

Fig. 1. An ORTEP (Johnson, 1965) projection of the molecule along [001].

this class of compounds. In fact, in $(UO_2 \text{saloden})$. CH-Cl₃ (Bombieri, Forsellini, Benetollo & Fenton, 1979) the O(1)-U-O(2) angle is 177.3 (6)° and the shortest contact is 2.88 Å: the bending diminishes as the contacts lengthen.

In the overall geometry of the molecule, there are no substantial differences from the previous determination.

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Structure of 1,20-Bis(8-quinolyloxy)-3,6,9,12,15,18-hexaoxaicosane-Rubidium Iodide*

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Abstract. $C_{32}H_{40}N_2O_8$. RbI, monoclinic, C2/c, a = 42.169 (13), b = 10.804 (7), c = 15.946 (8) Å, $\beta = 100.42$ (8)°, $M_r = 793.06$, Z = 8, $d_c = 1.474$, $d_o = 1.465$ Mg m⁻³ (flotation in bromobenzene/ethyl acetate), $\mu = 2.388$ mm⁻¹, $R_w = 0.074$ for 4668 unique data. The ligand displays a distorted helical conformation with one and a half turns which provides the cation with tenfold coordination. Eight coordination distances are slightly longer and two are considerably longer than expected for Rb⁺...O,N. There is no interaction between the shielded cation and the twofold-disordered anion.

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Introduction. The title compound was recrystallized from a mixture of methanol and ethyl acetate (Weber, Saenger, Vögtle & Sieger, 1979). Data were collected from a crystal $0.5 \times 0.5 \times 0.5$ mm with a four-circle diffractometer, Mo $K\alpha$ radiation, a graphite mono-chromator and the θ -2 θ step-scan mode up to sin $\theta = 0.3817$. They were corrected for polarization effects.

The structure was solved by direct methods and subsequent Fourier syntheses (Main, Lessinger, Woolfson, Germain & Declercq, 1977) and refined by full-matrix least squares (Sheldrick, 1976), omitting four reflexions because of obvious strong secondary extinction. The weighting scheme was based on counting statistics (Stout & Jensen, 1968). H-atom positions were located from difference Fourier syntheses and recalculated according to stereochemical criteria. H atoms were © 1979 International Union of Crystallography

^{*} Structures of Polyether Complexes. IX. Part VIII: Weber & Saenger (1979).

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Table 1. Fractional atomic coordinates (×10⁴) of the Table 2. Bond distances (Å) involving non-hydrogen non-hydrogen atoms and isotropic B values (mean e.s.d. ca 0.3-0.4 Å²) calculated from the deposited

atoms

	anisotropic U values				N(1)-C(2)	1.394 (11)	C(21)–O(22)	1.426 (11)
					N(1) - C(30)	1.305(13)	O(22) - C(23)	1.394 (13)
	x	У	Ζ	B (Å ²)	C(2) = C(3)	1.418 (13)	C(23) - C(24)	1.562 (15)
Rb	3771 (0)	2862 (1)	10927(1)	4.2	C(2) = C(39)	1.412(11)	C(24) = O(25)	1.442 (11)
	5000 (0)	2360(1)	7500 (0)	4.2	C(3) = O(4)	1.365 (11)	O(25) - C(26)	1.348 (11)
I(1)	2542 (1)	2300(1)	7500 (0) 4602 (2)	12.2	C(3) - C(42)	1.356 (11)	C(26)C(27)	1.418 (13)
N(1)	2022 (1)	2603 (2)	4092 (2)	13.2	O(4) - C(5)	1.393 (13)	C(26)–C(35)	1-374 (13)
$\Gamma(1)$	3923 (2) 4200 (2)	2097(7)	12935 (5)	0.0	C(5) - C(6)	1.450 (13)	C(27)–N(28)	1.345 (11)
C(2)	4209 (2)	21//(0)	13300 (5)	4.2	C(6)–O(7)	1.440 (11)	C(27)–C(32)	1.408 (13)
C(3)	4374 (2)	1338 (8)	12891 (6)	4.2	O(7)–C(8)	1.449 (13)	N(28)–C(29)	1.324 (11)
O(4)	4222 (2)	11/2(6)	12069 (4)	6.4	C(8)–C(9)	1.482 (15)	C(29)–C(30)	1.392 (13)
C(5)	4349 (2)	346 (10)	11546 (6)	6.3	C(9)–O(10)	1.420 (13)	C(30)–C(31)	1.325 (16)
C(0)	4101 (3)	-531 (9)	11184 (8)	7.8	O(10)–C(11)	1.398 (11)	C(31)–C(32)	1.384 (15)
0(7)	3840 (2)	119 (6)	10660 (4)	6.2	C(11)–C(12)	1.490 (15)	C(32)–C(33)	1.406 (16)
C(8)	3558 (3)	-672 (9)	10490 (8)	7.9	C(12)–O(13)	1.401 (11)	C(33)–C(34)	1.392 (20)
C(9)	3274 (3)	71 (9)	10101 (7)	7.0	O(13)-C(14)	1.412 (13)	C(34)C(35)	1.386 (16)
O(10)	3222 (1)	1005 (6)	10689 (4)	5.7	C(14)-C(15)	1.502 (15)	C(36)-C(37)	1.390 (13)
C(11)	2924 (2)	1589 (9)	10448 (7)	6.4	C(15)-O(16)	1.435 (11)	C(37)-C(38)	1.372 (15)
C(12)	2887 (2)	2605 (10)	11056 (7)	6.3	O(16) - C(17)	1.427 (11)	C(38)-C(39)	1.383 (13)
O(13)	3097 (1)	3571 (6)	10940 (4)	5.5	C(17) - C(18)	1.468(15)	C(39) - C(40)	1.374(11)
C(14)	3037 (2)	4648 (10)	11387 (7)	6.6	C(18) - O(19)	1.405(13)	C(40) - C(41)	1.321 (15)
C(15)	3275 (3)	5636 (9)	11269 (7)	6.7	O(19) - C(20)	1.409(11)	C(41) - C(42)	1.404(13)
O(16)	3589 (2)	5223 (6)	11676 (4)	5.7	C(20) - C(21)	1.476(16)	e(41) e(42)	1.404 (13)
C(17)	3820 (3)	6202 (9)	11761 (7)	6.5	0(20) 0(21)	1 470 (10)		
C(18)	4139 (3)	5684 (10)	12101 (7)	7.0				
O(19)	4236 (1)	4942 (6)	11469 (4)	5.7				
C(20)	4541 (3)	4388 (9)	11711 (7)	7.2	Table 2 Day	d analaa	(0) investigations	1
C(21)	4666 (2)	4012 (10)	10941 (7)	7.2	Table 5. Bon	a angles	(°) involving non-	nyarogen
O(22)	4458 (1)	3117 (6)	10469 (4)	5.6		(atoms	
C(23)	4501 (2)	3068 (11)	0623 (7)	5.0				
C(24)	4361 (2)	2082 (10)	9023(1)	6.0	C(36) - N(1) - C(2)	115.5 (8)	O(25)C(24)C(23)	106-1 (8)
O(25)	$\frac{4204}{2044}$	2082 (10)	9141(0)	0.8	C(3)-C(2)-N(1)	117.3 (7)	C(26)-O(25)-C(24)	116-8 (8)
C(25)	3944 (1)	2344 (0)	9145 (4)	5.0	C(39)-C(2)-N(1)	123.7 (8)	C(27)-C(26)-O(25)	114.2 (8)
C(20)	3099 (2)	1951 (9)	8044 (0)	5.3	C(39) = C(2) = C(3)	119.0 (8)	C(35) - C(26) - O(25)	124.8 (9)
$\mathcal{L}(27)$	3398 (2)	2571(9)	8554 (5)	4.8	C(4) = C(3) = C(2)	$114 \cdot 2(7)$	C(35) - C(26) - C(27)	120.9 (9)
N(28)	3381 (2)	3644 (7)	8972 (5)	4.9	C(42) = C(3) = C(2) C(42) = C(3) = O(4)	119.7 (0)	N(28) - C(27) - C(26)	119.1 (8)
C(29)	3100 (2)	4225 (10)	8851 (7)	5.9	C(5) = O(4) = C(3)	120.0 (3)	C(32) = C(27) = C(20) C(32) = C(27) = N(28)	118.4 (9)
C(30)	2831 (2)	3770 (11)	8298 (7)	7.3	C(6) - C(5) - O(4)	109.3 (9)	C(29) = N(28) = C(27)	122.3(3) 117.7(8)
C(31)	2844 (3)	2704 (10)	7895 (7)	7.0	O(7)-C(6)-C(5)	109.5 (8)	C(30)-C(29)-N(28)	121-8 (10)
C(32)	3131 (3)	2055 (10)	8008 (6)	6.1	C(8) - O(7) - C(6)	109.7 (7)	C(31)-C(30)-C(29)	$121 \cdot 1 (10)$
C(33)	3173 (3)	922 (13)	7608 (7)	8.9	C(9)-C(8)-O(7)	109.5 (8)	C(32)-C(31)-C(30)	119.2 (9)
C(34)	3467 (4)	304 (12)	7709 (8)	10.3	O(10)-C(9)-C(8)	108-5 (8)	C(31)-C(32)-C(27)	117.6 (10)
C(35)	3725 (3)	832 (9)	8253 (6)	6.9	C(11)-O(10)-C(9)	112.1 (7)	C(33)-C(32)-C(27)	118.3 (10)
C(36)	3779 (3)	3448 (9)	13388 (6)	6.5	C(12) - C(11) - O(10)	0) 110.4 (7)	C(33)–C(32)–C(31)	124.1 (10)
C(37)	3901 (3)	3785 (9)	14226 (7)	7.0	O(13)-C(12)-C(11)	l) 108·7 (9)	C(34)-C(33)-C(32)	123-2 (11)
C(38)	4180 (3)	3258 (9)	14650 (6)	5.8	C(14) - O(13) - C(12)	2) 111.9 (8)	C(35)-C(34)-C(33)	117-2 (11)
C(39)	4344 (2)	2432 (8)	14219 (6)	4.2	C(15) - C(14) - O(13)	109.7(9)	C(34) - C(35) - C(26)	121-8 (11)
C(40)	4626 (2)	1868 (9)	14596 (6)	5.6	C(10) - C(13) - C(14)	+) IU/·8(8) 5) 111.7(7)	C(37) - C(36) - N(1)	124.6 (10)
C(41)	4768 (2)	1098 (10)	14138 (6)	6.5	C(18) = C(17) = O(16)	(1) (1)	C(30) = C(37) = C(30)	120.0 (10)
C(42)	4651 (2)	808 (8)	13280 (6)	5.1	O(19) - C(18) - C(13)	7) 108.6(8)	C(38) = C(30) = C(37)	117.3 (8)
	• •		(*)		C(20) = O(10) = C(10)	1145(7)	C(40) = C(30) = C(2)	120 1 (0)
					-0(20)-0(13)-0(10)	5) 114.5(7)		120.1141
					C(20) = O(19) = C(10) C(21) = C(20) = O(19)	(7) (7)	C(40) - C(39) - C(2) C(40) - C(39) - C(38)	120.1 (9)
assigned	the isotropi	c thermal	narametera	of the	C(20) = O(19) = C(10) C(21) = C(20) = O(19) O(22) = C(21) = C(20)	$\begin{array}{c} 114.3(7) \\ 109.4(8) \\ 110.4(8) \end{array}$	C(40)-C(39)-C(2) C(40)-C(39)-C(38) C(41)-C(40)-C(39)	120.1 (9) 122.6 (8) 118.8 (9)

C(24) - C(23) - O(22)

a attached C atoms. Results are given in Tables 1, 2 and 3* and in Fig. 1. A stereoview of the complex is in Fig. 2.

Discussion. The structures of RbI–polyether complexes with similar but shorter ligands than the present one

* Lists of structure factors, temperature factors and H-atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34736 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

have been investigated before: The ligand with three O atoms wraps around the cation circularly (Saenger & Reddy, 1979), and the ligand with five O atoms wraps around the cation in a helical manner with nearly one turn (Saenger, Brand, Vögtle & Weber, 1977; Saenger & Brand, 1979).

C(41) - C(42) - C(3)

118.1 (9)

108.5 (9)

The present achiral linear polyether encloses the cation to form a chiral, helical complex with one and a



Fig. 1. Chemical structure, numbering scheme, torsion angles $(\pm 2^{\circ})$ along the polyether chain and coordination distances (Å) to Rb⁺.



Fig. 2. A stereoscopic view of the complex (Johnson, 1965). Radii are given arbitrary values.

half turns. This is achieved by a kink of the C(3)–O(4)-C(5)-C(6) torsion angle from *trans* to gauche (127°) and also by slight deviations from the expected *trans* orientations of the C(18)–O(19)–C(20)–C(21) (-160°) and C(20)–C(21)–O(22)–C(23) (159°) torsion angles.

In the ligand with three O atoms (Saenger & Reddy, 1979) the dihedral angle between the quinoline systems is about 70°, in the ligand with five O atoms (Saenger & Brand, 1979) it is about 90°, and in the present ligand with eight O atoms it is 147 (3)°. This latter angle shows the lack of stacking interactions between the two aromatic systems in the complex when the flexible polyether chain is long enough. In each of the two homologous RbI complexes mentioned above five hetero-atoms of the ligand are coplanar. In the shortest ligand both the N atoms of both the quinoline systems lie in this plane (Saenger & Reddy, 1979), whereas only one N is coplanar in the ligand with seven hetero-atoms



Fig. 3. A view of the cell looking down **b** (Johnson, 1965). Iodide anions are indicated with thermal ellipsoids (50% probability).

(Saenger & Brand, 1979). In the title compound the central six O atoms are only approximately coplanar (deviations ± 0.55 Å), the Rb⁺ also being located in this plane (0.03 Å). The hetero-atoms of both the terminal oxyquinoline groups, O(4), N(1) and O(25), N(28), deviate by 2.32, 3.04, and -2.51, -3.29 Å, respectively. This indicates that the occupation of the equatorial region of the coordination sphere of the cation is favoured over the polar regions.

All the hetero-atoms are arranged on a sphere with a mean radius of 3.07 (2) Å. This cation...hetero-atom distance is longer than the theoretical one (2.87 Å) calculated from van der Waals and ionic radii (*Handbook of Chemistry and Physics*, 1974) and slightly longer than the average observed (*International Tables for X-ray Crystallography*, 1968). The Rb⁺...N(28), 3.360 Å, and Rb⁺...O(22), 3.124 Å, distances exceed theoretical values by 0.4 and 0.25 Å, respectively, but most probably these atoms also interact with the cation.

Angles with Rb⁺ as vertex vary between 48 and 57°, a range observed before (Saenger, Brand, Vögtle & Weber, 1977). The unusual angle N(1)–Rb⁺–N(28) (159°), however, indicates that the two heterocycles are nearly opposite to one another and thus reflects the one and a half turns of the ligand in the helical structure. Because of the high coordination number the cation is totally shielded from the large I⁻ anion. The missing cation…anion interaction gives rise to high anisotropic thermal motions and twofold disorder of the anions which are located in channels between the stacked molecules of the ligand (see Fig. 3).

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Structure of (1,3,6,8,10,13,16,19-Octaazabicyclo[6.6.6]icosane)platinum(IV) Dithionate $2\frac{1}{2}$ Hydrate

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Abstract. $[Pt(C_{12}H_{30}N_8)](S_2O_6)_2.2\frac{1}{2}H_2O, C_{12}H_{30}N_8$ Pt⁴⁺.2S₂O₆²⁻.2 $\frac{1}{2}H_2O$, FW = 846.78, monoclinic, $P2_1/c$, a = 18.250 (3), b = 9.264 (1), c = 17.461 (3) Å, $\beta = 121.50$ (1)°, U = 2614.8 (5) Å³, Z = 4, $\mu = 6.04 \text{ mm}^{-1}$, $D_x = 2.151 \text{ Mg m}^{-3}$. The cage-shaped ligand in which the metal ion is encapsulated is sexidentate in this complex. The geometry of the cage structure depends on the nature of the central metal atom. The three non-equivalent N–C bonds differ significantly from each other [1.498 (7), 1.421 (8) and 1.532 (8) Å]. The tris(ethylenediamine)Pt^{IV} moiety of the complex has a *lel*₃ conformation. The complex is hydrogen bonded to dithionate ions and water molecules to form a network in the *c* and *b* directions.

Introduction. The macrocyclic title complex offers interesting prospects for the study of intramolecular rearrangements, electron transfer and spectroscopic properties. With this ligand, a metal ion could be in different oxidation states without seriously changing its coordination number or the structure. Moreover, cage complexes are usually mononuclear (Creaser, Harrowfield, Herlt, Sargeson, Springborg, Geue & Snow, 1977). In this connection, the crystal structure of the title complex, trivially represented as [Pt- $(sepulchrate)](S_2O_6)_2 \cdot 2\frac{1}{2}H_2O$, was determined. The [Pt(sepulchrate)]⁴⁺ was prepared by condensation of a 0567-7408/79/123096-03\$01.00 formaldehyde and an ammonia with an ethylenediamine complex of Pt. The prismatic transparent crystals were kindly supplied by A. Sargeson of the Australian National University. The crystal used for the intensity measurements was bounded by $\pm(110)$, $(\bar{1}10)$, (001)and (111), with interplanar spacings of 0.10, 0.16, 0.15 and 0.25 mm respectively. X-ray diffraction data were collected within the range $2\theta < 65^\circ$ on an automated four-circle diffractometer, using graphitemonochromated Mo K₀ radiation ($\lambda = 0.7107$ Å). Four standard reflections counted at 50-reflection intervals indicated considerable decay (5-15%) during the two weeks of data collection. The intensity measurements were completed by employing six different sets of setting parameters based on the same 18 reflections in order to obtain the average structure.

Structure determination was carried out on 6305 independent reflections with $|F_o| \ge 3\sigma(|F|)$. Corrections were applied to the net intensities to account for Lorentz and polarization effects and for absorption. The lattice constants showed 0.08 Å elongations in *a* and *c*, while that of *b* showed a shrinkage of 0.06 Å during the period of data collection. The coordinates of the Pt and S atoms, derived from the sharpened Patterson maps, were used for a structure factor calculation which gave an *R* value of 0.382. Successive Fourier and difference syntheses revealed the remaining © 1979 International Union of Crystallography