Conformation of the macro-ring

Similarity to 4-nitrobenzo-18-crown-6.CsSCN (Hašek, Hlavatá & Huml, 1977), the Rb^+ atom lies at the top of an irregular hexagonal pyramid, the base of which consists of O atoms. The mean distance of Rb from the O atoms of the macro-ring is 3·00 Å [compare with 3·02 Å for 18-crown-6.RbSCN (Dobler & Phizackerley, 1974)]. The Rb atom is situated at 1·17 Å from the weighted mean plane through six O atoms of the macro-ring [compare with 1·19 Å (Dunitz *et al.*, 1974)]. The distances between adjacent O atoms in the macro-ring vary between 2·79–2·86 Å (mean 2·833 Å), with the exception of 2·55 Å for O(2)—O(17). This short distance and the diminished angles C(18)—C(1)—O(2), 114·4°, and O(17)—C(18)—C(1), 117·4° (Fig. 1), can also be observed in the complex dibenzo-18-crown-6.RbSCN (Bright & Truter, 1970) and in the complex 4-nitrobenzo-18-crown-6.CsSCN (Hašek, Hlavatá & Huml, 1977).

Atoms in groups of C—C—O—C—C type in the macro-ring lie approximately in a plane. Similarly to the complex nitrobenzo-18-crown.CsSCN, one group has considerably larger deviations from the mean plane than the others. In the case of the Rb^+ cation this group is formed by atoms C(6), C(7), O(8), C(9), C(10); deviations of the atoms from their mean planes are 0·43 Å for C(7) and 0·52 Å for C(9).

Nitrobenzene substituent

The whole nitrobenzene group and the atoms O(2), C(3), O(17), C(16) lie, with a maximum deviation of 0·1 Å, in one plane. Deviations from the weighted mean plane through the benzene ring are given in Fig. 4.

Angles between the planes through the nitro group, benzene ring, C(1), O(2), C(3), C(18), O(17), C(16) group and six O atoms of the macro-ring are given in Table 4. Similarly to the case when Cs is the cation, the plane of the nitro group is rotated from the plane of the benzene ring by 3·4° towards the cation.

The authors are indebted to Dr J. Petránek and Dr O. Ryba for sample preparation and valuable discussions.

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The Crystal Structure of (+)589-*fac*-Tris(*meso*-2,4-pentanediamine)cobalt(III) Hexacyanocobaltate(III) Pentahydrate

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Crystals of the title compound are orthorhombic, space group $P2_12_12_1$, with $a = 17·953$ (2), $b = 18·382$ (2), $c = 10·161$ (2) Å and $Z = 4$. The structure has been refined to a residual of 0·042 with 4282 independent significant reflexions collected by diffractometry. The complex ion has approximate threefold symmetry. The six-membered chelate rings adopt the chair conformation with both $C—CH_3$ bonds in equatorial positions. The absolute configuration of the complex ion can be designated as Λ.

Introduction

The *mer* and *fac* isomers of $[Co(meso\text{-}ptn)_3]^{3+}$ have recently been separated and resolved by column chromatography on SP-Sephadex (Kojima & Fujita, 1976). Crystals of $(+)_{589}\text{-}[Co(meso\text{-}ptn)_3][Co(CN)_6].5H_2O$ were subjected to X-ray structure analysis in order to reveal the conformational details of

the complex ion and to establish its absolute configuration.

Experimental

Crystals used for the X-ray work were kindly provided by Professor Fujita of Nagoya University. They are orange-red plate-like crystals. A specimen with dimensions $0.2 \times 0.3 \times 0.4$ mm was selected for intensity measurement. Table 1 presents the crystallographic data. Intensities were collected on a Rigaku four-circle diffractometer with the θ–2θ scan technique and graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) to $2\theta = 60°$. 5416 reflexions were obtained, from which 4282 reflexions with $|F| > 3\sigma(|F|)$ were

selected and used for the refinement. The intensities showed a slight decrease of about 8% during the course of data collection because of dehydration and radiation damage. Data were corrected for this effect and Lorentz–polarization factors. No correction was made for absorption.

Table 1. *Crystal data*

$Co_2C_{21}H_{52}N_{12}O_5$, FW 670.6
Orthorhombic
$a = 17.953$ (2), $b = 18.382$ (2), $c = 10.161$ (2) Å
$U = 3353.4$ Å^3
$D_m = 1.32$, $D_x = 1.33$ g cm^{-3}, $Z = 4$
Mo $K\alpha$ ($\lambda = 0.7107$ Å), $\mu = 10.8$ cm^{-1}
Space group $P2_12_12_1$

Table 2. *Positional parameters* ($\times 10^4$ *for non-hydrogen atoms;* $\times 10^3$ *for hydrogen atoms*)

	x	y	z		x	y	z
Co(1)	4498 (0)	3690 (0)	6192 (1)	H(N3)1	498 (2)	253 (2)	545 (4)
Co(2)	2314 (0)	3077 (0)	1638 (1)	H(N3)2	445 (2)	269 (2)	472 (3)
N(1)	4619 (2)	3034 (2)	7719 (3)	H(N4)1	433 (2)	487 (2)	500 (4)
N(2)	3432 (2)	3364 (2)	6092 (4)	H(N4)2	403 (3)	435 (3)	458 (6)
N(3)	4799 (2)	2918 (2)	4931 (3)	H(N5)1	580 (2)	353 (2)	622 (4)
N(4)	4354 (2)	4369 (2)	4690 (3)	H(N5)2	572 (2)	432 (2)	567 (4)
N(5)	5567 (2)	3971 (2)	6344 (3)	H(N6)1	383 (2)	430 (2)	786 (4)
N(6)	4170 (2)	4481 (2)	7422 (3)	H(N6)2	405 (3)	492 (3)	683 (5)
N(7)	1064 (2)	2572 (2)	3435 (4)	H(C1)	454 (2)	198 (2)	703 (4)
N(8)	1795 (3)	1912 (3)	−269 (5)	H(C2)1	339 (2)	175 (2)	755 (4)
N(9)	3368 (2)	1992 (2)	2932 (5)	H(C2)2	327 (2)	250 (2)	818 (4)
N(10)	3561 (2)	3609 (2)	−146 (4)	H(C3)	342 (2)	236 (2)	555 (4)
N(11)	2801 (2)	4183 (2)	3680 (4)	H(C4)1	431 (2)	137 (2)	907 (4)
N(12)	1245 (2)	4210 (2)	554 (4)	H(C4)2	440 (2)	216 (2)	981 (4)
C(1)	4329 (2)	2270 (2)	7762 (4)	H(C4)3	492 (3)	174 (3)	921 (6)
C(2)	3493 (2)	2276 (2)	7548 (5)	H(C5)1	225 (2)	200 (2)	634 (4)
C(3)	3214 (2)	2584 (2)	6259 (4)	H(C5)2	220 (2)	272 (2)	546 (4)
C(4)	4554 (3)	1925 (3)	9047 (5)	H(C5)3	211 (3)	274 (3)	695 (5)
C(5)	2366 (2)	2526 (3)	6181 (5)	H(C6)	568 (2)	324 (2)	401 (4)
C(6)	5246 (2)	3053 (2)	3718 (4)	H(C7)1	442 (3)	349 (3)	271 (5)
C(7)	4881 (2)	3629 (2)	2882 (4)	H(C7)2	512 (2)	369 (2)	209 (3)
C(8)	4841 (2)	4374 (2)	3500 (4)	H(C8)	524 (2)	449 (2)	376 (4)
C(9)	5374 (2)	2345 (3)	2987 (5)	H(C9)1	565 (2)	239 (2)	220 (4)
C(10)	4581 (3)	4952 (3)	2531 (5)	H(C9)2	499 (2)	213 (2)	278 (4)
C(11)	5868 (2)	4312 (2)	7558 (4)	H(C9)3	555 (2)	195 (2)	356 (4)
C(12)	5431 (2)	4977 (2)	7921 (4)	H(C10)1	490 (3)	503 (3)	180 (5)
C(13)	4661 (2)	4813 (2)	8470 (4)	H(C10)2	460 (2)	546 (2)	292 (4)
C(14)	6700 (2)	4476 (3)	7379 (5)	H(C10)3	410 (3)	485 (3)	213 (5)
C(15)	4277 (3)	5479 (3)	9039 (5)	H(C11)	581 (2)	396 (2)	818 (4)
C(16)	1539 (2)	2763 (2)	2759 (4)	H(C12)1	564 (2)	529 (2)	857 (5)
C(17)	1995 (3)	2365 (3)	405 (5)	H(C12)2	540 (2)	528 (2)	718 (3)
C(18)	2978 (2)	2396 (2)	2436 (5)	H(C13)	469 (2)	443 (2)	912 (3)
C(19)	3091 (2)	3411 (2)	514 (5)	H(C14)1	689 (2)	466 (2)	827 (5)
C(20)	2608 (2)	3764 (2)	2903 (4)	H(C14)2	679 (2)	486 (2)	672 (4)
C(21)	1649 (2)	3779 (2)	915 (4)	H(C14)3	694 (2)	409 (2)	709 (5)
O(1)	1488 (3)	584 (3)	8539 (6)	H(C15)1	460 (2)	571 (2)	971 (4)
O(2)	1826 (2)	590 (2)	5897 (4)	H(C15)2	424 (2)	590 (2)	840 (4)
O(3)	3240 (3)	900 (2)	467 (6)	H(C15)3	387 (2)	535 (2)	949 (5)
O(4)	3303 (2)	770 (2)	4815 (4)	H(O1)1	208 (1)	72 (1)	884 (3)
O(5)	2442 (2)	4296 (2)	7788 (5)	H(O2)1	185 (3)	55 (3)	663 (6)
H(N1)1	508 (2)	304 (3)	798 (5)	H(O3)1	338 (3)	27 (3)	72 (6)
H(N1)2	446 (2)	324 (2)	841 (4)	H(O4)1	330 (3)	109 (3)	414 (6)
H(N2)1	322 (3)	363 (3)	504 (6)	H(O5)1	246 (1)	455 (1)	674 (3)
H(N2)2	315 (2)	358 (2)	681 (4)				

Structure solution and refinement

The positions of all the non-hydrogen atoms were derived by Patterson and Fourier methods, and refined by a block-diagonal least-squares program with aniso-tropic temperature factors. With $R = 0.061$ a difference synthesis was calculated which revealed all the positions of the H atoms, except those of the water molecules. The absolute structure was determined at this stage by the anomalous dispersion technique, as described later. Further refinement of the structure with the correct absolute configuration, including these H atoms, reduced the R value to 0.050 and all the H atoms, except five belonging to five water molecules, appeared on the difference synthesis. The final refinement was carried out with all the atoms included. The temperature factors of the H atoms were assumed to be isotropic and allowed to vary during the refinement. The final R became 0.042 for the 4282 observed reflexions. A weighting scheme, $w = 0.5$ for $|F_o| < 17$ and $w = 1$ for all other F_o's, was employed. The average shift:error ratio was 0.2 and a final difference map revealed no peaks of height >0.6 e $Å^{-3}$. Atomic scattering factors for Co, O, N and C were taken from *International Tables for X-ray Crystallography* (1974). For H the values given by Stewart, Davidson & Simpson (1965) were used. The atomic coordinates are listed in Table 2.*

Determination of the absolute configuration

The absolute configuration of the complex cation was assigned as Λ by the anomalous dispersion technique. Table 3 compares the calculated structure amplitudes

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32992 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Observed and calculated intensity relations between some hkl and h̄kl reflexions*

h	k	l	$|F_c(hkl)|$	Observed	$|F_c(\bar{h}kl)|$
1	7	1	27·1	>	6·8
3	8	1	30·7	>	14·1
3	10	1	16·8	<	28·4
4	6	1	23·0	>	12·5
4	9	1	18·9	<	35·6
2	6	2	34·4	>	15·2
3	10	2	23·8	<	40·0
5	4	2	25·8	<	50·2
1	2	3	26·5	>	14·2
3	1	3	25·6	>	14·1
6	3	3	41·0	>	23·5
4	1	4	35·7	>	15·8

of some Bijvoet pairs and observed relations on equi-inclination Weissenberg photographs taken with Cu Kα radiation.

Description of the structure and discussion

Fig. 1 presents a perspective view of the complex cation along its pseudo threefold axis. Bond lengths and angles are listed in Table 4. The N atoms of the three bidentate ligands form a slightly distorted octahedron around the Co atom. The three chelate rings take the stable chair conformation with the C–CH$_3$ bond equatorial, as expected. Unlike [Co(tn)$_3$]$^{3+}$, no anomalous thermal vibration of the ring C atoms was observed because of

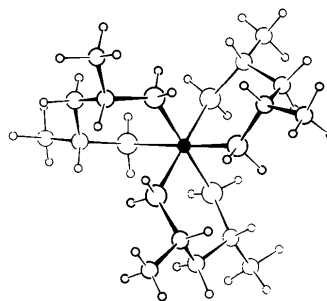Fig. 1. A perspective view of the complex cation, $\Lambda(+)_{589}$-[Co(meso-2,4-ptn)$_3$]$^{3+}$.

Table 4. *Interatomic distances (Å) and bond angles (°) in the chelate rings*

	Chelate rings			Calculated
	A	B	C	values*
Bond lengths				
Co–N	1·978 (3)	1·987 (3)	1·993 (3)	
	2·008 (3)	1·987 (3)	2·005 (3)	2·043
N–C	1·497 (5)	1·491 (5)	1·485 (5)	
	1·497 (5)	1·492 (5)	1·511 (5)	1·477
C–C	1·517 (6)	1·508 (6)	1·500 (6)	
	1·511 (6)	1·508 (7)	1·520 (6)	1·544
C–C$_{Me}$	1·507 (6)	1·516 (6)	1·535 (6)	
	1·530 (6)	1·521 (6)	1·520 (6)	1·549
Bond angles				
N–Co–N	87·8 (1)	89·3 (1)	92·7 (1)	93·85
Co–N–C	123·8 (2)	124·1 (2)	121·6 (2)	
	122·0 (2)	123·4 (2)	124·1 (2)	120·13
N–C–C	109·5 (3)	110·3 (3)	111·0 (3)	
	111·7 (3)	111·1 (4)	110·6 (3)	110·68
C–C–C	117·0 (4)	115·1 (4)	113·8 (3)	110·21
N–C–C$_{Me}$	109·0 (3)	110·1 (3)	109·8 (3)	
	108·7 (3)	110·4 (4)	109·2 (3)	109·38
C–C–C$_{Me}$	113·1 (4)	113·1 (4)	112·2 (4)	
	110·4 (4)	112·3 (4)	113·1 (3)	109·53

* Niketić, Rasmussen, Woldbye & Lifson (1976).

the substituted methyl groups. Accordingly, no unusual bond lengths or angles were observed. The geometry of the $Co(tn)_3$ portion is similar to that in $[Co(tn)_3]Cl_3.H_2O$ (Nagao, Marumo & Saito, 1973). An interesting feature is that the geometries of the three chelate rings are slightly, but significantly, different from each other. Fig. 2 presents the edge-on view of the three chelate rings to the plane formed by Co and two N atoms. Such changes appear to arise partly because of the specific packing forces in the crystal lattice and partly because of the flexibility of the six-membered chelate rings. As seen from Table 4 and Fig. 2, the following trend is observed: as the N—Co—N angle increases from 87·8 to 92·7°, the C—C—C angle decreases from 117·0 to 113·8°. Corresponding to this change in opposite bond angles in the six-membered chelate rings, the inner fragment (C—N—Co—N—C) flattens with slight puckering of the outer portion (N—C—C—C—N). These features can be seen in the dihedral angles between the C—C—C and N—C—C—N planes as shown in Table 5. This unique strain-relieving mechanism for chair rings in the present complex agrees with the general trend observed for other related complexes (Niketić, Rasmussen, Woldbye & Lifson, 1976).

A fast strain-energy minimization program was recently applied to calculate the equilibrium conformation of some tris-bidentate cobalt(III) complexes, including the present complex cation (Niketić et al., 1976). These calculations revealed that the C_3-chair conformer represents the most stable in the force field chosen. The minimized geometry of the complex ion is included in Table 5 for comparison. As discerned from the table the observed bond lengths and angles in the chelate ring C agree well with the calculation, indicating that ring C takes the most stable conformation.

The packing mode of the complex cations, anions and the water molecules is illustrated in Fig. 3. Relevant interatomic distances outside the complex ions are listed in Table 6. Four out of five water molecules are
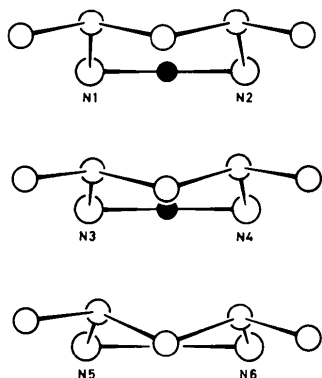
arranged around a twofold screw axis to form by O—H···O hydrogen bonds a helix parallel to the c axis. The bonds are drawn as dotted lines in Fig. 3. The closest approach to neighbouring complex ions occurs between O(1) and N(8) of the complex anion. The remaining water molecule, O(5), is hydrogen-bonded to N(11) of the complex anion and N(2) of the complex cation.

The circular dichroism (CD) spectra of $(+)_{589}$-fac-$[Co(meso\text{-}ptn)_3]^{3+}$ in an aqueous solution show a single positive peak in the region of the first absorption band ($\tilde{v} = 20 \times 10^3$ cm^{-1}, $\Delta\varepsilon = +0.62$) and a large negative peak ($\tilde{v} = 39.4 \times 10^3$ cm^{-1}, $\Delta\varepsilon = -8.7$) at the longer-wavelength side of the charge-transfer region (Kojima & Fujita, 1976). These authors assigned the absolute configuration of the present complex ion as Λ from the sign of the longest-wavelength CD band in the charge-transfer region in which the sign is insensitive to the conditions of measurement, such as whether in solution or the microcrystalline state, or whether with or without the presence of excess counter ions and so on. Generally, the CD spectra of tris-bidentate cobalt(III) complexes with six-membered chelate rings are particularly sensitive to the conditions

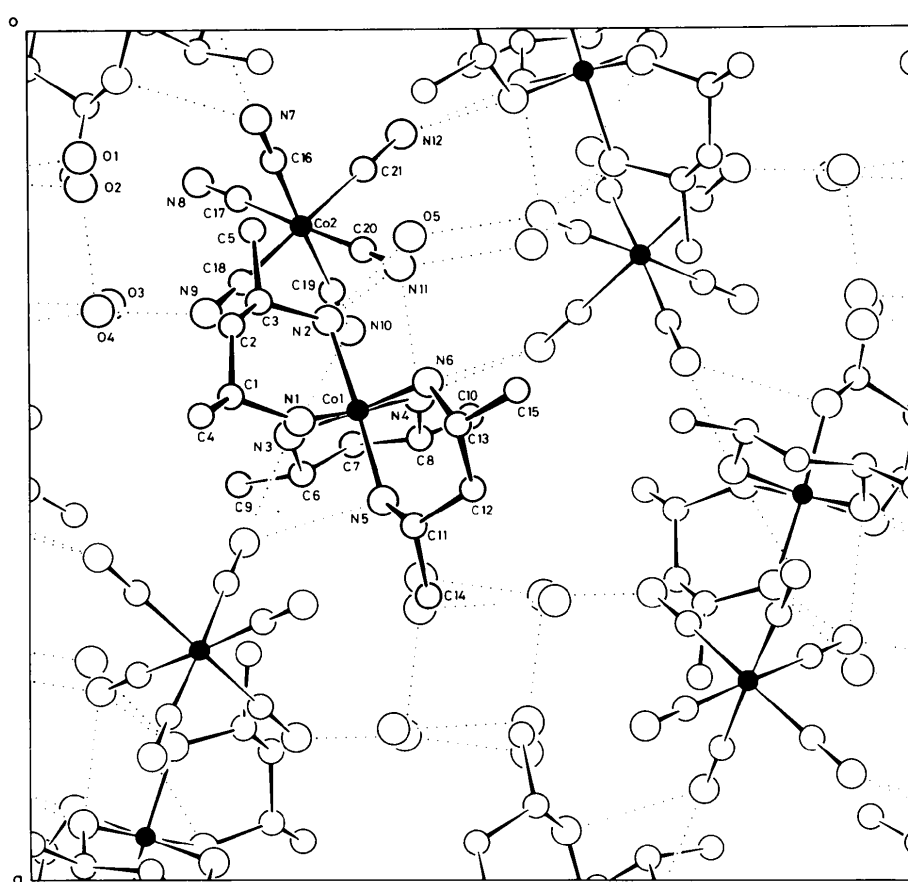Table 5. *Dihedral and torsion angles* (°) *in the chelate rings*

D_1: dihedral angle between NCoN and NCCN planes. D_2: dihedral angle between NCCN and CCC planes. The endocyclic torsion angles are labelled as follows:
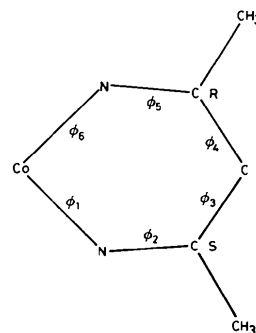
| | Chelate rings | | | Calculated |
	A	B	C	values*
Dihedral angles				
D_1	144·5	150·1	156·8	155·5
D_2	125·1	122·0	117·8	115·0
Torsion angles				
ϕ_1	44·8	36·9	29·4	30·20†
ϕ_2	−58·4	−54·4	−54·6	−57·18
ϕ_3	60·7	64·4	72·7	76·82
ϕ_4	−60·9	−64·9	−66·7	−71·60
ϕ_5	55·8	54·3	44·9	48·69
ϕ_6	−42·5	−36·5	−25·4	−26·34

* Niketić, Rasmussen, Woldbye & Lifson (1976).

† The sign of the torsion angle is determined according to the tentative rule adopted by IUPAC–IUB (1970).

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

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

of measurement (Kuroda, Fujita & Saito, 1975; Beddoe & Mason, 1968; Gollogly & Hawkins, 1968; Beddoe, Harding, Mason & Peart, 1971). This assignment was indeed verified by the present study. By reference to all the recorded CD data of tris-bidentate cobalt complexes of known absolute configuration an empirical rule relating the absolute configuration and CD spectra of tris-bidentate cobalt(III) complexes in the charge-transfer region was established: a tris(diamine)cobalt(III) complex whose sign of the lowest-frequency CD band in the charge-transfer region is negative has absolute configuration Λ; if it is positive, the absolute configuration is Δ.

Table 6. *Relevant interatomic distances* (Å) *less than* 3·4 Å *outside the complex ions, with their standard deviations in parentheses*

Key to symmetry operations

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

The asterisks indicate hydrogen bonding.

N(1)···N(7^i)	3·057 (4)	N(2)···O(5)	3·011 (6)*
N(1)···N(10^{ii})	3·070 (5)*	N(5)···O(2^i)	3·308 (5)
N(2)···N(11)	3·091 (5)*	N(6)···O(5)	3·144 (5)
N(3)···N(7^i)	2·954 (5)*	O(1)···N(8^{ii})	2·781 (7)
N(4)···N(11)	2·991 (5)*	O(3)···N(8)	3·278 (7)
N(4)···N(12^{iii})	2·959 (5)*	O(3)···N(9)	3·218 (7)
N(5)···N(7^i)	2·982 (5)	O(4)···N(9)	2·954 (6)*
N(6)···N(12^{iii})	3·154 (5)*	O(5)···N(11^{iii})	2·971 (6)*
N(6)···N(10^{ii})	3·142 (5)	C(4)···O(3^{ii})	3·346 (7)
C(1)···N(7^i)	3·356 (5)	C(14)···O(2^i)	3·339 (7)
C(2)···N(10^{ii})	3·392 (6)	O(2)···O(1)	2·752 (7)*
C(13)···N(10^{ii})	3·282 (6)	O(2)···O(4)	2·889 (6)*
		O(3)···O(2^{iv})	2·776 (6)*
		O(4)···O(1^{iv})	2·831 (6)*

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Etude Structurale du Complexe Racémique Actif [(+)Co(en)₃(−)Cr(en)₃]Cl₆.6,1H₂O à 123 K

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The structure of $[(+)Co(en)_3(-)Cr(en)_3]Cl_6.6 \cdot 1H_2O$ has been determined at 123 K. The unit cell is trigonal, space group $P321$. The lattice constants are $a = 11\cdot41$ (1), $c = 15\cdot46$ (1) Å and $\gamma = 120°$, and the volume of the unit cell loses 2% of its value on going from 293 to 123 K. At 123 K each complex ion recovers its individuality: the bonds Co–N and Cr–N become different, as in the racemic complexes.

Introduction

Les déterminations structurales, à température ambiante, des complexes racémiques actifs $[(+)Co(en)_3(-)Cr(en)_3]Cl_6.6,1H_2O$ (Whuler, Brouty, Spinat & Herpin, 1976) et $[(+)Co(en)_3(-)Cr(en)_3](SCN)_6.H_2O$ (Brouty, Whuler, Spinat & Herpin, 1977) ont montré que les ions complexes $(+)Co(en)_3^{3+}$ et $(-)Cr(en)_3^{3+}$ possèdent des longueurs de liaison métal–azote identiques. Il apparaît, par contre, qu'à 133 K, les ions complexes du racémique actif thiocyanate (Brouty *et al.*, 1977) retrouvent leur individualité.

L'affinement de la structure, à 123 K, de $[(+)Co(en)_3(-)Cr(en)_3]Cl_6.6,1H_2O$ va permettre de vérifier si ce phénomène peut être considéré comme général pour les complexes racémiques actifs triéthylènediamine.

Affinement de la structure à 123 K

L'étude à basse température est effectuée sur un diffractomètre quatre cercles Philips PW 1100, équipé d'un système de refroidissement par jet d'azote gazeux. La température du cristal est portée de 293 K à 123 K en six heures. A cette température, la maille cristalline a subi une contraction de 2% en volume et devient: $a =$ 11,41 (1), $c = 15,46$ (1) Å, $\gamma = 120°$, $V = 1743$ Å^3, groupe spatial $P321$.

Les intensités diffractées sont collectées dans les mêmes conditions de mesures qu'à l'ambiante [$4° < 2\theta < 70°$, intégration suivant ω, $\lambda(\text{Mo } K\alpha)$]; les fonds continus sont évalués en fonction de θ. 2784 réflexions sont ainsi recueillies et corrigées des facteurs de Lorentz et de polarisation.

Les affinements sont menés à partir des coordonnées atomiques établies à 293 K (Whuler *et al.*, 1976), après avoir calculé le facteur de température global à 123 K. Les positions de tous les atomes d'hydrogène sont déterminées par sections de série-différence et affinées. Les occupations des sites oxygène, affinées et vérifiées en série-différence, conduisent à une hydratation de 6,1H₂O, identique à celle observée à l'ambiante. Les coordonnées et coefficients d'agitation thermique définitifs ($R = 0,052$, 2058 réflexions telles que $F_{obs} > 4\sigma$) sont regroupés dans le Tableau 1.*