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Structures of Polyether Complexes. V.* Molecular Structure of Bis(8-quinolyloxyethyl) Ether–Rubidium Iodide, a Linear Polyether Circularly Embracing a Metal Ion

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(*Received* 3 *July* 1978; *accepted* 8 *August* 1978)

Abstract

The title compound (DGOE.RbI) crystallizes in space group *Pnma* with $a = 9{\cdot}955$ (2), $b = 18{\cdot}163$ (3), $c = 12{\cdot}242$ (3) Å. The structure was solved from 1821 X-ray diffractometer data and refined by least squares to $R = 6{\cdot}4\%$. The linear ligand wraps around the cation in a circular manner, with the quinoline planes tilted like the wings of a butterfly and forming a dihedral angle of 66·8°. Rb^+ is coordinated to two symmetry-related I^- ions at distances of 3·691 and 3·903 Å and to all heteroatoms of DGOE as follows: $Rb^+\cdots N$ 2·97, $Rb^+\cdots$O(quinoline) 3·067, $Rb^+\cdots$O(aliphatic) 3·174 Å. The latter distance is 0·3 Å longer than expected and might not represent true coordination.

Introduction

Relatively long, linear polyether ligands wrap around metal ions in more than one turn to form complexes displaying a helical or S-shaped configuration (Saenger, Brand, Vögtle & Weber, 1977; Saenger, Brand, Reddy, Suh & Weber, 1978; Suh & Saenger, 1978). In this connection it was of interest to study the structure of a complex formed by a short linear ligand, DGOE.RbI (Fig. 1) (Vögtle & Sieger, 1977).

Experimental

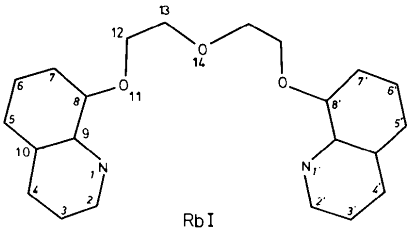

Fig. 1. Chemical structure of the DGOE.RbI complex.

When a hot, saturated methanol/ethyl acetate solution of DGOE.RbI was allowed to cool, yellowish, tabular crystals were obtained; crystal data are given in Table 1. The space-group ambiguity, *Pnma* or a reindexed $Pna2_1$, was resolved in favour of the former (with the *m* plane passing through the molecule) after the structure was solved with *MULTAN* (Main, Germain & Woolfson, 1970) and refined by full-matrix least squares in both space groups. The final *R* is 6·4% for all the measured 1821 data.

Results and discussion

Geometric data and the numbering scheme are displayed in Fig. 2, a diagram of the structure is in Fig. 3,

Table 1. *Crystallographic data*

Chemical formula: $C_{22}H_{20}N_2O_3.RbI$, $M_r = 572{\cdot}8$
Space group: *Pnma*
$a = 9{\cdot}955$ (2), $b = 18{\cdot}163$ (3), $c = 12{\cdot}242$ (3) Å
$V = 2213{\cdot}5$ Å^3, $Z = 4$, $D_c = 1{\cdot}719$ Mg m^{-3}, m.p. 498 K
1821 X-ray intensities were collected in the $2\theta/\omega$ scan mode; stationary background on both sides of scan.
Data were corrected for Lorentz-polarization, but not for absorption; size of crystal: 0·1 × 0·3 × 0·2 mm.
$R = \sum||F_o| - |F_c||/\sum|F_o| = 6{\cdot}4\%$ for all data.

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* Part IV: Suh & Saenger (1978).

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and atomic coordinates with e.s.d.'s obtained from the least-squares correlation matrix are in Table 2. Positions of H atoms were calculated on the basis of the C atom skeleton and not refined; in the refinement, H atoms were assigned an average temperature factor of 3·5 Å^2.* Fig. 4 shows the unit-cell contents.

All bond angles and distances within this structure are normal, the C(aromatic)–O–C(aliphatic) angles being greater than the C–O–C angles with both C atoms aliphatic; also, the C(aromatic)–O distance, 1·38 Å, is shorter than the C(aliphatic)–O distances, 1·45 and 1·43 Å (Fig. 2*a*). The torsion angles are *trans* for C–C–O–C and C–O–C–C but *gauche* for O–C–C–O, as previously observed (Fig. 2*b*) (Bright & Truter, 1970; Saenger, Brand, Reddy, Suh & Weber, 1978).

The quinoline heterocycle is slightly non-planar and displays a systematic puckering with C(3), C(4), C(7), C(8) below the least-squares plane through the ten atoms while the other six atoms are above this plane (Fig. 2*c*). The two heterocycles of the DGOE molecule form a dihedral angle of 66·8°, shaping the complex into a butterfly-like structure. This particular form was also observed for a cyclic crown ether complex, dibenzo-18-crown-6–(Na,Rb)SCN, where the two benzene rings enclose an angle of 71° (Fig. 5, Bright & Truter, 1970).

In this latter structure, the six O atoms ligating the Rb$^+$ ion are arranged in a nearly planar hexagon with the dimensions described in Fig. 5(*b*). The Rb$^+$ ion is 0·942 Å from this plane with Rb$^+\cdots$O coordination distances in the range 2·861 to 2·939 Å, comparable with the 2·87 Å calculated from the respective van der Waals radii (*Handbook of Chemistry and Physics*,

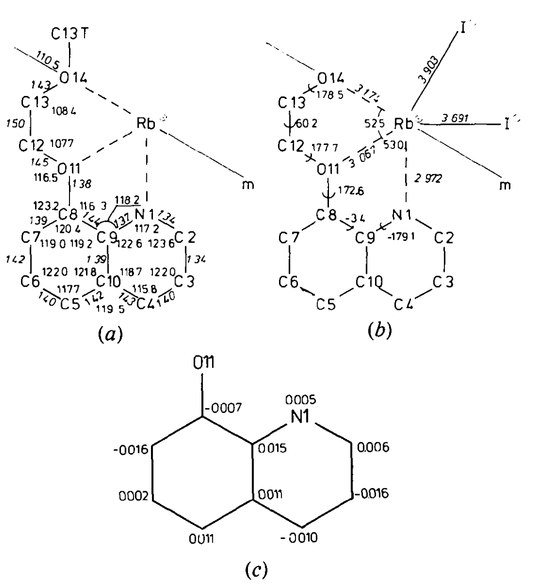

Fig. 2. (*a*),(*b*) Geometrical data for the DGOE.RbI complex. *m* indicates the crystallographic mirror plane passing through O(14), Rb$^+$, I$^-$. C(13*T*) is the mirror-equivalent C(13). The torsion angles in (*b*) are regarded as positive if the far atom moves clockwise; *cis* planarity is 0°. (*c*) Deviations of atoms (Å) from the quinoline least-squares plane.

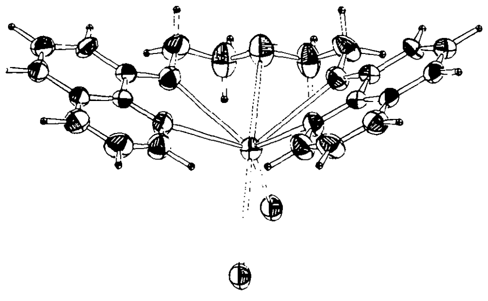

Fig. 3. A diagram illustrating the thermal ellipsoids at 50% probability (Johnson, 1965).

Table 2. *Positional parameters* (× 10^4)

	x	*y*	*z*
I	9038 (1)	2500 (0)	8274 (1)
Rb	10713 (1)	2500 (0)	5391 (1)
N(1)	8720 (7)	3657 (4)	4826 (6)
C(2)	7541 (9)	3602 (5)	5344 (7)
C(3)	6601 (10)	4128 (6)	5327 (8)
C(4)	6793 (9)	4794 (5)	4780 (7)
C(5)	8330 (10)	5537 (5)	3648 (7)
C(6)	9567 (11)	5589 (5)	3102 (7)
C(7)	10520 (10)	5005 (5)	3115 (7)
C(8)	10224 (9)	4367 (5)	3700 (7)
C(9)	8973 (8)	4300 (4)	4276 (6)
C(10)	8054 (9)	4876 (4)	4232 (6)
C(11)	11105 (6)	3787 (3)	3801 (4)
C(12)	12291 (10)	3810 (5)	3118 (7)
C(13)	13133 (9)	3148 (5)	3391 (8)
O(14)	12359 (9)	2500 (0)	3171 (8)
H(C2)1	7328	3089	5790
H(C3)1	5659	4043	5772
H(C4)1	6031	5230	4771
H(C5)1	7600	5986	3628
H(C6)1	9793	6084	2647
H(C7)1	11457	5053	2662
H(C12)1	12849	4308	3237
H(C12)2	11980	3766	2245
H(C13)1	13384	3165	4263
H(C13)2	14048	3143	2909

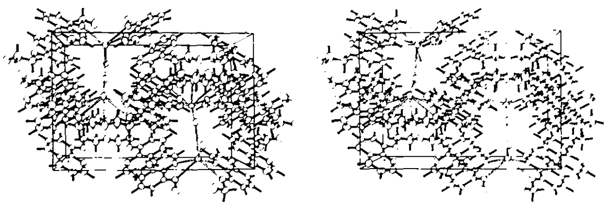

Fig. 4. Stereodiagram of the unit-cell contents (Johnson, 1965).

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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 33872 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

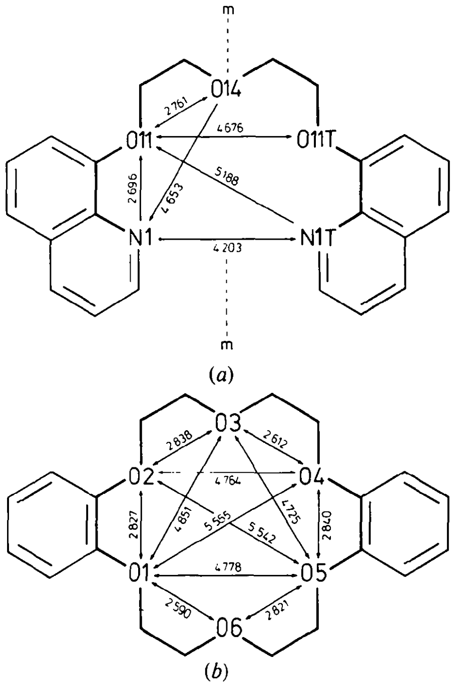

Fig. 5. Comparison of the hetero-atom geometry in (*a*) DGOE. RbI and (*b*) dibenzo-18-crown-6—(Na,Rb)SCN (Bright & Truter, 1970).

1964). The situation is similar for DGOE.RbI where the five hetero-atoms do not deviate from the common plane by more than 0·042 Å but the Rb$^+$ ion is displaced by 1·550 Å. In the coordination sphere, the Rb$^+\cdots$N distance, 2·972 Å, agrees with the theoretical value of 2·97 Å, but the Rb$^+\cdots$O distances significantly exceed the ideal 2·87 Å, being 3·067 for the aromatic O(11) and 3·174 Å for the aliphatic O(14). For the coordination of Rb$^+$ with aromatic O atoms in a similar complex, bis(8-quinolyloxyethoxyethyl) ether–RbI, comparable Rb$^+\cdots$O distances of 3·070 and 3·081 Å were observed. It was pointed out that the Rb$^+\cdots$O distance apparently increases with decreasing electronegativity of the O atom, Rb$^+\cdots$O(aromatic) distances being about 0·2 Å longer than Rb$^+\cdots$O(aliphatic) (Saenger, Brand, Vögtle & Weber, 1977).

The Rb$^+\cdots$O(14) distance, 3·174 Å, observed in the present study exceeds all the Rb$^+\cdots$O(aliphatic) distances reported thus far. An explanation for this can be found when the distances and angles between hetero-atoms in the dibenzo-18-crown-6—(Na,Rb)SCN complex and DGOE.RbI are compared (Fig. 5). The N$\cdots$N and N$\cdots$O distances in the latter are considerably shorter than the comparable O$\cdots$O distances observed in the former, indicating that the binding of the Rb$^+$ ion to the N(1) and O(11) atoms compresses the pentagon formed by the hetero-atoms of DGOE. As a consequence, O(14) moves out, giving rise to a decrease of angles N(1)$\cdots$O(11)$\cdots$O(14) and O(11)$\cdots$O(14)$\cdots$O(11*T*) from the ideal 120° to 117° and 115·8°, respectively, and a rather long Rb$^+\cdots$O(14) distance of 3·174 Å. Since this distance exceeds the ideal value by 0·3 Å it is questionable whether Rb$^+$ is really coordinated to O(14).

The authors are grateful to Professor F. Vögtle, Organisches Institut der Universität Bonn, for supplying the sample. The calculations were carried out on the Univac 1108 computer of the Gesellschaft für wissenschaftliche Datenverarbeitung, Göttingen.

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