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Absolute configuration of Λ-(+)$_{589}$-tris(ethylenediamine)cobalt(III) triiodide monohydrate

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Key indicators

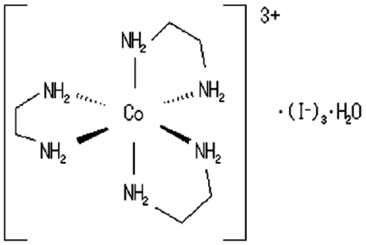
Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.005 Å
R factor = 0.023
wR factor = 0.066
Data-to-parameter ratio = 32.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure and absolute configuration of the title compound, Λ-(+)$_{589}$-[Co(C$_2$H$_8$N$_2$)$_3$]I$_3$·H$_2$O, has been determined. The configuration of the complex cation [Co(en)$_3$]$^{3+}$ is Λ(δδλ).

Comment

Compounds with the complex cation [Co(en)$_3$]$^{3+}$ (en = ethylenediamine) have played an important role in the development of crystallography for chiral crystals. [Co(en)$_3$]$^{3+}$ is the first transition metal complex not only to have its absolute configuration determined with anomalous scattering of X-rays (Saito *et al.*, 1955) but also to have its circular dichroism (CD) spectrum measured in both the solid and solution state (Mathieu, 1953; McCaffery & Mason, 1963). Therefore, it has been regarded as a model substance for investigating the relationship between a chiral crystal structure and the CD spectrum (Kuroda & Saito, 1976; Mason & Seal, 1976; Ernst & Royer, 1993).



(I)

In this study, we have examined the crystal structure and absolute configuration of the title compound, (I), for our study of the anisotropic character of optical activity (OA) and CD for [Co(en)$_3$]$^{3+}$ in the solid state. The ratio of the lattice constants is a:b:c = 0.449:0.600:1, explicitly different from that reported by Jaeger (1919) of a:b:c = 0.8276:1:0.7386. On the other hand, the ratio of the lattice constants of the racemic compound (Whuler *et al.*, 1980) is similar to Jaeger's report (Jaeger, 1919).

The configuration of the [Co(en)$_3$]$^{3+}$ complex in (I) is Λ(δδλ), meaning the lel$_2$ob form of the three ethylenediamine ligands. In the crystals of the racemate, the configuration is ob$_2$lel (Whuler *et al.*, 1980). Usually there occurs an inversion between conformations of ethylenediamine ligands δ and λ in solution. However, the difference of free energy of each ligand between δ and λ was reported to be about 2 kJ mol^{-1} (Beattie, 1971; Sudmeier & Blackmer, 1971). From a thermodynamic point of view, the magnitude of enthalpies in various config-

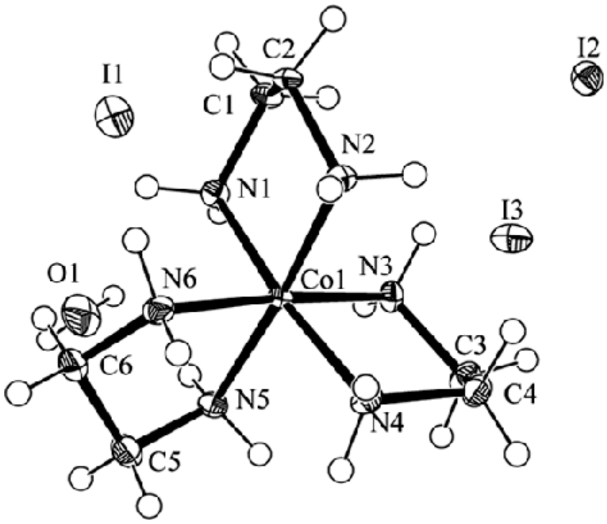


Figure 1
The molecular structure of the complex cation in (I) with displacement ellipsoids drawn at the 50% probability level.

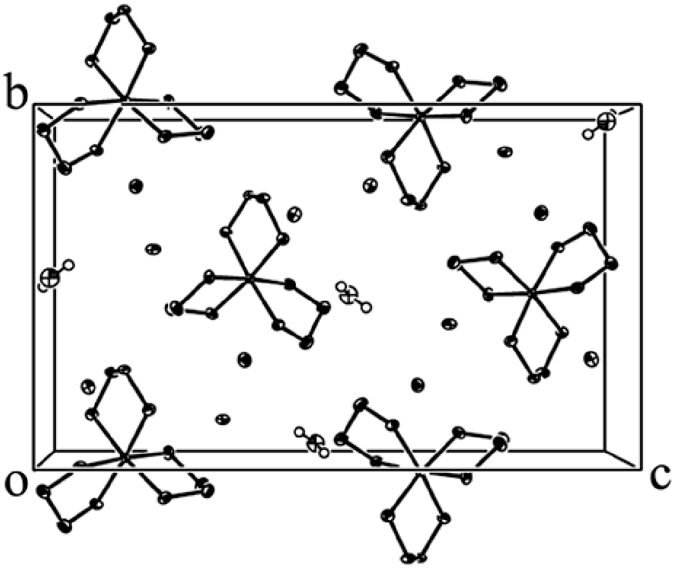


Figure 2
The crystal structure of (I) viewed along the the *a* axis.

urations of $[Co(en)_3]^{3+}$ was shown to be as follows; $lel_3 < lel_2ob < ob_2lel < ob_3$, where statistical and other entropy effects were not considered. The lel_2ob configuration is energetically more stable than ob_2lel. The complex cation in (I) may be energetically more stable than that in the racemate if the hydrogen bonding is not considered.

In (I), the Co—N bond distances are 1.949 (3)–1.981 (3) Å and the N—Co—N bond angles are 84.7 (1)–93.0 (1) and 173.3 (1)–175.8 (1)°. As shown in Fig. 2, the C_3 axis of the complex cation is approximately parallel to *a*.

Experimental

$[Co(en)_3]Cl·$D-tartrate$·5H_2O$ was prepared as described by Werner (1912) and was divided into its optical isomers by using solubility differences of the D-tartrate diastereoisomers. The optical isomer Λ-$(+)_{589}$-$[Co(en)_3]Cl·$d-tartrate$·5H_2O$ was converted into (I) by shaking with sodium iodide. The specific rotation of (I) in an aqueous solution at Na D line (589 nm) is +88.8° g^{-1} cm^3 dm^{-1}. Crystals of (I) were grown from 15% NaI aqueous solution by slow evaporation at 277 K. Because they effloresence in air, the specimen was protected by liquid paraffin and kept at 123 K during X-ray experiments.

Crystal data

$[Co(C_2H_8N_2)_3]I_3·H_2O$
$M_r = 637.96$
Orthorhombic, $P2_12_12_1$
$a = 8.4086$ (4) Å
$b = 11.2321$ (6) Å
$c = 18.7217$ (7) Å
$V = 1768.2$ (1) Å^3
$Z = 4$
$D_x = 2.397$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 10 070 reflections
$\theta = 2.2$–20.8°
$\mu = 6.21$ mm^{-1}
$T = 123.2$ K
Block, red
0.40 × 0.35 × 0.30 mm

Data collection

Rigaku R-AXIS–RAPID Imaging Plate diffractometer
ω scans
Absorption correction: by integration (*NUMABS*; Higashi, 1999)
$T_{\min} = 0.098$, $T_{\max} = 0.155$
20 028 measured reflections
5190 independent reflections
5024 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 30.1°$
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.066$
$S = 1.04$
5163 reflections
161 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^{\,2}) + \{0.05[{\rm Max}(F_o^{\,2},0) + 2F_c^{\,2}]/3\}^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.83$ e Å^{-3}
Absolute structure: (Flack, 1983), 2247 Friedel pairs
Flack parameter = 0.01 (3)

Table 1
Selected geometric parameters (Å, °).

Co1—N1	1.949 (3)	Co1—N4	1.968 (3)
Co1—N2	1.975 (3)	Co1—N5	1.981 (3)
Co1—N3	1.969 (3)	Co1—N6	1.963 (3)
N1—Co1—N2	85.4 (1)	N2—Co1—N6	90.6 (1)
N1—Co1—N3	90.2 (1)	N3—Co1—N4	85.4 (1)
N1—Co1—N4	173.3 (1)	N3—Co1—N5	91.7 (1)
N1—Co1—N5	92.3 (1)	N3—Co1—N6	175.8 (1)
N1—Co1—N6	92.3 (1)	N4—Co1—N5	92.9 (1)
N2—Co1—N3	93.0 (1)	N4—Co1—N6	92.4 (1)
N2—Co1—N4	89.8 (1)	N5—Co1—N6	84.7 (1)
N2—Co1—N5	174.7 (1)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N′···N6	0.95	2.59	2.821 (4)	94
N2—H2N′···N3	0.95	2.67	2.862 (4)	92
N3—H3N′···N2	0.95	2.66	2.862 (4)	92
N4—H4N′···N5	0.95	2.63	2.862 (4)	94
N5—H5N···N1	0.95	2.63	2.834 (4)	93
N6—H6N···N4	0.95	2.60	2.838 (4)	94
N1—H1N···O1	0.95	2.66	3.211 (4)	117
N5—H5N···O1	0.95	2.11	2.970 (4)	150

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All H atoms of the en ligands were placed in idealized positions and refined as riding atoms with isotropic displacement parameters. Those of the water molecule were located from difference Fourier maps and their positional parameters refined.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation and Rigaku, 1999); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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