Structures of Polyether Complexes.
II. Crystal Structure of the Bis[(8-quinolyloxy)ethoxyethyl] Ether Rubidium Iodide Complex*

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Abstract

$C_{26}H_{28}N_2O_5 \cdot RbI$ crystallizes in the monoclinic space group $P2_1/c$; $a = 9.649$ (2), $b = 17.666$ (3), $c = 15.868$ (3) Å, $\beta = 100.15$ (2)°, $D_x = 1.622$ Mg m^{-3}, $Z = 4$, m.p. 431–433 K. The final R is 8.6% for 4715 diffractometer data. Rb^+ is coordinated to all seven heteroatoms of the ligand which adopts a helical, chiral configuration by changing one C—O torsional angle from *trans* to *gauche*. The I$^-$ ion is located between molecules and not coordinated to Rb^+ because the cation is shielded by the ligand and by intermolecular stacking of quinoline heterocycles.

Introduction

In its ability to form complexes with cations, the linear polyether bis[(8-quinolyloxy)ethoxyethyl] ether (I, Fig. 1) (Weber & Vögtle, 1978) is reminiscent of the linear ionophore antibiotics of the nigericin family (Saenger,

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* Part I: Saenger, Brand, Vögtle & Weber (1977).

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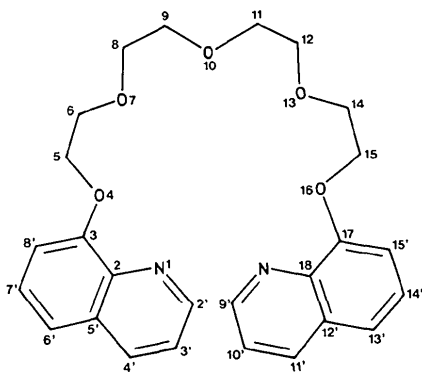
Brand, Vögtle & Weber, 1977). In the present contribution, structural details of the (I).RbI complex are described.

Experimental

The title compound crystallized in the form of yellowish needles (m.p. 431–433 K) when a hot, methanolic solution with ethyl acetate added near precipitation was allowed to cool slowly. 4715 diffractometer data were collected in the $2\theta/\omega$ scan mode with stationary background counts on each side of the scan and Ni-filtered Cu $K\alpha$ radiation. Three standard reflections monitored every 100 reflections showed about 10% loss of intensity. Data were corrected accordingly, as well as for Lorentz–polarization factors. The structure was solved by Patterson methods and refined by a full-matrix least-squares procedure with weights derived from counter statistics (Stout & Jensen, 1968). H atoms were located stereochemically and assigned the isotropic temperature factors of the attached C atoms; their atomic parameters were not refined. The final $R =$

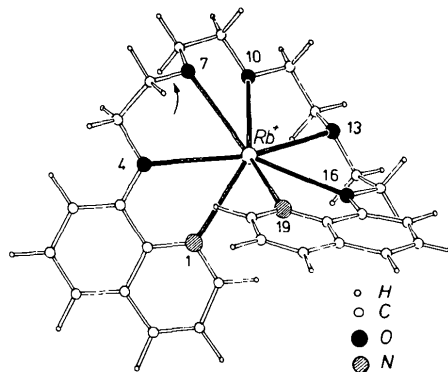Fig. 1. Chemical structure and numbering scheme of bis[(8-quinolyloxy)ethoxyethyl] ether.

Fig. 2. The structure of the (I).RbI complex. The C—O torsion angle in *gauche* conformation is marked by an arrow. Note the helical structure of the linear polyether.

Table 1. *Fractional atomic parameters for* (I). RbI; *e.s.d.'s are given in parentheses*

	x	y	z		x	y	z
I	−0·4018 (1)	−0·2365 (0)	0·1012 (1)	H(5,1)	0·1467	0·2805	0·1052
Rb	−0·1346 (1)	0·4570 (1)	0·2417 (1)	H(5,2)	−0·0342	0·2881	0·0530
N(1)	0·0757 (8)	0·5314 (4)	0·1545 (5)	H(6,1)	0·0742	0·2821	0·2462
N(19)	0·0836 (7)	0·5256 (4)	0·3704 (5)	H(6,2)	−0·0101	0·2066	0·1824
O(4)	0·0475 (7)	0·3838 (3)	0·1229 (4)	H(8,1)	−0·2581	0·2090	0·1397
O(7)	−0·1378 (7)	0·2933 (4)	0·2037 (4)	H(8,2)	−0·2571	0·2969	0·0840
O(10)	−0·3908 (7)	0·3743 (4)	0·1823 (5)	H(9,1)	−0·3908	0·2670	0·2374
O(13)	−0·4085 (6)	0·5081 (4)	0·2830 (5)	H(9,2)	−0·4783	0·2735	0·1280
O(16)	−0·1728 (6)	0·5799 (4)	0·3724 (4)	H(11,1)	−0·5265	0·3772	0·2700
C(5)	0·0415 (11)	0·3028 (5)	0·1114 (7)	H(11,2)	−0·6085	0·3839	0·1596
C(6)	−0·0025 (12)	0·2689 (6)	0·1884 (7)	H(12,1)	−0·6172	0·5062	0·2230
C(8)	−0·2600 (14)	0·2709 (6)	0·1481 (8)	H(12,2)	−0·4887	0·5092	0·1539
C(9)	−0·3895 (11)	0·2934 (7)	0·1762 (8)	H(14,1)	−0·5075	0·6107	0·2900
C(11)	−0·5169 (10)	0·4014 (8)	0·2076 (7)	H(14,2)	−0·3568	0·6113	0·2380
C(12)	−0·5143 (10)	0·4856 (8)	0·2141 (7)	H(15,1)	−0·3538	0·5834	0·4262
C(14)	−0·4012 (10)	0·5873 (7)	0·2906 (8)	H(15,2)	−0·3072	0·6703	0·3792
C(15)	−0·3103 (9)	0·6082 (6)	0·3743 (8)	H(2')	0·0428	0·6286	0·2218
C(2')	0·0984 (12)	0·6030 (6)	0·1749 (7)	H(3')	0·2086	0·7085	0·1591
C(3')	0·1895 (13)	0·6499 (6)	0·1386 (8)	H(4')	0·3250	0·6570	0·0468
C(4')	0·2553 (11)	0·6215 (6)	0·0757 (7)	H(8')	0·1689	0·3319	−0·0062
C(5')	0·2323 (9)	0·5454 (5)	0·0493 (6)	H(7')	0·3298	0·4106	−0·0801
C(2)	0·1417 (9)	0·5024 (5)	0·0931 (6)	H(6')	0·3602	0·5474	−0·0499
C(3)	0·1246 (9)	0·4232 (5)	0·0730 (6)	H(9')	0·2281	0·4619	0·3165
C(8')	0·1888 (10)	0·3925 (6)	0·0105 (7)	H(10')	0·4379	0·5032	0·4208
C(7')	0·2756 (11)	0·4369 (7)	−0·0318 (7)	H(11')	0·4100	0·5883	0·5359
C(6')	0·2957 (11)	0·5128 (6)	−0·0140 (7)	H(15')	−0·2016	0·6603	0·5133
C(9')	0·2133 (9)	0·5019 (6)	0·3678 (7)	H(14')	0·0074	0·7010	0·6241
C(10')	0·3322 (10)	0·5242 (6)	0·4288 (8)	H(13')	0·2442	0·6614	0·6163
C(11')	0·3175 (10)	0·5703 (6)	0·4913 (8)				
C(12')	0·1830 (10)	0·5957 (5)	0·4984 (6)				
C(18)	0·0680 (9)	0·5729 (5)	0·4365 (6)				
C(17)	−0·0695 (9)	0·6000 (5)	0·4393 (6)				
C(15')	−0·0943 (11)	0·6437 (5)	0·5073 (7)				
C(14')	0·0248 (14)	0·6650 (6)	0·5699 (7)				
C(13')	0·1597 (12)	0·6428 (6)	0·5664 (7)				

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

Atoms				Distance	Angle	Torsion angle
1	2	3	4	2–3	1–2–3	1–2–3–4
N(1)—C(2)—C(3)—O(4)				1·36 (1)	118·5 (8)	−3·6 (10)
C(2)—C(3)—O(4)—C(5)				1·37 (1)	114·7 (8)	−173·1 (7)
C(3)—O(4)—C(5)—C(6)				1·44 (1)	116·5 (8)	161·1 (8)
O(4)—C(5)—C(6)—O(7)				1·49 (2)	107·8 (9)	60·2 (10)
C(5)—C(6)—O(7)—C(8)				1·44 (1)	114·7 (8)	69·0 (11)
C(6)—O(7)—C(8)—C(9)				1·40 (1)	119·8 (8)	174·1 (9)
O(7)—C(8)—C(9)—O(10)				1·46 (2)	113·7 (10)	60·1 (12)
C(8)—C(9)—O(10)—C(11)				1·43 (1)	108·1 (10)	178·5 (9)
C(9)—O(10)—C(11)—C(12)				1·43 (1)	111·7 (8)	179·5 (9)
O(10)—C(11)—C(12)—O(13)				1·49 (2)	110·4 (9)	−67·3 (11)
C(11)—C(12)—O(13)—C(14)				1·42 (1)	109·6 (9)	179·2 (9)
C(12)—O(13)—C(14)—C(15)				1·41 (1)	111·4 (8)	168·3 (8)
O(13)—C(14)—C(15)—O(16)				1·50 (2)	109·5 (9)	62·3 (11)
C(14)—C(15)—O(16)—C(17)				1·42 (1)	107·2 (9)	173·2 (8)
C(15)—O(16)—C(17)—C(18)				1·37 (1)	116·5 (8)	−178·8 (8)
O(16)—C(17)—C(18)—N(19)				1·42 (1)	116·5 (8)	−3·8 (12)
N(19)—C(18)—C(17)				1·37 (1)	117·3 (7)	
N(1)—C(2)				1·36 (1)		

8·6%. Results are described in Tables 1 and 2 and in Figs. 2 and 3.*

Discussion

The stereoplot, Fig. 3, shows that the quinoline heterocycles of adjacent molecules are stacked at distances of 3·4 Å. This stacking formation and the enclosing of the Rb^+ by the ligand (Fig. 2) shields the cation such that I^- is not coordinated to Rb^+ but located between molecules of the complex.

The ligand is coordinated by all its heteroatoms to Rb^+. Distances between Rb^+ and the aromatic O(4) and O(16), 3·081 (7) and 3·070 (7) Å, are longer than distances to the aliphatic O atoms, probably a con-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34164 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
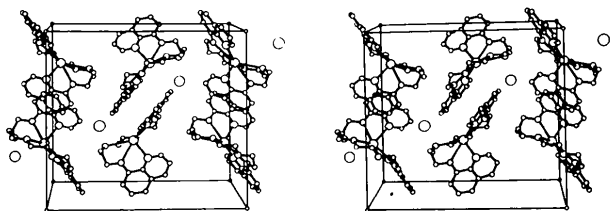
Fig. 3. Packing of molecules in the unit cell. Large circles indicate I⁻. Intermolecular stacking of quinoline heterocycles shields the Rb⁺ cation so that coordination with I⁻ is prevented.

Table 3. *Some data describing the coordination of* Rb⁺ *by* (I)

Atoms	Distance (Å)	Angle (°)	Distance (Å)
1–2–3	1–2	1–2–3	1–3
N(1)–Rb–O(4)	2·959 (8)	52·2 (2)	2·659 (9)
O(4)–Rb–O(7)	3·081 (7)	56·7 (2)	2·866 (10)
O(7)–Rb–O(10)	2·953 (7)	57·3 (2)	2·799 (10)
O(10)–Rb–O(13)	2·885 (7)	58·8 (2)	2·876 (10)
O(13)–Rb–O(16)	2·975 (7)	54·5 (2)	2·768 (8)
O(16)–Rb–N(19)	3·070 (7)	52·6 (2)	2·660 (9)
N(19)–Rb–N(1)	2·927 (7)	71·0 (2)	>3·2 Å

O(7), O(10), O(13), O(16), N(19) are coplanar; deviations (Å) from the least-squares plane are −0·154 (4), 0·197 (5), −0·077 (5), −0·088 (5), 0·122 (4). Rb⁺ is 0·745 (4) Å from this plane.

sequence of the lower electronegativity of the former (Table 3). Similar cation···O distances occur in other complexes of linear polyethers containing aromatic and aliphatic O atoms (Saenger & Reddy, 1979; Suh, Weber & Saenger, 1978).

The achiral, linear polyether wraps around the cation to form a chiral, helical complex. This could occur by adjustment of all the C—C and C—O torsion angles such that the fitting is achieved with the angles in the usually observed range, *gauche* for C—C and *trans* for C—O or O—C (Truter, 1973; Dunitz, Dobler, Seiler & Phizackerley, 1974). This is the case for the chain between O(7) and N(19), and the heteroatoms in this chain are nearly coplanar (Table 3). However, in order to avoid collision between the heterocycles, the torsion angle C(5)—C(6)—O(7)—C(8), 69°, is rotated from the usual *trans* into a *gauche* orientation.

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Crystallographic Studies on Metal–Nucleotide Base Complexes. X. *catena*-Tetraaqua-μ-(9-methylpurine)-copper(II) Sulphate Monohydrate

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Abstract

$[Cu(C_6H_6N_4)(H_2O)_4]^{2+}.SO_4^{2-}.H_2O$, monoclinic, space group $P2_1/n$, $a = 7 \cdot 310$ (1), $b = 13 \cdot 117$ (1), $c = 14 \cdot 628$ (2) Å, $\beta = 100 \cdot 98$ (1)°, $Z = 4$; final $R = 0 \cdot 029$. The Cu ion is octahedrally surrounded, the purine binding equatorially through both N(1) and N(7) producing a polymeric chain. N(9)-methylated purine is the only nucleobase ligand which has been found to be engaged in octahedral coordination simultaneously at N(1) and N(7). Since no exocyclic atom is attached to C(6), the stereoselectivity due to intracomplex hydro-