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The Crystal Structure and Absolute Configuration of $(+)_{589}$-Tris-(1,4-diaminobutane)-cobalt(III) Bromide

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Crystals of $(+)_{589}$-[Co(tmd)$_3$]Br$_3$, tmd = $H_2NCH_2CH_2CH_2CH_2NH_2$, are trigonal, $a = 15{\cdot}174$ (1), $c = 8{\cdot}376$ (1) Å, space group $P321$, and $Z = 3$. The structure has been refined by full-matrix least-squares calculations to an R value of 0·039 for 2213 independent reflexions (hkl and $\bar{h}\bar{k}\bar{l}$ included) collected by diffractometry. The complex ion has D_3 symmetry. The average Co–N distance is 1·991 Å and the average N–Co–N angle in the chelate ring is 89·2°. The chelate ring is puckered and chiral. The absolute configuration can be designated as $\Delta(\lambda\lambda\lambda)$. The CoN_6 chromophore is trigonally elongated and azimuthally contracted. The longer-wavelength circular dichroism band in the first absorption region was assigned to that of E symmetry on the basis of the single-crystal circular dichroism spectrum.

Introduction

Trisdiamine complexes of Co(III) and Cr(III) with D_3 symmetry have played a prominent role as model systems for natural optical activity in both experimental and theoretical investigations, since theoretical calculations are easier to perform owing to high symmetry of the complex ion, and many such complexes are stable and can be easily resolved into optical isomers. The origin of the optical activity exhibited by dissymmetric transition-metal complexes in the region of the first absorption band is ascribed in a number of theories to a certain kind of distortion of the ligands or their orbitals from a regular octahedral disposition (see *e.g.* Richardson, 1971; Strickland & Richardson, 1973). In his static-field one-electron approach, Richardson showed that the trigonal splitting parameter $K(=\tilde{\nu}_E - \tilde{\nu}_{A_2})$ of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of Co(III) may be controlled by whether the CoN_6 chromophore is trigonally elongated or compressed. All the D_3 complexes with five-membered chelate rings are trigonally compressed (Saito, 1974). Addition of CH_2 groups in the chelate ring might result in the trigonal elongation of the CoN_6 chromophore. Thus the crystal structure of the title compound has been determined and the symmetry of the circular dichroism band was assigned on the basis of the single-crystal circular dichroism spectrum.

Experimental

Crystals of $(+)_{589}$-[Co(tmd)$_3$]Br$_3$ were kindly provided by Professor Fujita. They are dark-red trigonal bipyramids.

Crystal data

$(+)_{589}$-[Co(tmd)$_3$]Br$_3$, $C_{12}H_{36}N_6CoBr_3$, F.W. 563·1. Trigonal, $a = 15{\cdot}174$ (1), $c = 8{\cdot}376$ (1) Å, $U = 1670{\cdot}1$ Å^3, $D_m = 1{\cdot}72$ g cm^{-3} (flotation, methyl iodide/chloroform), $D_x = 1{\cdot}68$ g cm^{-3}, $Z = 3$, μ for Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) = 64·9 cm^{-1}, space group: $P321$ (No. 150).

Reflexion intensities were measured on a Rigaku automated four-circle diffractometer using Mo $K\alpha$ radiation monochromated by a graphite plate. The specimen crystals were so small in quantity, and so brittle that it was extremely difficult to shape one into a sphere suitable for X-ray work. A crystal approximately spherical in shape with radius 0·17 mm was selected and used for the intensity measurement. Cell dimensions were derived in the usual way by least-squares analysis of setting angles of 48 high-angle reflexions. Intensity data were recorded using an ω–2θ scan mode. Intensities of three standard reflexions were monitored every 50 reflexions. Those reflexions which were non-equivalent as a result of anomalous dispersion were treated as independent reflexions. A total of 2952 reflexions were measured up to $2\theta = 55°$, of which 2213 reflexions with $|F| > 3\sigma$ were regarded as 'observed'. Data were subsequently corrected for Lorentz and polarization effects. Absorption correction was made by assuming the crystal to be spherical, but no correction was applied for extinction.

Solution and refinement of the structure

The coordinates of the non-hydrogen atoms were obtained by Patterson and Fourier methods and refined by least-squares calculations. With $R = 0{\cdot}049$ a difference synthesis was calculated which revealed all the hydrogen atoms in plausible positions. After inclusion of the hydrogen atoms further refinement was carried out, using full-matrix least-squares methods; the temperature factor of the hydrogen atoms was assumed to be isotropic and given the value 4·0 Å^2. The final R value was 0·039 for the 2213 observed reflexions, R_2 being 0·043. Unit weight was given to all the reflexions. Atomic scattering factors for Br, Co, N and C were taken from *International Tables for X-ray Crystallog-*

Table 2. *Positional and thermal parameters*

Atomic parameters for the non-hydrogen atoms ($\times 10^4$)

The U_{ij}'s are defined by: $\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots+2U_{12}hka^*b^*+\ldots)\times 10^{-3}]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	0	0	0	19 (1)	19 (1)	16 (1)			
Co(2)	6667	3333	4937 (1)	14 (1)	14 (1)	16 (1)			
Br(1)	0	0	5000	69 (2)	69 (2)	16 (1)			
Br(2)	6667	3333	−65 (1)	65 (1)	65 (1)	18 (1)			
Br(3)	−2921 (1)	0	0	16 (0)	47 (1)	44 (1)			−9 (1)
Br(4)	4415 (1)	0	5000	29 (0)	21 (0)	104 (1)			−2 (1)
N(1)	1223 (4)	572 (5)	1392 (6)	31 (3)	37 (3)	27 (2)	20 (3)	−5 (2)	−0 (3)
N(2)	5504 (4)	2437 (4)	6369 (6)	22 (2)	29 (2)	21 (2)	13 (2)	2 (2)	1 (2)
N(3)	5717 (4)	3508 (4)	3516 (6)	21 (2)	25 (2)	24 (2)	11 (2)	−5 (2)	−1 (2)
C(1)	1749 (5)	−6 (6)	1850 (9)	38 (4)	50 (4)	37 (4)	25 (4)	−9 (3)	2 (3)
C(2)	2664 (6)	235 (7)	832 (11)	34 (4)	52 (5)	61 (5)	23 (4)	−5 (4)	−3 (4)
C(3)	4671 (5)	2663 (6)	6795 (8)	37 (4)	38 (4)	34 (3)	20 (3)	14 (3)	5 (3)
C(4)	3753 (5)	2132 (6)	5760 (9)	25 (3)	36 (4)	51 (4)	13 (3)	6 (3)	3 (3)
C(5)	3839 (5)	2567 (6)	4092 (10)	22 (3)	39 (4)	50 (4)	17 (3)	−3 (3)	−2 (3)
C(6)	4684 (5)	2636 (6)	3060 (8)	24 (3)	39 (4)	36 (3)	12 (3)	−5 (3)	−7 (3)

Table 2 (*cont.*)

Positional parameters of the hydrogen atoms ($\times 10^3$).
The isotropic temperature factor of the hydrogen atom is 4·0 Å^2.

	x	y	z
H(1)	100 (6)	66 (6)	236 (9)
H(2)	187 (6)	132 (6)	115 (9)
H(3)	126 (6)	−70 (6)	176 (9)
H(4)	211 (6)	16 (6)	298 (10)
H(5)	303 (6)	−16 (6)	150 (9)
H(6)	302 (6)	89 (6)	84 (9)
H(7)	590 (5)	263 (6)	738 (9)
H(8)	514 (6)	174 (6)	591 (9)
H(9)	606 (7)	366 (6)	245 (9)
H(10)	564 (6)	403 (6)	369 (9)
H(11)	486 (7)	326 (7)	718 (10)
H(12)	435 (6)	235 (6)	793 (9)
H(13)	333 (7)	224 (6)	650 (9)
H(14)	360 (6)	160 (6)	600 (9)
H(15)	364 (6)	293 (6)	379 (10)
H(16)	336 (7)	218 (6)	334 (9)
H(17)	466 (6)	196 (6)	303 (10)
H(18)	440 (6)	260 (6)	181 (9)

raphy (1962). For H the values given by Stewart, Davidson & Simpson (1965) were used. Table 1 gives the observed and calculated structure amplitudes.* The atomic parameters and their standard deviations are listed in Table 2.

Determination of the absolute configuration

192 hkl and $\bar{h}\bar{k}\bar{l}$ pairs were examined. In Table 3 the observed and calculated differences in seven pairs are compared, for which $|F(hkl)|$ and $|F(\bar{h}\bar{k}\bar{l})|$ differed by more than 15%. The concordance in the table indicated that $(+)_{589}$-$[Co(tmd)_3]^{3+}$ has the absolute configuration Δ, as illustrated in Fig. 2. Before hydrogen atoms were included, the structure converged at residuals R=0·047 and R_2=0·054. At this stage the enantiomeric structure was refined, as confirmation, under identical conditions. It converged at residuals R= 0·062 and R=0·067. Application of the R factor ratio test shows that this structure may be rejected at the 0·005 level in favour of the former (Hamilton, 1965). The determined absolute configuration agrees with that deduced from the negative circular dichroism band in the first transition region (Fujita & Ogino, 1974).

Table 3. *Determination of the absolute configuration*

h	k	l	F_o	$\|F_c\|$
$\bar{10}$	11	1	20·2	20·2
10	$\bar{11}$	$\bar{1}$	12·3	13·7
$\bar{8}$	10	1	18·7	16·8
8	$\bar{10}$	$\bar{1}$	21·9	20·0
$\bar{7}$	12	1	17·7	16·7
7	$\bar{12}$	$\bar{1}$	20·6	20·6
$\bar{6}$	11	1	20·0	17·8
6	$\bar{11}$	$\bar{1}$	14·4	13·4
$\bar{5}$	8	1	10·4	10·9
5	$\bar{8}$	$\bar{1}$	14·6	14·3
7	5	1	20·7	20·6
$\bar{7}$	$\bar{5}$	$\bar{1}$	16·6	16·7
10	1	1	12·6	13·7
$\bar{10}$	$\bar{1}$	$\bar{1}$	18·3	20·2

Description of the structure and discussion

The crystal is composed of the complex cations and bromide ions. Fig. 1 represents a projection of the structure along the c axis. Two of the complex ions lie on the threefold axis of rotation, having approximate D_3 symmetry. The third has rigorous D_3 symmetry. A perspective drawing of the complex ion, $(+)_{589}$-$[Co(tmd)_3]^{3+}$ is shown in Fig. 2. Table 4 gives the interatomic distances and bond angles within the complex ion. Each ligand molecule is coordinated to the cobalt atom with an average Co–N distance of 1·991 (5) Å, which is significantly longer than that of 1·978 (4) in $[Co(en)_3]^{3+}$ (Iwata, Nakatsu & Saito, 1969). The N–Co–N angle in the chelate ring averages 89·2 (2)°. The chelate ring is strained. The angles

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30850 (35 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Co–N–C, N–C–C and C–C–C are all greater than the normal tetrahedral angle, as shown in Table 4. Fig. 3 shows a projection of a chelate ring along the twofold axis. The seven-membered chelate ring is puckered and chiral. The carbon atoms next to the nitrogen atoms are displaced by 0·85 Å on opposite sides of the plane formed by the cobalt and the two nitrogen atoms. The two remaining carbon atoms are nearly on this plane, the deviation being 0·11 Å. The chelate ring is chiral and can be designated as λ providing that the helicity is defined by the line joining the two ligating nitrogen atoms and by the line joining the two carbon atoms bonded to the nitrogen atoms. The latter line is inclined by about 0·6° with respect to the threefold axis of the complex ion. Accordingly the complex ion is the *lel*$_3$ isomer and can be designated as $\Delta(\lambda\lambda\lambda)$ as a whole. An octahedron formed by the six ligating nitrogen atoms is trigonally elongated and azimuthally contracted. Each Co–N bond is inclined at 53·5 (2)° on the average with respect to the trigonal axis of the complex ion. This angle is 54·75° for a regular octahedron. The upper triangle formed by the three nitrogen atoms is rotated clockwise by 4·3° with respect to the lower triangle of the three remaining nitrogen atoms from the position expected for a regular octahedron. Relevant interatomic distances outside the complex ions are listed in Table 5. In the crystal the complex ions are arranged with the threefold axis parallel to the *c* axis. Bromide ions and the complex ions are alternately stacked along the *c* axis. The shortest contact occurs between the nitrogen atom of the complex ion and bromide ion, with a N···Br distance of 3·389 Å. Among the alternate stacks of the complex ions and the bromide ions, other bromide ions are arranged. A complex is thus surrounded azimuthally by three

Table 4. *Interatomic distances* (Å) *and bond angles* (°) *within the complex ion with their standard deviations in parentheses*

Co(1)–N(1)	1·987 (5)	N(1)—Co(1)–N(1′)	88·6 (3)
Co(2)–N(2)	2·000 (4)	N(2)—Co(2)–N(3)	89·9 (2)
Co(2)–N(3)	1·986 (6)	Average	89·2 (2)
Average	1·991 (5)		
		Co(1)–N(1)—C(1)	123·2 (3)
N(1)—C(1)	1·501 (13)	Co(2)–N(2)—C(3)	122·8 (3)
N(2)—C(3)	1·507 (12)	Co(2)–N(3)—C(6)	122·7 (3)
N(3)—C(6)	1·509 (7)	Average	122·9 (3)
Average	1·506 (11)		
		N(1)—C(1)—C(2)	114·1 (5)
C(1)—C(2)	1·510 (12)	N(2)—C(3)—C(4)	113·8 (5)
C(3)—C(4)	1·490 (10)	N(3)—C(6)—C(5)	113·0 (5)
C(5)—C(6)	1·507 (11)		
C(2)—C(2′)	1·524 (18)	Average	113·6 (5)
C(4)—C(5)	1·522 (12)	C(1)—C(2)—C(2′)	115·6 (6)
Average	1·511 (13)	C(3)—C(4)—C(5)	116·5 (5)
		C(4)—C(5)—C(6)	116·3 (6)
		Average	116·1 (6)
Dihedral angles			
Co(1)–N(1)–C(1)–C(2)	97·2	C(1)–C(2)–C(2′)–C(1′)	124·5
Co(2)–N(2)–C(3)–C(4)	95·1	C(3)–C(4)–C(5)–C(6)	122·8
Co(2)–N(3)–C(6)–C(5)	96·3	Average	123·7
Average	96·2		
N(1)—C(1)–C(2)–C(2′)	104·4		
N(2)—C(3)–C(4)–C(5)	104·0		
N(3)—C(6)–C(5)–C(4)	104·0		
Average	104·1		

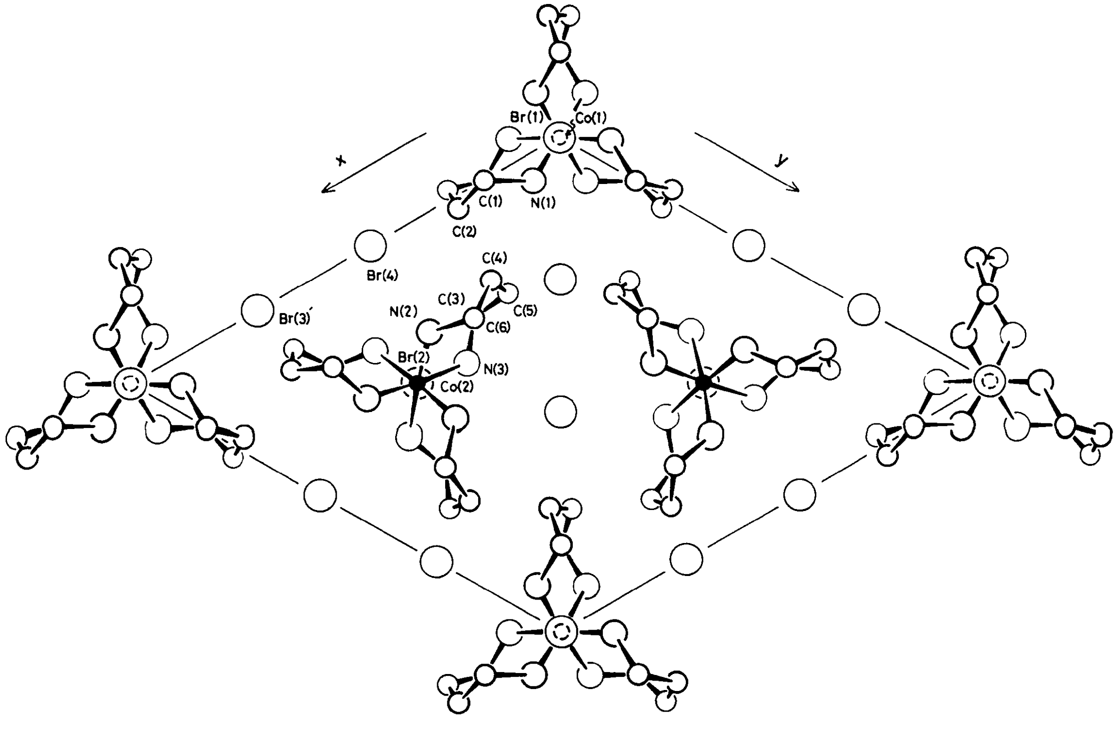

Fig. 1. A projection of the structure along the *c* axis.

Table 5. *Relevant interatomic distances* (Å) *outside the complex ions with their standard deviations in parentheses*

Key to symmetry operations

i	$-y$	$x-y$	z
ii	x	y	$1+z$
iii	$1-x+y$	$1-x$	z

Br(1)····N(1)	3·423 (5)	Br(3)·····N(1)	3·393 (7)
Br(2^{ii})···N(2)	3·389 (5)	Br(4)·····N(2)	3·408 (5)
Br(2)····N(3)	3·395 (6)	Br(4^{iii})···N(3)	3·486 (6)

bromide ions, the shortest contact between N and Br being 3·393 Å.

In aqueous solution this compound gives a weak negative and a strong positive circular dichroism band in the first absorption region, the former being at the lower frequency side (Fujita & Ogino, 1974). The negative peak was assigned to the E component based on single crystal c.d. spectra (Sato, Saito, Fujita & Ogino, 1974). On the other hand, the CoN_6 chromophore in Δ-$(-)_{589}$-$[Co(en)_3]^{3+}$ is trigonally compressed and azimuthally contracted (Saito, 1974). In an aqueous solution it shows a strong negative and a weak positive c.d. band. The negative band at the longer wavelength side is known to be that of E symmetry (Mason & Norman, 1965). Thus $\tilde{\nu}_E - \tilde{\nu}_{A_2}$ is negative irrespective of whether the CoN_6 chromophore is trigonally elongated or compressed. It is to be noted here that the rotatory strengths of the E and A_2 bands are reversed in the case of the seven-membered chelate rings. Such reversal of the rotatory strengths is also observed for $(-)_{589}$-$[Co(+cptn)_3]^{3+}$ in an aqueous solution (Ito, Marumo & Saito, 1971). A common feature in the two cases is that there is much strain in the chelate ring or in some part of the ligand. In fact, Strickland & Richardson (1973) calculated the rotatory strengths on a molecular-orbital model and showed that the *d–d* rotatory strength is very sensitive to various distortions within the chromophore, in agreement with our X-ray evidence.

The calculations were performed on the FACOM 270-30 of this Institute with a local version of the Universal Crystallographic Computation Program System UNICS (Crystallographic Society of Japan). A part of the calculations was carried out on a HITAC 8800/8700 at the Computer Centre of the University of Tokyo.

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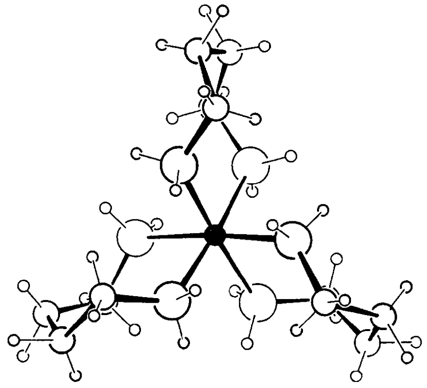

Fig. 2. A perspective drawing of the complex ion, $(+)_{589}$-$[Co(tmd)_3]^{3+}$.

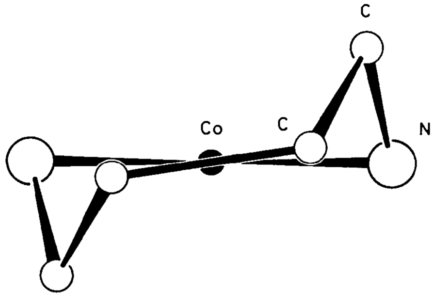

Fig. 3. A projection of the chelate ring along the twofold axis.

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