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

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The crystal structure of *cis*-$(+)_{589}$-$[CoCl_2en_2]Cl\cdot H_2O$ has been determined by the X-ray-diffraction method. The crystal is monoclinic with the cell constants: $a=12.07$, $b=11.52$, $c=8.33$ Å, and $\beta=96.9°$. The space group is $P2_1$, and $Z=4$. There are two crystallographically-independent complexes in the unit cell, but they have the same configuration and almost identical molecular dimensions. The absolute configuration of the complex cation is consistent with that proposed by McCaffery, Mason and Norman and should be denoted as $\Lambda(\delta\delta)$.

Several investigations have been made of the absolute configurations of optically-active *cis*-$[CoX_2en_2]$ or *cis*-$[Co\widehat{XX}en_2]$ complexes, making use of their Cotton effects or chemical interconversions.[1-7] Particularly, McCaffery, Mason and Norman[7] made a detailed study of the CD spectra in the first absorption-band region on the *cis*-series of bisdiamine complexes of cobalt(III) and established a definitive correlation between the major CD bands of these complexes and that of the thoroughly-examined $(+)_{589}$-$[Co\ en_3]^{3+}$;[8] they thus succeeded in making assignment of the absolute configurations to these bisdiamine cobalt(III) complexes.

We have been attempting to determine directly the absolute configurations of several metallic complexes by the X-ray method. We wish here to report on the results obtained for *cis*-$(+)_{589}$-$[CoCl_2en_2]Cl\cdot H_2O$.

Experimental

The racemic "violeo" compound was prepared by the method of Jörgensen and resolved into optical isomers by utilizing its reaction with ammonium (+)-α-bromocamphor-π-sulfonate.[9] The crude chloride obtained from the less soluble diastereoisomer yielded, upon crystallization from a saturated aqueous solution, needle-like, deep violet crystals of $(+)_{589}$-$[CoCl_2en_2]Cl\cdot H_2O$.

The unit cell dimensions were determined by the least-squares refinement of the $hk0$ and $h0l$ reflection data recorded on Weissenberg photographs. The aluminum powder diffraction lines were superimposed on the films for calibration. The systematic absences were: $0k0$ for k=odd. Hence, the space group could be either $P2_1$ or $P2_1/m$. However, the latter should be excluded, since the crystal contains only one form of the enantiomorphous isomers.

The crystal data are as follows:

monoclinic
space group $P2_1$
$a=12.07\ (0.008)$Å
$b=11.52\ (0.007)$
$c=8.33\ (0.005)$
$\beta=96.9\ (0.2)°$
$Z=4\ (D_m=1.71,\ D_c=1.75\ \mathrm{g\cdot cm^{-3}})$
$\mu=100.6\ \mathrm{cm^{-1}}$ (for Ni$K\alpha$)

Weissenberg multiple-film photographs were taken for the 0—4 and 0—6 layers about the c and [101] axes respectively, with Ni$K\alpha$ radiation ($\lambda=1.6591$ Å). The relative intensities of 1159 independent reflections were measured visually, and the Lorenz, polarization, spot-shape,[10] and absorption corrections were applied. The specimen crystal used was a rod with the approximate dimensions of $0.12\times0.07\times1.0$ mm.

Determination of the Crystal Structure

Prior to the complete collection of the three-dimensional reflection data, $hk0$ and $h0l$ data were obtained and the Patterson functions, $P(UV)$ and $P(UW)$, were calculated.*1 Since the unit cell

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1) J. P. Mathieu, *Bull. Soc. Chim. Fr.*, **3**, 463, 476 (1936).

2) F. P. Dwyer, T. E. McDermott and A. M. Sargeson, *J. Am. Chem. Soc.*, **85**, 661 (1963).

3) T. Bürer, *Helv. Chim. Acta*, **46**, 242 (1963).

4) T. E. McDermott and A. M. Sargeson, *Aust. J. Chem.*, **16**, 334 (1963).

5) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, **1964**, 1368.

6) F. P. Dwyer, A. M. Sargeson and I. K. Reid, *J. Amer. Chem. Soc.*, **85**, 1215 (1963).

7) A. J. McCaffery, S. F. Mason and B. J. Norman, *J. Chem. Soc.*, **1965**, 5094.

8) K. Nakatsu, M. Shiro, Y. Saito and H. Kuroya, This Bulletin, **30**, 158 (1957).

9) S. M. Jörgensen, *J. Prakt. Chem.*, **41**, 448 (1890).

10) D. C. Philips, *Acta Crystallogr.*, **7**, 746 (1954).

*1 At the early stages of the present work, the electronic computer available to us was OKITAC 5090D, with which it is difficult to deal with the three-dimensional data; hence, we started the structure analysis by the two-dimensional method.

TABLE 1. THE FINAL ATOMIC COORDINATES, TEMPERATURE FACTORS AND THELIR e.s.d.

Temperature factors are of the form: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$.

Atom	x	y	z	Atom	x	y	z
Co 1	0.2542(5)	0.5000(6)	0.0567(8)	N 4	0.265(2)	0.499(2)	0.298(3)
Co 2	0.1317(5)	0.0877(6)	0.5273(8)	N 5	0.134(2)	0.089(2)	0.286(3)
Cl 1	0.172(1)	0.324(1)	0.050(1)	N 6	0.291(2)	0.052(2)	0.545(4)
Cl 2	0.090(1)	0.595(1)	0.033(1)	N 7	0.097(2)	−0.078(2)	0.532(4)
Cl 3	−0.055(1)	0.122(1)	0.490(1)	N 8	0.135(2)	0.088(3)	0.765(3)
Cl 4	0.173(1)	0.281(1)	0.542(1)	C 1	0.345(3)	0.596(4)	−0.230(5)
Cl 5	0.322(1)	0.781(1)	0.431(1)	C 2	0.310(4)	0.691(4)	−0.117(6)
Cl 6	0.408(1)	0.124(1)	0.911(1)	C 3	0.427(4)	0.323(4)	0.269(6)
O 1	0.050(2)	0.858(2)	0.191(3)	C 4	0.384(4)	0.479(4)	0.370(5)
O 2	0.471(3)	0.349(3)	0.748(4)	C 5	0.251(3)	0.052(3)	0.246(5)
N 1	0.249(2)	0.500(3)	−0.182(3)	C 6	0.337(3)	0.092(3)	0.400(4)
N 2	0.326(2)	0.649(3)	0.054(4)	C 7	0.066(3)	−0.106(3)	0.701(5)
N 3	0.397(3)	0.418(3)	0.084(4)	C 8	0.146(3)	−0.034(3)	0.823(5)

Atom	B_{11}	B_{22}	B_{33}	Atom B_{12}	B_{13}	B_{23}
Co 1	0.0046(5)	0.0067(5)	0.0062(13)	0.0009(9)	−0.0014(12)	0.0001(14)
Co 2	0.0042(4)	0.0063(5)	0.0073(13)	0.0003(8)	−0.0019(12)	0.0001(14)
Cl 1	0.0063(8)	0.0047(7)	0.0121(22)	−0.0016(12)	−0.0045(19)	−0.0007(19)
Cl 2	0.0036(6)	0.0086(8)	0.0122(21)	0.0023(13)	−0.0035(17)	−0.0030(22)
Cl 3	0.0041(6)	0.0066(8)	0.0134(21)	0.0021(12)	0.0000(18)	0.0021(20)
Cl 4	0.0074(8)	0.0041(6)	0.0104(21)	0.0003(12)	−0.0011(19)	−0.0023(18)
Cl 5	0.0087(9)	0.0072(8)	0.0128(23)	0.0007(15)	0.0026(22)	0.0043(22)
Cl 6	0.0047(7)	0.0115(11)	0.0122(22)	0.0011(15)	−0.0008(19)	0.0022(24)

Atom	B	Atom	B
O 1	4.4(6)	N 8	2.9(6)
O 2	6.8(8)	C 1	5.2(9)
N 1	2.7(5)	C 2	5.1(9)
N 2	3.7(7)	C 3	5.0(9)
N 3	4.9(8)	C 4	4.9(9)
N 4	2.5(5)	C 5	4.2(9)
N 5	2.1(5)	C 6	3.2(7)
N 6	3.4(6)	C 7	3.4(7)
N 7	3.0(6)	C 8	2.8(7)

contains four formula units, there are eight heavy atoms (two cobalt and six chlorine atoms) in the asymmetric unit. $P(UW)$ was difficult to be solved because of the peculiar arrangement of the Patterson peaks. The coordinates of the two Co atoms and one Cl atom were found by an elaborate examination of $P(UV)$. These coordinates were used for a graphical derivation of the minimum function, on which we found seven additional heavy peaks (not including the above three atoms). Of these seven peaks, the five heaviest were assumed to be Cl-atoms. The remaining atoms were found on the electron-density map phased by the eight heavy atoms thus obtained. The z-coordinate of each atom was determined by the use of $P(UV)$ and the Fourier map, $\rho(xz)$. Subsequent refinement by the diagonal least-squares method reduced R to 0.14 for $hk0$ and to 0.19 for $h0l$.

Further refinement of the structure was made by the block-diagonal, least-squares method using the three-dimensional data. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[11] The real part of the anomalous dispersion correction was taken into account for Co.[12] The function minimized was $\sum w(|F_o|-|F_c|)^2$, and the following weighting scheme was employed:

$$w = 0.5 \qquad \text{if } F_0 < F_{\min} \ (= 5.0)$$

$$w = 1.0 \qquad \text{if } F_{\min} \leq F_0 \leq F_{\max} \ (= 44.6)$$

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

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

$$w = F_{max}/F_0 \quad \text{if } F_0 > F_{max}$$

Three cycles of the refinement with isotropic thermal parameters reduced R to 0.150. At this stage, anisotropic temperature factors were introduced for the heavy atoms, and three further cycles of the least-squares calculation improved R to 0.109. The atomic parameter shifts in the last cycle of the refinement were less than their standard deviations. The final atomic coordinates, the temperature factors, and their e.s.d.'s are listed in Table 1.

In order to determine the absolute configuration of the complex ion, the $hk1$ and $hk2$ Weissenberg photographs were taken with Cu$K\alpha$ radiation.[*2] The inequality relationships which were observed for some Bijvoet pairs of hkl and $h\bar{k}l$ are shown in Table 2. In this table, the calculated intensities which were obtained by the use of the atomic coordinates shown in Table 1 are also listed. The values of $\Delta f'_{Co}$ and $\Delta f''_{Co}$ were taken from the International Tables for X-ray Crystallography.[11] A comparison of the observed inequalities with the calculated ones indicates that the atomic coordinates shown in Table 1 can give the absolute structure of the crystal.

TABLE 2. CALCULATED AND OBSERVED INTENSITY

hkl	$F_c^2(hkl)$	obs.	$h\bar{k}l$	$F_c^2(h\bar{k}l)$
$\bar{5}11$	645	<	$\bar{5}\bar{1}1$	1050
$\bar{6}21$	1832	>	$\bar{6}\bar{2}1$	1005
$\bar{7}21$	713	<	$\bar{7}\bar{2}1$	900
$\bar{8}21$	829	<	$\bar{8}\bar{2}1$	1076
$\bar{5}12$	1798	>	$\bar{5}\bar{1}2$	882
$\bar{8}22$	361	<	$\bar{8}\bar{2}2$	1274
$\bar{7}22$	432	>	$\bar{7}\bar{2}2$	196
312	566	<	$3\bar{1}2$	1436
412	4330	>	$4\bar{1}2$	2621
422	1347	<	$4\bar{2}2$	2079

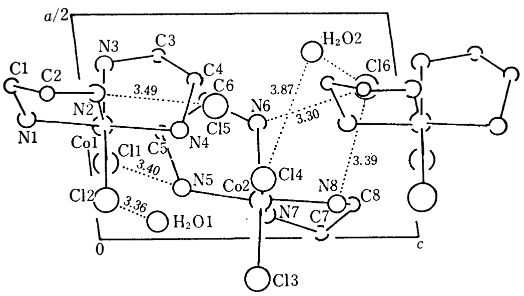

Fig. 1. The structure viewed along the b-axis.

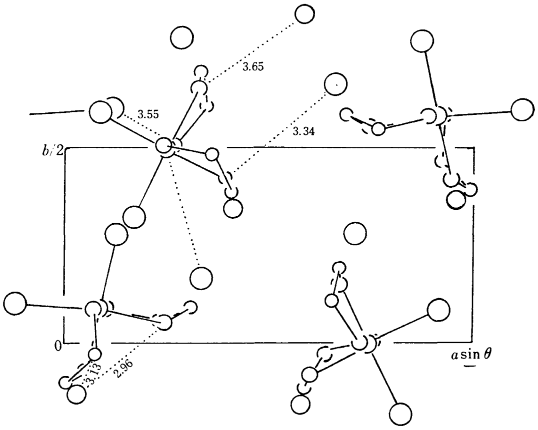

Fig. 2. The projection of the structure on the plane normal to the C-axis.

TABLE 3. THE BOND DISTANCES AND ANGLES IN THE COMPLEX IONS

Co1-Cl1	2.26(1)Å	Co2-Cl3	2.27(1)Å
Co1-Cl2	2.25(1)	Co2-Cl4	2.28(1)
Co1-N1	1.98(3)	Co2-N5	2.01(3)
Co1-N2	1.93(3)	Co2-N6	1.95(3)
Co1-N3	1.96(4)	Co2-N7	1.96(3)
Co1-N4	2.00(3)	Co2-N8	1.98(3)
N1-C1	1.52(6)	N5-C5	1.55(5)
N2-C2	1.49(6)	N6-C6	1.46(5)
N3-C3	1.59(6)	N7-C7	1.53(5)
N4-C4	1.50(5)	N8-C8	1.48(5)
C1-C2	1.47(7)	C5-C6	1.61(6)
C3-C4	1.53(6)	C7-C8	1.55(5)
∠Cl1-Co1-Cl2	93(1)°	∠Cl3-Co2-Cl4	92(1)°
∠N1-Co1-N2	87(1)	∠N5-Co2-N6	87(1)
∠N3-Co1-N4	86(1)	∠N7-Co2-N8	87(1)
∠Co1-N1-C1	108(2)	∠Co2-N5-C5	110(2)
∠Co1-N2-C2	107(2)	∠Co2-N6-C6	110(2)
∠Co1-N3-C3	109(3)	∠Co2-N7-C7	107(2)
∠Co1-N4-C4	110(2)	∠Co2-N8-C8	108(2)
∠N1-C1-C2	105(4)	∠N5-C5-C6	105(3)
∠N3-C3-C4	107(3)	∠N7-C7-C8	107(3)
∠N2-C2-C1	111(4)	∠N6-C6-C5	108(3)
∠N4-C4-C3	106(3)	∠N8-C8-C7	106(3)

Discussion

The crystal structure viewed along the b and c axes are shown in Figs. 1 and 2 respectively. The crystal is composed of $(+)_{589}$-$[CoCl_2en_2]^+$, Cl^-, and H_2O. Although, as has been stated previously, there are two crystallographically-independent complexes in an asymmetric unit, they have the same configuration and almost identical molecular dimensions, as is shown in Table 3. No significant differences are found in the corresponding bond lengths and angles. The absolute configuration of $(+)_{589}$-$[CoCl_2en_2]^+$ is illustrated in Fig. 3 (together with those of $(+)_{589}$-$[Co(CN)_2en_2]^+$[13] and $(+)_{589}$-$[Coen_3]^{3+}$,[8] which are given

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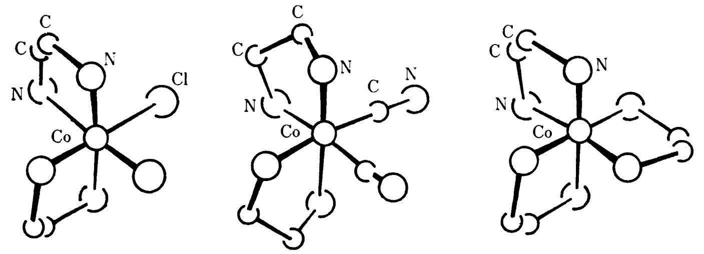
[*2] The right-handed coordinate system was used in the indexing of Weissenberg photographs throughout the present work.

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



$(+)_{589}$-$[CoCl_2en_2]^+$ $(+)_{589}$-$[Co(CN)_2en_2]^+$ $(+)_{589}$-$[Coen_3]^{3+}$

Fig. 3. The absolute configurations of $(+)_{589}$-$[CoCl_2en_2]^+$, $(+)_{589}$-$[Co(CN)_2en_2]^+$ and $(+)_{589}$-$[Coen_3]^{3+}$.

as references). This configuration is exactly in agreement with that proposed by Mason *et al.* and should be denoted as $\Lambda(\delta\delta)$, following the proposal of the IUPAC Commission.[14]

The conformation of the ethylenediamine molecules is of the "*lel-lel*" form in the present complex, whereas it is of the "*ob-ob*" form in $(+)_{589}$-$[Co(CN)_2en_2]Cl\cdot H_2O$[13] and of the "*ob-lel*" form in $(\pm)$-$[CoCl_2en_2]Cl\cdot H_2O$.[15]

On the basis of a conformational analysis of $[Coen_3]^{3+}$, Corey and Bailar predicted that the difference in the interaction energy between the three chelate rings would be 1.8 kcal/mole, the *lel-lel-lel* form being more stable, and the *ob-ob-ob* form, less stable.[16] This prediction was verified by the equilibrium study of $[Co(l\text{-}pn)_3]^{3+}$ by Dwyer *et al.*[17] In the case of *cis*-$[CoX_2en_2]$, however, if the X's are spherical (as in Cl) or cylindrical (as in CN): (1) the potential energy between the X's and each of the chelate rings is indifferent to the arrangement of the en-molecule—*ob* or *lel*—, and (2) the energy between the two chelate rings is one-third of that in the tris-ethylenediamine complex.[15] In short, though the degree of the steric interaction in the complex increases in the order of: *lel-lel*$<$*ob-lel*$<$*ob-ob*, (the *lel-lel* form being accordingly the most stable, and the *ob-ob* form, the least stable), the potential energy differences between these forms are quite small. This enables, on some occasions, the chelate ring to take the less-favored *ob-lel*[15] or *ob-ob*[13] form. The combination of *ob* and *lel* in a complex must, of course, be affected by the surroundings of the cation.

The distances of the notable short contacts are shown in Figs. 1 and 2. The nitrogen atoms of the ethylenediamine molecules form rather weak hydrogen bonds. That is, the cations are not very tightly bound by their environments; this must be the reason why the rings are of the *lel-lel* form in the crystal.[18]

The average value of Co-Cl is 2.26 Å, a value which is comparable to 2.286 Å in $[CoCl(NH_3)_5]Cl_2$[19] and 2.26 Å (average) in $(\pm)$-$[CoCl_2en_2]Cl\cdot H_2O$.[14] ∠Cl–Co–Cl is 91.8°, a value in good agreement with the 91.6° found in the racemate.[14] The bond lengths and angles in the ethylenediamine molecules are not accurate enough to be discussed in detail.

A complete list of the observed and calculated structure factors is preserved by the Chemical Society of Japan.*3

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[14] IUPAC Information Bull., No. **33**, 68 (1968).

[15] K. Matsumoto, S. Ooi and H. Kuroya, *Nippon Kagaku Zasshi*, **89**, 167 (1968).

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[17] F. P. Dwyer, F. L. Garvan and L. Shulman, *ibid.*, **81**, 290 (1959).

[18] K. N. Raymond, P. W. R. Corfield and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968); K. N. Raymond and J. A. Ibers, *ibid.*, **7**, 2333 (1968).

[19] G. G. Messmer and E. L. Amma, *Acta Crystallogr.*, **B24**, 417 (1968).

*3 The complete data of the F_0-F_c table are kept as Document No. 7008 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance, ¥600 for photoprints. Pay by check or money order, payable to: The Chemical Society of Japan.