Complexes of Alkali-metal Salts, including those of Chelating Anions, with Four Macrocyclic ' Crown ' Ethers

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An investigation of the effect of solvent, presence of water, and ratio of reactants on the isolation of complexes between LiX (X = Br, I, NCS) with benzo-15-crown-5(1) and of NaX and KX with (1), dibenzo-18-crown-6(2), dibenzo-24-crown-8(3), and dibenzo-30-crown-10(4) has led to several new complexes, particularly those with two metal atoms to one ligand. For sodium and potassium with X = 1-nitroso-2-naphtholate, 2-nitrophenolate, 2,4-dinitrophenolate, and 2-hydroxybenzoate, complexes have been made with ligands (1)—(3). These include [(sodium 2-nitrophenolate)$_2$(3)] and [potassium hydrogen(2-nitrophenolate)$_2$.(1)$_2$].

PEDERSEN'S original discovery[1] that the macrocyclic ethers which he synthesised and named ' crowns ' would react with alkali-metal salts led to the preparation first of many complexes with the ratio MX : L of 1 : 1, and later[2] with ratios of 1 : 2 and 2 : 3. All his compounds were dried before analysis. When he made crystalline complexes suitable for crystal structure analysis[3] several were found to contain water,[4,5] although the starting materials were anhydrous and of AnalaR quality.

We have explored the effect on complex isolation between simple salts, *i.e.* bromide, iodide, and thiocyanate of (i) the ratio of salt to ether, (ii) solvent (a feature known to affect the stability constant[6] and selectivity[7]), (iii) the anion, and (iv) the presence of water. This was intended as a preliminary to the study of alkali-metal salts of chelating anions with the crown ethers; in fact a new class of complexes was obtained, those with the ratio 2 : 1 of metal salt : ether.

TABLE 1

Polyether (trivial name) *	Molecular formula	M.p./ °C	Characteristic i.r. frequency/ cm^{-1}
(1) Benzo-15-crown-5	$C_{14}H_{20}O_5$	79	980
(2) Dibenzo-18-crown-6	$C_{20}H_{24}O_6$	167	990
(3) Dibenzo-24-crown-8	$C_{24}H_{32}O_8$	104	957
(4) Dibenzo-30-crown-10	$C_{28}H_{40}O_{10}$	107	960

* Systematic names are: (1), 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin; (2), 6,7,9,10,17,18,20,21-octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecin; (3), 6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[*b*,*n*][1,4,7,10,13,16,19,22]octaoxacyclotetracosin; (4), 6,7,9,10,12,13,15,16,23,24,26,27,29,30,32,33-hexadecahydrodibenzo[*b*,*q*][1,4,7,10,13,16,19,22,25,28]decaoxacyclotriacontin. These, in the Chemical Abstracts or Ring Index form, differ from the systematic names used in papers on the Crystal Structures of Complexes between Alkali-metal Salts and Cyclic Polyethers, Parts I—IV refs. 11, 4, 5, and 10, respectively.

In principle the synthesis of complexes is simple. The ligand and salt are dissolved in a common solvent and warmed, then the desired crystals separate on cooling. Usually ethanol is the most convenient solvent. In most systems one product is obtained whatever the ratio of the reactants. The criterion for complex formation was the isolation of a new solid phase which (i) if unsolvated has a higher melting point than the polyether, and (ii) does not absorb at the characteristic i.r. frequency of this polyether (Table 1). Hydroxy-group stretching bands in the i.r. spectrum indicated the presence of solvent in some species. Molecular weight determination by *X*-rays, where possible, was used in conjunction with elemental analysis to decide the composition of the product, *i.e.* the stoicheiometry salt : ether and the solvation. In practice the crystals were usually anhydrous or hydrated, only one ethanolate being obtained.

RESULTS AND DISCUSSION

Simple Salts.—Two lithium compounds with (1) were established as monohydrated 1 : 1 complexes, the bromide and iodide. For the thiocyanate however, the crystals (analysis and *X*-ray) corresponded to an anhydrous 1 : 1 form while the i.r. spectrum showed bands at 3240, 3310, and 3420 cm^{-1}, suggesting hydration so we do not regard it as satisfactorily characterised. No complexes were formed between lithium salts and the larger macrocyclic ethers.

For sodium and potassium compounds, Table 2 summarises the crystalline products obtained for all the individual systems, *i.e.* six salts with four macrocyclic ethers. Where the product is shown as hydrated the stoicheiometry 1 : 1 or 1 : 2 is the same as that given in refs. 1 or 2 respectively for dried samples. We report in Table 3 the analytical figures for the new phases with ligands (3) and (4), those for ligands (1) and (2) will be published.[3] Known and postulated structures are in the Figure.

For the potassium salts (1) forms 1 : 2 complexes, all may have potassium between the two molecules of ligand as in the iodide.[8] Dibenzo-18-crown-6 forms 1 : 1 complexes, potassium having the ideal radius to fit into the central hole of the complexed form. With X = SCN

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but not other salts, (3) gave a complex containing two metal atoms which shared two of the eight approximately coplanar oxygen atoms of the ligand and the two thiocyanate ions.[9] The ligand (4) wraps [10] round one potassium ion in the iodide.

For the sodium salts a different pattern emerges, 1 : 1 stoicheiometry for (1) and (2) was found in three crystal structures.[4,5,11] The pure NaNCS,(2),$2H_2O$ described here is not isomorphous with the sodium–rubidium compound which is anhydrous.[11] Hydrated 1 : 1

TABLE 2

Compositions of crystalline NaX and KX–crown ether complexes ratios are quoted metal : ether

	Na			K		
X =	I	Br	SCN	I	Br	SCN
(1)	1 : 1, H_2O [a,b]	1 : 1, $1{\cdot}5H_2O$ [c]	1 : 1 [d]	1 : 2 [e]	1 : 2 [c]	1 : 2,[c,d]
(2)	1 : 1, H_2O [c]	1 : 1, $2H_2O$ [c,f]	1 : 1, $2H_2O$ [a,c]	1 : 1, $1{\cdot}5H_2O$ [a,c]	1 : 1 [c]	1 : 1 [a]
(3)	1 : 1, H_2O		1 : 1, H_2O 2 : 1			2 : 1 [g]
(4)	2 : 1, H_2O		2 : 1	1 : 1 [h]		1 : 1, H_2O [a]

[a] Ref. 1. [b] Ref. 5. [c] Ref. 3. [d] Ref. 2. [e] Ref. 8. [f] Ref. 4. [g] Ref. 9. [h] Ref. 10.

TABLE 3

			Found (%)					Calc. (%)				
Compound	M.p., t.p.	Description	C	H	N	Metal	*M*	C	H	N	Metal	*M*
(*a*) Simple salts												
[LiI(1)H_2O]	150 [t] 174 [t] 197 [m]	Colourless crystals	39·9	5·2				40·0	5·2			
[LiBr(1)H_2O]	185— 187 [m]	Colourless crystals	44·5	5·8				45·1	5·9			
[NaI(3)H_2O]	70 [t] 153 [m]	Colourless crystals	46·7	5·6		3·5		46·8	5·5		3·7	
[NaNCS(3)H_2O]	83 [t] 185 [m]	Colourless crystals	54·9	6·2	2·7	4·4	566	54·8	6·2	2·6	4·2	547
[$(NaNCS)_2$(3)]	208 [m]	Colourless laths	51·5	5·4	4·7	8·1	576	51·0	5·3	4·6	7·5	610
[$(KNCS)_2$(3)]	132 [m,d]	Colourless crystals	48·9	5·1	4·4	13·0	659	48·6	5·0	4·4	12·2	642
[$(NaI)_2$(4)H_2O]	172 [m,d]	Colourless crystals	40·2	5·0		5·1	875	39·4	4·9		5·4	854
[$(NaNCS)_2$(4)]	145 [b] 176 [m]	Colourless crystals	51·3	5·9	4·1	6·4	695	51·6	5·8	4·0	6·6	698
[KNCS(4)H_2O]	105 [t] 135 [m]	Colourless crystals	53·4	6·4	2·3	5·5		53·5	6·4	2·2	5·9	
(*b*) Salts of chelating anions												
[Na(1-nitroso-2-naphtholate)(1)]	162 [m,d]	Bright green crystals	61·7	5·7	3·1		464	62·2	5·6	3·0	5·0	463
[Na(2,4-dinitrophenolate(1)]	90— 95 [m]	Yellow crystals	50·6	4·9	5·9	5·0		50·6	4·8	5·9	4·8	
[KH$(2\text{-nitrophenolate})_2(1)_2$]	125— 130 [m]	Pale yellow flakes	56·3	5·6	3·2	4·7	856	56·4	5·7	3·3	4·6	852
[K(2,4-dinitrophenolate)$(1)_2$]	105— 110 [t] 135 [m]	Yellow crystals	52·7	5·1	3·9	5·0		53·8	5·7	3·7	5·1	
[K(2-hydroxybenzoate)$(1)_2H_2O$]	119 t 129 [m]	Colourless crystals	58·1	6·5		5·1	725	57·5	6·4		5·3	730
[K(2-hydroxybenzoate)$(1)_2$]	90 [t] 115 [m]	Colourless crystals	60·9	6·0		5·8	705	59·0	6·3		5·4	712
[Tl(2,4-dinitrophenolate(1)]	121— 124 [m]	Dark orange crystals	36·7	3·5	4·2		692	36·6	3·5	4·3		655
[Na(2,4-dinitrophenolate)(2)H_2O]	115— 125 [m]	Fine yellow needles	53·2	5·3	4·2	4·1		53·4	5·0	4·8	3·9	
[K(2-nitrophenolate)(2)H_2O]	112— 114 [m]	Yellow crystals	56·5	5·4	2·6	6·9		56·2	5·4	2·5	7·0	
[K(2,4-dinitrophenolate)(2)EtOH]	118 [t] 135 [m]	Yellow crystals	53·5	5·3	4·5	6·2	642	54·4	5·3	4·5	6·3	618
[K(2-hydroxybenzoate)(2)H_2O]	120 [m]	Colourless crystals	58·6	6·1		7·3		58·0	5·6		7·0	
[K(2-hydroxybenzoate)(2)]	255 [m]	Colourless chunks	60·2	5·6		7·5		60·1	5·4		7·3	
[Tl(2,4-dinitrophenolate(2)H_2O]	75 77 [m]	Yellow crystals	40·2	4·0	3·4			40·7	3·8	3·7		
[$\{Na(2\text{-nitrophenolate})\}_2$(3)]	182— 187 [m,d]	Orange lozenge crystals	56·0	5·1	3·4	5·7	784	56·0	5·2	3·6	6·0	770
[$\{Na(2\text{-hydroxybenzoate})\}_2$(3)]	213 [m]	Colourless flakes	59·0	5·5				59·5	5·5		6·0	
[$\{K(2\text{-hydroxybenzoate})\}_2$(3)]	145— 150 [m,d]	Colourless crystals	56·2	5·3				57·0	5·3		9·8	

Transition. [m] Melting. [b] Blackening. [d] Decomposition.

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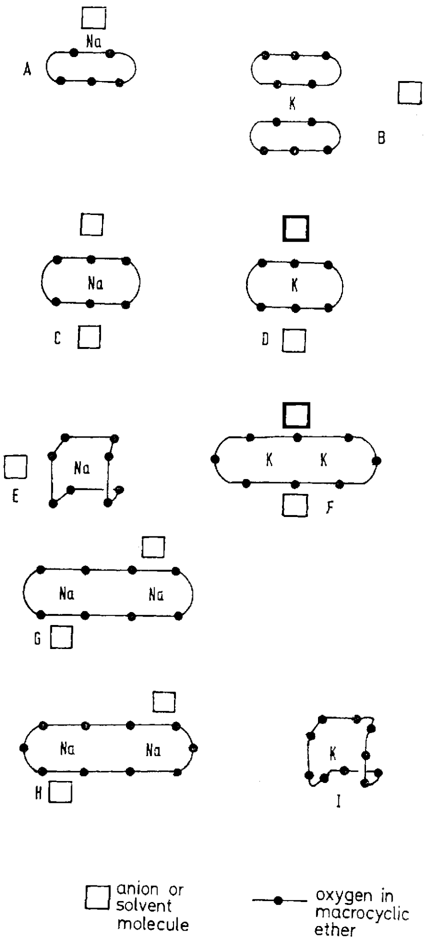
compounds are found for two anions with (3), but the preparation of the iodide complex could not be repeated. It may be that the ligand adopts a conformation in which the eight oxygen atoms are not coplanar and partially or completely encloses the sodium ion. For sodium thiocyanate the 2 : 1 anhydrous complex analogous to the potassium one has also been obtained by careful exclusion of water. Both the products of reaction of (3) with NaNCS have been characterised by a preliminary single crystal *X*-ray investigation. For (4) two sodium salts gave 2 : 1 complexes but no reaction was obtained with the bromide. Experiments with models show that the centrosymmetrical uncomplexed form of dibenzo-30-crown-10 has two sets of five oxygen atoms arranged so that each set could co-ordinate a sodium ion in a similar way to (1);[5] preliminary *X*-ray investigation showed that in the [$(NaNCS)_2$(4)] complex the two sodium ions must be related by symmetry. Failure to form complexes with bromides may result from their having higher lattice energies than the corresponding iodides or thiocyanates.



Representation of known and postulated sodium and potassium interactions with macrocyclic ethers, (1)—(4). Specific compounds of known structure are labelled with the chemical formula, postulates with a general formula MX; A, [Na(1)-H_2O], ref. 5; B, [$KI(1)_2$], ref. 8; C, [NaBr(2)2H_2O], ref. 4; D, [KX(2)solv.]; E, [NaX(3)solv.]; F, [$(KNCS)_2$(3)], ref. 9; G, [$(NaX)_2$(3)]; H, [$(NaX)_2$(4)]; I, [KI(4)], ref. 10

Chelating Anions.—For these compounds the solvent was not critical, methanol, ethanol, and acetone with various contents of water always gave the same product. The chelating anions used were those derived from 8-hydroxyquinoline, isonitrosoacetophenone, 1-nitroso-2-naphthol, 2-nitrophenol, 2-aminobenzoic acid, 2,4-dinitrophenol, 2-hydroxybenzoic acid, and 2-nitrobenzoic acid. Only four of these gave complexes with sodium or potassium salts, *viz.* 1-nitroso-2-naphthol, 2-nitrophenol, 2,4-dinitrophenol, and 2-hydroxybenzoic acid, Table 3(b).

With the ligand (1), the ratio of metal to ether is the same as that for the simple salts, 1 : 1 for sodium and 1 : 2 for potassium. The sodium compounds are anhydrous, possibly because the chelating anion occupies the position opposite the ligand like the water in [NaI(1),H_2O][5] (Figure). For the potassium compounds we postulate a sandwich structure as in [$KI(1)_2$][8] with the anion not co-ordinated. The behaviour of potassium 2-nitrophenolate is of special interest because the anion in the complex isolated is [$H(2\text{-nitrophenolate})_2]^-$ which has presumably been formed by partial solvolysis of the original potassium salt. Solvolysis may take place in the other systems and be one reason for the difficulty of isolating a pure product. Another difficulty is illustrated by K(2-hydroxybenzoate)$(1)_2$; the anhydrous form was clearly different from the hydrate (the single crystals being orthorhombic with a density of 1·37 g ml^{-1} whereas the monohydrate is triclinic with density 1·29 g ml^{-1}) as shown by the i.r. spectra (Table 4). Both products are formed in the same reaction, the hydrate appearing on the side of the beaker. To obtain a homogeneous sample for analysis it is necessary to study the products under the microscope and pick crystals of the same habit.

TABLE 4

I.r. absorptions, cm^{-1}, observed >3100 cm^{-1}

[LiI(1)H_2O]	3450, 3400
[LiBr(1)H_2O]	3440, 3770br
[NaI(3)H_2O]	3560, 3500, 3430
[NaNCS(3)H_2O]	3600, 3565, 3500
[$(NaI)_2$(4)H_2O]	3430br
[KNCS(4)H_2O]	3500, 3390
[K(2-hydroxybenzoate)$(1)_2H_2O$]	3490, 3370
[Na(2,4-dinitrophenolate)(2)H_2O]	3590, 3500, 3430
[K(2-nitrophenolate)(2)H_2O]	3300br
[K(2,4-dinitrophenolate)(2)EtOH]	3400
[K(2-hydroxybenzoate)(2)H_2O]	3600, 3540
[Tl(2,4-dinitrophenolate)(2)H_2O]	3400v.br

For dibenzo-18-crown-6 both metals give 1 : 1 complexes usually solvated, suggesting that the metal is in the cyclic ether ring and available for interaction on both sides. One preparation yielded both the anhydrous and the hydrated forms of [K(2-hydroxybenzoate)(2)]. With (2) only [Na(2,4-dinitrophenolate)] gave a well characterised complex, Table 3.

2 : 1 Complexes were formed by dibenzo-24-crown-8. No complex could be isolated from dibenzo-30-crown-10.

Thallium(I) derivatives of simple salts have been reported by other workers.[1,12] Like the sodium and potassium complexes, the Tl : (2) ratio is 1 : 1 and the same ratio is maintained for Tl : (1) in contrast to the behaviour of potassium; possibly the stereochemically active lone pair of electrons in Tl^{I} prevents ' sandwich ' formation. We found that [Tl(2,4-dinitrophenolate)] was the only thallium salt with a chelating anion which yielded cyclic ether complexes; this may indicate that dissociation of the salt is a preliminary requirement, this salt has a much larger conductivity than the others.[13]

The structures of the [MX(2)] complexes, see Figure, suggest the possibility of forming complexes with linear polyatomic cations having suitable equatorial radii such as dialkyl thallium, R_2Tl^+,[14,15] and uranyl, UO_2^{2+}. No reaction could be obtained with halides of these cations, probably because complex formation is normally stepwise and these ions could only fit into a ligand preformed in the complex conformation.

Apart from the disappearance of the characteristic i.r. frequency of the macrocyclic ether on complex formation, two other features are of interest. In the thiocyanates there is the possibility of finding evidence for $>$N–C–S bridging which is known to occur for [$(KNCS)_2$(3)] [9] in contrast with –N–C–S co-ordination in [(Rb,Na)NCS(2)].[11] Unfortunately, the ν(C–S) and δ(NCS) frequencies are obscured by the ligand and the strong ν(C–N) at 2057 cm^{-1} appears at the usual frequency for the NCS^- anion.[16] For two complexes, however, the band is split, into 2075 and 2080 cm^{-1} for [$(NaNCS)_2$(4)], and into 2055 and 2085 cm^{-1} for [(NaNCS)(2)$2H_2O$]. In the solvates the i.r. bands in the hydroxy stretching region, Table 4, can be compared with those for [NaI(1)H_2O] containing a co-ordinated water molecule hydrogen-bonded to the anion and [NaBr(2)$2H_2O$] containing both co-ordinated and unco-ordinated water with some, but not all, the hydrogen atoms taking part in hydrogen bonding. None is as complicated as the latter. It seems probable that in most the water is co-ordinated to the metal, the exceptions being the four compounds (including the ethanolate) for which only one broad band is recorded, suggesting that the solvent is merely in the lattice. The complex [KH(2-nitrophenolate)$_2$(1)$_2$] shows the broad absorption from 1600 to 700 cm^{-1} characteristic of short hydrogen bonds [17] as in type A acid salts.[18]

EXPERIMENTAL

Complexes were synthesised by dissolving the required amount of the polyether with the alkali-metal salt in ethanol or 1 : 1 ethanol–methanol. The solvent was slowly evaporated at room temperature until crystals appeared or the whole of the solvent was driven off. In the latter case the product before being subjected to authentication, was examined under the microscope and separated from unreacted material, if any. In the former case the homogeneity of the crystals was ascertained under the microscope and the filtrate was again subjected to crystallisation or evaporation to dryness to discover if there was a second new product.

M.p.s were recorded using hot-stage (0—360°) microscopy and i.r. spectra on a Perkin-Elmer 457 spectrometer. Elemental (C, N, and H) analysis was carried out at University College, London, whereas alkali metals were estimated by flame photometry. Molecular weights were determined from measurements on single crystal *X*-ray Weissenberg and precession photographs with densities measured by flotation.

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