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References

BEDDOE, P. G., HARDING, M. J., MASON, S. F. & PEART, B. J. (1971). *Chem. Commun.* p. 1283.
 GEUE, R. J. & SNOW, M. R. (1971). *J. Chem. Soc. (A)* pp. 2981–2987.

GOLLOGLY, J. R. & HAWKINS, C. J. (1972). *Inorg. Chem.* **11**, 156–161.
International Tables for X-ray Crystallography. (1962). Vol. III. Birmingham: Kynoch Press.
 IWATA, M., NAKATSU, K. & SAITO, Y. (1969). *Acta Cryst.* **B25**, 2562–2571.
 LIQUORI, A. M., DAMIANI, A. & ELEFANTE, G. (1968). *J. Mol. Biol.* **33**, 439–444.
 NIKETIĆ, S. Q. & WOLDBYE, F. (1973). *Acta Chem. Scand.* **27**, 621–642.
 NOMURA, T., MARUMO, F., SAITO, Y. (1969). *Bull. Chem. Soc. Japan*, **42**, 1016–1020.

Acta Cryst. (1973). **B29**, 2443

The Crystal Structure of $(-)_546$ -Tris- $(R,R$ -2,4-diaminopentane)cobalt(III) Chloride Dihydrate, $(-)_546$ -[Co(R,R -ptn) $_3$]Cl $_3$ ·2H $_2$ O

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The structure of $(-)_546$ -[Co(R,R -ptn) $_3$]Cl $_3$ ·2H $_2$ O has been determined from three-dimensional X-ray data collected by the diffractometer method. The compound forms tetragonal crystals with $a = 11.395$ (1), $c = 20.242$ (1) Å and $Z = 4$ in space group $P4_32_12$. The structure has been refined by least-squares methods with anisotropic temperature factors to an R value of 0.039 for 3016 observed reflexions. The complex cation has an approximate D_3 symmetry. The six-membered chelate ring has a twisted-boat form. The two methyl groups are in equatorial positions with respect to the average plane of the chelate ring. The mean N–Co–N angle is 89.1° . The absolute configuration is Δ and that of the three chelate rings is λ . The line joining the two asymmetric carbon atoms makes an angle of 2° with respect to the quasi-threefold axis of rotation.

Introduction

$(-)_546$ -Tris- $(R,R$ -2,4-diaminopentane)cobalt(III) chloride dihydrate, $(-)_546$ -[Co(R,R -ptn) $_3$]Cl $_3$ ·2H $_2$ O is one of the two isomers of tris- $(R,R$ -2,4-diaminopentane)cobalt(III) salts (Mizukami, Ito, Fujita & Saito, 1970). This isomer was assigned as a Δ isomer from the negative circular dichroism band in the first transition region. The crystal structure was determined in order to gain conformational details of the complex ion. The crystal structure of the other isomer has already been determined (Kobayashi, Marumo & Saito, 1972).

Experimental

Crystals of $(-)_546$ -[Co(R,R -ptn) $_3$]Cl $_3$ ·2H $_2$ O were kindly supplied by Professor J. Fujita of Tohoku University. They are needle-like orange-red crystals. The unit-cell dimensions determined from higher-order reflexions recorded on Weissenberg photographs were later re-

fined by employing data obtained on a single-crystal diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å).

Crystal data are: $(-)_546$ -Co(C $_5$ H $_{14}$ N $_2$) $_3$ Cl $_3$ ·2H $_2$ O, F.W. 507.9; tetragonal, $a = 11.395$ (1), $c = 20.242$ (1) Å, $U = 2630$ Å 3 ; $D_m = 1.280$ g cm $^{-3}$, $Z = 4$, $D_x = 1.283$ g cm $^{-3}$. Space group $P4_32_12$ (No. 96). Linear absorption coefficient for Mo $K\alpha$, $\mu = 9.99$ cm $^{-1}$.

The intensity data were collected on a Rigaku automated four-circle diffractometer. The specimen was ground into a sphere of about 0.23 mm diameter. The ω - 2θ scan technique was employed. Mo $K\alpha$ radiation monochromated by a graphite crystal was used. A set of standard reflexions was measured every 50 reflexions during the data collection. A total of 3500 reflexions were measured up to $2\theta = 55^\circ$. Those reflexions which were non-equivalent as a result of anomalous dispersion were treated as independent reflexions. The reflexions of which the intensities were less than three times their standard deviations were regarded as 'unobserved' and were not included in subsequent calculations. Thus, 3016 independent reflexions were collected. The intensities were corrected for Lorentz and polarization effects, but corrections for absorption and extinction were not applied.

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Table 1. *Atomic parameters*

The values of β_{ij} refer to the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Here and elsewhere in this paper the estimated standard deviations in the last figure are given in parentheses.

(a) Heavy atoms. Values are $\times 10^4$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	5286 (0)	4714 (0)	7500	30 (0)	30 (0)	13 (0)	0 (0)	0 (0)	0 (0)
Cl(1)	7002 (1)	7002 (1)	0	70 (1)	70 (1)	30 (0)	-22 (1)	-7 (1)	7 (1)
Cl(2)	7598 (1)	7082 (1)	6832 (1)	79 (1)	72 (1)	27 (0)	-30 (1)	1 (0)	7 (0)
N(1)	5298 (2)	3007 (3)	7291 (1)	37 (2)	42 (2)	16 (1)	-2 (2)	1 (1)	0 (1)
N(2)	5662 (2)	5051 (2)	6561 (1)	42 (2)	46 (2)	15 (1)	-1 (2)	0 (1)	-2 (1)
N(3)	5243 (2)	6436 (3)	7670 (1)	50 (2)	36 (2)	19 (1)	1 (2)	-3 (1)	0 (1)
C(1)	6758 (5)	4765 (4)	5528 (2)	94 (4)	85 (4)	20 (1)	-6 (4)	4 (2)	-11 (2)
C(2)	6437 (4)	4228 (3)	6194 (2)	69 (4)	54 (3)	17 (1)	-3 (1)	-4 (1)	-6 (1)
C(3)	4973 (3)	2640 (3)	6606 (2)	40 (2)	62 (3)	21 (1)	2 (2)	-7 (1)	4 (1)
C(4)	5868 (4)	3017 (4)	6103 (2)	59 (3)	103 (4)	21 (1)	6 (3)	-10 (2)	-11 (2)
C(5)	4812 (3)	1316 (4)	6579 (2)	43 (3)	92 (4)	35 (1)	10 (3)	-13 (2)	-5 (2)
C(6)	4371 (3)	7142 (3)	7286 (2)	48 (3)	56 (3)	28 (1)	-6 (1)	6 (1)	3 (2)
C(7)	4679 (3)	8466 (5)	7353 (3)	45 (3)	99 (4)	53 (2)	-6 (3)	4 (2)	6 (3)
C(8)	3121 (3)	6879 (3)	7500	55 (5)	55 (5)	27 (2)	-18 (3)	0 (4)	0 (4)
O	4756 (3)	6719 (3)	9089 (1)	86 (3)	77 (2)	24 (1)	-6 (3)	12 (1)	2 (1)

Table 1 (cont.)

(b) Hydrogen atoms. Values are $\times 10^3$. The average isotropic temperature factor of hydrogen atoms is 3.5 \AA^2 .

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	488 (4)	509 (4)	631 (2)
H(2)	605 (4)	587 (4)	655 (2)
H(3)	593 (4)	269 (4)	744 (2)
H(4)	469 (4)	268 (4)	750 (2)
H(5)	600 (4)	681 (4)	752 (2)
H(6)	524 (4)	651 (4)	765 (2)
H(7)	546 (5)	301 (5)	565 (2)
H(8)	653 (5)	240 (5)	610 (2)
H(9)	294 (4)	744 (4)	797 (2)
H(10)	431 (4)	305 (4)	662 (2)
H(11)	719 (5)	410 (5)	647 (2)
H(12)	441 (5)	691 (5)	679 (2)
H(13)	602 (5)	505 (4)	528 (2)
H(14)	719 (5)	407 (5)	525 (2)
H(15)	733 (5)	547 (4)	559 (3)
H(16)	468 (4)	100 (5)	616 (2)
H(17)	430 (4)	98 (4)	690 (2)
H(18)	545 (4)	82 (5)	677 (2)
H(19)	481 (4)	870 (5)	781 (2)
H(20)	543 (5)	864 (5)	708 (2)
H(21)	400 (5)	897 (5)	717 (3)

Determination of the structure

The general position of the space group $P4_32_12$ is eightfold. The four cobalt atoms and four of the chloride ions are required to lie on twofold axis of rotation. This fact was confirmed by examining three-dimensional Patterson maps and the positions of the heavy atoms were easily fixed. The positions of the other lighter atoms except hydrogen were determined by routine application of the heavy-atom method. Block-diagonal least-squares refinement using anisotropic temperature factors reduced the *R* value (defined by $\sum||F_o| - |F_c|| / \sum|F_o|$) to 0.045. At this stage a difference Fourier synthesis was carried out, which revealed all the hydrogen atoms in plausible positions. Further refinement was carried out including the hydrogen atoms, where the thermal parameters of the hydrogen atoms

were assumed to be isotropic. The final *R* value was 0.039 for the 3016 observed reflexions. At the final stage of the refinement all the parameter shifts of the non-hydrogen atoms were less than one half of their standard deviations. A weighting scheme $w=1$ if $|F_o| \geq 15$ and $w=0.2$ otherwise was employed. The atomic scattering factors and the corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1962). Table 1 lists the final atomic parameters and their standard deviations. The observed structure amplitudes are compared with the calculated values in Table 2.

Determination of the absolute configuration

An equi-inclination Weissenberg photograph was taken, with Cu *K* α radiation, of the third layer-line around the *b* axis. The differences in intensity between the reflexions and the counter-reflexions were clearly

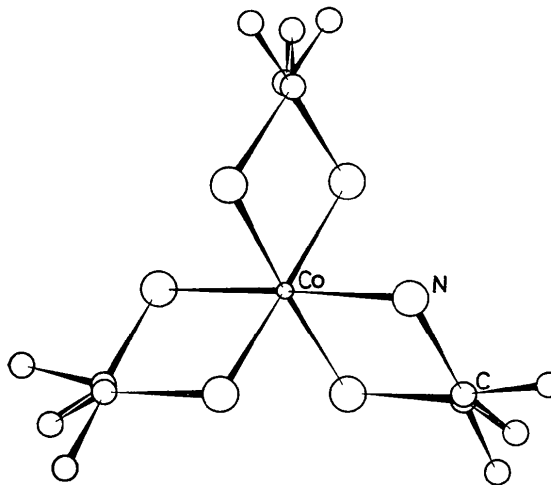


Fig. 1. A perspective drawing of the complex ion, $(-)_546\text{-[Co}(R,R\text{-ptn})_3\text{]}^{3+}$.

discernible, as shown in Table 3. Comparison of the observed and calculated differences indicates that $(-)_546\text{-[Co}(R,R\text{-ptn})_3]^{3+}$ has the absolute configuration Δ (IUPAC Information Bulletin, 1968), as illustrated in Fig. 1. The absolute configuration agrees with that deduced from the negative circular dichroism band in the first transition region.

Description of the structure and discussion

A perspective drawing of the complex ion $(-)_546\text{-[Co}(R,R\text{-ptn})_3]^{3+}$ is presented in Fig. 1, which correctly represents the absolute configuration. The complex ion has rigorous C_2 symmetry, but has approximate D_3 symmetry. Table 4 lists the interatomic distances and bond angles within the complex ion, together with

Table 2. Observed and calculated structure amplitudes

hkl	$I(hkl)$	Obs.	$I(h\bar{k}l)$
134	4160	>	2362
135	697	>	350
138	2153	>	900
631	441	<	942
632	2970	>	2218
733	282	<	762
734	1739	>	1354

Table 2 (cont.)

834	1000	>	1000
835	1000	>	1000
836	1000	>	1000
837	1000	>	1000
838	1000	>	1000
839	1000	>	1000
840	1000	>	1000
841	1000	>	1000
842	1000	>	1000
843	1000	>	1000
844	1000	>	1000
845	1000	>	1000
846	1000	>	1000
847	1000	>	1000
848	1000	>	1000
849	1000	>	1000
850	1000	>	1000
851	1000	>	1000
852	1000	>	1000
853	1000	>	1000
854	1000	>	1000
855	1000	>	1000
856	1000	>	1000
857	1000	>	1000
858	1000	>	1000
859	1000	>	1000
860	1000	>	1000
861	1000	>	1000
862	1000	>	1000
863	1000	>	1000
864	1000	>	1000
865	1000	>	1000
866	1000	>	1000
867	1000	>	1000
868	1000	>	1000
869	1000	>	1000
870	1000	>	1000
871	1000	>	1000
872	1000	>	1000
873	1000	>	1000
874	1000	>	1000
875	1000	>	1000
876	1000	>	1000
877	1000	>	1000
878	1000	>	1000
879	1000	>	1000
880	1000	>	1000
881	1000	>	1000
882	1000	>	1000
883	1000	>	1000
884	1000	>	1000
885	1000	>	1000
886	1000	>	1000
887	1000	>	1000
888	1000	>	1000
889	1000	>	1000
890	1000	>	1000
891	1000	>	1000
892	1000	>	1000
893	1000	>	1000
894	1000	>	1000
895	1000	>	1000
896	1000	>	1000
897	1000	>	1000
898	1000	>	1000
899	1000	>	1000

Table 3. Determination of the absolute configuration

hkl	$I(hkl)$	Obs.	$I(h\bar{k}l)$
134	4160	>	2362
135	697	>	350
138	2153	>	900
631	441	<	942
632	2970	>	2218
733	282	<	762
734	1739	>	1354

their estimated standard deviations. The cobalt atom has a slightly distorted octahedral coordination of nitrogen atoms. The Co-N distances range from 1.981 to 1.989 Å. They agree with those observed in other tris(diamine)cobalt(III) complexes. The C-N and C-C distances are quite normal, as can be seen from Table 4. The six-membered chelate ring has a twisted-boat form. The N-Co-N angles are close to 90°, the mean value being 89.1 (3)°. The distortion of the octahedron formed by the six nitrogen atoms is less than that observed in $(+)_546\text{-[Co}(R,R\text{-ptn})_3]^{3+}$: the upper triangle formed by the three nitrogen atoms is rotated clockwise around the threefold axis of D_3 by about 3° with respect to the lower triangle of the remaining three nitrogen atoms from the position expected for a regular octahedron. The two methyl groups are in equatorial positions with respect to the average plane of the chelate ring. The conformation of the chelate rings can be designated as lel_3 , since the line joining the two asymmetric carbon atoms is inclined at an angle of about 2° with respect to the quasi-threefold axis of the complex ion. The six-membered chelate ring is chiral and its absolute configuration can be designated as λ , provided the helicity is defined by the line joining the two nitrogen atoms and the line joining the two asymmetric carbon atoms that are neighbours to each of the coordinating atoms.

Table 4. *Interatomic distances and bond angles within the complex ions*

Co—N(1)	1.986 (9) Å
Co—N(2)	1.981 (8)
N(1)—C(3)	1.490 (14)
N(2)—C(2)	1.484 (15)
C(1)—C(2)	1.521 (19)
C(2)—C(4)	1.533 (19)
C(3)—C(4)	1.501 (18)
C(3)—C(5)	1.517 (17)
Co—N(3)	1.989 (9)
N(3)—C(6)	1.493 (16)
C(6)—C(7)	1.551 (19)
C(6)—C(8)	1.515 (17)
N(1)—Co—N(2)	89.1 (3)°
Co—N(1)—C(3)	118.0 (7)
Co—N(2)—C(2)	118.9 (7)
N(1)—C(3)—C(4)	112.3 (10)
N(2)—C(2)—C(4)	112.0 (10)
N(1)—C(3)—C(5)	110.0 (9)
N(2)—C(2)—C(1)	109.3 (10)
C(3)—C(4)—C(2)	117.5 (11)
C(4)—C(3)—C(5)	109.9 (10)
C(4)—C(2)—C(1)	110.8 (11)
N(3)—Co—N(33)	88.9 (4)
Co—N(3)—C(6)	117.2 (7)
N(3)—C(6)—C(8)	111.6 (10)
C(6)—C(8)—C(66)	116.9 (10)
N(3)—C(6)—C(7)	109.0 (10)
C(7)—C(6)—C(8)	121.2 (10)

In Table 5, the observed bond angles in the complex ion are compared with those of Niketić & Woldbye's (1973) minimized conformation. The observed values were averaged by assuming D_3 symmetry. A major difference is observed in the symmetry of the complex ion. In the minimized conformation, the complex ion has a threefold axis of rotation, whereas the actual complex ion in the crystal has an approximate D_3 symmetry. As shown in Fig. 1, the two methyl carbon atoms are on the opposite sides of the plane formed by the three methylene carbon atoms. In the minimized conformation, however, the two methyl carbon atoms and two of the three remaining carbon atoms are roughly in one plane and this plane makes an angle of about 20° with respect to the plane defined by the threefold axis and the line joining the central methylene carbon atom and the cobalt atom. The observed bond angles agree well with the calculated (minimized) values except Co—N—C, C—C—C and C—C—C' angles. The difference in the overall symmetry and in some bond angles may be caused by specific packing forces in the crystal. The calculation of conformational energy has shown that the six-membered chelate ring is flexible, *i.e.* the potential energy surface appears to have shallow minimum (Niketić & Woldbye, 1973).

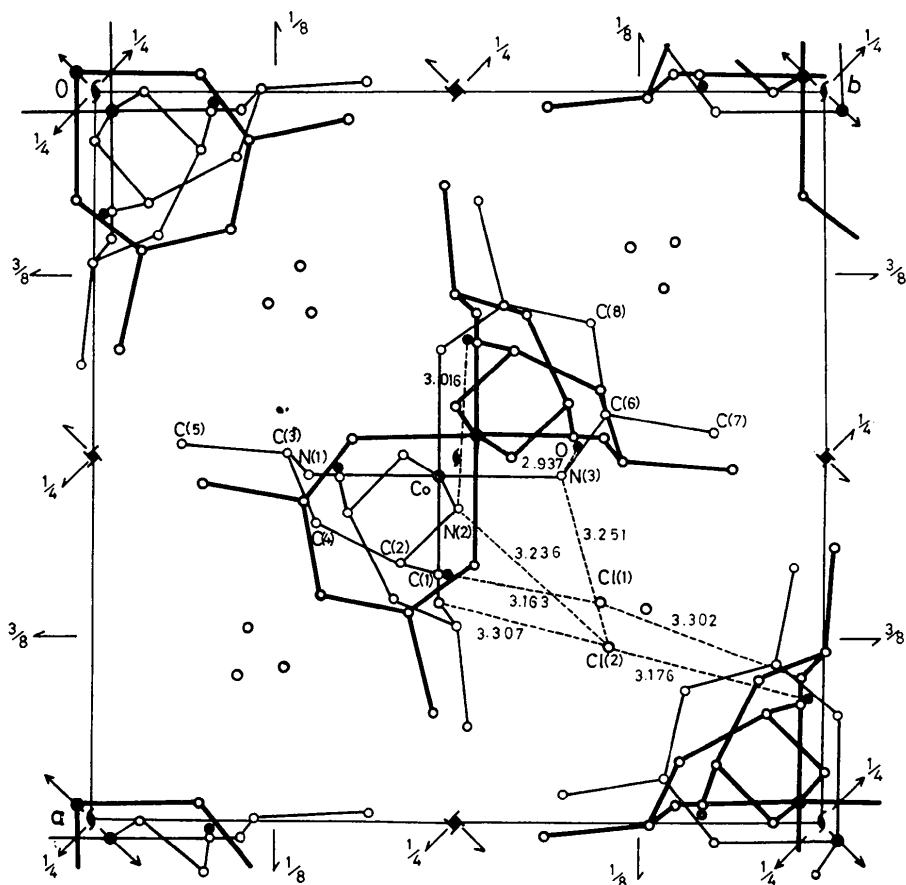
Fig. 2. A projection of the structure along the c axis. Broken lines indicate close contacts.

Table 5. Observed and calculated molecular geometries of the complex ion, $[\text{Co}(\text{R},\text{R}\text{-ptn})_3]^{3+}$

Angles in the chelate* ring	Obs.	Calc.†
N—Co—N	89.1°	89.2°
Co—N—C	118.0	113.5
N—C—C	112.0	111.5
C—C—C	117.3	113.4
N—C—C'‡	109.4	113.4
C—C—C'	111.0	109.9
Dihedral angles		
Co—N—C—C	67.7°	74.5°
Co—N—C—C'	168.8	163.4
N—C—C—C	33.0	37.7

* Averaged by assuming D_3 symmetry.

† Niketić & Woldbye (1973).

‡ C': methyl carbon atom.

The crystal structure projected along the c axis is presented in Fig. 2. Intermolecular contacts less than 3.5 Å are given in Table 6 and in Fig. 2. The cobalt atom lies on the twofold axis and is close to the twofold screw axis parallel to the c axis. Close contacts between the complex ions and chloride ions occur between amino nitrogen atoms and chloride ions. The Cl...N distances range from 3.236 to 3.307 Å. A water molecule is associated with N(2), N(3) and Cl(1).

All the calculations were carried out on the FACOM 270-30 of this Institute and on the HITAC 5020 of the Computation Centre of this University. The authors are grateful to Professor J. Fujita of Tohoku University for providing the crystals. They would like to thank Professor Flemming Woldbye for communicating the

Table 6. Interatomic distances less than 3.5 Å outside the complex ion

Superscript	x	y	z
None	x	y	z
i	y	x	\bar{z}
ii	\bar{y}	\bar{x}	$\bar{z} + \frac{1}{2}$
iii	$\bar{y} + \frac{1}{2}$	$x + \frac{1}{2}$	$z + \frac{3}{4}$
iv	$y + \frac{1}{2}$	$\bar{x} + \frac{1}{4}$	$z + \frac{1}{4}$
Cl(1)...N(1 ^{iv})*			3.302 (9) Å
Cl(1)...O ⁱ			3.163 (10)
Cl(2)...N(1 ⁱⁱ)*			3.307 (9)
Cl(2)...N(2)*			3.236 (9)
Cl(3)...N(3)*			3.251 (10)
Cl(2)...O ⁱⁱⁱ			3.176 (10)
N(2)...O ⁱⁱ *			3.016 (12)
N(3)...O*			2.937 (13)

* Asterisk indicates hydrogen bonding.

results of their conformational analysis prior to its publication. 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.

References

- International Tables for X-ray Crystallography*. (1962). Vol. III. Birmingham: Kynoch Press.
IUPAC Information Bulletin (1968). No. 33, pp. 68–77.
 KOBAYASHI, A., MARUMO, F. & SAITO, Y. (1972). *Acta Cryst. B* **28**, 3591–3595.
 MIZUKAMI, F., ITO, H., FUJITA, J. & SAITO, K. (1970). *Bull. Chem. Soc. Japan*, **43**, 3633, 3973.
 NIKETIĆ, S. R. & WOLDBYE, F. (1973). *Acta Chem. Stand.* **27**, 621–642.