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Field Desorption Mass Spectrometry of Complexes of Sodium and Potassium with Macrocyclic Polyethers

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Four alkali metal complexes of crown ether derivatives have been examined by field desorption mass spectrometry after deposition from acetone. The base peak at low emitter currents corresponded to [metal cation + crown]. Loss of the central alkali metal was also observed. Of the three compounds of known crystal structure, [Na-15-crown-5(H_2O)]$^+I^-$, [K-dibenzo-30-crown-10]$^+I^-$ and [NaBr-dimethoxy-benzo-15-crown-5]$^\circ$, only the last exhibited [alkali metal$_2$ halide]$^+$ ions at higher emitter currents, suggesting a diagnostic feature of halide-coordinated complexes. On this basis an aquated complex of a macrobicyclic crown ligand, L, with sodium bromide has been assigned the ionic form [NaL]$^+$Br$^-$xH_2O.

Introduction

A common problem in the characterisation of crown ether complexes of alkali metals is establishing the coordination number of the metal. In particular, confirmation of the coordination of water or anionic ligands (in addition to the ring oxygens) has generally required X-ray crystallographic studies. It seemed possible that field desorption (f.d.) mass spectrometry could provide a novel and rapid solution to this problem, since this method has recently been successfully applied to a wide variety of organometallic [1–5] and coordination complexes [6–8] (both neutral and ionic). In the great majority of such complexes examined to date the f.d. mass spectra exhibited molecular [P]$^+$ ions as strong or base peaks, leading to ready identification.

We report here f.d. mass spectral studies on a series of crown ether complexes of sodium and potassium, namely**

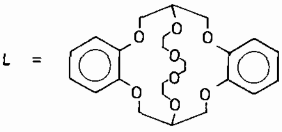

Fig. 1. The formula of the macrobicyclic ligand L in (4).

[Na(benzo-15-crown-5)(H_2O)]I (1)
[K(dibenzo-30-crown-10)]I (2)
[Na(dimethoxy-benzo-15-crown-5)Br] (3)
and
NaL·BrxH_2O (4)
with x ≈ 3.

The formula of the macrobicyclic ligand L in (4) is shown in Fig. 1. In complexes (1) and (2) X-ray crystallographic studies [9, 10] have established that the iodide ion is not coordinated to the central alkali metal, and that a water ligand is attached to sodium in (1) [9]. In contrast, the bromide ion in (3) is known [11] to be bonded to the sodium. The coordination sphere of the sodium ion in the crown ether complex (4) is yet to be established. This series should therefore provide a crucial test of the ability of f.d. mass spectra to establish metal coordination numbers in crown ether complexes.

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**Systematic names are cumbersome and have been subject to change. 1980 versions are: benzo-15-crown-5: 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin; dimethoxybenzo-15-crown-5: 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-(17,18-dimethoxybenzo)pentaoxacyclooctadecin; dibenzo-30-crown-10: 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; macrobicyclic molecule (L): named as 7,8,16,17-tetrahydro-6H,15H-5,9,14,18,19,22,25,28-octaoxa-7,16-decanodibenzo[a,h] cyclotetradecene in ref. 12, or in the cyclophane scheme as 1,5,12,16,23,26,29,32-octaoxa-[$10^{3,14}$] [5:5]-orthocyclophane.

TABLE I. Field Desorption Mass Spectra of Crown Ether Complexes.

Complex	Mol. wt.	Emitter current/mA	m/z (% rel. int.)
(1)	309[a]	9	292(51), 291(100), 269(40), 268(64), 159(19)
		12	292(13), 291(20), 270(6), 269(28), 268(100), 226(11)
(2)	575[a]	7	577(41), 576(41), 575(100), 431(62)
		10	577(13), 576(23), 575(100), 560(6), 559(6), 536(34), 439(9)
(3)	431	14	353(19), 352(9), 351(100), 253(4)
		17	328(14), 261(8), 127(94), 125(100), 81(6), 79(16)
(4)	567[b]	11	471(8), 470(46), 469(100)
		20	471(10), 470(15), 469(67), 448(11), 447(24), 446(100), 401(7), 223(5)

[a] Mol. wt. for cation only. [b] Mol. wt. for formula NaL, Br, H_2O.

Experimental

Complexes (1) and (2) were crystallised from methanol as described previously [9, 10]. Compound (3) was obtained by slow evaporation from methanol of an equimolar mixture of the crown compound and sodium bromide. The ligand [12], L, in (4) is sparingly soluble in water but dissolved in aqueous sodium bromide from which the crystalline complex was obtained solvated with approximately three molecules of water. *Anal.* Found: C, 47.77; H, 5.70; Br, 12.96%. M: 594.5. $C_{24}H_{30}O_8$, NaBr, $3H_2O$ requires: C, 47.78; H, 6.01; Br, 13.24%. M: 603.5.

Field desorption mass spectra were recorded using a combined F.D./F.I./E.I. source on a Varian CH5D mass spectrometer linked to a Varian Spectro System 100 data system. Solutions of the complexes in acetone were applied to an activated tungsten emitter wire. Emitter currents between 6 and 20 mA were employed. The source temperature was 74 °C and an accelerating voltage of 3 kv was employed. Spectra were recorded over a mass range *m/z* 50–1200.

Results and Discussion

Field desorption mass spectra for each of the complexes (1–4) at selected emitter currents are summarised in Table I. The spectra obtained varied with the conditions employed, generally showing somewhat greater fragmentation with higher emitter currents. However, the most notable feature of all the spectra, in common with other coordination complexes [6–8], is their simplicity.

For salt (2), in which the iodide ion is known [10] not to be coordinated to potassium, the base peak at low emitter currents (*m/z* 575) corresponds to the expected molecular $[P]^+$ ion for the cationic portion. The only fragment ion is one at *m/z* 431 of unknown origin, the other observed being $[P + 1]^+$ and [P + 2] ions. At higher emitter currents a further medium intensity peak appears at *m/z* 536 arising from the $[P - K]^+$ ion. Loss of the central metal has not been previously observed in the f.d. mass spectra of any transition metal coordination complexes studied by us [6]. However, the present observation is consistent with the relatively weak coordinating ability of alkali metals.

During the course of this work a paper by Bursey *et al.* [8] appeared describing essentially similar features for the f.d. mass spectra of a variety of cationic 18-crown-6 complexes of alkali metals, in agreement with an earlier brief report [13]. A notable observation in the studies by Bursey *et al.* [8] was facile exchange of the central metal, leading to memory effects in successive samples containing different metals. This explains the weak peaks at *m/z* 559 and 560 observed here for complex (2) in all spectra recorded with emitter currents greater than 8 mA. They correspond to the molecular $[P]^+$ and $[P + 1]^+$ ions for [Na(dibenzo-30-crown-10)]I since the spectra of (2) were recorded after those for the sodium complex (1).

Interestingly, the spectra of complex (1) do not exhibit a molecular $[P]^+$ ion peak under any of the conditions employed. At low emitter currents the base peak at *m/z* 291 corresponds to the $[P - H_2O]^+$ ion. This suggests either that the water ligand in complex (1) is only weakly coordinated to the central sodium although it has the shortest Na–O bond or that the water ligand has been displaced in the initial dissolution of (1) in acetone. Similar loss of a solvate ligand has been recently observed [3] in the f.d. mass spectra of neutral $[(\eta\text{-}C_6H_6)RuX_2(DMSO)]$ (X = Cl, Br) complexes.

A further strong peak is observed for (1) at *m/z* 268 (the base peak at high emitter currents) which indicates loss of the central sodium to give the $[P - H_2O - Na]^+$ ion. No other fragmentation is observed except for ions of unknown origin at *m/z* 226 and 159. In addition, in some spectra weak peaks were also noted at *m/z* 709 and 710 as expected for the cluster species $[(P - H_2O)_2I]^+$ and $[(P - H_2O)_2I] + I^+$, respectively.

The neutral complex (3), although known from X-ray crystallographic studies [11] to contain a coordinated bromide ligand, does not show the anticipated molecular $[P]^+$ ion at any of the emitter currents used (11–20 mA). The only significant peaks observed at low emitter currents are those arising from $[P - Br]^+$ (*m/z* 351, base peak) and associated $[P + 1 - Br]^+$ and $[P + 2 - Br]^+$ ions. As with (1) and (2), loss of the central alkali metal occurs at higher emitter currents ($[P - NaBr]^+$ at *m/z* 328). A further striking feature of the spectrum run at 17 mA is the intense peaks at *m/z* 125 and 127 corresponding to the isotopic $[Na_2Br]^+$ species and the weaker $[Br]^+$ ion peaks at *m/z* 79 and 81. The absence of related $[M_2I]^+$ and $[I]^+$ ions in any of the spectra for salts (1) and (2) and the failure of Bursey *et al.* [8] to observe $[M_2\text{halide}]^+$ or $[\text{halide}]^+$ peaks in their spectra of cationic crown-ether complexes desorbed off wires previously coated with alkali metal halides, suggests that the presence of such peaks in complex (3) may be a feature associated only with coordinated halides.

Finally, the f.d. spectra of compound (4), of overall stoichiometry $NaL{\cdot}BrxH_2O$, are again simple. The only intense peaks are those due to $[\text{“P”} - xH_2O - Br]^+$ (*m/z* = 469) and $[\text{“P”} - xH_2O - NaBr]^+$ (*m/z*) ions. In view of the absence of $[Na_2Br]^+$ or $[Br]^+$ peaks we therefore tentatively assign this complex the ionic structure $[NaL]BrxH_2O$ analogous to the crystalline form [14] of a potassium chloride complex with the benzo derivative of L; in this the non-stoichiometric water of crystallisation is not coordinated to the potassium which is encapsulated only by the ligand.

The above results indicate that f.d. mass spectra are useful in the characterisation of crown ether complexes of alkali metals. Strong peaks for the M(crown ether) moiety are invariably detected at low emitter currents for neutral or ionic complexes, despite the general weakness of the alkali metal–oxygen bonds. In addition, while the method appears to be unsuccessful as a diagnostic tool for the presence of coordinated water molecules in such complexes, it may provide a novel and simple test for the presence of coordinated halides. Further studies are in progress.

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