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Crystal Structure of a Complex Between Sodium Perchlorate and a Bicyclic Polyether

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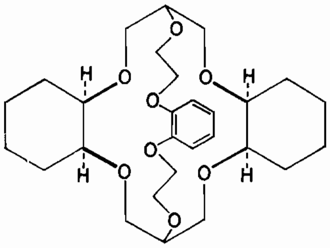
Abstract

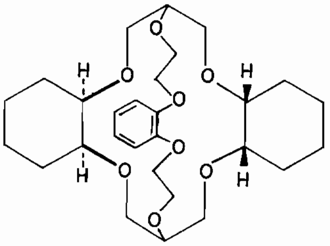
The ligand, *rel*-21*R*,26*S*,29*S*,34*R*-21,22,23,24,25,26,29,30,31,32,33,34-dodecahydro-1,4,7,14,17,20,28,35-octaoxa($2^{3,29}$*syn*$2^{18,34}$*syn*) (7.7) orthocyclophane, L, is one of three isomers based on a dicyclohexano-14-crown-4 ring with two carbon bridge-head atoms linked by $-OCH_2CH_2O-(o\text{-}C_6H_4)-OCH_2CH_2O-$. The crystal structure of the 1:1 complex with sodium perchlorate has been determined on 2697 observations, $R = 0.11$. In a monoclinic unit cell, $a = 18.889(5)$, $b = 12.473(4)$, $c = 13.401(4)$ Å, $\beta = 99.21(3)°$, $V = 3116.6$ Å^3, space group *Pn*, the asymmetric unit consists of two complex cations $(NaL)^+$ which are approximate mirror images enclosing a water molecule to give $[\mu H_2O(NaL)_2]^{2+}$ and two independent perchlorate ions. Each sodium ion is coordinated by six of the eight ligand oxygen atms, Na–O = 2.40 to 2.73 Å, and the shared water molecule Na(1)–O = 2.88 and Na(2)–O = 2.54 Å while the Na–O distances to the oxygen atoms on the benzene rings are greater than 3.0 Å.

Introduction

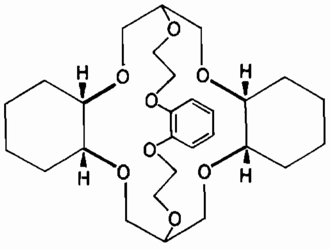
Three isomeric macrobicyclic polyethers were synthesised and their stability constants for complex formation with alkali metal cations found to vary widely with configuration [1, 2]. The formulae **IA**, **B**, **C** indicate the relative positions of the ring junction hydrogen atoms with respect to the $-OCH_2CH_2O-(o\text{-}C_6H_4)-OCH_2CH_2O-$ link. Similar isomeric compounds with $-O(CH_2CH_2O)_n-$ links ($n = 2$ or 3) all show a consistent pattern that for a given cation the stability constants for complex formation in methanol are in the ratio $10^4:10^2:1$ for **B**:**A**:**C**. The crystal structures of **IB** and its complexes with potassium perchlorate [3] and lanthanum nitrate [4] have been published as have those of **IC** and its methanol solvate [5] and of **IA** [3]. So far it has not proved possible to obtain any crystalline complexes of metal salts for isomer **IC** or for isomer **IA** except with sodium perchlorate. This complex, which was used in the purification of the ligand [2] L (isomer **IA**), is the subject of the present paper.



IA (L)



IB



IC

Experimental

Crystals were obtained from methanol/water [2]. The infrared spectrum was measured as a Nujol mull on a Perkin-Elmer 457 spectrometer. Preliminary X-ray photographs and setting of the crystal on a CAD-4 diffractometer showed the space group to be *Pn* or *P*2/*n* with four formula units $NaClO_4C_{28}H_{42}O_8$ in the cell and Guinier photographs of a powdered

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sample showed the crystal to be characteristic of the whole [6].

Crystal Structure Determination

Crystal Data

$C_{28}H_{42}O_8 \cdot NaClO_4 \cdot \frac{1}{2}H_2O$, $M = 638.1$, monoclinic, space group *Pn* (No. 7, non-standard setting of *Pc*, equivalent positions x, y, z; $\frac{1}{2} + x, -y, \frac{1}{2} + z$), $a = 18.889(5)$, $b = 12.473(4)$, $c = 13.401(4)$ Å, $\beta = 99.21(3)°$, $V = 3116.6$ Å^3, $F(000) = 1356$, $D_m = 1.350$ g cm^{-3}, $Z = 4$, $D_c = 1.360$ g cm^{-3}, μ(Mo Kα) = 1.88 cm^{-1}, λ(Mo Kα) = 0.71069 Å.

One of the colourless crystals, 0.40 × 0.30 × 0.35 mm, was mounted on the Philips PW1100 4-circle diffractometer in the Polytechnic of North London by Dr M. McPartlin. Observations were collected by $\omega/2\theta$ scan from $5 < 2\theta < 50°$ for $h = \pm 22$, $k = \pm 12$, $l = 0-13$ giving 7472 measurements of which 3533 were unique, the *R* factor of merging being 0.055. Corrections for Lorentz and polarization but not absorption effects were applied. The unit cell dimensions are within 0.002 Å and 0.04° of the mean of those from the CAD-4 and Guinier measurements, although those differed by 0.1%.

The complex originally appeared to be unsolvated so that there would be one or two formula units in the asymmetric unit in space groups *P*2/*n* and *Pn* respectively. A three-dimensional Patterson synthesis did not show many peaks at $v = 0$ and the statistics in SHELX-76 [7] indicated a non-centrosymmetric structure so there were 84 non-hydrogen atoms to locate. It was not until the structure solving program SHELX-86 [8] became available that the structure was solved. Its clear output allowed two perchlorate ions to be recognized, one sodium surrounded by seven oxygen atoms and eight probable carbon atoms, i.e. $Cl_2NaO_{15}C_8$. This gave a discouraging $R = 0.38$. Further search of the SHELX output suggested the second complex cation with sodium, six oxygen and seven carbon atoms. $Cl_2Na_2O_{21}C_{15}$ now gave $R = 0.32$ after two cycles of refinement. Despite this high value the difference map revealed peaks corresponding to all the rest of the complex cations and, unexpectedly, a water molecule shared by the two sodium ions. Isotropic refinement with SHELX-76 proceeded smoothly, normally two blocks were used, (i) the scale, both perchlorate ions, Na(1) and L(1); and (ii) the scale, Na(2), L(2) and the water molecule, O(9). At $R = 0.13$ a full matrix cycle showed no correlations greater than 0.5. The chlorine and sodium ions were allowed anisotropic vibration; four hydrogen atoms were added in positions calculated to give C–H = 1.08 Å and complete tetrahedra around the ring junction carbon atoms and their common isotropic vibration parameter allowed to refine, it finally being 0.09(3) Å^2. Although there is no disorder in the structure, the crystals diffract weakly and there were only 2697 observations with $I \geqslant 3\sigma(I)$. As there are 362 parameters improvement in *R* by allowing more anisotropy or adding more hydrogen atoms seemed unlikely to be meaningful and refinement was concluded with $R = 0.11$ and the weighting scheme $1/(\sigma F_o)^2 + 0.0018(F_o^2)$, the maximum shift/e.s.d. was 0.3 and the highest peak in the final difference map was 1 e Å^{-3} and not in a reasonable position to be a hydrogen atom. The scattering factors for Na, Cl, C, O and H were calculated from the analytical coefficients in ref. 9. The programs of the Nicolet R3/m diffractometer [10] were used for some molecular geometry and to generate Figs. 1 and 3. See also 'Supplementary Material'.

Results and Discussion

The complete asymmetric unit is shown in Fig. 1 for the coordinates in Table 1.

All four cyclohexane rings are in the chair form so the *cis* substituted hydrogen atoms at the junctions with the macrocyclic rings are axial and equatorial in pairs. The numbering scheme for the ligands is displayed in Fig. 2 so that the axial hydrogen atoms on ligand (1), H(126) and H(129) and those on ligand (2) H(234) and H(221) correspond as do their configurations relative to the links O(n4)...O(n17). As appears in Fig. 1 and is confirmed by the torsion angles in Fig. 2, the $(Na(1)L(1))^+$ and $(Na(2)L(2))^+$ entities are mirror images within experimental error. They are not related by pseudosymmetry in the crystal. Their bond lengths and angles are the same as, but less accurate than, those in the uncomplexed molecule [3].

The peak O(9) was assigned as a water molecule on the basis of its electron density, the absence of a peak attributable to carbon as required for CH_3OH, and the better agreement with the observed density than either an unsolvated or a hemi-methanolated form. There is no absorption in the infrared spectrum

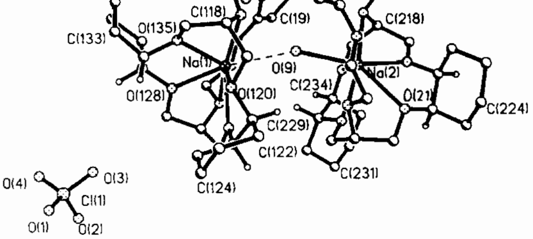

Fig. 1. The asymmetric unit showing the designations of the atoms in the perchlorate ions, the sodium ions, the water molecule and some atoms in each of the two macrobicyclic ether ligands.

TABLE 1. Fractional atomic coordinates and isotropic vibration parameters, U ($\AA^2$)[a]

(Cl(1)	0.3483(–)	0.4295(4)	0.4651(–)	0.074(4)
(O)1	0.4226(8)	0.4089(11)	0.4707(10)	0.089(4)
(O)2	0.3330(7)	0.4661(11)	0.5599(10)	0.082(4)
(O)3	0.3106(9)	0.3265(15)	0.4491(14)	0.124(6)
(O)4	0.3238(8)	0.5041(13)	0.3918(12)	0.101(5)
Cl(2)	0.2359(3)	−0.2185(4)	−0.0614(4)	0.077(4)
O(5)	0.2639(8)	−0.2354(12)	−0.1524(12)	0.096(5)
O(6)	0.2017(8)	−0.3099(14)	−0.0309(12)	0.106(5)
O(7)	0.2902(9)	−0.1885(13)	0.0176(13)	0.104(5)
O(8)	0.1855(10)	−0.1341(16)	−0.0760(14)	0.129(6)
O(9)	0.0170(8)	−0.2764(13)	0.4357(12)	0.101(5)
Na(1)	0.0816(4)	−0.0849(5)	0.3714(5)	0.073(5)
O(11)	0.1575(7)	−0.0395(11)	0.5319(10)	0.079(4)
C(12)	0.1435(10)	0.0524(17)	0.5877(17)	0.083(6)
C(13)	0.0939(11)	0.1252(18)	0.5202(16)	0.084(6)
O(14)	0.0311(7)	0.0716(11)	0.4838(10)	0.075(4)
C(15)	−0.0249(12)	0.1348(19)	0.4273(17)	0.092(7)
C(16)	−0.0893(11)	0.0686(17)	0.4159(15)	0.078(6)
O(17)	−0.0767(7)	−0.0206(11)	0.3493(10)	0.079(4)
C(18)	−0.1352(10)	−0.0874(14)	0.3186(13)	0.059(5)
C(19)	−0.2045(12)	−0.0734(18)	0.3469(17)	0.088(7)
C(110)	−0.2584(12)	−0.1518(19)	0.3113(17)	0.088(7)
C(111)	−0.2399(13)	−0.2336(19)	0.2511(18)	0.097(7)
C(112)	−0.1739(11)	−0.2431(17)	0.2198(16)	0.078(6)
C(113)	−0.1177(10)	−0.1682(15)	0.2542(14)	0.064(5)
O(114)	−0.0525(7)	−0.1696(10)	0.2301(9)	0.073(4)
C(115)	−0.0384(12)	−0.2536(18)	0.1632(18)	0.084(6)
C(116)	0.0387(11)	−0.2378(17)	0.1504(16)	0.077(6)
O(117)	0.0840(6)	−0.2461(10)	0.2485(9)	0.066(3)
C(118)	0.1559(10)	−0.2546(15)	0.2407(14)	0.062(5)
C(119)	0.1954(12)	−0.2847(19)	0.3489(17)	0.093(7)
O(120)	0.2001(6)	−0.1809(10)	0.4091(10)	0.069(4)
C(121)	0.2196(11)	−0.1962(16)	0.5148(5)	0.074(6)
H(121)	0.1790(11)	−0.2471(16)	0.5383(15)	0.095(31)
C(122)	0.2905(14)	−0.2548(21)	0.5478(19)	0.106(8)
C(123)	0.3571(15)	−0.1856(24)	0.5150(22)	0.127(9)
C(124)	0.3531(14)	−0.0747(21)	0.5643(20)	0.112(8)
C(125)	0.2846(12)	−0.0207(18)	0.5354(17)	0.088(7)
C(126)	0.2240(11)	−0.0882(17)	0.5634(17)	0.084(6)
H(126)	0.2359(11)	−0.0961(17)	0.6446(17)	0.095(31)
C(127)	0.1267(10)	0.1735(16)	0.4282(15)	0.076(6)
O(128)	0.1262(7)	0.0896(11)	0.3551(10)	0.080(4)
C(129)	0.1403(10)	0.1234(16)	0.2569(14)	0.070(6)
H(129)	0.1688(10)	0.1987(16)	0.2591(14)	0.095(31)
C(130)	0.0733(11)	0.1396(17)	0.1911(16)	0.081(6)
C(131)	0.0862(13)	0.1711(21)	0.0832(19)	0.101(8)
C(132)	0.1273(12)	0.0714(19)	0.0406(18)	0.092(7)
C(133)	0.1969(12)	0.0614(18)	0.1141(17)	0.093(7)
C(134)	0.1859(8)	0.0407(14)	0.2214(13)	0.058(5)
H(134)	0.2381(8)	0.0405(14)	0.2679(13)	0.095(31)
O(135)	0.1487(6)	−0.0613(8)	0.2258(8)	0.050(3)
C(136)	0.1852(11)	−0.1551(17)	0.1920(15)	0.076(6)
Na(2)	−0.0115(4)	−0.4161(5)	0.5614(5)	0.063(4)
O(21)	0.0370(6)	−0.5107(9)	0.7290(8)	0.062(3)
C(22)	0.0972(10)	−0.4633(16)	0.7881(15)	0.073(6)
C(23)	0.1324(9)	−0.3815(15)	0.7219(14)	0.065(5)
O(24)	0.1227(6)	−0.4193(9)	0.6198(8)	0.055(3)
C(25)	0.1605(10)	−0.5195(14)	0.6108(13)	0.062(5)
C(26)	0.1664(10)	−0.5391(14)	0.5027(13)	0.063(5)
O(27)	0.0924(6)	−0.5490(9)	0.4507(9)	0.063(3)
C(28)	0.0836(9)	−0.5521(13)	0.3468(12)	0.052(5)
C(29)	0.1402(9)	−0.5530(14)	0.2926(13)	0.061(5)
C(210)	0.1242(10)	−0.5491(16)	0.1866(15)	0.071(6)
C(211)	0.0581(10)	−0.5469(15)	0.1377(14)	0.071(5)
C(212)	−0.0062(10)	−0.5450(15)	0.1905(15)	0.073(6)
C(213)	0.0127(9)	−0.5483(15)	0.3001(14)	0.063(5)
O(214)	−0.0380(7)	−0.5458(10)	0.3611(10)	0.077(4)
C(215)	−0.1137(9)	−0.5445(15)	0.3106(13)	0.060(5)
C(216)	−0.1594(12)	−0.5363(18)	0.3947(16)	0.090(7)
O(217)	−0.1392(6)	−0.4368(10)	0.4467(9)	0.069(4)
C(218)	−0.1883(10)	−0.4168(15)	0.5169(15)	0.068(5)
C(219)	−0.1753(11)	−0.4937(17)	0.6085(16)	0.083(6)
O(220)	−0.1005(6)	−0.5023(10)	0.6423(9)	0.066(3)
C(221)	−0.0803(9)	−0.5886(13)	0.7085(13)	0.054(5)
H(221)	−0.1230(9)	−0.6116(13)	0.7489(13)	0.095(31)
C(222)	−0.0613(10)	−0.6863(15)	0.6456(14)	0.066(5)
C(223)	−0.0355(13)	−0.7781(20)	0.7172(18)	0.104(8)
C(224)	0.0325(12)	−0.7410(18)	0.7967(18)	0.094(7)
C(225)	0.0143(11)	−0.6451(18)	0.8569(16)	0.088(7)
C(226)	−0.0144(10)	−0.5525(15)	0.7839(14)	0.064(5)
H(226)	−0.0287(10)	−0.4896(15)	0.8324(14)	0.095(31)
C(227)	0.0953(12)	−0.2724(18)	0.7161(17)	0.092(7)
O(228)	0.0220(6)	−0.2796(10)	0.6958(9)	0.067(3)
C(229)	−0.0134(11)	−0.1793(16)	0.6722(16)	0.076(6)
H(229)	0.0053(11)	−0.1504(16)	0.6051(16)	0.095(31)
C(230)	0.0065(14)	−0.0863(21)	0.7532(21)	0.116(8)
C(231)	−0.0190(13)	−0.1168(20)	0.8524(19)	0.103(7)
C(232)	−0.0964(12)	−0.1403(20)	0.8357(17)	0.098(7)
C(233)	−0.1163(10)	−0.2337(16)	0.7539(15)	0.076(6)
C(234)	−0.0905(10)	−0.1978(17)	0.6553(15)	0.075(6)
H(234)	−0.1188(10)	−0.1249(17)	0.6303(15)	0.095(31)
O(235)	−0.1037(7)	−0.2777(10)	0.5842(10)	0.076(4)
C(236)	−0.1756(11)	−0.2999(17)	0.5444(15)	0.077(6)

[a] For anisotropic vibration parameters $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^*$.

3040 cm^{-1} as is expected for hydroxy stretching. The calculated elemental analysis for the hemihydrate is in slightly better agreement with the observed than the published data [2]. The IR spectrum shows a single sharp band at 630 cm^{-1} indicative of non-coordinated perchlorate ions as found. The Na--O(9) distances, Table 2, constitute the only significant differences between the environments of the two sodium ions so the stereoviews Fig. 3a and b are of one complex cation.

From the dimensions for the perchlorate ions, Table 2, it is apparent that caution is required in the quantitative interpretation of the results. Nevertheless, it is clear that the sodium ions are not coordinated by the oxygen atoms on the benzene rings, nor are they completely encapsulated by the ligands because of the interaction with water. This interaction is through a benzo-cyclo-hexano-18-crown-6 ring of the ligand and is comparable with that found to one anion in the potassium complex of **IB** and to

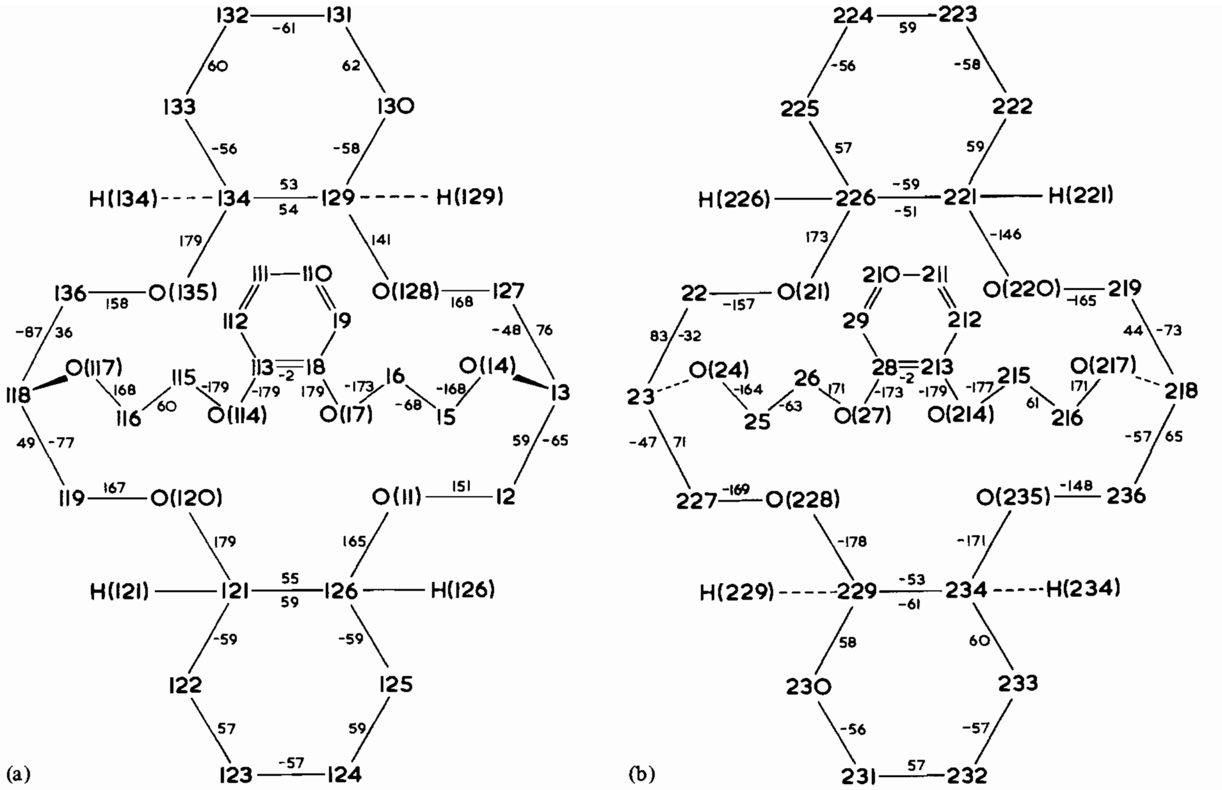

Fig. 2. The numbering schemes for the atoms of the macrobicyclic ligands. Oxygen atoms and hydrogen atoms are designated specifically, carbon atoms are shown by numbers only. The ligand with atoms O(11) to C(136) is coordinated to Na(1), that with atoms O(21) to C(236) to Na(2) where Na(1) and Na(2) share a water molecule O(9) as depicted in Fig. 1. Also displayed are the torsion angles in the ligands of the asymmetric unit in Table 1. The other molecule in the unit cell has the signs reversed. The estimated standard deviations are 1.4° at 180° and 3.8° at 0°. Not shown are two angles at each bridgehead carbon atom *viz.* C(12)–C(13)–O(14)–C(15), 173 °; C(127)–C(13)–O(14)–C(15), −61°; C(116)–O(117)–C(118)–C(119), −169°; C(116)–O(117)–C(118)–C(136), 63°; and C(236)–C(218)–O(217)–C(216), −165°; C(219)–C(218)–O(217)–C(216), 72°; C(25)–O(24)–C(23)–C(227), 175°; C(25)–O(24)–C(23)–C(22), −65°. Also omitted are angles round the benzene rings which are 0° or 180° within 4°.

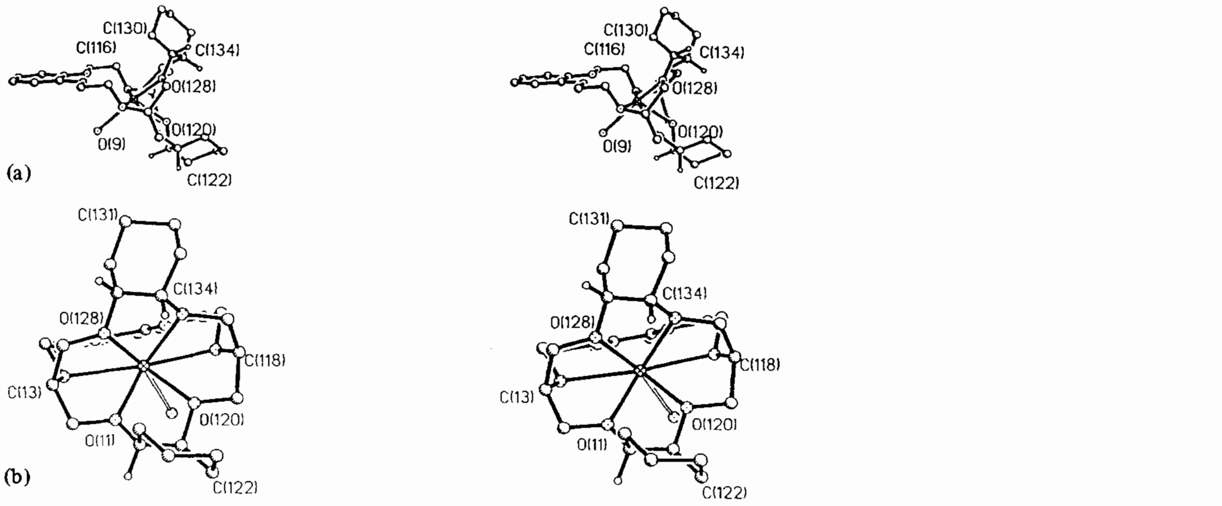

Fig. 3. Stereoviews of the complex cation $(Na(1)L(1)H_2O)^+$: (a) tilted slightly from the view with the bridgehead carbon atom C(13) eclipsing C(118) and O(14) eclipsing the other end-capping oxygen atom, O(117), of the triangular prism of oxygen atoms; (b) projected onto the plane of the four oxygen atoms of the dicyclohexano-14-crown-4 entity, O(11), O(120), O(135) and O(128).

TABLE 2. Selected bond lengths and angles

(a) Coordination round the sodium ions

Na–O bond lengths (Å), e.s.d. 0.013–0.017 Å

Na(1)–O(11)	2.45	Na(2)–O(235)	2.51
Na(1)–O(14)	2.73	Na(2)–O(217)	2.66
Na(1)–O(117)	2.61	Na(2)–O(24)	2.53
Na(1)–O(120)	2.51	Na(2)–O(228)	2.48
Na(1)–O(128)	2.36	Na(2)–O(220)	2.40
Na(1)–O(135)	2.51	Na(2)–O(21)	2.57
Na(1)–O(9)	2.88	Na(2)–O(9)	2.54

Other Na–O distances

Na(1)–O(17)	3.07	Na(2)–O(214)	3.11
Na(1)–O(114)	3.10	Na(2)–O(27)	3.12

Angles subtended at Na(1) (°), e.s.d. 0.4–0.6°

	O(14)	O(117)	O(120)	O(128)	O(135)	O(9)
O(11)	64	132	64	73	111	98
O(14)		161	127	63	128	103
O(117)			70	128	62	66
O(120)				98	71	87
O(128)					66	166
O(135)						129

Angles subtended at Na(2) (°), e.s.d. 0.4–0.5°

	O(217)	O(24)	O(228)	O(220)	O(21)	O(9)
O(235)	64	131	63	73	112	80
O(217)		162	126	65	129	87
O(24)			70	126	62	85
O(228)				95	71	87
O(220)					65	148
O(21)						144

Na(1)–O(9)–Na(2) 156.0(6)°

(b) Bond lengths in the perchlorate ions (Å), e.s.d. 0.014 – 0.020 Å

Cl(1)–O(1)	1.42	Cl(2)–O(5)	1.42
Cl(1)–O(2)	1.42	Cl(2)–O(6)	1.40
Cl(1)–O(3)	1.47	Cl(2)–O(7)	1.40
Cl(1)–O(4)	1.38	Cl(2)–O(8)	1.41

two anions through both such rings in the lanthanum complex of **IB**.

The cage formed by eight oxygen atoms of isomer **IA** in the complexed form is essentially the same as that of isomer **IB** with potassium perchlorate. It can be seen as an end-capped triangular prism, Fig. 3a. The triangular faces are about 2.6 Å apart, with right angles at O(128), O(135), O(21) and O(220). In neither structure is the metal ion on the mid-point of a line joining the end-capping oxygen atoms, O(n4) and O(n17). The sodium ion is about 0.5 Å nearer to the plane of the four oxygen atoms on the cyclohexano rings and the angles subtended by the chelate oxygen atoms on these rings are 64–66°. A shift towards the 14-crown-4 oxygen atoms for a smaller cation was found by NMR studies [11] to persist in solutions of the corresponding dibenzo-14-crown-4 macrobicyclic complexes. The potassium ion is situated off the mid-point towards the perchlorate ion so that it is coordinated to all eight of the ligand oxygen atoms, but only weakly to the one corresponding to O(135) and O(21).

Kinetic measurements on crown and cryptate complexes [12–14] have generally shown that, in a given solvent, the differences in equilibrium formation constants result mainly from differences in the rates of decomplexation so it is reasonable to hope that comparison of complexed forms may throw light on the reasons for variations in stability constant. If we compare the behaviour of sodium and potassium in an eight oxygen atom cage, the smaller number of Na–O interactions seems a simple explanation for its lower formation constant. The log K_e values in methanol are for isomer **IA** 5.86 (Na$^+$) and 6.50 (K$^+$) and for isomer **IB** 7.86 (Na$^+$) and 8.18 (K$^+$). However, it is much more difficult to explain the larger difference between different isomers for the same cation. For isomer **IA** the complexed form differs from the uncomplexed by changes in torsion angles from *trans* to *gauche* round the bridgehead carbon atoms C(n3) and C(n18) and also C(15)–C(16) or C(215)–C(216) while O(17)–C(18) or C(213)–O(214) change from *gauche* to *trans* with the effect that the CH$_2$ group of C(16) or C(15) is outside the cavity in the complex. Other changes *gauche* to *trans* are at O(n1)–C(n26) and O(n35)–C(n34), i.e. six major changes per molecule. For isomer **IB** there were eight major changes per molecule to give the conformation in the complex with potassium perchlorate so possibly the greater conformational change makes decomplexation slower.

There is no hydrogen bonding from the water molecule to ligand oxygen atoms or to perchlorate ions i.e. no O(9)···O contact is less than 3.0 Å. Apart from electrostatic forces between the complex cations and the anions, there are possible C–H··· OClO$_3$ interactions from H(221) and H(226) at 2.66 and 2.42 Å respectively to O(4) and O(1) of the perchlorate ion at $-\frac{1}{2}+x, -y, \frac{1}{2}+z$.

Supplementary Material

Tables of structure factors and of anisotropic vibration parameters, all bond lengths and angles, and planes through various groups of atoms are available from the author on request.

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