SHORT STRUCTURAL PAPERS

(+)589-Tris-[(−)-*trans*-1,2-diaminocyclohexane]rhodium(III) Nitrate Trihydrate

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Abstract. $(+)_{589}$-[Rh(−chxn)$_3$] (NO$_3$)$_3$.3H$_2$O, hexagonal, $P6_3$, $a=13\cdot339(2)$, $c=9\cdot848(2)$ Å, $Z=2$, $D_m=1\cdot50$, $D_x=1\cdot50$ g cm^{-3}. The complex ion has a threefold axis of rotation. The rhodium atom is surrounded nearly octahedrally by six nitrogen atoms at an average distance of $2\cdot082(3)$ Å. This is an *ob* isomer and the central C–C bond in the puckered chelate ring is inclined at an angle of $65\cdot9(2)°$ to the threefold axis. The absolute configuration can be designated as $A(\lambda\lambda\lambda)$.

Introduction. The absolute configurations of about 60 complexes had been determined by the end of 1972 and the number is still growing at an increasing rate (Saito, 1974). The X-ray determination of the absolute configuration of transition metal complexes is an elegant means of evaluating many assignments of the chirality of the complex ions on the basis of circular dichroism. About 80% of the complex ions of which the absolute configurations have been established by means of X-rays are cobalt(III) complexes. The paucity of absolute configurations of complexes of elements other than cobalt is still a distinct handicap. The *lel*$_3$ and *ob*$_3$ isomers of tris-(*trans*-1,2-diaminocyclohexane)-rhodium(III) salts were isolated as chlorides and nitrates and were characterized by their electronic and circular dichroism spectra, optical rotation and thermogravimetry (Galsbøl, Steenbøl & Sørensen, 1972). The absolute configurations were assigned by correlation of the *lel*$_3$ isomer with $(−)_{589}$-[Co(−chxn)$_3$]Cl$_3$.5H$_2$O using the method of an active racemate, whose absolute configuration was already determined by means of X-rays (Marumo, Utsumi & Saito, 1970). Crystals of $(+)_{589}$-[Rh(−chxn)$_3$] (NO$_3$)$_3$.3H$_2$O were subjected to X-ray crystal structure analysis in order to verify the absolute configuration and to obtain conformational details.

Crystals of $(+)_{589}$-[Rh(−chxn)$_3$] (NO$_3$)$_3$.3H$_2$O (which were kindly supplied by Dr Galsbøl of H. C. Ørsted Institute) are colourless transparent needles. Unit-cell dimensions were determined from Weissenberg photographs and refined on a diffractometer.

The intensities of reflexions were measured on a Rigaku automated four-circle diffractometer using Mo $K\alpha$ radiation monochromated by a graphite plate. A crystal of dimensions $0\cdot18 \times 0\cdot18 \times 0\cdot19$ mm was used. Of 1750 accessible reflexions below $2\theta=60°$ 1611 with $|F| \geq 3\sigma$ were used for the refinement. The intensity data were corrected for the usual Lorentz and polarization effects. No corrections were made for absorption or extinction.

The structure was solved by routine application of the heavy-atom method and refined by the block-diagonal least-squares method assuming anisotropic thermal parameters. The R value dropped to $0\cdot038$. At this stage a difference synthesis was calculated and the positions of all the hydrogen atoms except those of the water molecules could be determined. After inclusion of the hydrogen atoms, a final set of least-squares calculations was carried out assuming isotropic thermal parameters for the hydrogen atoms. The final R value was $0\cdot027$ for the 1611 observed reflexions. Unit weight was given to all the reflexions. The scattering factors for all the atoms were those listed in *International Tables for X-ray Crystallography* (1962). Observed and calculated structure factors are compared in Table 1.* Table 2 lists the final atomic parameters, together with their estimated standard deviations.

Equi-inclination Weissenberg photographs were taken of the zeroth to the third layer lines around the *a* axis with Cu $K\alpha$ radiation. Some of the calculated intensities and the observed relations between *hkl* and its counter-reflexion *hkl̄* are compared in Table 3. The agreement in the table indicates that the complex ion

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* Table 1 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30466 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Positional and thermal parameters*

(a) Fractional atomic coordinates and thermal parameters for the non-hydrogen atoms ($\times 10^4$), with estimated standard deviations. The β_{ij}'s are defined by: exp $[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	3333	6667	0 (1)	32 (0)	32 (0)	38 (0)	0	0	0
N(1)	2179 (3)	5213 (3)	1122 (3)	44 (2)	42 (2)	56 (3)	45 (4)	28 (5)	3 (5)
N(2)	3494 (3)	5445 (3)	−1135 (3)	44 (2)	36 (2)	56 (3)	38 (4)	24 (5)	−1 (4)
C(1)	1886 (3)	4165 (3)	291 (4)	42 (2)	35 (2)	85 (6)	28 (4)	34 (5)	−3 (5)
C(2)	3005 (3)	4352 (3)	−342 (4)	48 (3)	34 (2)	69 (4)	39 (4)	32 (5)	7 (4)
C(3)	2802 (4)	3331 (4)	−1231 (5)	72 (4)	41 (3)	126 (6)	49 (6)	66 (8)	−19 (7)
C(4)	2232 (5)	2211 (4)	−389 (6)	108 (5)	41 (3)	189 (11)	69 (6)	109 (11)	−2 (8)
C(5)	1089 (5)	2018 (4)	231 (11)	91 (4)	32 (2)	276 (16)	14 (6)	152 (17)	−21 (13)
C(6)	1304 (4)	3050 (4)	1142 (5)	78 (4)	36 (3)	134 (6)	35 (5)	105 (9)	26 (7)
N(3)	4822 (3)	952 (3)	−1054 (4)	64 (3)	51 (3)	86 (4)	44 (5)	−1 (6)	8 (6)
O(1)	4737 (3)	532 (3)	104 (6)	99 (3)	66 (2)	99 (4)	58 (4)	8 (10)	53 (9)
O(2)	5080 (4)	1979 (3)	−1159 (3)	198 (6)	56 (3)	93 (4)	106 (7)	−27 (9)	17 (6)
O(3)	4691 (4)	370 (4)	−2078 (4)	142 (5)	82 (3)	104 (4)	124 (7)	−39 (8)	−45 (7)
O(4)	4934 (4)	2913 (4)	1457 (4)	158 (5)	98 (4)	96 (4)	160 (8)	−65 (8)	−26 (7)

Table 2 (*cont.*)

(b) Positional parameters for the hydrogen atoms with estimated standard deviations ($\times 10^3$).

Mean isotropic temperature factor of the hydrogen atoms is 3·5 (1·5) Å².

	x	y	z
H(1)	154 (5)	518 (4)	146 (6)
H(2)	253 (5)	511 (5)	198 (6)
H(3)	417 (4)	560 (5)	−139 (5)
H(4)	302 (5)	522 (5)	−202 (6)
H(5)	141 (4)	410 (4)	−49 (5)
H(6)	355 (4)	446 (4)	32 (6)
H(7)	218 (6)	323 (6)	−227 (7)
H(8)	354 (5)	350 (5)	−168 (5)
H(9)	206 (6)	140 (6)	−126 (7)
H(10)	282 (5)	219 (6)	50 (6)
H(11)	42 (6)	192 (6)	−88 (8)
H(12)	54 (6)	141 (5)	1 (12)
H(13)	56 (5)	275 (5)	163 (6)
H(14)	191 (5)	311 (5)	198 (5)

shown in Fig. 1 corresponds to $(+)_{589}$-[Rh(–chxn)₃]³⁺. The absolute configuration can be designated as $\Lambda(\lambda\lambda\lambda)$ according to the *IUPAC Information Bulletin* (1968), in agreement with the assignment by the method of active racemates (Galsbøl et al., 1973).

Table 3. *Determination of the absolute configuration*

h	k	l	$F_c^2(hkl)$	Observed relations	$F_c^2(hkl)$
0	2	1	353	<	605
0	6	4	110	<	428
1	3	2	3856	>	3069
1	3	3	467	<	824
2	0	1	353	<	707
2	4	2	2540	>	2043
3	1	3	1303	<	1673
3	1	1	1697	>	980
3	2	1	2314	>	1490

Discussion. A partial projection of the structure is shown in Fig. 1. The structure consists of the complex cations, nitrate ions and water molecules. The complex

ion has rigorous C_3 symmetry but has a pseudosymmetry D_3. The geometry of the complex ion is very similar to that of $(+)_{589}$-[Co(–chxn)₃]³⁺ (Kobayashi, Marumo & Saito, 1972). The bond distances and angles within the complex ion are listed in Table 4. Each ligand molecule is coordinated to the rhodium atom through its nitrogen atoms. The Rh–N distances of 2·089(3) and 2·074(3) Å are longer than the Co–N distance of 1·984(5) Å. The angle N–Rh–N in the chelate ring is reduced to 82·7(1)°, being smaller than the corresponding angle of 84·3(1)° in the cobalt analogue. All other bond distances and angles are normal. The cyclohexane ring takes a chair conformation. The C–C bonds in the chelate rings are inclined at an angle of 65·9(2)° with respect to the threefold axis. Consequently this is an ob_3 isomer. The six coordinating nitrogen atoms are slightly distorted from a regular octahedral arrangement. The upper triangle formed by the three nitrogen atoms is rotated counterclockwise by about 5·2° with respect to the lower triangle of the three remaining nitrogen atoms. This is much smaller than the observed angle of 9° in the cobalt analogue. The Rh–N bond is inclined by 58·3(1)° with respect to the threefold axis of rotation. If the six nitrogen atoms were exactly on the apices of an octahedron this angle would be 54·75°. Accordingly
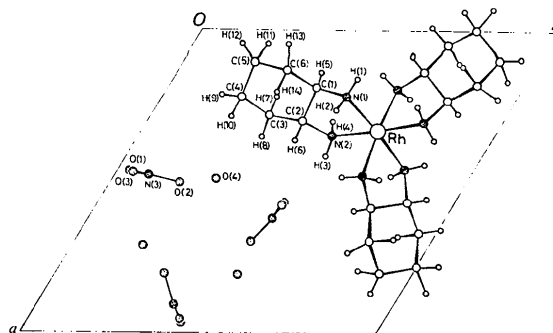

Fig. 1. A partial projection of the structure viewed along the c axis.

Table 4. *Interatomic distances and bond angles in the complex ion and the nitrate ion*

Rh—N(1)	2·089 (3) Å	Rh—N(2)	2·074 (4) Å	N(1)–C(1)	1·493 (5) Å
N(2)–C(2)	1·487 (5)	C(1)–C(2)	1·518 (6)	C(2)–C(3)	1·524 (7)
C(3)–C(4)	1·537 (7)	C(4)–C(5)	1·540 (10)	C(5)–C(6)	1·545 (9)
C(6)–C(1)	1·537 (6)	N(3)–O(1)	1·251 (7)	N(3)–O(2)	1·239 (8)
N(3)–O(3)	1·231 (7)				

N(1)–Rh—N(2)	82·71 (9)°	Rh—N(1)–C(1)	107·8 (2)°
Rh—N(2)–C(2)	108·7 (2)	N(1)–C(1)–C(2)	107·2 (2)
N(2)–C(2)–C(1)	106·9 (3)	C(2)–C(1)–C(6)	111·2 (2)
C(1)–C(2)–C(3)	111·6 (3)	C(2)–C(3)–C(4)	109·8 (4)
C(3)–C(4)–C(5)	110·1 (4)	C(4)–C(5)–C(6)	110·7 (4)
C(5)–C(6)–C(1)	108·9 (4)	O(1)–N(3)–O(2)	119·0 (5)
O(2)–N(3)–O(3)	120·2 (5)	O(3)–N(3)–O(1)	120·8 (5)

the RhN_6 chromophore is slightly compressed. The corresponding angle in $(+)_{589}\text{-}[Co(-chxn)_3]^{3+}$ is 55·2°.

The nitrate ion is almost planar. The average N–O distance is 1·240(7) Å and the average O–N–O angle is 120·0(4)°. The ions are arranged with their planes parallel to, and with N–O(2) nearly perpendicular to,

the threefold axis. Pertinent short contacts are listed in Table 5. Hydrogen bonds are formed between amino nitrogen atoms and oxygen atoms of the nitrate ions. They are marked in Table 5 by an asterisk. Although the hydrogen atoms of the water molecule could not be located, the $O(2)\cdots O(4)$ distance of 2·910 Å suggests an $O-H\cdots O$ hydrogen bond. Thus the complex cations, water molecules and nitrate ions are linked by a zigzag sequence of hydrogen bonds along the c axis.

Table 5. *Interatomic distances less than 3·5 Å outside the complex and the nitrate ions*

Key to symmetry operations

(i)		$x,$	$y,$	z
(ii)		$1-y,$	$x-y,$	z
(iii)	$1-x+y,$		$1-x,$	z
(iv)		$1-x,$	$1-y,$	$-0·5+z$
(v)		$y,$	$1-x+y,$	$0·5+z$
(vi)		$x-y,$	$x,$	$0·5+z$
(vii)		$1-x,$	$-y,$	$-0·5+z$
(viii)		$-y,$	$x-y,$	z
(ix)		$x-y,$	$x,$	$-0·5+z$

N(1)···O(2ᵛⁱ)	2·989 (5) Å*	N(1)···O(1ᵛⁱⁱⁱ)	3·321 (6) Å
N(1)···O(3ᵛ)	3·295 (7)	N(2)···O(4ⁱᵛ)	3·197 (5)
N(2)···O(4ⁱˣ)	2·937 (5)*	N(2)···O(1ⁱⁱⁱ)	3·422 (6)
N(2)···O(3ⁱⁱⁱ)	3·149 (7)	C(1)···O(1ᵛⁱⁱⁱ)	3·258 (7)
C(2)···O(1ⁱⁱⁱ)	3·316 (5)	O(1)···O(4ⁱⁱ)	3·050 (7)
O(1)···O(4ⁱ)	3·333 (7)	O(2)···O(4ⁱ)	2·910 (6)*
O(2)···O(2ⁱⁱ)	3·429 (14)	O(3)···O(1ᵛⁱⁱ)	3·262 (7)
O(4)···O(3ᵛⁱ)	3·211 (9)		

* An asterisk indicates hydrogen bonding.

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