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Field Desorption and Chemical Ionization Mass Spectra of 'Crown' and Macrobicyclic Polyether Complexes of Potassium

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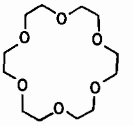
The potassium complexes of five crown ethers have been investigated by field desorption and by chemical ionization desorption mass spectrometry with ammonia as the carrier. Three have also been investigated by the latter technique with methane as the carrier. For two macrobicyclic crown ethers simple F.D. spectra corresponding to $[L + K]^+$ were obtained; benzo-15-crown-5 showed the $[L_2 + K]^+$ sandwich and dibenzo-2-crown-8 gave an ion corresponding to $[L + K]^+$, the ligand 18-crown-6 appeared to volatilise without ionizing and yielded spectra in F.D. corresponding to potassium thiocyanate. With ammonia all five ligands gave $[L + NH_4]^+$ as the most abundant ion, benzo-15-crown-5 also gave some $[L_2 + NH_4]^+$; some fragmentation was obtained. With methane there is more extensive fragmentation although the parent $[L + H]^+$ was in fair abundance.

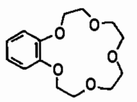
Introduction

Alkali metals have been regarded as an advantage and as a disadvantage in field desorption mass spectrometry; the former from their use in 'cationization' to help volatilise a sample [1], and the latter from the poor reproducibility and the appearance of peaks at unexpected M/z [2]. Although it has been suggested [3] that the interference from alkali metal cations might be avoided by removing them with dibenzo-18-crown-6, the technique does not seem to have been generally adopted. We are interested in complexes of alkali metal cations *per se* and have investigated those formed with crown ethers and their derivatives by various techniques [4].

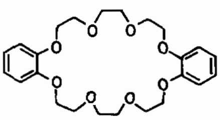
In a preliminary investigation [5] of the use of field desorption mass spectrometry to distinguish ion paired $(LC^+X^-)^o$ from cationic $(LC)^+X^-$ complexes we found the latter to give no species containing both the cation and the anion X, while the former did so. To explore the potential of the method for complexes of various stoichiometries L:C^+ we have now examined five potassium complexes, three of known crystal structure. The same cation was used to avoid the possibility of exchange [6]. Desorption chemical ionization techniques have been applied to the same compounds.



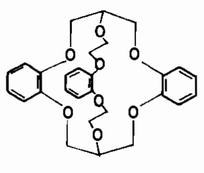
L(1)



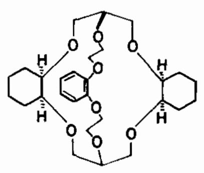
L(2)



L(3)



L(4)



L(5)

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TABLE I. Field Desorption Mass Spectra Abundances decrease from left to right. In one run samples were measured in the order (iii), (ii), (v), (iv), (i).

Compound	Mass of ligand	M/z
(i) KNCS·L(1)	264	39, 136, 233, 41, 138, 235
(ii) $KBr(L(2))_2$	268	575, 573, 39, 576
(iii) $(KNCS)_2$ L(3)	448	487, 97, 489
(iv) KNCS L(4)	494	534, 39, 536, 41
(v) $K^+ClO_4^-$ L(5)	506	529, 59, 545, 530, 546, 504, 506

The compounds are

(i) KNCS·L(1) where
L(1) is a monocyclic crown ether, 18-crown-6, giving a 1:1 complex which in the crystal was found [7] to consist of $[KL(1)]^+$ equidistant from two NCS^- ions.

(ii) $KBr(L(2))_2$ where
L(2) is monocyclic benzo-15-crown-5, which forms in the crystals [8] and in solution species of 1:2 stoichiometry [4]. In the corresponding iodide crystal structure analysis revealed [9] a sandwich complex cation $[K(L(2))_2]^+$ and I^-.

(iii) $(KNCS)_2L(3)$ where
L(3) is dibenzo-24-crown-8; this compound was shown [10] by crystal structure analysis to contain a complexed dimeric ion pair.

(iv) KNCS L(4) where
L(4) is a macrobicyclic ligand, benzo-224, which encapsulates potassium to yield a complex cation shown by crystal structure determination [11] in the chloride to be $[KL(4)]^+Cl^-$, $5H_2O$.

(v) $K^+ClO_4^-$, L(5) where
L(5) is a hydrogenated derivative [12] of L(4), dicyclohexyl-benzo-224 isomer B, the complexed ion pair having been found by crystal structure analysis [13].

We wished to see whether stoichiometries other than CX:L of 1:1 would be retained in the experimental conditions and whether the ion paired complexes would be distinguishable.

Experimental

Ligands were synthesised and purified, complexes were crystallised from mixtures of the ligand compounds and salts, usually from methanol and characterised by the melting points, IR and NMR spectra and elemental analysis. Compounds (iii) [10] and (v) [13] had been subjected to crystal structure analyses in one of our laboratories.

For field desorption measurements the crystalline compounds were dissolved in acetone, allowed to dry on the emitter (activated carbon) and inserted in a V.G. ZAB. The source temperature was kept as low as possible *ca.* 80 °C to avoid any decomposition effects, however the absence of the ligand L(1) and the very fast desorption of this compound may be due to the temperature of the source being too high. The mass spectrometer was operated at 8 kv accelerating voltage and the data were acquired into a V.G. Multispec data system. The data system was calibrated in the Electron Impact mode using perfluorokerosene, then switched into the combined F.I./F.D. mode. The mass spectrometer was scanned at 3 seconds per decade from M/z 800-20 in the exponential down mode.

The same compounds were also examined using the Desorption Chemical Ionisation technique on a V.G. 7070HS mass spectrometer coupled to a V.G. 2235 FB data system. The compounds were dissolved in methanol and spotted onto the D.C.I. probe which consists of a platinum spiral. The probe was inserted into the ion source and programmed from 0–1500 m.A. to obtain a desorption profile. The mass spectrometer was scanned at 1 second per decade from M/z 800-20 in the exponential down mode. The reagent gasses used were ammonia and methane at a source pressure of 0.5 torr. It was noted that compound L(1) desorbed without any heating being applied to the filament wire.

Results and Discussion

Results of field desorption are shown in Table I. A notable feature is the simplicity of the spectra and lack of fragmentation. Compound (iv) gives mainly $[KL(4)]^+$ with some potassium but no free L(4). Compound (ii) gives $[K(L(2))_2]^+$ and potassium, neither $[L(2))]^+$ nor a 1:1 $[KL(2))]^+$ species. This is of particular interest because of the possibility of distinguishing the true sandwich from the 1:2 stoichiometry metal:ligand shown by systems in which only one ligand is coordinated to the cation, the other being a molecule of crystallisation as in calcium 3,5-dinitrobenzoate trihydrate $(L(2))_2$ which consists in the crystals [14] of $[CaL(2), X_2]^\circ$, L(2),

TABLE II. Desorption Chemical Ionization Mass Spectra M/z (rel.%) in Order of Decreasing Mass in (a) NH_3, (b) CH_4.

(i)	(a)	282(40)	281(100)	264(15)	176(10)		
	(b)	266(14)	263(100)	177(47)	133(49)	89(22)	87(26)
(ii)	(a)	553(8)	286(11)	285(26)	269(13)	268(33)	267(100)
(iii)	(a)	466(29)	465(100)	448(5)	447(8)	136(24)	121(25)
	(b)	466(23)	448(43)	225(30)	181(51)	163(43)	
				137(100)	136(46)	121(60)	
(iv)	(a)	512(33)	511(100)	494(9)	493(10)	149(19)	121(28)
	(b)	493(26)	205(43)	193(12)	187(18)	177(10)	
			175(12)	163(12)	148(100)	137(39)	
			136(12)	121(44)			
(v)	(a)	525(14)	524(33)	523(100)	506(7)	155(8)	136(25)

$3H_2O$. Measurements of stability constants in methanol solution and of nuclear magnetic resonance spectra in deuteroacetone solution show that the ligand (2) forms 1:2 K^+:L(2) species [4]. On the other hand with ligand (3) measurements in solution give evidence only for 1:1 stoichiometry [15]. Only on crystallization does L(3) yield compounds containing two complexed ion pairs.

The M/z values in Table I for compound (iii) correspond to $[KL(3)]^+$ not the K:L(3) 2:1 species found in the crystal. It is probable that evaporation gives the solution species because crystallization of the least soluble species which is present in very small concentration takes time. However, our observations may merely reflect the ease of desorption.

Compound (v) shows peaks for $[KL(5)]^+$ and for $L(5)^+$ but there appears to be contamination with sodium, the largest peak corresponding to $[NaL(5)]^+$. The stoichiometry is the same as that found [12] in solution in methanol for C^+X:L(5). Unfortunately, the batch of compound was lost in the post but the presence of a small contamination with sodium (Na:K = 1:20) was found [16] by electron probe microanalyses in another crystalline sample. The relative peak heights reveal the relative ease of loss of metal not the relative percentages of the ions as found in comparison of Li^+, Na^+ and K^+ with D-glucose [17]. Loss of metal in (v) to give $[M^+]$ and not in (iv) is consistent with the presence of sodium. The sodium from this sample did not exchange onto the complexes of L(1), and L(4).

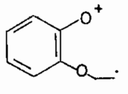
For compound (i) the results are unexpected and were confirmed by repetition with a new sample after an interval of five months. The existence of isotope 41 gives a characteristic appearance to K-containing species without hydrogen but the usual ±1 and ±2 mask this otherwise. The peaks correspond to K^+, K_2NCS^+ and $K_3(NCS)_2^+$, *i.e.* the clusters from a solution of a salt. The ligand may have volatilized without ionizing. These results contrast with the findings of Bursey and coworkers who have used cobalt [6] or nickel [18] dendrite emitters, and found many species containing L(1) for alkali metal halides and for nitrates of other cations with exchange and memory effects.

Compounds (ii) and (iv) as expected, show no evidence for ion pairing. Compound (iii) gave a peak at 97 M/z, possibly $[KNCS]^+$, compound (v) gave no peak corresponding to K (or Na) andClO_4^-, the strong peak at 59 M/z is not accompanied by one at 61 M/z as might be expected for a chlorine-containing fragment and may be acetone. Further work is required to show whether the technique gives a useful indication of ion pairing in solution as shown by evaporation.

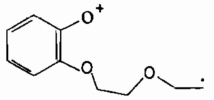
Results of desorption chemical ionization are in Table II. When the flow gas was ammonia, there was no indication of any species containing potassium. The major products correspond to complexes of the ammonium ion, with the usual ±1, ±2 found by this technique. For L(1) we did get the (1:1) ammonium complex. For compounds L(4) and L(1) the 1:1 complex was the major product. From L(2) a 1:2 sandwich complex was a minor product, the main one being the uncomplexed ligand and a subsidiary being a 1:1 complex with the ammonium ion, this corresponding to the species isolated from solutions of ammonium thiocyanate [19], ammonium picrate [20], or ammonium 2,4-dinitrophenolate [20] with L(2). Dibenzo-24-crown-8, L(3), gives mainly the 1:1 complex with the ammonium ion not 2:1 as in a compound isolated from solutions of ammonium thiocyanate with L(3) [19]. There is a small amount of uncomplexed ligand.

Desorption chemical ionization with ammonia gave some fragmentation of the ligands. For L(1), the species $(CH_2CH_2O)_n$ with n = 4, for L(3) and L(4) a species M/z 121 probably A, for L(3) and L(5), a species M/z 136 probably B, for L(4) a species M/z 149 and for L(5) at M/z 155 these are probably D and the corresponding cyclohexane fragment E. Species **A**, B and C are all found in E. I. fragmentation of dibenzo-18-crown-6 and confirmed by study of three of its nitro derivatives [21] and similarly fragmentation of acetylbenzo-18-crown-6 [22].

When methane was used as the carrier gas in desorption chemical ionization no potassium-containing entities were found and more extensive fragmentation was observed, L(1) yielding also the n = 2 and n = 3 species; L(3) yielding A, B, C and, at M/z 163, $(B + C_2H_5)^+$ while L(4) yields A, B, $(B + C_2H_5)^+$, and D.



B



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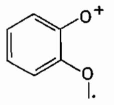
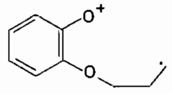
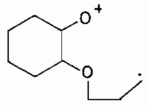


A



D



E

The high abundance of the parent ion $[M + H]^+$ of L(1) in desorption chemical ionization with methane confirms [23] the superiority of this technique over E.I. mass spectrometry for aliphatic crown ethers.

Acknowledgements

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