

Table 5. *Torsion angles (°) for the glutamate anion*

E.s.d.'s are 0.3°. Signs of the angles reflect the convention of Klyne & Prelog (1960).

O(1)–C(1)–C(2)–N(1)	–18.2
O(2)–C(1)–C(2)–N(1)	163.7
O(1)–C(1)–C(2)–C(3)	105.6
O(2)–C(1)–C(2)–C(3)	–72.6
C(1)–C(2)–C(3)–C(4)	–179.6
N(1)–C(2)–C(3)–C(4)	–56.0
C(2)–C(3)–C(4)–C(5)	–160.7
C(3)–C(4)–C(5)–O(3)	15.7
C(3)–C(4)–C(5)–O(4)	–166.4

glutamate conformation in these calcium glutamate salts are similar to those found in other glutamate crystal structures.

These studies of crystalline calcium–glutamate complexes suggest that the carboxyl groups of glutamate residues in proteins may serve as either bidentate or unidentate ligands in calcium binding sites. If the bidentate mode is employed, one should expect a higher Ca coordination number (*e.g.* 7 or 8) and somewhat larger Ca–O distances on average. On the other hand, if the unidentate mode is employed, lower Ca coordination numbers are possible and one should expect shorter Ca–O distances on average. A preliminary survey of calcium–carboxyl interactions in a variety of crystalline complexes has been made (Einspahr & Bugg, 1977). This survey suggests that the bidentate mode cannot be accommodated in sixfold calcium coordination polyhedra, although the unidentate mode often contributes to calcium-binding sites of coordination numbers seven and eight. In addition, the ratio of numbers of unidentate to bidentate examples in the survey is about four to one.

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The Crystal Structure of (+)₄₇₀-*cis*-Diamminebis(*R,R*-2,4-diaminopentane)cobalt(III) Trichloride Monohydrate

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Abstract

Crystals of [Co(C₃H₁₄N₂)₂(NH₃)₂]Cl₃·H₂O, C₁₀H₃₄Cl₃CoN₆·H₂O, are orthorhombic, space group *P*2₁2₁2₁, with *a* = 11.575 (1), *b* = 17.023 (1), *c* = 10.679 (1) Å and *Z* = 4. Block-diagonal least-squares

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refinement reduced the *R* value to 0.033 for 3784 independent reflexions collected by diffractometry. The complex cation has an approximate twofold symmetry. The six-membered chelate rings take the skew-boat conformation with both C–CH₃ bonds in equatorial positions. The absolute configuration of the complex

ion can be designated as *Δ*. The average Co–N(NH₃) distance [1.992 (3) Å] is slightly longer than that in the chelate rings [1.977 (2) Å].

Introduction

There exist three isomers of the complex ion, [Co(NH₃)₂(*R,R*-ptn)₂]³⁺, *trans*, *Δ*-*cis*, and *Λ*-*cis* forms, all of which have been synthesized and characterized (Kojima, Fujita & Fujita, 1977). Crystals of (+)₄₇₀-*cis*-[Co(NH₃)₂(*R,R*-ptn)₂]Cl₃·H₂O were subjected to X-ray crystal structure analysis in order to gain the conformational details of the complex ion and to verify its absolute configuration assigned on the basis of the solution CD spectrum.

Experimental

Orange-red platy crystals were kindly provided by Professor Fujita of Nagoya University.

Crystal data: (+)₄₇₀-*Δ*-*cis*-[Co(NH₃)₂(*R,R*-ptn)₂]Cl₃·H₂O; C₁₀H₃₄Cl₃CoN₆·H₂O, FW 421.4, orthorhombic, *a* = 11.575 (1), *b* = 17.023 (1), *c* = 10.679 (1) Å, *U* = 2104.2 Å³, *D_m* = 1.32 (floatation, nitrobenzene/trichloroethylene), *D_x* = 1.33 Mg m⁻³, μ(Mo *K*α) = 1.23 mm⁻¹, space group *P*2₁2₁2₁, *Z* = 4.

A crystal specimen used for intensity measurements was shaped into an approximate sphere of diameter 0.46 mm. Intensity data were collected on a Rigaku automated four-circle diffractometer using Mo *K*α radiation monochromated by a graphite plate. The *θ*–2*θ* scan technique was employed up to 2*θ* = 65°. 4242 reflexions were measured, from which 3784 independent reflexions with *I* > 3σ(*I*) were used for the structure refinement. Data were corrected for Lorentz–polarization factors, but an absorption correction was not applied.

Structure determination and refinement

The weak intensities of odd-layer reflexions on the oscillation photographs around the *b* axis indicated that the Co atoms lie close to the twofold screw axis. The positions of Co, six N and two Cl atoms were deduced from three-dimensional Patterson map; however, such an unusual location of the Co atom did not exhibit the full phase-determining power. Thus attempts to solve the structure by the heavy-atom method failed.

The structure was solved by the direct method with program *TANGEN* written by Ohashi (unpublished) using 500 *|E|*'s greater than 1.70. The origin was specified by reflexions 507 (*E* = 2.5), 1,12,0 (*E* = 2.7) and 052 (*E* = 1.8). In addition, the phases for the 682 and 2,14,7 reflexions (*E* = 2.5) were chosen as follows:

$\pm\pi/4$, $\pm 3\pi/4$ to ensure that the starting phases were within $\pi/4$ of their true values, and the enantiomorph was fixed by 682. The *E* map based on the set with the lowest *R* value revealed the CoN₆ group and two possible arrangements of the Cl atoms.

Starting with the positions of the CoN₆ group, the positions of all non-hydrogen atoms were derived by the Fourier method. They were refined by a block-diagonal least-squares program with anisotropic temperature factors. With *R* = 0.067, all the H were located from a difference synthesis, except those of the water molecules. Further refinement was carried out with all atoms included. The final *R* became 0.033 for the 3784 observed reflexions. The average isotropic temperature factor for the H atoms was 5.5 (1.2) Å². A weighting scheme, *w* = 0.5 for *F_o* < 20, and *w* = 1 for all other *F_o*'s, was employed. The largest shift: error ratio was 0.6 and a final difference synthesis showed no peaks of height greater than 0.5 e Å⁻³. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The atomic coordinates are listed in Table 1.*

Determination of the absolute configuration

The absolute configuration of the complex cation was assigned as *Δ* with reference to the known absolute configuration of *R,R*-2,4-diaminopentane (Kobayashi, Marumo & Saito, 1972, 1973). In order to confirm the absolute configuration, equi-inclination Weissenberg photographs were taken with Cu *K*α radiation.*

Description of the structure and discussion

The structure of the complex cation

A perspective view of the cation along the axis of the complex is presented in Fig. 1.† The complex has *C*₂ pseudosymmetry. Bond distances and angles within the complex are listed in Table 2. The average Co–N(NH₃) bond distance is longer by 0.015 Å than that in the chelate rings. Each Co–N bond in the chelate ring is inclined at a mean angle of 53.8° with respect to the axis of the complex, whereas the Co–N(NH₃) is inclined at a mean angle of 54.9°. The

* Lists of structure factors and anisotropic temperature factors, and a table of observed and calculated intensity relations between some Bijvoet pairs have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33963 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The axis of the complex ion is defined as a normal to the plane through the midpoint of the line joining the two N atoms of each chelate ligand and the two NH₃ molecules, respectively.

Table 1. Positional parameters ($\times 10^4$ for non-hydrogen atoms; $\times 10^3$ for hydrogen atoms)

	x	y	z
Co	4924 (0)	600 (0)	2405 (0)
Cl(1)	5124 (1)	3059 (1)	1638 (1)
Cl(2)	7648 (1)	4178 (1)	4689 (1)
Cl(3)	2216 (1)	4649 (1)	386 (1)
N(1)	3211 (2)	567 (2)	2289 (3)
N(2)	4964 (3)	1221 (1)	846 (2)
N(3)	4806 (2)	1533 (1)	3507 (2)
N(4)	6614 (2)	680 (1)	2490 (3)
N(5)	5083 (3)	-372 (1)	1376 (3)
N(6)	4863 (3)	-72 (1)	3930 (2)
C(1)	1327 (4)	1228 (3)	2012 (5)
C(2)	2623 (3)	1284 (2)	1790 (4)
C(3)	2887 (4)	1415 (3)	404 (5)
C(4)	4004 (4)	1086 (2)	-70 (4)
C(5)	4336 (5)	1436 (4)	-1341 (4)
C(6)	5344 (4)	2265 (3)	5419 (4)
C(7)	5727 (3)	1643 (2)	4488 (3)
C(8)	6887 (3)	1828 (3)	3924 (4)
C(9)	7138 (3)	1484 (2)	2636 (4)
C(10)	8439 (3)	1434 (3)	2392 (5)
OW	2714 (6)	3489 (4)	2727 (6)
H(N1)1	318 (5)	15 (4)	164 (6)
H(N1)2	305 (4)	45 (3)	305 (4)
H(N2)1	589 (5)	107 (3)	31 (6)
H(N2)2	518 (4)	171 (2)	90 (4)
H(N3)1	454 (4)	195 (3)	322 (4)
H(N3)2	396 (3)	146 (2)	398 (4)
H(N4)1	682 (3)	40 (2)	182 (4)
H(N4)2	671 (4)	45 (3)	299 (5)
H(N5)1	566 (5)	-38 (3)	76 (5)
H(N5)2	422 (4)	-59 (3)	110 (4)
H(N5)3	596 (5)	-75 (4)	187 (6)
H(N6)1	433 (5)	-47 (3)	390 (5)
H(N6)2	578 (4)	-3 (2)	436 (4)
H(N6)3	408 (6)	11 (4)	477 (7)
H(C1)1	104 (4)	171 (2)	159 (4)
H(C1)2	106 (3)	86 (2)	173 (3)
H(C1)3	112 (4)	130 (2)	274 (4)
H(C2)1	294 (3)	171 (2)	216 (4)
H(C3)1	317 (4)	203 (3)	4 (5)
H(C3)2	164 (5)	125 (4)	15 (6)
H(C4)1	388 (3)	56 (2)	-15 (4)
H(C5)1	375 (3)	140 (2)	-185 (4)
H(C5)2	443 (4)	198 (3)	-134 (4)
H(C5)3	486 (5)	128 (3)	-164 (5)
H(C6)1	553 (4)	265 (2)	523 (5)
H(C6)2	430 (5)	218 (3)	598 (5)
H(C6)3	606 (4)	229 (2)	603 (4)
H(C7)1	592 (4)	113 (2)	494 (4)
H(C8)1	670 (5)	234 (3)	378 (5)
H(C8)2	749 (5)	166 (3)	453 (5)
H(C9)1	670 (3)	185 (2)	205 (4)
H(C10)1	864 (4)	132 (2)	156 (4)
H(C10)2	878 (3)	187 (2)	249 (4)
H(C10)3	873 (3)	109 (2)	293 (4)

two chelate rings take a skew-boat conformation with the C-CH₃ bonds equatorial. Edge-on views of the chelate rings with respect to the plane formed by the Co and the two N atoms are shown in Fig. 2. Although the N-C bond distances and Co-N-C angles are slightly different, the geometries of the two chelate rings in the present complex are similar to each other and to that

Table 2. Interatomic distances (Å) and bond angles (°) within the complex ion with their standard deviations in parentheses

	A	B	NH ₃	[Co(R,R-ptn) ₃] ³⁺ *
Co-N	1.987 (2)	1.982 (2)	1.994 (2)	1.985 (9)
N-C	1.973 (2)	1.964 (2)	1.990 (3)	1.498 (15)
C-C	1.498 (5)	1.504 (4)		1.530 (19)
C-C _{Me}	1.498 (5)	1.524 (6)		1.516 (18)
N-Co-N	89.2 (1)	89.1 (1)	88.7 (1)	89.0 (4)
Co-N-C	117.0 (2)	117.6 (2)		118.0 (7)
N-C-C	116.8 (2)	118.1 (2)		112.0 (10)
N-C-C _{Me}	112.0 (3)	112.3 (3)		109.1 (10)
C-C-C	111.2 (3)	111.5 (3)		117.2 (11)
C-C-C _{Me}	110.1 (3)	109.6 (3)		113.9 (10)
	109.5 (3)	109.2 (3)		
	116.4 (4)	116.8 (3)		
	111.0 (4)	112.1 (3)		
	111.7 (4)	111.2 (3)		
Dihedral angles				
N-Co-N-C	36.0 (2)	35.5 (2)		
Co-N-C-C	29.3 (2)	31.1 (2)		
Co-N-C-C _{Me}	67.7 (4)	68.1 (3)		67.7
	71.2 (4)	69.1 (3)		
N-C-C-C	168.3 (3)	166.7 (2)		168.8
	164.9 (3)	167.6 (2)		
	26.3 (5)	30.5 (5)		33.0
	41.8 (5)	35.8 (4)		
C-C-C-C _{Me}	149.6 (4)	154.4 (3)		
	164.4 (4)	157.9 (3)		

* Kobayashi, Marumo & Saito (1973).

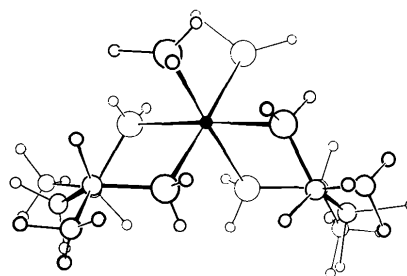
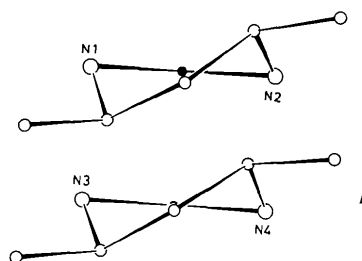
Fig. 1. A perspective view of the complex cation, (+)₄₇₀ [Co(NH₃)₂(R,R-ptn)₂]³⁺.

Fig. 2. Edge-on views of the chelate rings, A and B, with respect to the plane formed by the Co and the two N atoms.

observed in (-)₅₄₆-[Co(R,R-ptn)₃]Cl₃·H₂O (Kobayashi *et al.*, 1973).

The crystal packing

The packing mode of this crystal is illustrated in Fig. 3. Short interatomic distances outside the complex ion are listed in Table 3. Cl(1) connects two complex cations by Cl···H—N hydrogen bonds. Two Cl⁻ ions, Cl(2) and Cl(3), are arranged nearly on the axis of the

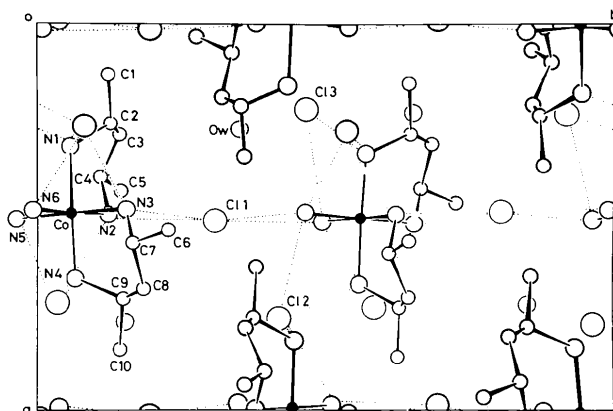


Fig. 3. A projection of the crystal structure along *c*.

Table 3. Interatomic distances (Å) outside the complex ion less than 3.5 Å

Symmetry code

(i)	<i>x</i> ,	<i>y</i> ,	<i>z</i>	(iv)	$\frac{1}{2} + x$,	$\frac{1}{2} - y$,	$-z$
(ii)	$-\frac{1}{2} + x$,	$\frac{1}{2} - y$,	$1 - z$	(v)	$-1 + x$,	<i>y</i> ,	<i>z</i>
(iii)	$1 - x$,	$\frac{1}{2} + y$,	$\frac{1}{2} - z$				

Cl(1)—N(2)	3.246 (3)*	N(1)—Cl(2 ⁱⁱ)	3.321 (3)*
Cl(1)—N(3 ⁱ)	3.296 (3)*	N(2)—Cl(3 ^{iv})	3.274 (3)*
Cl(1)—O ^w ⁱ	3.106 (7)	N(3)—Cl(2 ⁱⁱ)	3.379 (3)*
Cl(1)—N(5 ⁱⁱⁱ)	3.419 (3)*	N(4)—Cl(3 ^{iv})	3.199 (3)*
Cl(1)—N(6 ⁱⁱⁱ)	3.240 (3)*	N(5)—Cl(3 ^{iv})	3.339 (3)*
Cl(2)—N(1 ⁱⁱⁱ)	3.323 (3)*	N(6)—Cl(2 ⁱⁱ)	3.326 (3)*
Cl(2)—N(5 ⁱⁱⁱ)	3.446 (3)*	OW···N(5 ⁱⁱⁱ)	3.344 (8)
Cl(3)—O ^w ⁱ	3.240 (6)	C(1)—C(10 ^v)	3.385 (6)
Cl(3)—N(4 ⁱⁱⁱ)	3.171 (3)*		
Cl(3)—N(6 ⁱⁱⁱ)	3.492 (3)*		

* Hydrogen bonding.

complex. Each of these two Cl⁻ ions forms three Cl···H—N hydrogen bonds with a complex cation. A similar hydrogen-bonding scheme was observed in (+)₅₈₉-[Co(en)₃]Cl₃·H₂O (Iwata, Nakatsu & Saito, 1969). The closest approach occurs between OW and two Cl⁻ ions [Cl(1) and Cl(3)].

The CD spectra of (+)₄₇₀-Δ-[Co(NH₃)₂(R,R-ptn)₂]³⁺ in aqueous solution show two peaks of opposite sign in the region of the first absorption band ($\nu = 19.3 \times 10^2 \text{ mm}^{-1}$, $\Delta\epsilon = -0.22$ and $\nu = 21.5 \times 10^2 \text{ mm}^{-1}$, $\Delta\epsilon = +0.09$; Kojima, Fujita & Fujita, 1977). These authors observed the CD variation on the addition of sulfate ions. This phenomenon was explained by an ion-pair formation. Our X-ray evidence indicates that when the R,R-ptn chelate rings take a skew-boat form, a set of three N—H bonds, two from R,R-ptn and one from an ammonia molecule, are oriented favorably for hydrogen-bond formation with a sulfate ion (see Fig. 1). Thus it may be reasonable to assume that the conformation of the flexible R,R-ptn chelate rings is stabilized in the skew-boat conformation by forming such hydrogen bonds in solution.

The calculations were carried out on the FACOM 230-48 of this Institute. The program *TANGEN* was used on the HITAC 8700/8800 at the Computer Center of the University of Tokyo. The authors are grateful to Dr Y. Ohashi of Tokyo Institute of Technology for providing the program. Part of the cost of this research was met by a Scientific Research Grant from the Ministry of Education, to which the authors' thanks are due.

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