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A Fast Atom Bombardment Mass Spectrometric Analysis of Crown Ether Complexes [1]

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Abstract. Analyses of crown ether complexes of alkali metal ions and characterization of the complexes formed in *m*-nitrobenzyl alcohol have been carried out by fast atom bombardment (FAB) mass spectrometry. By using *m*-nitrobenzyl alcohol as a matrix for measurements, the stoichiometry of the complexes was assessed on the basis of the observed FAB peaks. In addition, the formation of crown ether–alkali metal complexes at a 2 : 1 molar ratio was enhanced by increasing the ionic radius of the metal ion in agreement with previous observations. On these grounds, FAB mass spectrometry may provide a rapid means for investigation of the complexation behavior of crown ethers and the stoichiometry of the complexes.

Key words. Crown ether complex, FAB-mass spectrometry.

1. Introduction

Since crown ethers show an unusual ability to form relatively stable complexes with alkali metal ions, the formation of complexes between crown ethers and alkali metal ions has been extensively studied. The complexation behavior in solution has most often been investigated by means of calorimetry, potentiometry, and absorption spectrometry. In practice, however, these methods tend to be somewhat cumbersome for the determination of the stability constants. By contrast, fast atom bombardment (FAB) mass spectrometry provides a rapid means for investigation of the complexation between crown ethers and alkali metal ions [2–5]. Johnstone and Lewis suggested that the complexation of crown ethers can be assessed readily and semi-quantitatively by the FAB technique [2]. Recently, Vignon and co-workers developed a method for the evaluation of stability constants for crown ether complexes by FAB mass spectrometry [3]. In this paper, we report on characterization of the complexation behavior of crown ethers in *m*-nitrobenzyl alcohol and the stoichiometry of the complexes by the FAB technique.

2. Experimental

FAB mass spectrometry was performed on a JEOL JMS DX 303 mass spectrometer. The spectra were obtained in the positive ion mode. The atom gun was operated at 6 kV, and xenon was employed at the bombarding gas. For the analysis of the complexes formed in *m*-nitrobenzyl alcohol as a matrix, peak heights at the

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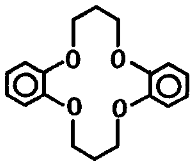
required m/z values were averaged over 4 scans by using a JEOL DA 5000 data system. The linked scanning techniques [6] were employed to study fragmentation in the first field-free region of the spectrometer. The linked scan involves two of the spectrometer variables; i.e., magnetic (**B**) and electric (**E**) fields and accelerating voltage (**V**), being scanned simultaneously with a constant relationship. The **B**/**E** scan provides information with respect to daughter ions, while the $\mathbf{B}^2/\mathbf{E}$ scan provides information as regards parent ions.

2.1. MATERIALS

Benzo-15-crown-5 (**2**) and dibenzo-18-crown-6 (3) were purchased from Aldrich Chemical Co., and dibenzo-14-crown-4 (**1**) was prepared according to a previously published method [7]. Other reagents were the purest grade commercially available and were used without further purification.



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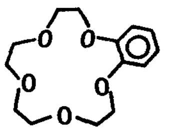

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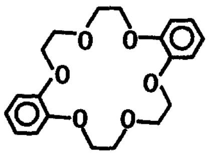

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Alkali metal complexes, i.e. dibenzo-18-crown-6·KSCN (**4**), dibenzo-18-crown-6·NaSCN (**5**), (benzo-15-crown-5)$_2$·KSCN (**6**), and (benzo-15-crown-5)$_2$·KI (**7**) were prepared according to literature procedures [8, 9].

2.2. ANALYSIS OF COMPLEXATION

A 1 μL sample of *m*-nitrobenzyl alcohol was loaded onto the probe, and 1 μL of a crown ether solution (50 mM in $CHCl_3$) and a metal salt solution (50 mM in H_2O) were carefully added to the alcohol. The mixture was allowed to stand for 20 min at room temperature and then carefully stirred. After being allowed to stand at room temperature for an additional 10 min, the mixture was stirred again and placed in the ion source. Spectra were recorded immediately after the sample was installed.

When the organophosphate salts of metal ions were used, 1 μL of aqueous metal hydroxide (50 mM), 0.5 μL of a bis(2-ethylhexyl)phosphoric acid solution (100 mM in $CHCl_3$), and 0.5 μL of a crown ether solution (100 mM in $CHCl_3$) were added to a matrix, *m*-nitrobenzyl alcohol.

3. Results and Discussion

3.1. FAB SPECTRA OF CROWN ETHER COMPLEXES

In the first step of our present investigation, four crown ether complexes were synthesized and examined by means of the FAB technique. On the basis of preliminary experiments, *m*-nitrobenzyl alcohol was selected as a matrix for FAB measurements.

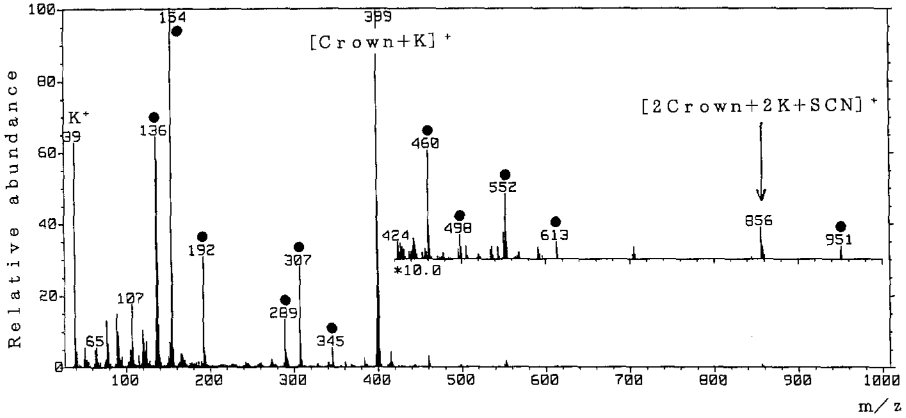

Fig. 1. FAB mass spectrum of dibenzo-18-crown-6 · KSCN complex; ●, peak originated from the matrix system.

For the dibenzo-18-crown-6 complex of KSCN (**4**) at a 1 : 1 molar ratio, the spectrum shows an intense peak at *m/z* 399, which is assigned to [Crown + K]$^+$, and a weak peak at *m/z* 856 which is referred to [2 Crown + 2K + SCN]$^+$ (see Figure 1).

As for the dibenzo-18-crown-6 complex of NaSCN (**5**) at a 1 : 1 molar ratio, [Crown + Na]$^+$ (*m/z* 383) and [2Crown + 2Na + SCN]$^+$ (*m/z* 824) were also identified. These results suggest that the ionization occurs via dissociation and loss of the anion to form [Crown + Metal]$^+$, and the resulting ion, [Crown + Metal]$^+$, undergoes association with a neutral assembly of [Crown + Metal + Anion] to form [2Crown + 2Metal + Anion]$^+$.

As regards (benzo-15-crown-5)$_2$·KSCN (**6**), a 2 : 1 crown ether–alkali metal complex, an ion peak at *m/z* 575, which is assigned to [2Crown + K]$^+$, was observed in addition to ion peaks attributable to [Crown + K]$^+$ (*m/z* 307) and [2Crown + 2K + SCN]$^+$(*m/z* 672). Linked scan studies (**B**^{2}/**E** and **B**/**E**) showed

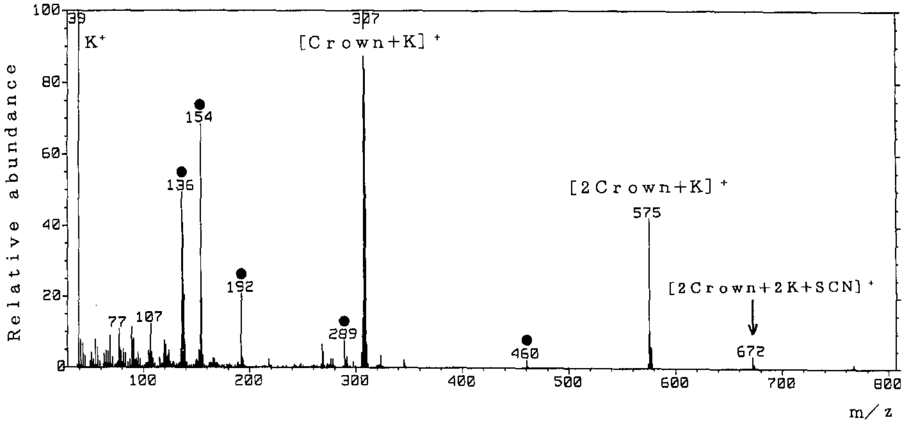

Fig. 2. FAB mass spectrum of benzo-15-crown-5 · KSCN complex; ●, peaks originated from the matrix system.

that $[\mathrm{Crown} + \mathrm{K}]^+$ was formed by loss of the crown ether molecule from $[2\mathrm{Crown} + \mathrm{K}]^+$, not by loss of SCN^- from [Crown + K + SCN].

The spectrum for (benzo-15-crown-5)$_2$·KI (**7**) was similar to that for **6**, showing that an ion is generated by the loss of I^- from [2Crown + K + I]. These data suggest that the stoichiometry of crown ether complexes can be assessed by fragment peaks observed in FAB mass spectra.

3.2. ANALYSIS OF COMPLEXATION BETWEEN CROWN ETHERS AND ALKALI METAL IONS IN *m*-NITROBENZYL ALCOHOL

Since FAB mass spectrometry provides a good method for the analysis of the complexes, we investigated the complex formation of crown ethers with alkali metal ions and the stoichiometry of the resulting complexes in *m*-nitrobenzyl alcohol by the FAB technique.

The crown ether–metal salt complexes were prepared in the alcohol on a probe of the mass spectrometer for measurements as described in the Experimental Section.

When a 1 : 1 mixture of dibenzo-18-crown-6 (DB18C6) and KSCN was examined, the spectrum showed an intense peak at *m/z* 399, attributable to $[\mathrm{Crown} + \mathrm{K}]^+$, and a weak peak at *m/z* 856 for $[2\mathrm{Crown} + 2\mathrm{K} + \mathrm{SCN}]^+$. There was no observed peak that is attributable to $[2\mathrm{Crown} + \mathrm{K}]^+$. The result indicates that the DB18C6 complex of KSCN at a 2 : 1 molar ratio was not formed in the matrix.

For a 1 : 1 mixture of dibenzo-14-crown-4 (DB14C4) and NaSCN, $[2\mathrm{Crown} + \mathrm{Na}]^+$ was observed along with $[\mathrm{Crown} + \mathrm{Na}]^+$ and $[2\mathrm{Crown} + 2\mathrm{Na} + \mathrm{SCN}]^+$. Furthermore, the DB14C4 – NaSCN mixture at a 2 : 1 molar ratio gave a peak of $[2\mathrm{Crown} + \mathrm{Na}]^+$ that is more intense than that of the 1 : 1 mixture. Thus, it may be concluded that both 1 : 1 and 2 : 1 complexes were formed in the alcohol matrix, and the formation of the 2 : 1 complex is enhanced by increasing the molar ratio of the crown ether to Na^+.

In order to assess a structural effect of the crown ethers on the stoichiometry of the complexes, a series of crown ethers having different ring sizes were treated with alkali metal salts in the alcohol matrix and examined by the FAB technique.

The crown ether and the alkali metal salt were mixed at a 1 : 1 molar ratio, and a relative abundance of the corresponding 2 : 1 complexes in the matrix was determined by evaluating the peak intensity of $[2\mathrm{Crown} + \mathrm{Metal}]^+$ relative to that of $[\mathrm{Crown} + \mathrm{Metal}]^+$. The relative abundance of the ions are summarized in Table I and Figure 3. The data in Table I indicate the following facts. First, the formation of the 2 : 1 complex is enhanced by increasing an ionic radius of the metal ion, and the results are consistent with previous observations showing that 2 : 1 complexes are often observed in cases where an internal size of the crown ether ring is smaller than a size of the complexing ion [10]. Second, the formation of the 2 : 1 complex becomes less favorable as the anion size is increased. Though the location of the counter anion is not obvious in the matrix, it seems reasonable to assume that the anion is located in a vicinity of the cation and prevents formation of the bulky 2 : 1 complex.

In summary, the FAB method provides a rapid means for investigating the complexation behavior of crown ethers with alkali metal salts and the stoichiometry of the resulting complexes.

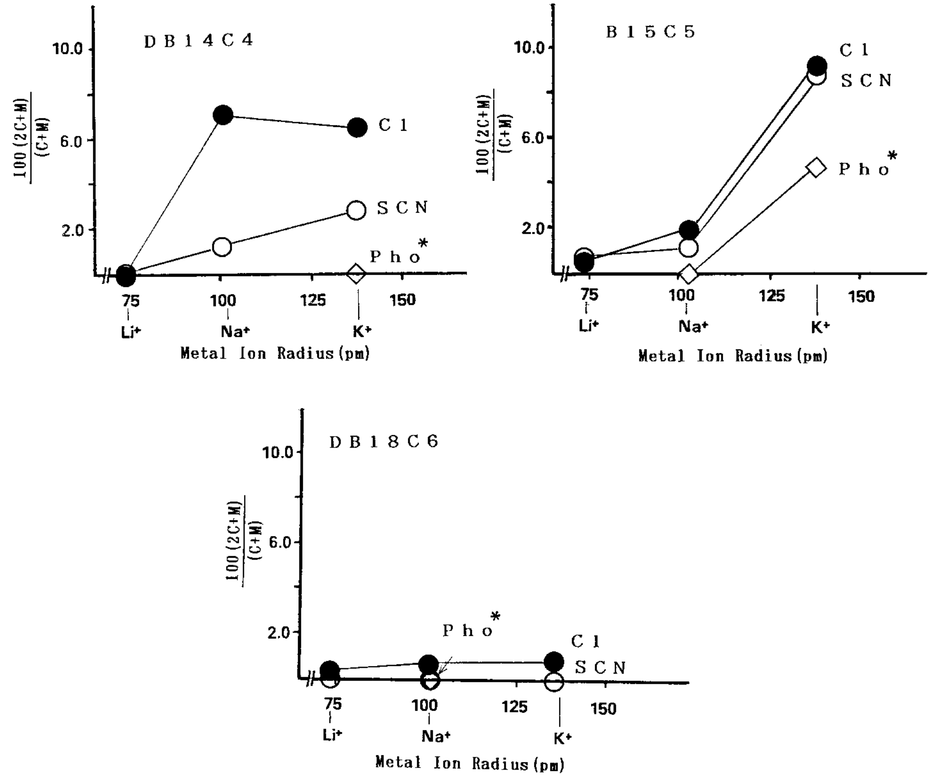

Fig. 3. Intensity of (2C + M)/(C + M) vs ionic radius of metals: DB14C4, dibenzo-14-crown-4; B15C5, benzo-15-crown-5; DB18C6, dibenzo-18-crown-6; Pho*, Bis(2-ethylhexyl) phosphate ion.

Table I. Relative abundance of [2C + M] peaks[a]

	DB14C4			B15C5			DB18C6		
Anion	Li	Na	K	Li	Na	K	Li	Na	K
Cl	0	7.1	6.4	0.4	2.1	9.1	0.2	0.4	0.7
SCN	0.1	1.2	3.0	0.5	1.2	8.9	0.1	0	0
Pho[b]	0	–	0	0	0.3	4.7	0	0	–

[a] Relative abundance of a [2C + M] peak was evaluated in terms of 100[2C + M]/[C + M], where [2C + M] and [C + M] refer to peak intensities of complexes at 2 : 1 and 1 : 1 molar ratios of a crown ether to an alkali metal salt, respectively.

[b] Bis(2-ethylexyl)phosphate ion.

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