[{Ru(C$_5$H$_5$N)$_4$}$_2$(C$_2$O$_4$)](BF$_4$)$_2$ and by Curtis *et al.* (1973) for [(Ni{NH$_2$(CH$_2$)$_2$NH$_2$}$_2$)$_2$(C$_2$O$_4$)](NO$_3$)$_2$. The bond lengths within the oxalate group are normal and do not show any asymmetry arising from the unequal Ni—O distances.

The water molecule is hydrogen-bonded to O(11) [3·009 (10) Å *via* H1(O3)], N(2) [2·983 (7) Å *via* H(N2)] and N(6) [2·867 (8) Å, presumably *via* the unlocated H2(O3)] of three different molecules. A consequence of the first-mentioned contact is a reduction in the static disorder and/or the vibrational freedom of O(11), as reflected in its thermal parameters, compared with the other perchlorate O atoms. This causes the observed Cl—O distance to be longer for O(11) than for O(12–14); after application of a Busing & Levy (1964) riding-motion correction, assuming the O atoms to be riding on Cl, all four Cl—O bond lengths lie in the range 1·48 to 1·52 (1) Å.

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Crystal Structures of Complexes Between Alkali-Metal Salts and Cyclic Polyethers. 12.* The Complex between Sodium Bromide and 2,3-Dimethoxybenzo-15-crown-5 {Bromo(2,3-dimethoxy-6,7,9,10,12,13,15,16-octahydrobenzo[1,4,7,10,13]pentaoxacyclopentadecene)sodium}

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Abstract

C$_{16}$H$_{24}$BrNaO$_7$, $M_r = 431·3$, is monoclinic, $P2_1/c$, with $a = 12·036$ (2), $b = 8·222$ (6), $c = 20·210$ (4) Å, $\beta = 102·21$ (4)°, $U = 1954·8$ Å^3, $D_m = 1·432$, $Z = 4$, $D_c = 1·436$ Mg m^{-3}, μ(Mo Kα) = 2·13 mm^{-1}. The structure was determined by the heavy-atom method and refined by full-matrix least squares to $R = 0·069$ for 1377 observed reflections from measurements on a four-circle X-ray diffractometer. There are discrete molecules consisting of

C$_{16}$H$_{24}$NaO$_7^+$.Br$^-$ ion pairs [Na–Br 2·763 (3) Å] with the Na$^+$ ion additionally coordinated by the five O atoms of the crown-ether ring [Na–O 2·37 (1) to 2·45 (1) Å]. The *ortho*-dimethoxy groups do not take part in coordination.

Introduction

The crown-ether ligand 2,3-dimethoxybenzo-15-crown-5 (1*a*) differs from the parent (1*b*) in being soluble in water. It was synthesized as part of a general study of complexing agents for d^0 cations with controlled changes in physical properties and it forms complexes with alkali-metal salts. With sodium iodide

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* Part 11: Owen (1980).

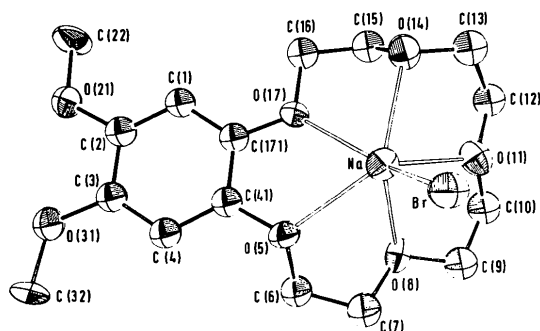† To whom correspondence should be addressed.

Fig. 1. One molecule of the complex showing the designations of the atoms, and vibration ellipsoids at the 50% level. H atoms are omitted.

the compound obtained was shown, by elemental analysis, preliminary X-ray investigation and infrared spectroscopy, to be a hydrate, and hence possibly similar to the known [Na(1b)(H$_2$O)]$^+$.I$^-$ complex (Bush & Truter, 1972). By contrast, the sodium bromide complex crystallizes without solvent and has the formula NaBr(1b). To discover whether the *ortho*-dimethoxy groups formed a chelating entity additional to the 15-crown-5 ring, the crystal structure of the complex was determined. The molecule was found to consist of Na$^+$Br$^-$ ion pairs coordinated only by the macrocyclic ring as shown, with the numbering of the atoms, in Fig. 1.

(Ia) R = OCH$_3$

(Ib) R = H
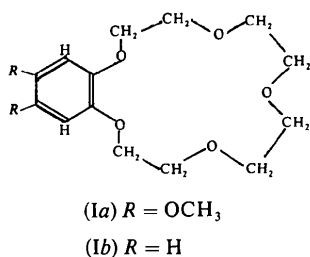
Experimental

The ligand (350 mg) and sodium bromide (110 mg) dissolved in methanol (3 ml) were treated with ethyl acetate (5 ml), the complex slowly crystallized after a period of 2 h as thick colourless needles, m.p. 467 K.

The crystals are unstable in the X-ray beam. The first one exploded, so for further investigation a crystal 0·38 × 0·40 × 0·23 mm was mounted in a capillary tube with **b** parallel to the sides. Preliminary photographs established the space group as $P2_1/c$ and showed that observations to $2\theta\,50°$ should be obtainable with Mo $K\alpha$ radiation.

Intensity measurements were made on a FACS-I four-circle Picker diffractometer in the θ–2θ scan mode at 0·50° min^{-1} from 0·5° below the $K\alpha_1$ to 0·6° above

the $K\alpha_2$ peak and backgrounds were counted for 25s at the end of each scan. Accurate cell dimensions were obtained from 25 manually centred reflections. Observations were collected in shells of reciprocal space from 2·5 < 2θ < 38°; the intensities of the two standard reflections 530 and 606 had then fallen by 25%. The four octants with $k = 0$ or positive were measured and scaled to the standards; equivalent reflections were averaged. For strong reflections at low θ values the use of filtered radiation gave an unreliable value of the low-θ background so that measurements were repeated without a filter and the average of the values obtained with and without a filter was scaled to those of the standard reflections measured in the same way. Lorentz and polarization factors were applied and standard deviations calculated from the formula $\sigma^2(I)$ = total count + (0·25 × background sum) × (scan time/background time)^2. Of 1585 unique reflections measured 1377 had $|F| > 4\sigma_{F_o}$ and were treated as observed.

A Patterson synthesis with the 730 reflections having $2\theta < 30°$ revealed the Br atoms which yielded an R value of 0·47 after two cycles of isotropic refinement. All the non-hydrogen atoms were located by standard electron density and difference syntheses. After refinement with anisotropic vibration parameters for Na, Br, O and the methyl C atoms until all shifts in parameters were less than the corresponding standard deviations, a difference synthesis showed some peaks in positions close to those calculated for H atoms on the benzene rings or the CH$_2$ groups at C—H = 0·96 Å. Full-matrix refinement including the aromatic H atoms and the methylene H atoms each with a common U_{iso} parameter gave an R factor of 0·076. A difference synthesis revealed three peaks of about 0·5 e Å^{-3} in positions corresponding to two H atoms on C(32) and one on C(22); these allowed the coordinates of all six methyl H atoms to be calculated. In the final cycles of refinement the H atoms on C(22) and those on C(32) were each assigned a common isotropic vibration parameter. Refinement ceased when the most significant shift was 0·055 of the corresponding standard deviation. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weighting scheme $w = 0·4355/(\sigma_{F_o}^2 + 0·00387\ F_o^2)$. The final R was 0·069 and R_w 0·093. Correlation factors greater than 0·5 in the matrix were found between the scale and the U_{ij} values for Br.

Atomic scattering factors and coefficients for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974).

Computing with the programs *SHELX* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965) was carried out on the ICL System 4 in Rothamsted Experimental Station. Geometrical calculations and the control and processing of the intensity collection on the Picker diffractometer were carried out with *XRAY-ARC* (1973) on the IBM 1130 computer.

Discussion

The fractional atomic coordinates and isotropic vibration parameters are in Table 1.* As shown in Fig. 1, the Na^+ ion is six-coordinated by the Br^- ion and five O atoms; distances are in Table 2. The Na–Br distance of 2·763 (3) Å is intermediate between that in sodium bromide [2·983 (3) Å] and that in the gaseous ion pair [2·502 Å (*International Tables for X-ray Crystallography*, 1962)]; it is significantly shorter than the value of 2·82 (1) Å found (Bush & Truter, 1971) for an ion pair when the sodium was coordinated by another seven atoms: six O atoms from dibenzo-18-crown-6 and one water molecule. The Na–Br bond is at 14·8 (6)° from the normal to the rather poor plane through the five O atoms (Table 3). As shown by the torsion angles in Table 4 there is no pseudosymmetry in the 15-membered ring and this one is the most irregular found so far; the torsion angle C(171)–C(41)–O(5)–C(6) contrasts with the usual *trans* conformation found in benzo crown complexes. Structures of Na complexes with benzo-15-crown-5 are known for $[Na(Ib)H_2O]^+.I^-$ (Bush & Truter,

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36328 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates (×10⁴) and isotropic vibration parameters (Å² × 10³)

	x	y	z	U_{iso}/U_{eq}
Br	2241·1 (8)	5623 (1)	3931·2 (5)	75·2 (6)†
Na	1274 (3)	2573 (4)	3918 (2)	77 (2)†
C(1)	−2453 (7)	1215 (11)	3007 (4)	68 (3)
C(2)	−3458 (8)	1618 (11)	3168 (4)	65 (2)
C(3)	−3479 (8)	2435 (10)	3774 (4)	65 (2)
C(4)	−2462 (7)	2852 (11)	4198 (5)	66 (3)
C(41)	−1446 (8)	2443 (11)	4038 (4)	66 (3)
C(171)	−1426 (7)	1565 (10)	3451 (4)	64 (3)
O(5)	−387 (4)	2870 (7)	4432 (3)	70 (2)†
C(6)	−207 (7)	2435 (11)	5138 (5)	80 (3)
C(7)	1013 (7)	2615 (12)	5435 (5)	86 (3)
O(8)	1604 (5)	1547 (8)	5070 (3)	83 (3)†
C(9)	2801 (8)	1536 (13)	5296 (5)	91 (3)
C(10)	3269 (10)	477 (14)	4837 (6)	101 (4)
O(11)	3009 (5)	1126 (8)	4184 (3)	90 (3)†
C(12)	3284 (9)	107 (15)	3667 (5)	95 (3)
C(13)	2792 (9)	834 (13)	3009 (5)	96 (3)
O(14)	1604 (5)	1195 (8)	2909 (3)	87 (3)†
C(15)	915 (8)	−216 (13)	2826 (5)	88 (3)
C(16)	−287 (8)	275 (13)	2764 (5)	82 (3)
O(17)	−368 (5)	1156 (8)	3348 (3)	80 (3)†
O(21)	−4501 (5)	1288 (9)	2777 (3)	86 (3)†
C(22)	−4574 (9)	503 (19)	2161 (7)	139 (8)†
O(31)	−4527 (5)	2718 (8)	3899 (3)	74 (3)†
C(32)	−4592 (8)	3739 (12)	4452 (5)	82 (4)†

† For these atoms U_{eq} is defined as $\sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* \times (a_i \cdot a_j)$.

Table 2. Environment of the sodium ion

Na–Br	2·763 (3) Å	Na–O(11)	2·365 (7) Å
Na–O(5)	2·452 (6)	Na–O(14)	2·437 (7)
Na–O(8)	2·428 (7)	Na–O(17)	2·372 (6)

Angles (°) subtended at a–Na–b

a \ b	Br	O(5)	O(8)	O(11)	O(14)
O(5)	106·6 (2)				
O(8)	108·8 (2)	67·1 (2)			
O(11)	96·0 (2)	135·5 (2)	69·5 (2)		
O(14)	106·7 (2)	133·8 (2)	128·2 (2)	70·4 (2)	
O(17)	139·2 (2)	65·5 (2)	104·2 (2)	117·9 (3)	68·4 (2)

Table 3. Deviations (Å) of atoms from best planes

	Plane-defining atoms		Other atoms	
Plane 1	O(5)	0·417 (6)	Na	0·861 (5)
	O(8)	−0·333 (7)	Br	3·533 (5)
	O(11)	0·095 (7)		
	O(14)	0·284 (7)		
	O(17)	−0·481 (6)		
Plane 2	C(1)	0·018 (8)	O(5)	0·082 (11)
	C(2)	0·004 (9)	O(17)	−0·065 (11)
	C(3)	−0·016 (8)	O(21)	0·007 (12)
	C(4)	0·005 (9)	C(22)	0·046 (19)
	C(41)	0·017 (9)	O(31)	−0·087 (12)
	C(171)	−0·026 (8)	C(32)	0·085 (16)
			Na	0·617 (16)

Angle between normals: 20·1 (4)°.

Table 4. Torsion angles (°) in the macrocyclic ring

O(5)–C(41)–C(171)–O(17)	3·0 (11)	C(12)–O(11)–C(10)–C(9)	−172·1 (9)
C(41)–C(171)–O(17)–C(16)	−179·7 (8)	O(11)–C(10)–C(9)· O(8)	62·5 (11)
C(171)–O(17)–C(16)–C(15)	−171·6 (7)	C(10)–C(9)–O(8)–C(7)	−175·9 (8)
O(17) C(16)–C(15)–O(14)	−57·8 (10)	C(9)· O(8) C(7)–C(6)	178·9 (7)
C(16)–C(15)–O(14)–C(13)	177·0 (8)	O(8)·· C(7) C(6)–O(5)	−59·7 (9)
C(15)–O(14)· C(13)· C(12)	−71·1 (10)	C(7)· C(6) O(5)–C(41)	166·9 (7)
O(14)···C(13)–C(12)–O(11)	−52·6 (11)	C(6)–O(5)–C(41)· C(171)	−128·0 (8)
C(13)–C(12)–O(11)–C(10)	170·7 (8)		

1972), $[Na(Ib)]_2UO_2Cl_4$ (Moody & Ryan, 1979), $[Na(Ib)ClO_4]^0$, $[Na(Ib)_2]^+.ClO_4^-$ and $[Na(Ib)_2]^+.BPh_4^-$ (Owen, 1980). The Na···O distances in the 1:2 complexes are longer than any in the 1:1 complexes. For the latter, the range of values and absence of systematic distinction between distances to O atoms on the aromatic rings and to O atoms between two CH_2 groups is similar to that found here.

The bond lengths and angles, Table 5, within the macrocyclic and benzene rings have the usual values for crown compounds. There are many examples of *ortho*-dimethoxy groups on aromatic rings; a common feature is the $C_{aromatic}$–O bond length (*ca* 1·36 Å) attributed to some delocalization. The methyl groups may both be coplanar with the benzene ring or one or both may be significantly out of this plane; there is a

Table 5. *Dimensions of the ligand* (Å *and* deg)

C(1)–C(2)	1·36 (1)	C(41)–O(5)	1·40 (1)
C(171)–C(1)	1·40 (1)	O(5)–C(6)	1·44 (1)
C(2)–C(3)	1·40 (1)	C(6)–C(7)	1·47 (1)
C(3)–C(4)	1·38 (1)	C(7)–O(8)	1·43 (1)
C(4)–C(41)	1·37 (1)	O(8)–C(9)	1·42 (1)
C(41)–C(171)	1·39 (1)	C(9)–C(10)	1·47 (1)
C(2)–O(21)	1·361 (9)	C(10)–O(11)	1·40 (1)
O(21)–C(22)	1·39 (1)	O(11)–C(12)	1·43 (1)
C(3)–O(31)	1·36 (1)	C(12)–C(13)	1·47 (1)
O(31)–C(32)	1·41 (1)	C(13)–O(14)	1·43 (1)
		O(14)–C(15)	1·42 (1)
		C(15)–C(16)	1·48 (1)
		C(16)–O(17)	1·41 (1)
		O(17)–C(171)	1·375 (9)
C(171)–C(1)–C(2)	120·6 (9)	C(41)–C(171)–O(17)	116·1 (7)
C(1)–C(2)–C(3)	120·5 (9)	C(171)–C(41)–O(5)	116·0 (7)
C(1)–C(2)–O(21)	124·8 (8)	C(41)–O(5)–C(6)	115·4 (6)
O(21)–C(2)–C(3)	114·7 (8)	O(5)–C(6)–C(7)	107·8 (7)
C(2)–C(3)–C(4)	119·0 (8)	C(6)–C(7)–O(8)	106·9 (8)
C(2)–C(3)–O(31)	115·7 (8)	C(7)–O(8)–C(9)	114·9 (7)
O(31)–C(3)–C(4)	125·3 (8)	O(8)–C(9)–C(10)	107·4 (9)
C(3)–C(4)–C(41)	120·6 (9)	C(9)–C(10)–O(11)	109·3 (9)
C(4)–C(41)–C(171)	120·3 (8)	C(10)–O(11)–C(12)	115·3 (8)
C(1)–C(171)–C(41)	118·8 (8)	O(11)–C(12)–C(13)	108·3 (9)
C(2)–O(21)–C(22)	119·3 (7)	C(12)–C(13)–O(14)	114·3 (9)
C(3)–O(31)–C(32)	117·2 (7)	C(13)–O(14)–C(15)	112·9 (8)
C(1)–C(171)–O(17)	125·1 (8)	O(14)–C(15)–C(16)	108·9 (8)
C(4)–C(41)–O(5)	123·7 (8)	C(15)–C(16)–O(17)	108·0 (8)
		C(16)–O(17)–C(171)	119·0 (7)
Na–O(5)–C(6)	115·4 (5)	Na–O(11)–C(12)	117·2 (6)
Na–O(5)–C(41)	117·4 (5)	Na–O(14)–C(13)	108·3 (5)
Na–O(8)–C(7)	106·4 (5)	Na–O(14)–C(15)	106·6 (5)
Na–O(8)–C(9)	105·1 (5)	Na–O(17)–C(16)	117·5 (5)
Na–O(11)–C(10)	114·7 (6)	Na–O(17)–C(171)	120·6 (5)
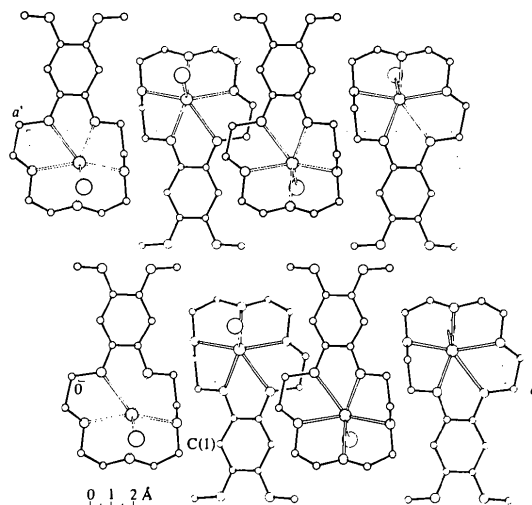
Fig. 2. The structure projected down **b**. The crystal-chemical unit with coordinates in Table 1 is distinguished by the designation of C(1).

wide range of O–CH$_3$ bond lengths (1·41–1·48 Å) (Perdikatsis, Catsoulacos & Filippakis, 1979; Villa, Manfredotti & Guastini, 1979; von Deuten, Kopf & Klar, 1979a,b).

In this compound the apparent shortening of the O–CH$_3$ bonds may be a result of libration, or there might be disorder with the true positions of the methyl groups, particularly C(22), being on either side of the benzene plane, and the apparent coplanarity shown in Table 3 a space average; this would be consistent with the apparent large vibration of C(22) normal to the plane as shown in Fig. 1.

Large vibration parameters were not expected from the preliminary photographs, which showed reflections to the edge of the Cu $K\alpha$ sphere; the probable explanation is that decomposition of the crystal reduced most intensities by more than those of the two standard reflections. Vibration and/or disorder is consistent with the relatively loose packing depicted in Fig. 2. The shortest Br· · ·H distance is 2·81 (1) Å to a H atom on C(6) in the molecule at $-x$, $1 - y$, $1 - z$, and there are seven other Br· · ·H contacts up to 3·3 Å to four different molecules. The other shortest intermolecular contact is between a H atom on C(10) and its equivalent related by a centre of symmetry at $\frac{1}{2}$, 0, $\frac{1}{2}$, 2·31 (2) Å. There are no H· · ·O or H· · ·C contacts < 2·73 Å.

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