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Structures of Polyether Complexes.
VI.* Change of Configuration of a Cation–Oligoether Complex by Methylation of the Ligand: The Structure of Bis(2-methyl-8-quinolyloxyethoxyethyl) Ether–Rubidium Iodide

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Abstract

$C_{28}H_{32}N_2O_5.RbI$, orthorhombic, $Pca2_1$, $a = 9{\cdot}309$ (6), $b = 14{\cdot}465$ (7), $c = 21{\cdot}724$ (7) Å, $M_r = 688{\cdot}99$, $Z = 4$, $d_o = 1{\cdot}560$, $d_c = 1{\cdot}564$ Mg m^{-3} (flotation in bromobenzene/ethyl acetate), m.p. 467–469 K, $\mu = 11{\cdot}350$ mm^{-1}. The cation is coordinated to the anion and to all seven hetero-atoms. The ligand forms a helical structure with the heterocycles stacked parallel to each other 3·4 Å apart. This configuration contrasts with that found for the quinoline analog where the heterocycles are nearly perpendicular to each other and the cation is not coordinated to I^-.

Experimental

The title compound was recrystallized from a mixture of methanol and ethyl acetate (Vögtle & Sieger, 1977). Intensities for 2383 unique reflexions were obtained from a crystal 0·5 × 0·3 × 0·3 mm with a four-circle diffractometer, Ni-filtered Cu $K\alpha$ radiation, and the θ–2θ step scan up to $\sin\theta/\lambda = 0{\cdot}57$ Å^{-1}. The pseudocentrosymmetric structure was solved by direct methods combined with Fourier syntheses (Main, Lessinger, Woolfson, Germain & Declercq, 1977) and refined by full-matrix least squares (Sheldrick, 1976). Absorption or extinction corrections were not applied and the weighting scheme was based on counting statistics (Stout & Jensen, 1968). H-atom positions were calculated from stereochemical considerations after each cycle and only refined at the very end. H atoms of the methyl groups could not be located.

The final $R_w = 0{\cdot}076$ with all data included. Atomic coordinates of non-hydrogen atoms are presented in Table 1; bond distances, angles and torsion angles along the oligoether chain are listed in Table 2.‡ Coordination distances and the numbering scheme are given in Fig. 1.

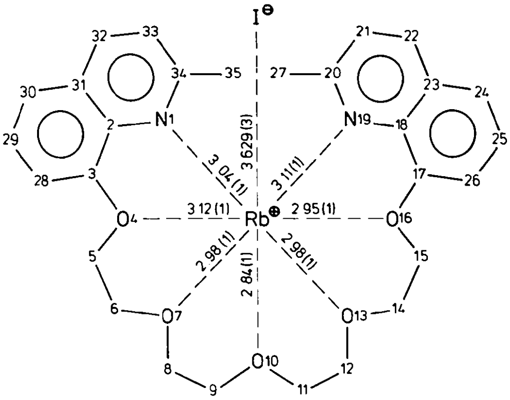

Fig. 1. Chemical structure, atom numbering and coordination distances (Å) to Rb^+.

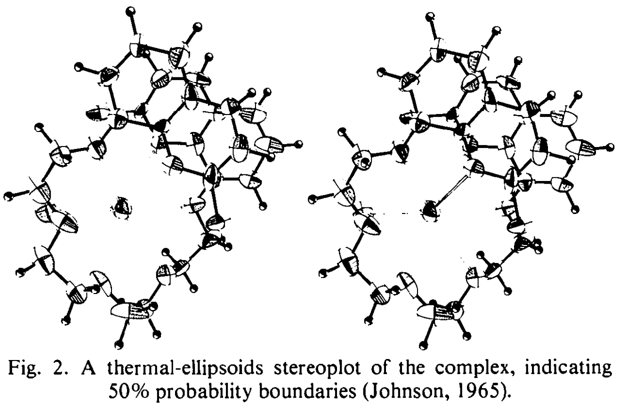

Fig. 2. A thermal-ellipsoids stereoplot of the complex, indicating 50% probability boundaries (Johnson, 1965).

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* Part V: Saenger & Reddy (1979).

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‡ Lists of structure factors, anisotropic thermal parameters, H-atom positions and bond distances and angles in the aromatic systems have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34299 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *of the non-hydrogen atoms*

	x	y	z
Rb	6571 (2)	2477 (1)	7232 (1)
I	9936 (2)	2630 (1)	6395 (1)
N(1)	7759 (13)	1850 (8)	8466 (6)
C(2)	6846 (15)	1292 (9)	8789 (8)
C(3)	5995 (21)	588 (13)	8451 (9)
O(4)	6140 (15)	577 (9)	7883 (6)
C(5)	5303 (24)	−110 (14)	7526 (9)
C(6)	5583 (21)	72 (14)	6847 (3)
O(7)	4892 (18)	938 (10)	6672 (6)
C(8)	4814 (24)	1015 (17)	6000 (10)
C(9)	4055 (24)	1957 (16)	5934 (10)
O(10)	5148 (16)	2629 (9)	6079 (6)
C(11)	4620 (20)	3536 (15)	5887 (9)
C(12)	5851 (15)	4203 (11)	6006 (9)
O(13)	5819 (17)	4300 (10)	6680 (6)
C(14)	6938 (23)	4875 (13)	6886 (9)
C(15)	6537 (23)	5124 (12)	7552 (9)
O(16)	6595 (16)	4256 (8)	7899 (6)
C(17)	6370 (20)	4301 (12)	8463 (9)
C(18)	5246 (17)	3663 (14)	8707 (3)
N(19)	4601 (16)	3094 (10)	8311 (7)
C(20)	3563 (19)	2522 (12)	8483 (8)
C(21)	3250 (20)	2411 (11)	9105 (9)
C(22)	3938 (21)	2941 (13)	9550 (9)
C(23)	4976 (21)	3605 (12)	9358 (9)
C(24)	5658 (15)	4186 (9)	9774 (4)
C(25)	6636 (21)	4828 (12)	9558 (8)
C(26)	7030 (19)	4888 (11)	8916 (11)
C(27)	2882 (21)	1912 (13)	7955 (9)
C(28)	5074 (23)	−6 (14)	8798 (7)
C(29)	4983 (23)	144 (13)	9448 (6)
C(30)	5837 (21)	784 (12)	9790 (10)
C(31)	6730 (21)	1388 (11)	9440 (8)
C(32)	7569 (13)	2027 (9)	9733 (4)
C(33)	8560 (18)	2531 (12)	9412 (9)
C(34)	8575 (15)	2490 (10)	8771 (8)
C(35)	9633 (20)	3071 (13)	8339 (8)

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *along the oligoether chain*

A	*B*	*C*	*D*	*B*–*C*	∠*A*–*B*–*C*	∠*A*–*B*–*C*–*D*
C(34)	N(1)	C(2)	C(3)	1·37 (2)	120 (1)	−179 (2)
N(1)	C(2)	C(3)	O(4)	1·48 (2)	119 (1)	−2 (2)
C(2)	C(3)	O(4)	C(5)	1·24 (2)	116 (2)	−180 (2)
C(3)	O(4)	C(5)	C(6)	1·48 (2)	118 (2)	176 (4)
O(4)	C(5)	C(6)	O(7)	1·52 (1)	108 (1)	−70 (2)
C(5)	C(6)	O(7)	C(8)	1·46 (2)	109 (1)	−165 (3)
C(6)	O(7)	C(8)	C(9)	1·47 (2)	110 (0)	180 (1)
O(7)	C(8)	C(9)	O(10)	1·54 (3)	101 (3)	75 (6)
C(8)	C(9)	O(10)	C(11)	1·44 (3)	105 (2)	167 (4)
C(9)	O(10)	C(11)	C(12)	1·46 (2)	108 (2)	−176 (6)
O(10)	C(11)	C(12)	O(13)	1·52 (1)	106 (1)	−75 (3)
C(11)	C(12)	O(13)	C(14)	1·47 (2)	102 (1)	178 (3)
C(12)	O(13)	C(14)	C(15)	1·41 (2)	111 (1)	165 (2)
O(13)	C(14)	C(15)	O(16)	1·54 (3)	105 (2)	65 (5)
C(14)	C(15)	O(16)	C(17)	1·47 (2)	106 (1)	177 (4)
C(15)	O(16)	C(17)	C(18)	1·25 (2)	117 (1)	128 (3)
O(16)	C(17)	C(18)	N(19)	1·49 (3)	116 (1)	1 (3)
C(17)	C(18)	N(19)	C(20)	1·33 (1)	118 (1)	−178 (3)

Results and discussion

A stereoscopic view of the complex is shown in Fig. 2. The Rb$^+$ ion is eightfold coordinated to I$^-$ and to all the hetero-atoms of the ligand. The latter displays a helical configuration with both heterocycles stacked parallel [*i.e.* 2 (3)°] to each other 3·4 (3) Å apart.

Wrapping of the ligand

Along the oligoether chain, C—O torsion angles are *trans* and ethyleneglycol C—C torsion angles are *gauche* as observed earlier for crown-ether complexes (Truter, 1973). Only the O(16)—C(17) torsion angle next to the second quinaldine (2-methylquinoline) residue is forced into a *gauche* conformation (128°) thus avoiding a collision of the two quinaldine ring systems and allowing their parallel packing. A kink in torsion angles was also observed in the quinoline complex but it occurred three bonds earlier at O(13)—C(14) (Saenger, Brand, Vögtle & Weber, 1977; Saenger & Brand, 1979).

In that complex the kink gives rise to nearly perpendicular orientations of the heterocycles with respect to each other, a situation differing substantially from the parallel stacking found in the present study. Since in both complexes the same cation is coordinated it is clear that only the chemical difference of the ligands accounts for the structural change. In Fig. 3 the two complexes are superimposed for ease of comparison.

As in other linear oligoether complexes (Saenger, Brand, Vögtle & Weber, 1977; Saenger & Brand, 1979; Suh, Weber & Saenger, 1978; Saenger & Reddy, 1979) N(1), O(4), O(7), and O(10) are coplanar within 0·03 Å. The Rb$^+$ ion is also located in this plane but O(13), O(16), and N(19) lie 0·91, 1·50 and 2·86 Å, respectively, out of this plane. The continuous increase in these three distances indicates the helical character of the ligand. In the quinoline complex Rb$^+$ is located 0·9 Å from the plane described by the atoms mentioned

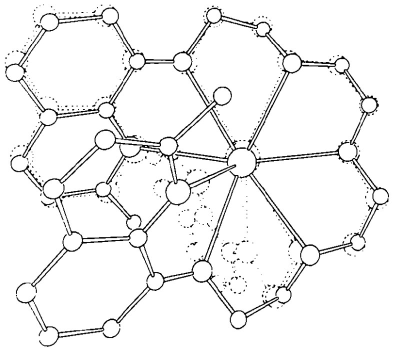

Fig. 3. A comparison of bis(8-quinaldineoxyethoxyethyl) ether–RbI and the 8-quinolyloxy analog (broken lines). The two molecules are superimposed such that the O atoms of the ligands are in similar positions.

above (Saenger, Brand, Vögtle & Weber, 1977). This geometry gives rise to a smaller radius of the polyether chain around the cation but the difference of only 0·15 Å is too small to account for the different configurations of the two complexes (Fig. 3).

Coordination to the cation

From van der Waals and ionic radii the $Rb^+\cdots O$, $Rb^+\cdots N$, and $Rb^+\cdots I^-$ distances should be about 2·87, 2·97 and 3·67 Å respectively (*Handbook of Chemistry and Physics*, 1974). In the title complex all the coordination distances except $Rb^+\cdots O(10)$, 2·84, and $Rb^+\cdots I^-$, 3·629 Å, exceed these values, especially $Rb^+\cdots O(4)$, 3·12 Å.

Compared to the quinoline complex (Saenger, Brand, Vögtle & Weber, 1977) the $Rb^+\cdots N$ distances are about 0·13 Å longer. This could be explained by (1) the change in electronegativity of N in the two heterocyclic systems, (2) the difference in ligand structures, and (3) the additional coordination to I^- in the quinaldine complex, probably resulting in weaker Rb^+–hetero-atom interactions.

In general, $Rb^+\cdots O$(aliphatic) distances are shorter than $Rb^+\cdots O$(aromatic) (Saenger, Brand, Vögtle & Weber, 1977; Suh, Weber & Saenger, 1978; Saenger & Reddy, 1979). This holds for $Rb^+\cdots O(4)$ but not for $Rb^+\cdots O(16)$ in the present complex. On the other hand, $Rb^+\cdots N(19)$ is noticeably longer than the corresponding $Rb^+\cdots N(1)$. In the quinoline complex, coordination distances to O(7) and O(13), to O(4) and O(16), and to N(1) and N(19) are pairwise nearly identical. It seems that in the quinaldine complex the stacking of the heterocycles limits the steric freedom of the oligoether chain, and therefore the coordination distances to Rb^+ are unsymmetrically distributed. In the quinoline analog, the heterocycles do not interact with each other and the oligoether chain can wrap around the cation without restrictions, giving rise to a symmetrical distribution of coordination distances.

Angles with Rb^+ as vertex are similar in both complexes: $N{-}Rb^+{-}O = 52\,(1)$, $O{-}Rb^+{-}O = 57\,(2)°$. The $N{-}Rb^+{-}N$ angle of 67 (2)° differs because the folding of the ligands is not comparable. The hetero-atoms do not surround the cation in a regular scheme as, for instance, in valinomycin (Steinrauf, Pinkerton & Dawkins, 1969); not even a bicapped triangular prism is evident as is sometimes found for octacoordinated Rb^+ (Metz, Moras & Weiss, 1970). It seems that in a long heptadentate ligand like the present one the geometry of the coordination sphere of the cation is mainly determined by the flexibility and stereochemical constraints of the ligand.

Packing in the unit cell

There are left- as well as right-handed helices in the unit cell (Fig. 4). The quinaldine planes of molecules related by the *a* glide are arranged perpendicular to each other [93 (4)°] thus forming a fishbone-like packing. Individual complex molecules represent $Rb^+\cdots I^-$ ion pairs wrapped by the organic ligand. They are stacked in channels of ligands without any interactions between a cation of one molecule and an anion of a neighbouring one since the shortest distance is 6·44 (1) Å.

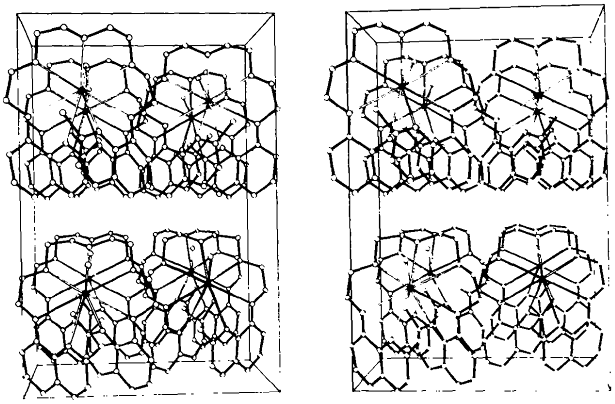

Fig. 4. A stereoplot of the unit-cell contents, looking down **a**. Note that the heterocycles of adjacent molecules are not stacked, in contrast to the 8-quinolyloxy analog (Saenger, Brand, Vögtle & Weber, 1977).

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Calculations were carried out on the Univac 1108 computer of the Gesellschaft für wissenschaftliche Datenverarbeitung, Göttingen.

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X-ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems.

X. The Crystal Structure of Dithieno[1,2-*b*:5,4-*b*′]tropylium Tetrafluoroborate at 143 and 295 K

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Abstract

$(C_{11}H_7S_2)^+BF_4^-$ is triclinic, space group $P\bar{1}$, with a = 7·1949 (12), b = 8·7203 (12), c = 9·5967 (20) Å, α = 105·787 (15), β = 99·074 (13), γ = 96·817 (13)° at 143 K, Z = 2. The structure was refined to an R of 0·043 for 1448 non-zero counter reflexions at 143 K. The cation is almost planar; the angle between the planes of the two thiophene rings is 175·3 (4)°. Aromatic character is indicated by the relatively uniform C—C lengths. The S—C bonds are equal. The BF_4^- ion is disordered and has been described by two different orientations.

Introduction

The title compound is composed of dithienotropylium cations and BF_4^- anions. The cation has aromatic character and is relatively stable to hydrolysis. The chemical properties of tropylium ions substituted with thiophene rings have been studied by Yom-Tov (1972). The structure of one of these compounds of aromatic character, dithieno[2,1-*b*:4,5-*b*′]tropylium perchlorate, has been determined (Aurivillius, 1974) and the cation found to be planar.

The present compound ($E.BF_4^-$, Fig. 1) is the first of a series (E,A,B), the structures of which have been determined. The second (A) is 4H-cyclohepta[1,2-*b*:5,4-*b*′]dithiophen-4-one (Andersson, 1978) and the third (B) is 8,9-dihydro-4H-cyclohepta[1,2-*b*:5,4-*b*′]-dithiophen-4-one (Andersson, 1975). Chemical and spectroscopic data indicate a decrease of aromaticity from the first to the last compound, and the structures of A and B have been correlated with their chemical properties (Andersson, 1978). With the present structure determination the series will be completed.

The packing of the ions has been studied. The BF_4^- ions are disordered, which is also the case for ClO_4^- in the compound studied by Aurivillius (1974). The present structure was determined at both 143 and 295 K.

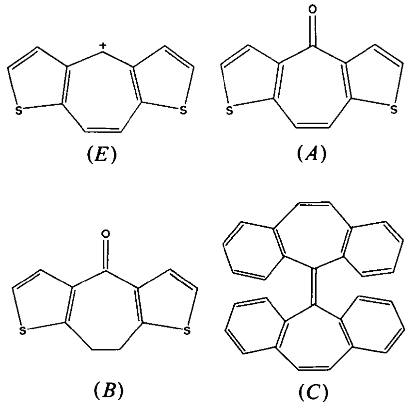

Fig. 1. Schematic drawings of the molecules: (E) dithieno-[2,1-*b*:5,4-*b*′]tropylium tetrafluoroborate; (A) 4H-cyclohepta-[1,2-*b*:5,4-*b*′]dithiophen-4-one; (B) 8,9-dihydro-4H-cyclohepta-[1,2-*b*:5,4-*b*′]dithiophen-4-one; (C) 2,3:6,7:2′,3′:6′,7′-tetrabenzoheptafulvalene.

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