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The Crystal Structure of Bis[(R)-2-methyl-1,4,7-triazacyclononane]cobalt(III) Iodide Pentahydrate

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Crystals of $\{Co[(R)\text{-}MeTACN]_2\}I_3.5H_2O$ are trigonal, $R32$, with $a = 8.799\,(1)$, $c = 32.180\,(4)$ Å and $Z = 3$. The structure was refined by full-matrix least-squares methods to an R value of 0.039 for the 902 observed reflexions collected by diffractometry. The complex ion exhibits orientational disorder on a site of symmetry D_3 around the triad axis. Three of the nine I^- ions and the O atoms of water molecules show positional disorder. Two cyclic ligand molecules are spanned on opposite faces of an octahedron, being coordinated to the central Co atom with six N atoms. The Co–N distance is 1.974 Å. The conformation of each five-membered chelate ring is λ. The substituted methyl group is attached in an equatorial position with respect to the average plane of the chelate ring. The $[CoN_6]$ chromophore is elongated along the threefold axis, the Co–N bond being inclined at an angle of $51.3°$ with respect to the threefold axis. The chromophore is twisted around the threefold axis in the same way as in Δ-$[Co(en)_3]^{3+}$.

Introduction

Mason & Peacock (1976) synthesized the cyclic tridentate (R)-$(-)$-2-methyl-1,4,7-triazacyclononane and its Co^{III} complex, $\{Co[(R)\text{-}MeTACN]_2\}^{3+}$. They found that the complex exhibits the largest ring-conformation d-electron optical activity for the (CoN_6) chromophore yet recorded (Mason & Peacock, 1976). Crystals of $\{Co[(R)\text{-}MeTACN]_2\}I_3.5H_2O$ were subjected to X-ray crystal-structure analysis in order to provide structural data for the analysis of the observed optical activity for this complex ion (Mason & Seal, 1976).

Experimental

Crystals of $\{Co[(R)\text{-}MeTACN]_2\}I_3.5H_2O$ were kindly supplied by Professor S. F. Mason. They were re-

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crystallized from water. The crystals are yellow transparent hexagonal prisms. The diffraction symmetry on Weissenberg photographs is $3m$. The observed systematic absences, hkl for $-h + k + l = 3n$, indicated that the possible space group is $R3m$, $R32$ or $R3c$. Since the crystal is optically active, the space group was uniquely determined to be $R32$.

Crystal data

$(-)_{589}$-$\{Co[(R)\text{-}MeTACN]_2\}I_3.5H_2O$, $C_{14}H_{44}N_6O_5$-CoI_3, $M_r = 816.19$, trigonal, $a = 8.799\,(1)$, $c = 32.180\,(4)$ Å, $U = 2157.6$ Å^3, $Z = 3$, $D_x = 1.88$ g cm^{-3}, μ for Mo $K\alpha$ ($\lambda = 0.7107$ Å) $= 35.3$ cm^{-1}, space group $R32$ (No. 155).

A crystal with dimensions $0.26 \times 0.23 \times 0.33$ mm was used for intensity measurement. Intensity data were collected on a Rigaku four-circle diffractometer by ω scans at $4°$ min^{-1}, with graphite-monochromated Mo $K\alpha$ radiation. The scan range was calculated according to $1.1° + 0.5° \tan\theta$. Of the 2404 reflexions

recorded for $2\theta \leq 100°$, 902 intensities greater than $3\sigma(F)$ as estimated from counting statistics were regarded as 'observed' and used for the refinement.

The usual correction was made for Lorentz and polarization effects, but no correction was applied for absorption or extinction.

Structure determination

In the space group $R32$ the general positions are eighteenfold. The Co atom must lie on a set of three-fold special positions, since there are three formula units in the unit cell. The positions for the Co atoms were chosen as 0,0,0. The complex ion is thus required to have symmetry D_3. This means that the complex ions exhibit some orientational disorder, since they do not possess D_3 symmetry, because of the substituted methyl groups.

Three-dimensional sharpened Patterson maps showed four prominent peaks on 0,0,w, indicating that the I⁻ ions are on 0,0,z. Since the special position 0,0,z in the space group $R32$ is sixfold, nine I⁻ ions may be accommodated on two sets of sixfold positions with appropriate population parameters. The calculation of the structure amplitudes based on the coordinates of the Co atom and the two I⁻ ions gave an R value of 0.28. The positions of the N atoms that form an octahedron around the Co atom were also deduced from the Patterson maps. Successive Fourier syntheses including these atoms revealed the positions of the other lighter atoms of the ligands. At this stage, the difference syntheses revealed that six I⁻ ions are on a set of sixfold special positions with population 1.00 and the remaining three I⁻ ions are situated closer to the complex cation than the former and are distributed on two sets of sixfold positions and a set of general positions with different populations. Taking the disorder of the I⁻ ions into account and applying anisotropic thermal parameters for the heavy atoms, the R value

dropped to 0.14. Other small peaks on the difference syntheses were attributed to the O atoms of the water molecules. The population parameters of I⁻ ions in each site as well as those of O atoms were refined by the full-matrix least-squares program LINUS (Coppens & Hamilton, 1970). The R value became 0.078. The thermal parameters of the C atoms in the chelate ring became about 10 Å², unusually large compared with those of the remaining atoms; moreover, the difference syntheses at this stage suggested positional disorder in the ethylene portion of the chelate ring. Calculation of the interatomic distances and bond angles based on the possible positions of the C atoms deduced from the difference maps suggested that the positions of the substituted and unsubstituted methylene C atoms can have slightly different values. When this disorder was taken into account, the positions of the H atoms attached to all the C atoms in the chelate ring came out clearly on the difference maps and the map became flat at the region where the C atoms of the chelate ring were located. Final cycles of the refinement were then carried out where the isotropic thermal parameter of each H atom was fixed and given the value 3.5 Å². The R value dropped to 0.039 for the 902 observed reflexions. The final difference map became flat within 0.2 e Å⁻³. At the final stage of the refinement almost all the parameter shifts were less than one tenth of the corresponding standard deviations. The atomic scattering factors were taken from International Tables for X-ray Crystallography (1962). The scattering factor curve of Stewart, Davidson & Simpson (1965) was used for H. Table 1 lists the atomic parameters.*

A test was made for the absolute configuration of the molecule by changing the indices of all reflexions hkl to $\bar{h}\bar{k}\bar{l}$. The converged R value was 0.041. With the for-

Table 1. The final positional and thermal parameters with estimated standard deviations ($\times 10^4$)

The U_{ij} are defined by $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^*)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}	Population
Co	0	0	0	28 (0)	28 (0)	37 (1)	14 (0)	0	0	1.0000
N	1125 (20)	2017 (6)	384 (2)	38 (6)	36 (2)	44 (7)	23 (3)	1 (3)	−5 (2)	1.0000
C(A)	2556 (18)	416 (23)	577 (3)	35 (5)	46 (6)	52 (5)	21 (5)	−3 (4)	3 (5)	1.0000
C(1B)	2203 (51)	1820 (41)	716 (11)	51 (18)	70 (17)	62 (20)	29 (14)	−8 (13)	17 (11)	0.6667
C(2B)	2094 (69)	1799 (82)	699 (21)	22 (15)	69 (26)	55 (32)	10 (16)	−15 (18)	−47 (24)	0.3333
C(3)	3716 (38)	3348 (36)	877 (7)	69 (18)	58 (16)	44 (13)	26 (14)	−18 (13)	−12 (11)	0.3333
I(1)	0	0	3513 (0)	35 (0)	35 (0)	105 (1)	17 (0)	0	0	1.0000
I(2)	0	0	1953 (8)	67 (7)	67 (7)	44 (7)	34 (7)	0	0	0.19 (4)
I(3)	0	0	1837 (19)	92 (16)	92 (16)	421 (65)	46 (16)	0	0	0.12 (2)
I(4)	473 (84)	566 (177)	1874 (13)	76 (21)	164 (57)	47 (12)	20 (35)	−23 (16)	−32 (25)	0.06 (−)
O(1)	3806 (207)	118 (164)	1643 (26)	669 (211)	562 (170)	60 (31)	560 (190)	−82 (62)	−90 (69)	0.35 (6)
O(2)	3306 (196)	3892 (169)	1566 (18)	200 (54)	382 (114)	87 (46)	157 (77)	−3 (57)	−59 (54)	0.34 (6)
O(3)	437 (157)	33 (149)	4659 (16)	67 (83)	31 (40)	224 (46)	32 (56)	20 (36)	−24 (38)	0.14 (1)

mer value of 0·039, Hamilton's (1965) R test indicated the first choice to be significantly valid at the 99·5% confidence level. Equi-inclination Weissenberg photographs were taken, with Cu $K\alpha$ radiation, of the zero and third layer lines around the c axis. Table 2 lists the calculated F values and observed intensity relations between hkl and $\bar{k}hl$ pairs. The concordance in the table confirms the absolute configuration deduced by the test mentioned above. The absolute configuration of MeTACN was determined to be (R) in agreement with that of the starting substance (R)-(−)-propylenediamine (Mason & Peacock, 1976).

Table 3 lists some relevant interatomic distances.

Table 2. Determination of the absolute configuration

h k l	$F_c (hkl)$	Observed	$F_c (\bar{k}hl)$
2 2 0	277·7	<	291·9
2 5 0	168·9	>	161·9
5 5 0	74·8	<	81·3
2 5 3	134·4	>	128·3
5 5 3	60·8	<	64·8

Table 3. Relevant interatomic distances (Å)

Key to symmetry operations

(i)	$x,$	$y,$	z	(v)	$-x,$	$-x + y,$	$-z$
(ii)	$-x + y,$	$-x,$	z	(vi)	$x - y,$	$-y,$	$-z$
(iii)	$-y,$	$x - y,$	z	(vii)	$\frac{2}{3} - x, \frac{1}{3} - x + y,$		$\frac{1}{3} - z$
(iv)	$y,$	$x,$	$-z$	(viii)	$\frac{1}{3} + x, \frac{2}{3} + y,$		$-\frac{1}{3} + z$

H · · · H distances within the complex

N(H)—H(1^i)(C1B)	2·69		H(3)(CA)—H(2^i)(C1B)	2·18
N(H)—H(2^i)(C1B)	2·02		H(1)C1B)—H(4^i)(CA)	2·51
N(H)—H(3^{iv})(CA)	2·21		H(1)(C1B)—H(4^{iii})(CA)	2·06
N(H)—H(3^{iii})(CA)	2·11		H(1)(C1B)—H(1^{ii})(C1B)	2·55
N(H)—H(4^{iii})(CA)	2·17			

C · · · I distances shorter than 4·70 Å and I · · · O, O · · · C and O · · · O distances shorter than 3·90 Å. The distances that may not occur because of the disorder are indicated by an asterisk for comparison.

C(3)—I(2^i)	4·66 (4)		C(3)—I(^{vii})	3·83 (3)
C(3)—I(3^i)	4·39 (5)		C(3)—I(2^{vii})	3·07 (4)*
C(3)—I(4^i)	4·18 (6)		C(3)—I(3^{vii})	3·28 (5)*
C(3)—I(4^{iii})	4·59 (9)		C(3)—I(4^{vii})	3·88 (9)
C(3)—I(1^{viii})	4·28 (3)			2·85 (9)*
I(1)—O(3^i)	3·71 (5)		I(4)—O(2^{vii})	2·79 (18)*
I(2)—O(1^{iii})	3·45 (24)		O(1)—I(2^{ii})	3·45 (19)
I(2)—O(1^{vii})	2·82 (22)*		O(1)—I(3^{iii})	3·36 (19)
I(3)—O(1^i)	3·36 (19)		O(1)—I(4^{iii})	3·83 (26)
I(3)—O(1^{vii})	2·73 (22)*		O(1)—I(4^{vii})	2·67 (17)*
I(4)—O(1^i)	3·24 (23)		O(2)—I(3^{iii})	3·32 (11)
I(2)—O(2^i)	3·43 (16)		O(2)—I(3^{vii})	3·24 (19)
I(2)—O(2^{vii})	3·79 (15)		O(2)—I(4^{ii})	3·59 (13)
I(3)—O(2^i)	3·32 (17)		O(3)—I(1^{iii})	3·71 (5)
I(4)—O(2^{vii})	2·91 (14)*		O(2)—C(3^i)	2·34 (9)*
O(1)—C(3^i)	3·79 (15)		C(3)—O(3^{viii})	3·27 (14)
O(1)—C(3^{vii})	3·95 (16)		O(1)—O(2^i)	3·57 (25)
O(1)—O(2^{ii})	2·94 (18)			
O(2)—O(3^{viii})	2·42 (20)*			

Description of the structure and discussion

The structure (Fig. 1) is essentially ionic, comprising the complex cation, I⁻ ions and water molecules. The Co atom lies on a threefold special position and the complex is required to have D_3 symmetry. The methyl group is attached to one of the three chelate rings of the cyclic tridentate ligand, so that the complex ion exhibits orientational disorder. There are three possible geometrical isomers for the complex ion in respect of the positions of the two methyl groups. No conclusion can be drawn concerning the isomerism due to the orientational disorder, since the X-ray analysis only indicates the average structure.

Two molecules of the cyclic tridentate ligand coordinate to the Co atom with six secondary N atoms from above and below the metal atom to form an octahedral complex. A ligand molecule is spanned on a face of an octahedron. There are six five-membered chelate rings, with λ conformation. The C—CH$_3$ bond is equatorial with respect to the mean plane of the chelate rings. The conformations of the chelate rings with and without a substituted methyl group are different. Co—N—C(A)—C(1B)—N form two chelate rings without a methyl group and Co—N—C(A)—C(2B)—N
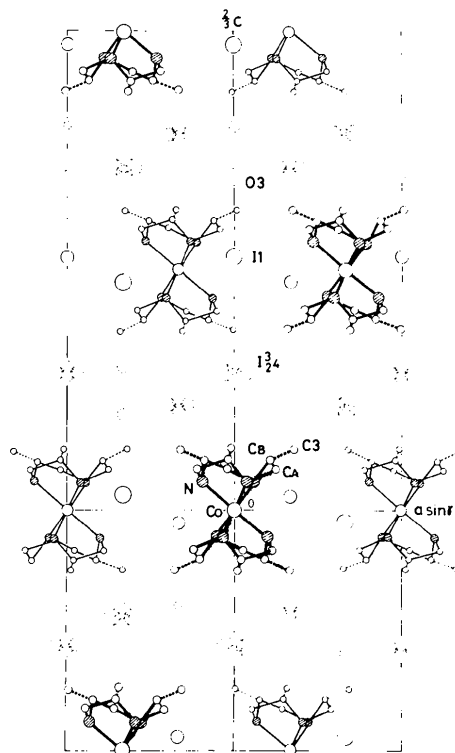

Fig. 1. The structure viewed along **b**. Atoms exhibiting positional disorder are indicated by broken circles. Disordered methyl groups are connected by broken lines. For clarity, O(1) and O(2) are not illustrated.

form the other one with a methyl C(3) atom bonded to C(2B). C(1B) and C(2B) are only 0.1 Å apart in the average structure. The complex {Co[(R)-MeTACN]₂}³⁺ is expected to owe its d-electron optical activity to the dissymmetric potential arising from distortion of the (CoN₆) chromophore and from the dissymmetric puckered chelate rings with the same type of ring conformation. The λλλ configuration may contribute to the large optical activity taking account of its additivity. In fact, a circular dichroism spectrum showed a magnitude of rotatory strength of more than twice that expected for six individual λ chelate rings (Mason & Peacock, 1976). The bond lengths and bond angles are shown in Fig. 2. Co—N is 1.974 Å, which is in good accordance with 1.978 Å reported for [Co(en)₃]³⁺ (Iwata, Nakatsu & Saito, 1969). The N—Co—N angle is 85.0°. As can be seen from Fig. 2, the bond distances and angles which involve C atoms are not sufficiently accurate. This may be a result of the orientational disorder and the resulting parameter interactions. The coefficients of the correlation matrix in the full-matrix least-squares calculation indicated large correlations between the coordinates and temperature factors of C(1B) and C(2B), the populations of O(1) and O(2) and of the I⁻ ions.

The (CoN₆) chromophore is elongated along and twisted around the threefold axis. The Co—N bond is inclined at an angle of 51.3 (2)° with respect to the threefold axis; 54.75° is the value for a regular octahedron. The triangle formed by the three N atoms of the upper ligand is rotated clockwise from an octahedral position by about 7.6° with respect to that of the lower ligand. This rotation of one cyclic ligand with respect to the other may be attributed to the steric repulsion between non-bonded H atoms. The closest approach of 2.02 Å occurs between the H atom bonded to the N atom of one ligand and that bonded to the C atom in the other ligand. If the direction of twist were counterclockwise, the non-bonded H distances would be much shorter than the sum of the van der Waals radii. Thus the direction of the distortion seems to be
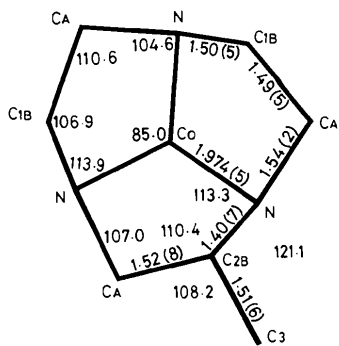
uniquely determined by the steric effects of the H atoms. A similar distortion of the (CoN₆) chromophore is present in a sandwiched complex, (+)ₓ₄₆-bis-(tribenzo[b,f,j][1,5,9]triazacycloduodecene)cobalt(III) ion (Wing & Eiss, 1970), which is reported to be about 8°.

A complex cation {Co[(R)-MeTACN]₂}³⁺ is surrounded by six I⁻ ions located approximately in one plane through the Co atom and perpendicular to the c axis. The I⁻ ions which are closer to the Co atom exhibit positional disorder. Three I⁻ ions are distributed among two sets of sixfold positions and a set of general positions with an approximate population ratio of 3:2:1. The interatomic distances between the methyl C and the I⁻ ions on general positions range from 2.85 to 4.28 Å. Since the van der Waals radii of the I⁻ ion and the methyl group are 2.20 and 2.0 Å respectively, it would be impossible for an I⁻ ion to approach a methyl group at a distance shorter than 3.9 Å. Thus the positional disorder of the I⁻ ions might occur to accommodate the bulky methyl group. The water molecules are arranged in a space between the complex cation and the I⁻ ions. 15 water molecules are distributed on a set of sixfold positions and two sets of general positions.

The single-crystal circular dichroism spectrum shows a single negative peak at 487 nm with light parallel to the optic axis, while that in an aqueous solution has a positive peak at about 477 nm.

The difference syntheses at the final stage revealed eight peaks around the Co atom which appear to be at least partly due to the asphericity of the d electrons (Fig 3a and b). They are arranged at eight corners of a distorted cube (Iwata & Saito, 1973). Six of them are 0.67 Å from the Co atom and two of them are on the threefold axis 0.96 Å away from the Co atom. It seems certain that the maps contain information on the nature of the Co—N bonding; however, the intensity data are not sufficient to warrant detailed analysis. Moreover, various errors tend to accumulate on the threefold axis.
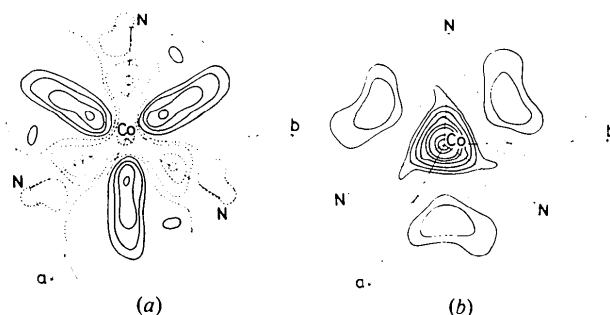

Fig. 2. Bond lengths (Å) and bond angles (°).

Fig. 3. Sections of final difference Fourier syntheses perpendicular to c. The contours are at intervals of 0.1 e Å⁻³. (a) A section 0.3 Å above the cobalt atom. (b) A section 0.96 Å above the cobalt atom.

All the computations were carried out on the FACOM 270-30 at this Institute and on the HITAC 8700/8800 at the Computer Centre of the University of Tokyo with a local version of the Universal Crystallographic Computation Program System (*UNICS*, 1967). This research was aided by a Scientific Research Grant from the Ministry of Education, to which the authors' thanks are due. The authors wish to express their gratitude to Professor Mason for kindly supplying the crystals and for the CD results in advance of publication.

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Synthèse et Structure Cristalline du Bis[difluorooxostannate(II)] d'Etain (II), (Sn₂O₂F₄)Sn₂

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The synthesis and the crystal structure of a new tin(II) fluoride oxide are described. The crystal structure of $(Sn_2O_2F_4)Sn_2$ has been determined by single-crystal X-ray techniques. The symmetry is monoclinic, and the space group is $C2/m$ with $a = 9.296$ (2), $b = 8.076$ (2), $c = 5.074$ (3) Å and $\beta = 97.9$ (1)°. The final R value is 0.036 for the 381 observed reflexions. The Sn atoms have a stereochemically active lone pair of electrons E. In the lattice, the geometry of the Sn^{II} coordination is of two types: the tetrahedron $Sn(1)OF_2E(1)$ with the lone pair at the apex; and the trigonal bipyramid $Sn(2)O_2F_2E(2)$, E being at one corner of the equatorial plane $Sn(2)O_2E(2)$; these bipyramids form a dimer by sharing the O–O edge: $(Sn_2O_2F_4E_2)^{4-}$. These new anion complexes are connected along c by Sn^{II} atoms [Sn(1)], forming infinite strings $[(Sn_2O_2F_4)Sn_2]_n$. The strings are held together by weak Sn(1)–F bonds. The trigonal-bipyramidal coordination around Sn(2) by light elements (O and F) is rather uncommon.

Au cours de l'étude du système SnO–SnF₂, un oxyfluorure inédit a été isolé: Sn₂OF₂. Sa synthèse, sa caractérisation et la détermination de sa structure font l'objet du présent mémoire.

La phase mise en évidence résulte de l'interaction directe d'un mélange équimolaire d'oxyde d'étain(II), (SnO) et du difluorure (SnF₂) en tube scellé, à une température de 200 °C. La durée de chauffe a été de 24 h. La poudre qui en résulte, de couleur blanche, est bien cristallisée.

Le spectre X de poudre est reporté au Tableau 1.

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Etude radiocristallographique

Un petit bloc monocristallin de forme prismatique a été isolé de la poudre et étudié par voie radiocristallographique (dimensions 0,02 × 0,02 × 0,03 mm).

Les diagrammes obtenus à l'aide d'une chambre de précession de Buerger ont permis de déterminer les paramètres cristallins et le groupe spatial; à partir de ces données, le spectre X de poudre est totalement indexé (Tableau 1): $a = 9,296 \pm 0,002$, $b = 8,076 \pm 0,002$, $c = 5,074 \pm 0,003$ Å; $\beta = 97,9 \pm 0,1°$. Extinctions: $hkl, h + k = 2n + 1$; groupes spatiaux: $C2$, Cm ou $C2/m$.

La masse spécifique déterminée par pycnométrie sur poudre dans l'orthophtalate de diéthyle, $D_m = 5,11 \pm 0,02$, est en bon accord avec la valeur calculée, $D_c = 5,13$ g cm^{-3}, pour quatre motifs Sn₂OF₂ par maille.