Complexes between Macrobicyclic Polyethers[†] and Hydrogen Bond Donors; the Crystal Structure of Ammonium Iodide and 1,5,12,16,23,26,29,32-Octaoxa[$10^{3,14}$][5.5]orthocyclophane

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Interaction between hydrogen bonding donor molecules and four macrobicyclic polyethers derived from dibenzo-14-crown-4 with the bridge which forms the second ring containing (1) three, (2) four, (4) five oxygen atoms separated by $(CH_2)_2$ units, or else (3) by two aliphatic and two more oxygen atoms on a benzene ring has been investigated by potentiometric titration, and by i.r. and u.v. spectroscopy. Hydrated complexes have been isolated from (2), with ammonium salts, glycine, hydrochloric acid, picric acid, and trichloroacetic acid and from (4) with ammonium bromide. Crystal structure of the ammonium iodide complex of (2), with stoicheiometry NH_4I : (2) : H_2O of 1 : 1 : n, has shown it to contain centrosymmetric dimeric $[NH_4^+(2)]_2$ cations and iodide anions with n *ca.* 1.5 in a unit cell a = 22.734(3), b = 14.288(3), c = 17.514(4) Å, β = 100.46(2)°, space group $C2/c$. The phase problem was solved by direct methods and the parameters refined to R = 0.062 for 3 021 observations. Each ammonium nitrogen atom is nearly coplanar with six oxygen atoms of one ligand [N–O, 2.718(7)–2.868(7) Å], and is hydrogen bonded to one oxygen atom [N–O, 2.981(7) Å] of the other ligand in the dimer. The complex dimeric cations pack to form channels which contain iodide ions and water molecules held by hydrogen bonding.

We have described the syntheses of macrobicyclic polyethers having high formation constants for complexation of alkali metal cations in water[1] and even higher ones in methanol.[2] To test the potential of the compounds for molecular recognition *via* hydrogen bonding and to discover the extent to which such interactions might interfere with binding by metallic cations, we have carried out investigations with a variety of hydrogen bonding donors. The compounds tested were ammonium salts $NH_4^+X^-$ (X = Cl, Br, I, NCS, ClO_4, BPh_4), guanidinium salts $C(NH_2)_3^+X^-$ (X = NO_3 and Cl), amino acids, $NH_3^+CHRCO_2^-$ [R = H, Me, CH_2OH, CH(OH)Me, and CH_2CO_2H], proline and hydroxyproline, and acids HY (Y = chloride, picrate, trichloroacetate). Interactions with four macrobicyclic polyethers (1), (2), (3), and (4) were investigated. These have the formulae and systematic names listed in Figure 1.

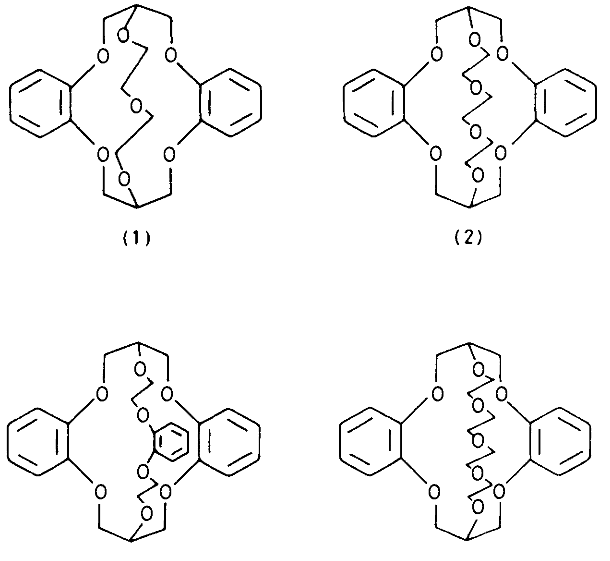
(1) (2) (3) (4)

Figure 1. Formulae of the macrobicyclic molecules. Systematic names are: (1) 1,5,12,16,23,26,29-heptaoxa[$7^{3,14}$][5.5]orthocyclophane; (2) 1,5,12,16,23,26,32-octaoxa[$10^{3,14}$][5.5]orthocyclophane; (3) 1,4,7,14,17,20,28,35-octaoxa[$2^{3,29}.2^{18,34}$][7.7]orthocyclophane; and (4) 1,5,12,16,23,26,29,32,35-nonaoxa[$13^{3,14}$][5.5]orthocyclophane

Results and Discussion

The ligand molecules are insoluble in water, but slightly soluble in solutions of alkali metal halides giving complexes that crystallise with varying amounts of water.[2] We have now found a similar solubilising effect with a typical mineral acid, hydrochloric acid, and with strong organic acids; complexes of these acids have been isolated from water. Ammonium salts showed a lesser solubilising effect and no complexes were isolated from water

To measure formation constants by the e.m.f.[3] method we used methanol as a solvent because ammonium bromide is freely soluble and the ligands sufficiently soluble in it to allow potentiometric titrations. Results showed formation of 1 : 1 complexes with all four ligands, Table 2. Except for the rather inaccurate β_2 value for ligand (2) there was no evidence for stoicheiometry other than 1 : 1. This is similar to the behaviour of potassium and contrasts with that of caesium which gives 1 : 2 complexes with (2) and (3).[2] In the u.v. spectrum, complex formation is shown by a shift in the π–π‡ transitions of the crown ethers derived from catechol.[4] We found a maximum absorbance at 275 nm for the uncomplexed molecule (2) at all ratios of ligand to salt; on addition of ammonium bromide a shoulder at 282 nm appeared and its relative intensity increased as more ammonium bromide was added, confirming interaction in solution.

In attempts to isolate complexes of each of the four ligands with ammonium salts, guanidinium salts, or amino acids, the 1 : 1 stoicheiometry indicated by solution studies was used. Methanol was the usual solvent but others were sometimes required. Complexes were obtained with ligand (2) for six ammonium salts.

The anion affects the nature of the product isolated. NH_4X

[†] Systematic names of the three polyethers not given in the title: 1,5,12,16,23,26,29-heptaoxa[$7^{3,14}$][5.5]orthocyclophane; 1,4,7,14,17,20,28,35-octaoxa[$2^{3,29}.2^{18,34}$][7.7]orthocyclophane; and 1,5,12,16,23,26,29,32,35-nonaoxa[$13^{3,14}$][5.5]orthocyclophane.

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Table 1. Analyses of complexes with (2), $C_{24}H_{30}O_8$

		Found (%)						
Other components	$T_{decomp.}$/°C	C	H	N	Cl	Br	I	S
NH_4Br	150	40.67	6.56	2.15		13.07		
NH_4Cl	140	49.13	7.12	3.36	8.45			
NH_4ClO_4	250	38.81	4.84	1.82	5.83			
NH_4NCS	200	54.07	6.55	4.98				5.53
NH_4I	250	45.51	5.65	2.15			19.5	
$NH_2CH_2CO_2H$	120	56.45	7.32	2.42				
Cl_3CCO_2H	100	43.47	4.39		25.94			
$C_6H_2(NO_2)_3OH$		50.03	4.74	6.95				
HCl (5N)		50.41	6.36		9.96			
HCl (4N)		49.92	6.32		9.22			
HCl (2N)		51.36	6.57		8.69			
NH_4BPh_4		72.86	6.94	1.69				
Analysis of complex with (4), $C_{26}H_{34}O_9$								
$NH_4Br(4)$	192	51.10	6.46	2.26		14.33		

Other components	M[a]	N : C	R : C	Stoicheiometry	Anhydrous mol. wt. (i)	Calculated mol. wt. from C (ii)	nH$_2$O
NH_4Br		1 : 22	1 : 21[b]	1 : 1	544.4	708.8	9
NH_4Cl		1 : 17	1 : 17[c]	1 : 1	500.0	586.7	5
NH_4ClO_4		1 : 25	1 : 20[c]	1 : 1	564.0	742.8	10
NH_4NCS		2 : 26	1 : 26[d]	1 : 1	522.6	555.3	2
NH_4I	623.4	1 : 24	1 : 25[e]	1 : 1	601.5	633.4	2
$NH_2CH_2CO_2H$	564.5	1 : 27		1 : 1	521.6	553.2	2
Cl_3CCO_2H			6 : 30[c]	2 : 1	773.3	773.7	0
$C_6H_2(NO_2)_3OH$	740	3 : 25		1 : 1	675.6	720.2	2
HCl (5N)			1.6 : 24[c]	1.6 : 1	504.8	571.8	4
HCl (4N)			1.5 : 24[c]	1.5 : 1	501.2	577.5	4
HCl (2N)			1.4 : 24[c]	1.4 : 1	497.6	561.3	4
NH_4BPh_4		1 : 50		1 : 1	783.8	805.0	1
Analysis of complex with (4), $C_{26}H_{34}O_9$							
$NH_4Br(4)$		1 : 26	1 : 24[b]	1 : 1	590.5	611.0	1

[a] By *X*-ray methods, see Table 2. [b] R = Br. [c] R = Cl. [d] R = S. [e] R = I.

with X Br, I, NCS, or ClO_4 yielded crystals of composition $NH_4X(2)nH_2O$. For X Cl, the solubility of the salt was similar to that of the complex. For X BPh_4, the salt was recovered after the mixture had been heated under reflux in methanol. However, from ethanol the $NH_4BPh_4(2)$ complex was obtained. With other ligands, (1) and (4), the product isolated from reaction with ammonium bromide in methanol was the uncomplexed ligand. However, from acetone the ammonium bromide complex of (4) could be isolated. Previous work[5] has shown that with alkali metal and alkaline earth metal complexes of crown ethers, isolation depends upon relative solubilities and is not only related to the formation constant at equilibrium.

Glycine required the addition of a little water and gave a complex with (2), but the other amino acids and the guanidinium salts yielded crystals of the uncomplexed (2). Glycine was treated with each of the other three ligands in aqueous methanol; no new product was isolated.

All the crystals of each complex decomposed at the same temperature, indicating homogeneity; however this temperature varied from day to day within 5 °C. The ammonium perchlorate and the ammonium thiocyanate complexes of (2) decomposed significantly above 154 C, the m.p. of (2).

The analyses of new products are in Table 1, together with an approximate indication of the stoicheiometry using the ratios of C to N and to Cl, Br, I and S. The former is more reliable because the elements C, H, and N are determined simultaneously. Also shown is the calculated molecular weight (i) for an unsolvated complex of a particular stoicheiometry, and (ii) the apparent molecular weight of the sample calculated from the carbon analysis (assumed to be correct). The ratios indicate that water, not methanol, is the probable solvent of crystallisation and an estimate of the number of water molecules calculated from the difference, (ii) (i), is given.

To investigate the effect of amino acids on the ligands the chromatographic R_F values were measured on paper with propan-2-ol–water (4 : 1) as the solvent. Only aspartic acid (R CH_2CO_2H) showed a significant effect; the R_F value increased from 0.05(1) to 0.14(1) in the presence of the ligand (2). This suggests that the carboxy-group of uncomplexed aspartic acid interacts with the paper and possibly with the ligand. However, in our attempts to isolate a complex in the presence of hydrochloric acid, the ligand formed a crystalline $HCl(2)nH_2O$ complex, confirmed by microanalysis and the i.r. spectrum, and not an aspartic acid complex.

I.r. Spectra.—The band at 1 280 cm^{-1} in the i.r. spectrum of the uncomplexed ligand (2) was absent in those of the ammonium and glycine complexes. Other diagnostic features were changes in the fingerprint region 900—1 200 cm^{-1}, and also in the N–H and O–H stretching region compared with unreacted mixtures of the compounds.

For the glycine complex, the strong characteristic, ' zwitterion ' absorptions in the regions 2 200—3 200 and 1 300—

Table 2. Stability constants at 25 °C. $K_1 = [M^+L]/[L][M^+]$ $\beta_2 = [ML_2]/[L]^2[M^+]$. Units of K_1, l mol^{-1} and β_2, l^2 mol^{-2}. Numbers in parentheses are percentage standard deviations in K or β

	Ammonium complex						Potassium [c]	Caesium [c]	
Ligand	C_L [a]	C_{NH_4Br} [b]	logK_1	logK_1'	logβ_2	Solvent	logK_1	logK_1'	logβ_2
(1)	5	5	1.24(16.6)			methanol	3.2		
(2)	10	5	4.91(8.6)	4.93(5.5)	6.9(40.5)	methanol	7.48(2.8)	4.66(1.2)	7.58(2.5)
	6.7	3.3	4.09(2.1)	4.10(0.7)	6.20(10.2)	methanol–water 2 : 1			
(3)	0.5	0.5	4.24(5.5)			methanol	8.75(2.8)	4.25(1.2)	7.70(1.8)
(4)	5	5	5.91(6.6)			methanol	7.52(0.9)	7.52(1.1)	

[a] C_L = concentration of ligand (mmol l^{-1}). [b] C_{NH_4Br} = concentration of ammonium bromide (mmol l^{-1}). [c] Ref. 2.

Table 3. Unit cell dimensions of complexes with (2)

Parameter	NH_4I	$NH_2CH_2CO_2H$	Cl_3CCO_2H	$C_6H_2(NO_2)_3OH$
System	monoclinic	monoclinic	monoclinic	triclinic
a/Å	22.734(3)	12.691(5)	11.007(3)	14.035(12)
b/Å	14.288(3)	12.662(5)	18.586(3)	17.079(12)
c/Å	17.514(4)	18.806(9)	17.407(8)	18.143(21)
α/°	90	90	90	109.12(7)
β/°	100.46(2)	100.07(3)	90.0(3)	119.55(5)
γ/°	90	90	90	94.08(7)
U/Å^3	5 594.6	2 975.4	3 561	3 428
Space group	$C2/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$ (or $P1$)
D_m/Mg m^{-3}	1.480	1.26		1.44
Z	8	4		4
D_x	1.51 ($2H_2O$) 1.49 ($1.5H_2O$)	1.25 ($2H_2O$)		1.44 ($3.5H_2O$) 1.39 ($2H_2O$) 1.449 ($4H_2O$)

1 620 cm^{-1} were replaced by a band at 3 240 cm^{-1}, three centred on 3 160 cm^{-1}, and an inflection at 3 360 cm^{-1}. The fingerprint region differed from that of the uncomplexed molecule diagnostically, but to a lesser extent than for the ammonium complexes. This suggested that glycine has induced a different conformation.

The ammonium complexes of (2) had similar spectra in the fingerprint region to those of its alkali metal complexes. They also gave a band at 3 250 cm^{-1} which persisted on prolonged drying; (it is probably the stretching frequency of a hydrogen-bonded N–H group). Bands removed by drying were a broad one at 3 450 cm^{-1} and a shoulder at 3 190 cm^{-1}. In addition the ammonium perchlorate complex gave a single band at 625 cm^{-1} indicating that the perchlorate ion was not co-ordinated.[6] Crystals of different habits of the ammonium thiocyanate complex gave identical spectra including the characteristic sharp N–C stretching band at 2 060 cm^{-1}.

Although the stoicheiometry of the HCl(2) complex was variable, all samples gave similar i.r. spectra with subtle differences from that of (2) in the fingerprint region, with the addition of a broad band at 3 400—3 200, another at 2 200—2 100, a small one at 1 630, and bands at 1 070 and 930 cm^{-1}, even from samples dried *in vacuo*. These bands are consistent with the presence of H_3O^+ and $H_5O_2^+$ entities,[7] possibly co-ordinated as in the complex formed between perchloric acid monohydrate and dicyclohexano-18-crown-6,[8] but also possibly in a lattice with water molecules and chloride ions, as found in the hydrochloric acid hydrates first identified by melting points,[9] and shown by crystal structure analysis to contain H_3O^+ (the monohydrate),[10] $H_5O_2^+$ (the dihydrate),[11] $H_5O_2^+$, and H_2O (the trihydrate)[12] with hydrogen bonding to the chloride ions. With H_3O^+ or $H_5O_2^+$ in the lattice the co-ordinated entity might be water giving [H_2O(2)], comparable with H_2O(1) naphthalene-2,3-diol.[13]

There were several changes in the i.r. spectrum of (4) on formation of the ammonium bromide complex, which was the same in the fingerprint region as the potassium bromide complex; principal features were the disappearance of bands at 1 040 and 1 280 cm^{-1} and the appearance of one at 1 340 cm^{-1}. Above 3 000 cm^{-1} the bands attributable to water were at 3 425 and 3 380 cm^{-1}. The N–H stretching gave a broad band at 3 205 cm^{-1}, a lower frequency than for the complexes with (2) which may indicate that there is stronger hydrogen bonding consistent with the higher formation constants, Table 2.

X-Ray Diffraction.—The compounds which gave suitable crystals were investigated by *X*-ray diffraction. The crystal data are given in Table 3. It was not possible to measure the density of the trichloroacetic acid complex but, for the other three compounds, the molecular weights obtained in this way are given in Table 1 and are in fair agreement with those calculated from the carbon analyses. In Table 3 the calculated density is based on the assumption given there about the number of water molecules.

Crystal Structure.—The ammonium iodide complex proved sufficiently stable in the *X*-ray beam for collection of intensities and structure determination. The numbering of the atoms is given in Figure 2 and their co-ordinates in Table 4. The structure consists of complex cations with iodide ions and water molecules in channels. Figure 3 shows one dimeric complex cation; the dimensions involving the ammonium ion are given in Table 5.

Each nitrogen atom is nearly equidistant (mean 2.795 Å) from six oxygens of the macrocyclic ring which is formed by including O(1) and O(16) and those oxygens which are separated from them by two carbon atoms, *i.e.* atoms O(23)—O(32) inclusive. This forms a pseudo benzo-18-crown-6 ring. The atoms from C(4)—C(13) inclusive can then be seen as the bridge forming a bicyclic molecule. The six oxygen atoms form a moderately good plane with O(5) and O(12) on one side and

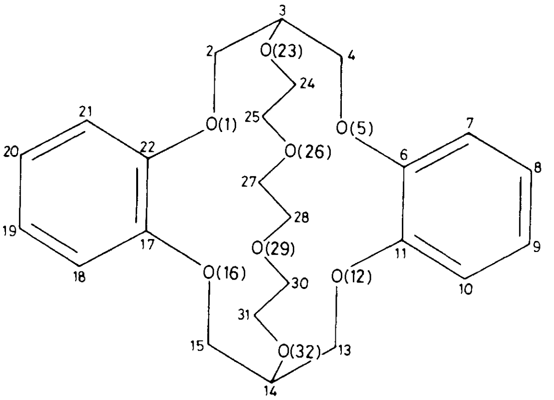


Figure 2. The atomic designations of (2) in the crystal structure of the ammonium iodide complex. Hydrogen atoms were numbered to correspond to the carbon atoms, those of methylene groups being further distinguished by a and b. In addition, co-ordinates were obtained for the iodide ion, I, the nitrogen atom of the ammonium ion, N, and four water molecules O(01), O(02), O(101), and O(102)

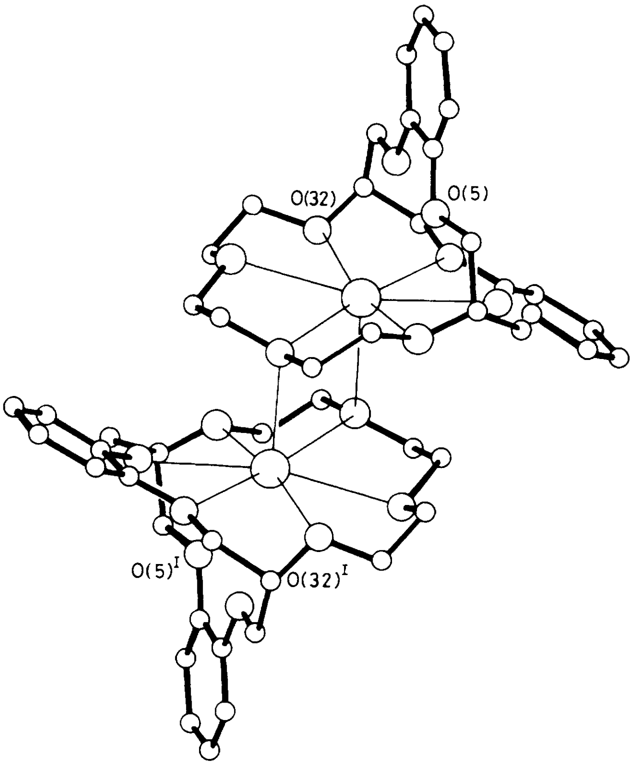


Figure 3. The molecular structure of the dimeric cation. Carbon, oxygen, and nitrogen are shown as small, medium, and large circles respectively; hydrogen atoms are omitted. Some atoms are designated. The Roman numeral, I, refers to atoms related to the crystal chemical unit of Table 4 by the centre of symmetry at ½, 1, ½ with the equivalent position $1 - x, 2 - y, 1 - z$

nitrogen at 0.191(6) Å on the other side towards the contact which forms the dimeric entity, O(26)^{I} at 3.156(5) Å. The angle between this contact and the normal to the six-oxygen plane is 6°. The bond angles subtended do not suggest a tetrahedral distribution about the nitrogen; our failure to locate the hydrogen atoms is probably due to their being disordered.

Table 4. Fractional atomic co-ordinates (× 10^4) and thermal parameters (Å^2 × 10^4)

Thermal parameters marked * are U_{eq}. $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*(\mathbf{a}_i \cdot \mathbf{a}_j)$. SOF is site occupation factor, 1.0 unless given.

Atom	*x*	*y*	*z*	U_{iso}/U_{eq} *	SOF
I	8 890.9(3)	9 248.3(4)	9 346.4(4)	916(3) *	
O(1)	6 223(2)	7 887(3)	5 146(2)	468(16) *	
C(2)	5 859(3)	7 073(4)	5 024(4)	456(23) *	
C(3)	5 433(3)	7 048(4)	5 594(4)	476(24) *	
C(4)	5 728(3)	6 918(5)	6 441(4)	516(25) *	
O(5)	6 045(2)	7 752(3)	6 711(2)	486(16) *	
C(6)	6 404(3)	7 728(4)	7 432(3)	420(22) *	
C(7)	6 384(3)	7 024(5)	7 978(4)	501(26) *	
C(8)	6 772(4)	7 091(6)	8 699(4)	591(30) *	
C(9)	7 166(4)	7 786(7)	8 852(4)	649(32) *	
C(10)	7 196(3)	8 493(5)	8 307(4)	559(27) *	
C(11)	6 804(3)	8 465(5)	7 603(3)	416(22) *	
O(12)	6 775(2)	9 132(3)	7 036(2)	513(16) *	
C(13)	7 203(3)	9 866(6)	7 164(4)	612(28) *	
C(14)	7 116(3)	10 517(5)	6 475(5)	612(29) *	
C(15)	7 288(3)	10 107(5)	5 749(4)	604(28) *	
O(16)	6 908(2)	9 331(3)	5 490(3)	547(18) *	
C(17)	7 015(3)	8 812(5)	4 872(4)	471(24) *	
C(18)	7 455(3)	9 024(6)	4 445(4)	611(29) *	
C(19)	7 526(4)	8 419(7)	3 836(5)	730(36) *	
C(20)	7 171(4)	7 659(7)	3 652(4)	683(33) *	
C(21)	6 716(3)	7 448(5)	4 072(4)	545(26) *	
C(22)	6 652(3)	8 023(5)	4 686(3)	430(22) *	
O(23)	5 067(2)	7 855(3)	5 470(2)	460(15) *	
C(24)	4 600(4)	7 866(6)	5 925(5)	720(34) *	
C(25)	4 215(4)	8 663(6)	5 737(6)	835(39) *	
O(26)	4 494(2)	9 571(3)	5 815(3)	505(17) *	
C(27)	4 404(3)	10 147(6)	6 453(4)	598(29) *	
C(28)	4 731(4)	11 028(5)	6 443(4)	553(27) *	
O(29)	5 358(2)	10 904(3)	6 661(2)	496(17) *	
C(30)	5 700(4)	11 719(5)	6 588(4)	608(30) *	
C(31)	6 352(4)	11 499(5)	6 818(4)	656(31) *	
O(32)	6 522(2)	10 869(3)	6 273(3)	525(17) *	
N	5 740(2)	9 482(4)	5 727(3)	432(18) *	
O(01)	10 341(5)	9 919(8)	8 795(6)	1 250	0.82(2)
O(02)	8 750(7)	9 351(10)	7 188(9)	1 250	0.58(2)
O(101)	10 000	8 451(49)	7 500	1 250	0.09(1)
O(102)	10 000	10 656(42)	17 500	1 250	0.10(1)

The arrangement about the ammonium ion contrasts with that in the ammonium bromide complex of 18-crown-6,[14] in which the nitrogen atom is *ca.* 0.8 Å from the plane of the six oxygen atoms and clearly forms three hydrogen bonds to the upper oxygen atoms. This is described by Cram and Trueblood [15] as ' perched,' and had until recently been assumed to be the normal arrangement. However, while the $NH_4{}^+$(2) complex is the first example of an unsubstituted ammonium ion inside an 18-crown-6 ring, it is the fourth of an $RNH_3{}^+$ entity being ' nested.' [15] One example is the hydrazinium ion which was found [16] to have the quaternary ammonium nitrogen atom 0.11 Å from the plane of the six oxygen atoms of 18-crown-6 and with hydrogen bonds to the three ' lower ' oxygen atoms (N–O) and the NH_2 group hydrogen bonding to the ' upper ' oxygen atoms (N–O). In the hydroxylammonium complex of 18-crown-6, the nitrogen atom was found 0.68 Å from the plane through the six oxygen atoms and nearly equidistant from all six.

A third example is the ethylenediammonium complex of 18-crown-6 1,2,10,11-tetracarboxylate.[17] Here the nitrogen atom of one $NH_3{}^+$ group is 0.56 Å from the mean plane through the six ether oxygen atoms and approximately equidistant from them. The hydrogen atoms were assumed to occupy positions staggered with respect to the CH_2–CH_2 bond

Table 5. Environment of the nitrogen atom

Distances (Å) to oxygen atoms

O(1)	2.799(7)	O(16)	2.769(7)
O(32)	2.718(7)	O(29)	2.842(7)
O(26)	2.868(7)	O(23)	2.774(7)
O(26)^1	2.981(7)		
O(5)	3.021(7)	O(12)	3.015(7)

Angles (°) subtended at nitrogen by oxygen atoms within 3.0 Å, e.s.d. 0.2°

	O(16)	O(32)	O(29)	O(26)	O(23)	O(26)^1
O(1)	55.4	116.6	166.4	120.8	60.0	93.3
O(16)		61.7	122.9	174.3	115.3	85.3
O(32)			61.6	122.6	167.0	89.2
O(29)				61.9	118.4	100.0
O(26)					61.6	90.8
O(23)						103.4

Deviations (Å) of atoms from a mean plane; atoms included in the calculation are in italics

O(1)	*0.013(5)*	*O(16)*	*−0.166(6)*	*O(32)*	*−0.006(6)*	*O(29)*	*0.271(6)*
O(26)	*−0.922(6)*	*O(23)*	*0.235(5)*	N	−0.191(6)	O(26)^1	−3.156(5)
N^1	−3.388(6)	O(5)	2.421(5)	O(12)	2.262(5)		

giving three nearly linear N–H···O bonds with N···O 2.84, 2.86, and 2.87 Å, whereas the other three contacts were 2.76, 2.84, and 2.92 Å.

The formation constant (Table 2) for the ammonium ion with (2) is greater than those for ammonium, hydrazinium, and hydroxylammonium ions [logK_c 4.27, 4.21, and 3.99 (± 0.02), respectively] with unsubstituted 18-crown-6 in methanol determined thermochemically.[18] There is, as yet, no correlation with 'perching' or 'nesting.' Our structure is the second example of two ammonium ions being 'sandwiched' between two ligand molecules;[19] from it the possibility of NH_4^+:(2) in the ratio 1 : 2 can be envisaged.

There are no significant differences in the bond lengths and angles from those in the uncomplexed form[20] [even to the apparently short bond C(24)–C(25) 1.44(1) Å which probably results from some disorder; atom C(25) has a large anisotropic vibration parameter]. Mean values for the various kinds of bond are in Table 6; for the carbon–oxygen bonds the standard deviation from the spread about the mean agrees with that from the refinement, but for the carbon–carbon bonds it is double. The ligand is more symmetrical than in its uncomplexed form;[20] the torsion angles are in Table 6. Major changes are that C(27)–C(28) is *gauche* in the complex and *trans* in the uncomplexed molecule, and the bridgehead at C(3) has changed to be in a simple pseudo mirror relation to that at C(14), the torsional angle O(5)–C(4)–C(3)–O(23) being *gauche* in the complex and *trans* in the free molecule.

The pseudo benzo-18-crown-6 entity differs from the conformation of 18-crown-6 itself in the idealised complexed form, *i.e.* with all C–C bonds *gauche* and all C–O bonds *trans*, in two ways. The existence of the benzene ring forces the O(1)–C(22)–C(17)–O(16) angle to be *cis* and the torsion angle C(24)–C(25)–O(26)–C(27) is found to be 107 instead of 180°. Similar effects have been noted in complexes of benzo-18-crown-6 and macrocyclic ligands giving a pseudo benzo-18-crown-6 grouping.[21]

Co-ordination to the oxygen atoms of the corresponding pseudo crown compound has been found for water with (1)[13] (pseudo benzo-15-crown-5), rubidium with (4)[22] (pseudo benzo-21-crown-7), and potassium with (3)[23] (pseudo dibenzo-18-crown-6).

The crystals contain the complex dimeric cations packed to form channels along the crystallographic c axis. These channels at 0, 0, z and $\frac{1}{2}$, $\frac{1}{2}$, z contain iodide ions occupying single sites about which they vibrate with relatively large amplitude, Table 4; there are also water molecules, O(01) and O(02), in general positions with occupation factors of 0.82(1) and 0.58(2), respectively, while water molecules O(101) and O(102) are on two-fold axes with low occupation factors, 0.09(1) and 0.10(1), respectively. This gives a total of 12 water molecules per unit cell, or n = 1.5 in the empirical formula. As the occupation factors depend upon the vibration parameter chosen, we made an independent check. The value of n obtained from the density and volume, Table 3, is 1.2. Calculation from the volume alone provides a further test; of the 699.3 Å^3 per formula unit, 566.8 Å^3 is attributable to the ligand,[20] 81.6 Å^3 to ammonium iodide,[24] leaving 50.9 Å^3 for water. A survey[25] of crystalline hydrates gave an average volume of 24.5 Å^3 per water molecule, so the volume here corresponds to a stoicheiometry of n = 2.0.

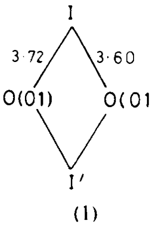
The minimum contact between a non-hydrogen atom in the cation and one in the channel is C(2)···O(101), 3.65(1) Å; there are no contacts less than 4.0 Å between the nitrogen atom and any in the channels (the N···I separation is greater than 6.0 Å). Apart from the N···O(26)^1 contact, all the contacts between the two ligands in the dimers, and between dimers, are greater than the sum of the van der Waals radii. It is probable that the ammonium complexes of (2) with smaller anions, and more water of crystallisation, have channel structures like this and the KCl(3)nH$_2$O complex.[23] With the larger values of n the water is more labile.

Orange crystals of this complex are formed immediately from colourless solutions; the colour does not result from decomposition. The nearest contacts for the iodide ion to the carbon atoms of the ligands are 4.096(7) Å to C(10) and 4.122(7) to C(18), *i.e.* they are to aromatic carbon atoms, but greater than 3.9 Å, the sum of the van der Waals radii. Its nearest neighbours are three oxygen atoms of the water molecules in the channels: these are within hydrogen bonding distance.

In the columns the main hydrogen-bonded entities are at centres of symmetry separated by c/2. The angle subtended at water O(01) is 99.1(2)°, and this molecule with 82% occupancy could be acting as a donor only to iodine [see (1)]. The angles subtended at it by contacts from O(02) and O(101) are compatible only with accepting from them. A water molecule O(02) could serve to link entities at adjacent centres of symmetry by hydrogen bonding to an iodide ion (3.74 Å) in one

Table 6. Dimensions in the ligand

Type of bond	Range (Å)	Mean (σ) individual (Å)
$C_{(sp^2)}$–O	1.370—1.388	1.375(8)
$C_{(sp^3)}$–O	1.416—1.440	1.425(8)
$C_{(sp^2)}$–$C_{(sp^2)}$	1.332—1.406	1.388(22)
$C_{(sp^3)}$–$C_{(sp^3)}$	1.463—1.524	1.503(22)
	Torsion angles (°)	
C(22)–O(1)–C(2)–C(3)		179(1)
C(17)–C(22)–O(1)–C(2)		–177(1)
C(21)–C(22)–O(1)–C(2)		5(1)
O(1)–C(2)–C(3)–C(4)		–67(1)
O(1)–C(2)–C(3)–O(23)		60(1)
C(2)–C(3)–C(4)–O(5)		71(1)
O(23)–C(3)–C(4)–O(5)		–54(1)
C(2)–C(3)–O(23)–C(24)		174(1)
C(4)–C(3)–O(23)–C(24)		–57(1)
C(3)–C(4)–O(5)–C(6)		–172(1)
C(4)–O(5)–C(6)–C(7)		–14(1)
C(4)–O(5)–C(6)–C(11)		166(1)
O(5)–C(6)–C(7)–C(8)		–179(1)
C(11)–C(6)–C(7)–C(8)		1(1)
O(5)–C(6)–C(11)–C(10)		–178(1)
O(5)–C(6)–C(11)–O(12)		2(1)
C(6)–C(11)–O(12)–C(13)		–176(1)
C(10)–C(11)–O(12)–C(13)		4(1)
C(11)–O(12)–C(13)–C(14)		178(1)
O(12)–C(13)–C(14)–C(15)		–70(1)
O(12)–C(13)–C(14)–O(32)		54(1)
C(13)–C(14)–C(15)–O(16)		64(1)
O(32)–C(14)–C(15)–O(16)		–64(1)
C(13)–C(14)–O(32)–C(31)		69(1)
C(31)–O(32)–C(14)–C(15)		–163(1)
C(14)–C(15)–O(16)–C(17)		–175(1)
C(15)–O(16)–C(17)–C(18)		–4(1)
C(15)–O(16)–C(17)–C(22)		176(1)
O(16)–C(17)–C(18)–C(19)		179(1)
C(22)–C(17)–C(18)–C(19)		–1(1)
O(1)–C(22)–C(17)–O(16)		2(1)
C(3)–O(23)–C(24)–C(25)		–176(1)
O(23)–C(24)–C(25)–O(26)		–57(1)
C(24)–C(25)–O(26)–C(27)		–107(1)
C(25)–O(26)–C(27)–C(28)		179(1)
O(26)–C(27)–C(28)–O(29)		–72(1)
C(27)–C(28)–O(29)–C(30)		174(1)
C(28)–O(29)–C(30)–C(31)		–179(1)
O(29)–C(30)–C(31)–O(32)		67(1)
C(30)–C(31)–O(32)–C(14)		–173(1)



(1)

and to O(01) in the next. Water molecules O(011) and O(102) on the sparsely occupied sites on two-fold axes may also bridge the centres of symmetry, by forming donor bonds to O(01), or to O(02). Although the sites of O(101) and O(102) are 3.15(9) Å apart, their low occupation numbers and the fact that a hydrogen bond along here is geometrically incompatible with another bonding to O(01) or O(02), suggests that these sites are not occupied simultaneously in any channel.

Experimental

Formation constants were measured by potentiometric titration method. The cell, described previously,[3] was immersed in a water-bath at 25 °C. The silver–silver chloride reference standard electrode was in a saturated solution of sodium chloride in methanol and in contact with the test solution through a porous plug. The EIL potassium-ammonium sensitive glass electrode was conditioned by soaking in a solution of ammonium chloride in methanol overnight; its decade shift was found to be 54.0 mV compared with the Nernstian 59.2 mV. For each run, ammonium bromide (15 ml) was titrated with a solution of the ligand. The concentrations given in Table 3 were limited by the solubility of the ligand. The e.m.f. was measured initially and, after addition of portions of titrant, the reading was taken when the e.m.f. stabilised. At least two runs were made for each polyether each involving about 20 readings, up to a stoicheiometric excess of over 2 : 1 for the ligand. By means of the MINIQUAD program [26] formation constants were determined allowing for stoicheiometries of 2 : 1 and 1 : 2 as well as 1 : 1. Results are given in Table 2.

U.v. spectra were measured on a Pye Unicam SP 500 spectrophotometer. Ammonium bromide (0.1 mM in methanol) was added to the ligand to give molar ratios up to 1 : 1 and their spectra measured from 254 to 290 nm.

Ammonium Iodide-(2)nH$_2$O.—A mixture of (2) (40 mg) and ammonium iodide (20 mg) (purified by powdering and washing with acetone) in ethanol (10 ml) was warmed, the solution filtered and the complex allowed to crystallise by slow evaporation at room temperature. The crystals were obtained as orange needles (55 mg). On heating, the crystals lost solvent (water) at 100 °C giving an amorphous mass, m.p. *ca.* 250 °C (decomp.).

Ammonium Bromide-(2)nH$_2$O.—Ammonium bromide (9.8 mg AnalaR) and (2) (44.6 mg) were dissolved in methanol (25 ml, AnalaR) and the mixture warmed until a clear solution was obtained. The solution was concentrated to about 2 ml and the crystals were filtered off.

Similar treatments with (2) yielded complexes of ammonium chloride, ammonium thiocyanate, and ammonium perchlorate. For ammonium tetraphenylborate, ethanol was used instead of methanol. Analyses are given in Table 1. No complexes could be isolated with ammonium bromide or ammonium chloride with ligands (1), (3), or (4) from methanol.

Ammonium Bromide-(4).—Ammonium bromide (15 mg) and (4) (50 mg) were dissolved in warm methanol (1 ml), and the solution concentrated to about 0.5 ml. Ethyl acetate (2 ml) was added, causing a little ammonium bromide to separate; this was filtered off. On addition of more ethyl acetate (3 ml) the complex separated as a microcrystalline solid (45 mg), m.p. 192 °C.

Glycine-(2)nH$_2$O.—Glycine (7.5 mg) and (2) (44.6 mg) were dissolved in methanol (25 ml) with water (1—2 ml) added. The resulting clear solution was warmed. After concentration and cooling, a crystalline *complex* was obtained. No new crystalline products were prepared with other amino acids. Aspartic acid (0.1 mequiv.) did not dissolve in aqueous methanol (25 ml); addition of five drops of concentrated hydrochloric acid (2.5 mequiv.) gave a clear solution. The isolated product was found to be a hydrated (2)-hydrochloric acid complex.

Hydrochloric acid-(2)nH$_2$O.—The ligand (50 mg) was warmed with hydrochloric acid (2 ml) (4 or 5M) for 30 min, and then allowed to stand at room temperature overnight.

The modified crystals were collected and air dried; the composition of the complex depended on the concentration of the acid used.

Microanalyses were carried out in University College, London. Results are given in Table 1.

For paper chromatography, the amino acid, dissolved in water, was spotted at the origin on Whatman No. 1 chromatography paper. The solvent, propan-2-ol : water [4 : 1 (v/v)], was allowed to ascend for 3 h. The spots were developed by spraying with ninhydrin (indan-1,2,3-trione) (1.25 g in 250 ml of n-butanol). Compound (2) was added (100 mg in 200 ml of solvent) and the procedure repeated.

I.r. spectra of compounds dried in the oven at 60—100 °C, or, for the HCl complex, *in vacuo* were obtained as Nujol mulls in a Perkin-Elmer 457 grating spectrophotometer.

Most crystals tended to decompose in the *X*-ray beam. Where necessary they were enclosed in Lindeman glass capillaries. Preliminary *X*-ray photographs were taken with Cu-K_α radiation. More precise unit cell dimensions were obtained from high angle θ reflections on a CAD4 diffractometer with monochromated Mo-K_α radiation, $\lambda = 0.7107$ Å. For powder photography a Nonius-Guinier camera with monochromated Cu-K_α radiation, $\lambda = 1.5405$ Å was used. Densities were measured by flotation where possible. Results are given in Table 3.

Crystal Structure Determination.—The ammonium iodide–(2) complex proved stable in the *X*-ray beam. A crystal ($0.30 \times 0.35 \times 0.45$ mm) was mounted in Araldite (but no capillary) on an Enraf-Nonius CAD4 diffractometer. The cell dimensions given in Table 3 were obtained from 22 reflections in the range $2\theta = 15—16°$. The intensities were measured up to $2\theta = 50°$. 5 487 Planes were recorded of which 4 777 were unique. The intensities of three reference reflections 060, 510, and 002 showed no decline during the period of collection. 3 021 Were considered observed at $|F| > 2\sigma_F$. The data were checked for absorption; the maximum transmission factor was 0.998 and the minimum 0.870, and no correction was applied. The program CAD4 [27] was used to bring intensities to structure amplitudes. The structure was solved by the centrosymmetric direct methods program in SHELX.[28] The majority of the atoms were located in the first *E*-map. Successive electron density difference maps revealed a nitrogen atom and two water molecules O(01) and O(02) in general positions which, at $R = 0.25$, appeared to have electron densities of 2.5 e Å^{-3}. After further refinement to $R = 0.11$, two peaks of 0.45 e Å^{-3} appeared on a two-fold axis. It was considered that these were water molecules O(101) and O(102) with low occupation numbers. Hydrogen atoms of the ligand were included in the fixed calculated positions at 0.98 Å from the corresponding carbon atoms. Attempts to locate the hydrogen atoms at the ammonium ion and the water molecules were unsuccessful. Even in the final electron density difference map the four highest peaks, in the range 0.45—0.35 e Å^{-3} were 0.48 Å from nitrogen, 1.0 Å from iodine, close to the C(24)–C(25) bond and 1.3 Å from water O(02), so two were clearly spurious.

In the final refinement the iodine, carbon, oxygen, and nitrogen atoms were allowed anisotropic refinement while the water molecules were treated as oxygen atoms with a fixed isotropic vibration parameter 0.125 Å^2. The occupation numbers were allowed to vary. The final *R* value was 0.062, weighted $R' = 0.072$ with the weight at $1/[\sigma^2(F_0) + 0.002F_0^2]$.

Three reflections, 110, 200, and 220, which appeared to be suffering from extinction, were omitted from the refinement. The scattering factors for neutral carbon, oxygen, nitrogen, and iodine were used. The large vibration parameters for the last did not suggest that use of I$^-$ was necessary.

The anisotropic vibration parameters, the hydrogen atom co-ordinates, and the full bond lengths and angles, as well as the tables of structure factors, have been deposited as Supplementary Data, Sup. No. 23785 (23 pp.).*

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