogen bonding, while in another ring only one hydrogen atom of the individual NH_2

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[9] M. J. Buerger, "Vector Space," John Wiley & Sons, New York (1959), p. 271.

[10] "International Tables for X-ray Crystallography," Vol. III. Kynoch Press, Birmingham (1962), p. 202.

[11] R. W. James, "The Optical Principles of the Diffraction of X-rays," G. Bell & Sons, London (1948), p. 608.

[12] The complete data of the F_o-F_c table are kept as Document No. 7116 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and remitting, in advance, ¥400 for photoprints. Pay by check or money order payable to: Chemical Society of Japan.

[13] W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York (1968), p. 260.

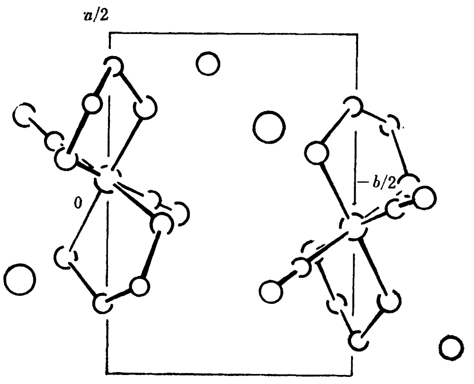


Fig. 1. The structure projected upon the (001) plane

Tablr 4a. Possible N-H···B bonds with N···B distances less than 3.50 Å

$(+)_{589}$-$[Co(CN)_2en_2]^+$

N	B	N···B	H···B	∠N-H-B
N_1	Cl	3.49 Å	2.58 Å	147°
N_1	$N_6(-x, -1/2+y, -z)$	3.31	2.41	157
N_2	O	3.08	2.12	154
N_2	$Cl(-x, -1/2+y, 1-z)$	3.20	2.17	180
N_3	$Cl(x, y, -1+z)$	3.33	2.30	180
N_4	$N_6(x, y, 1+z)$	3.14	2.24	145

Table 4b.

$(+)_{589}$-$[CoCl_2en_2]^+$ containing Co_1[a] as a central matal atom

N	B	N···B	H···B	∠N-H-B
N_1	$Cl_4(x, y, -1+z)$	3.46 Å	2.72 Å	129°
N_1	$O_2(x, y, -1+z)$	3.31	2.55	130
N_2	Cl_5	3.49	2.65	139
N_3	$Cl_6(1-x, 1/2+y, 1-z)$	3.34	2.39	153
N_3	$O_2(x, y, -1+z)$	3.15	2.51	120
N_4	Cl_5	3.47	2.65	138

$(+)$-$_{589}$-$[CoCl_2en_2]^+$ containing Co_2[a] as a central metal atom

N	B	N···B	H···B	∠N-H-B
N_5	Cl_1	3.40 Å	2.52 Å	143°
N_5	$O_1(x, y, -1+z)$	2.96	2.06	145
N_6	Cl_6	3.30	2.32	159
N_6	Cl_5	3.30	2.38	148
N_7	$O_1(x, y, -1+z)$	3.13	2.23	145
N_8	Cl_6	3.39	2.52	142
N_8	$Cl_2(-x, -1/2+y, 1-z)$	3.36	2.48	143

a) The atoms are labelled in the same way as in the previous paper.[15] There are two crystallographically-independent complex ions in the $(+)_{589}$-$[CoCl_2en_2]Cl\cdot H_2O$ crystal.

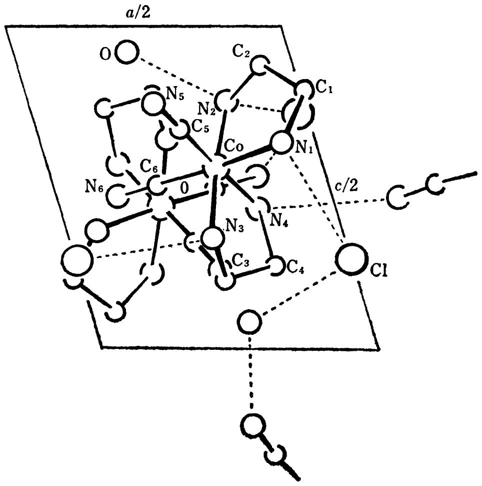
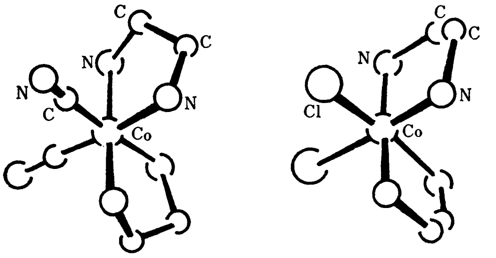


Fig. 2. The structure viewed along the *b* axis.

group takes part in the hydrogen bonding. The interatomic distance between $O(-x, 1/2+y, -z)$ and $N_5(x-1, y, z)$ is 3.08 Å, and that between $O(-x, 1/2+y, -z)$ and Cl is 3.27 Å, the Cl–O–N_5 angle being 102°. Thus, both of the hydrogen atoms of the water molecule seem to participate in the hydrogen bonding. The hydrogen bonds are shown in Fig.2 by the dashed lines.

The absolute configuration of $(+)_{589}$-$[Co(CN)_2en_2]^+$ is depicted in Fig. 3. This is in accordance with that proposed by Mason *et al.*[4] and can be denoted as $\Lambda(\lambda\lambda)$.[14] In the figure the absolute configuration of $(+)_{589}$-$[CoCl_2en_2]^+$ is also shown as a reference.[15] Both of the ethylenediamine molecules have the *ob* conformation in the present complex; thus, the complex cation can be described as having the *ob*-*ob* conformation. According to the conformational analysis made by Corey and Bailar,[16] the *ob*-*ob*-*ob* conformer is the least stable among the possible conformers of the trisethylenediamine complex. This probably holds true for the case of the *cis*-bisethylenediamine complex as well. As was stated in the previous paper,[15] however, the difference in the intramolecular potential energy between the most stable



$(+)_{589}$-$[Co(CN)_2en_2]^+$ $\Lambda(\lambda\lambda)$ $(+)_{589}$-$[CoCl_2en_2]^+$ $\Lambda(\delta\delta)$

Fig. 3. The absolute configurations of the complex ions.

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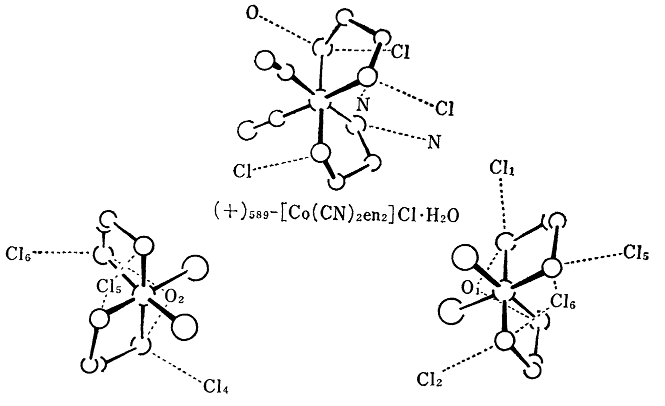
14) "Tentative Proposals (of the Commission on the Nomenclature of Inorganic Chemistry of IUPAC) for Nomenclature of Absolute Configurations," *Inorg. Chem.*, **9**, 1 (1970).

15) K. Matsumoto, S. Ooi, and H. Kuroya, This Bulletin, **43**, 3801 (1970).

16) E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

lel-lel conformer and the least stable *ob-ob* conformer is quite small in the bisethylenediamine complex, as compared with the case of the trisethylenediamine complex.

Ibers *et al.*[17] pointed out that the *lel-lel-lel* conformer of [Cr $en_3]^{3+}$ has fewer amine hydrogens which are free to form hydrogen bonds than does the *ob-ob-ob* conformer, and that the less stable latter conformer is favoured in the cases where strong hydrogen bonds can be formed. Though, in the bisethylenediamine complex, the situation is different from the case of the trisethylenediamine complex, their results seem also to be applicable to $(+)_{589}$-$[Co(CN)_2en_2]^+$ and $(+)_{589}$-$[CoCl_2en_2]^+$. In Fig. 4 are illustrated the hydrogen bonds coming out of the amine hydrogens of $(+)_{589}$-$[Co(CN)_2en_2]^+$ (*ob-ob*) and $(+)_{589}$-$[CoCl_2en_2]^+$(*lel-lel*), while the numerical data of the latter cation are listed in Table 4b. A comparison of these data with those of $(+)_{589}$-$[Co(CN)_2en_2]^+$ indicates that there are no appreciable differences in number and in length of the hydrogen bonds between these *lel-lel* and *ob-ob* conformers. Thus, the role of the hydrogen bonding in stabilizing the energetically-unfavourable *ob-ob* conformer does not seem so important in the bisethylenediamine complex as in the trisethylenediamine complex.



$(+)_{589}$-$[Co(CN)_2en_2]Cl\cdot H_2O$

$(+)_{589}$-$[CoCl_2en_2]Cl\cdot H_2O$ $(+)_{589}$-$[CoCl_2en_2]Cl\cdot H_2O$

Fig. 4. Possible hydrogen bonds around the complex ions.

TABLE 5. THE BOND DISTANCES AND ANGLES IN THE COMPLEX ION

Co-N_1	2.00(2) Å	N_1-Co-N_2	85(1)°
Co-N_2	1.94(3)	N_3-Co-N_4	86(1)
Co-N_3	1.98(3)	Co-N_1-C_1	109(2)
Co-N_4	1.96(2)	Co-N_2-C_2	111(2)
Co-C_5	1.88(3)	Co-N_3-C_3	109(2)
Co-C_6	1.85(3)	Co-N_4-C_4	109(2)
N_1-C_1	1.49(4)	N_1-C_1-C_2	110(3)
N_2-C_2	1.50(5)	N_2-C_2-C_1	106(3)
N_3-C_3	1.48(5)	N_3-C_3-C_4	108(3)
N_4-C_4	1.52(4)	N_4-C_4-C_3	109(3)
C_1-C_2	1.49(5)	Co-C_5-N_5	174(3)
C_3-C_4	1.50(5)	Co-C_6-N_6	175(3)
C_5-N_5	1.18(4)		
C_6-N_6	1.19(4)		

The bond distances and angles are given in Table 5. The Co–C bond is nearly collinear with the C–N bond. The average value of the Co–C bond length (1.87 Å) is in good agreement with that (1.869 Å) found in [Cr $en_3][Co(CN)_6]\cdot 6H_2O$,[18] but slightly less than the value (1.92 Å) in $(+)_{589}$-$[Co(C_{10}H_{28}N_6)][Co(CN)_6]\cdot 2H_2O$.[19] All the bond distances and angles in the chelate rings are normal.

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