

Tris(3,6-dioxaheptyl)amine Alkali-metal Cation Complexes. A Fast Atom Bombardment Mass Spectrometry, Infrared, and Nuclear Magnetic Resonance Study†

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Tris(3,6-dioxaheptyl)amine (tdoha, industrial name TDA-1) is shown to complex with a series of alkali-metal cations in solution, complexation being observed by fast atom bombardment mass spectrometry (f.a.b.m.s.; observation of a metal–tdoha cation), i.r., and ^{19}F n.m.r. Approximate values of the relative concentrations of the tdoha and crown ether complexes are obtained by f.a.b.m.s. by competitive complexation experiments with a range of cations.

Fast atom bombardment mass spectrometry (f.a.b.m.s.) is a 'soft ionization' technique that requires no sample heating and often results, for inorganic, organometallic, or co-ordination compounds, in the formation of a molecular ion, quasi-molecular ion, or in the case of ionic systems, simply the monocharged anion or cation or matrix-molecule–anion or –cation clusters. This is contrary to biochemical applications of f.a.b. where quasi-molecular ions predominate. Fragmentation to help in structural elucidation is observed, but not at the expense of the peaks essential in identifying the molecular formulation of the complex.¹

The methods used for the investigation of complexation between macrocyclic or acyclic polyethers and various metal cations tend to be somewhat cumbersome and usually require calorimetry, potentiometry, or absorption spectroscopy for the determination of stability constants. Complexes formed in solution between polyethers and metallic cations have been widely studied because of their excellent selective transport. Crown ether type compounds, apart from their synthetic value, also provide good model systems for the investigation of membranes in living systems. F.a.b.m.s. has previously been used to investigate complex formation between metallic cations and macrocyclic ligands.^{2,3} Johnstone and co-workers^{2,3} suggest that f.a.b.m.s. can be used routinely to examine complex formation between metal cations and macrocyclic ligands in solution.

We have studied the complex formation between tris(3,6-dioxaheptyl)amine (tdoha, industrial name TDA-1) and alkali-metal cations using f.a.b.m.s. In the light of the controversy surrounding the ability of f.a.b. to give an accurate picture of solution behaviour, we have obtained i.r. and n.m.r. data supporting our f.a.b. results in this regard. Systems in which a crown ether and tdoha competed for an alkali-metal cation were also investigated (all components being equimolar).

Experimental

Saturated solutions of alkali-metal halides in tdoha were prepared and left to stand at 45 °C for at least 24 h. F.a.b. spectra were obtained using an AEI MS-30 (Kratos Ltd., Manchester) retrofitted with a saddle field f.a.b. gun (Ion tech, Teddington) and a Kratos f.a.b. source in beam no. 1. Xenon was used as the bombarding atom, the energy of the beam was 6–8 keV and a stainless steel probe tip was used. All spectra were peak averaged from a minimum of ten scans using a DS55 data

system. Mass conversions were done off-line based on a tris-(perfluoroheptyl)-1,3,5-triazine calibration. I.r. spectra were obtained as thin films of the neat material using an Analect FX-6260 FT-IR instrument at a resolution of 4 cm^{-1} . ^1H N.m.r. spectra were obtained on a Bruker WP-80 as neat material at 303 K. ^{19}F N.m.r. spectra were obtained at 303 K on a Bruker WP-60 operating at 56.45 MHz (sample as neat material with external lock). CFCl_3 was used as an external reference.

The crown ether–tdoha–alkali-metal halide solutions were prepared in a 1:1:1 molar ratio. F.a.b. mass spectra were obtained after standing for 24 h at 40 °C. The ligand tdoha was obtained from May and Baker; the alkali-metal halides were from BDH, Alfa, or Aldrich and were of reagent grade. All the crown ethers were from Aldrich and were used unpurified.

The crude solid NaI–tdoha complex was prepared from a saturated solution of NaI in tdoha at 130 °C. This was allowed to cool to room temperature to leave a dark brown hygroscopic solid. This was then washed with cyclohexane followed by diethyl ether to remove any excess tdoha. The pale brown hygroscopic solid thus obtained was dried under vacuum (0.1 mmHg) at ambient temperature.

Results and Discussion

Saturated solutions of LiCl, LiF, LiBr, LiI, NaF, NaCl, NaI, KF, KCl, KI, RbF, CsCl, CsF, and CsI in tdoha were prepared and analysed by f.a.b.m.s. The solutions did not need a matrix liquid as the boiling point of tdoha alone is > 330 °C. Scans could be obtained over a period of 15 min without change. The f.a.b. mass spectrum of tdoha is shown in Figure 1, major ions being formed at $M + 1$ and $M - 1$ (m/z 324 and 322 respectively). The $M + 1$ ion presumably arises from the protonation of the molecule at the nitrogen and $M - 1$ from protonation of the nitrogen followed by cyclization involving loss of a hydrogen molecule. The base peak in the spectrum at m/z 234 corresponds to the fragment $\text{C}_{11}\text{H}_{24}\text{NO}_4$. Other intense peaks occur at m/z 59 (92% base) and 248 (38% base) corresponding to $\text{C}_3\text{H}_7\text{O}$ and $\text{C}_{12}\text{H}_{26}\text{NO}_4$ respectively. The ligand tdoha itself may be useful as a matrix liquid for f.a.b.m.s. because of its simple spectrum and the persistent nature of the sample in the mass spectrometer. Sharp *et al.*⁴ have used crown ethers as matrix liquids for f.a.b.m.s. In particular, 18-crown-6 (1,4,7,10,13,16-hexaoxacyclo-octadecane) mixed with 10% tetraglyme, $\text{CH}_3(\text{OCH}_2\text{CH}_2)_4\text{OCH}_3$, to depress its melting point has been used in the study of a series of rhodium, iridium, and platinum organometallic compounds. The routine use of

† Non-S.I. units employed: eV $\approx 1.60 \times 10^{-19}$ J, mmHg ≈ 133 Pa.

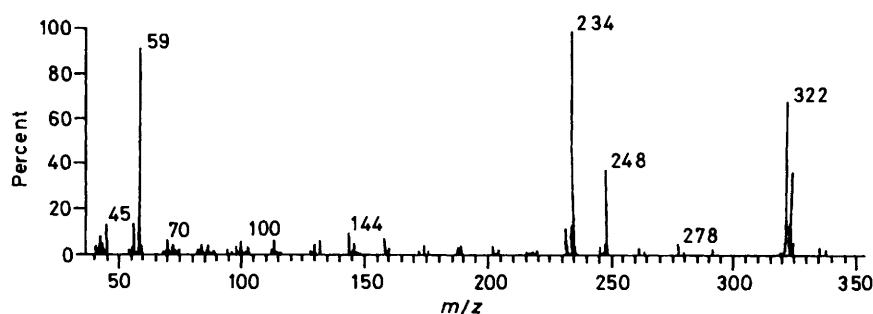


Figure 1. F.a.b.m.s. spectrum of tdoha (no peaks above m/z 350)

Table 1. F.a.b.m.s. of alkali halide-tdoha saturated solutions

Halide in MX-tdoha species	m/z 324 (MH ⁺)	m/z 234	Percentage of t.i.c. (tdoha + cation) peak
tdoha	5.8	14.6	—
LiF	4.2	13.5	0.0
LiCl	0.9	5.1	27.9
LiBr	0.0	0.0	45.1
LiI	0.0	0.0	38.8
NaF	6.8	14.0	0.0
NaCl	5.6	16.7	0.2
NaI	3.4	11.2	4.9
KF	5.8	14.8	0.2
KCl	4.8	12.4	0.3
KI	0.0	0.4	22.8
RbF	4.6	13.9	0.2
CsF	4.9	14.0	0.1
CsCl	4.1	13.3	0.0
CsI	5.4	14.3	0.0

crown ethers as matrix liquids is not to be recommended because of the toxic and hygroscopic nature of these compounds. The similar complexing properties of tdoha may mean that it is a useful alternative.

It can be seen from the data (Table 1) that there is no apparent periodic trend for the alkali metals. In the case of the lithium cation, tdoha demonstrated a high complexing affinity which was supported by the i.r. data (e.g. a change in the C—O—C asymmetric stretching frequency of 33 cm^{-1} for the iodide). From the f.a.b.m.s. data (Table 1) it appears that potassium is more strongly co-ordinated to tdoha than is sodium, since the percentage of the total ion current (t.i.c.) for the cation-tdoha peak is 22.8 for KI compared to 4.9 for NaI. However, the same frequency shift in the O—C—O asymmetric stretching band was obtained for potassium and sodium.

Caesium chloride showed no complex formation, but in the case of CsF and RbF a small amount of complex formation was observed, the cation-tdoha complex being 0.1 and 0.2% of the t.i.c. respectively. Because of the hygroscopic nature of these salts some water contamination was present in each of these solutions, as demonstrated by the i.r. spectrum, and this may account for the anomalous behaviour of these salts.

The stability constants of tdoha with alkali-metal cations have been determined previously by potentiometric titration in water-methanol solution.⁵ The order was found to be $\text{K,Na} > \text{Rb} > \text{Li,Cs}$. Our f.a.b.m.s. results give the order of complexation as $\text{Li} > \text{K,Na} > \text{Rb} > \text{Cs}$. The lower complexation of lithium when measured potentiometrically compared to our f.a.b.m.s. results may be reconciled by the higher affinity of the lithium cation for water in the water-methanol solvent. This competition between the solvent and tdoha for the cation is avoided in the f.a.b.m.s. method, in which no water is present.

Table 2. F.a.b.m.s. of LiCl-tdoha saturated solution

m/z	Percentage of t.i.c.	Assignment
330	27.9	[tdoha + Li] ⁺
324	0.9	[tdoha + H] ⁺
322	3.2	[tdoha - H] ⁺
234	5.1	[C ₁₁ H ₂₄ NO ₄] ⁺
138	2.0	[C ₆ H ₁₃ NO ₂ Li] ⁺
59	10.2	[C ₃ H ₇ O] ⁺

In the case of Li⁺ and K⁺, where strong complexation occurs, the fragmentation pattern of tdoha was also changed, fragments containing the alkali metal being observed in addition to the complex peak itself (Table 2).

It is believed by Johnstone *et al.*⁶ that to a first approximation the intensities of the molecular ions observed by f.a.b.m.s. are proportional to the concentrations of the species present in the matrix. We have investigated a series of competitive systems between tdoha and a range of crown ethers. We assume since in each case the electrostatic forces that have to be overcome on volatilisation are the same (to a first approximation) for the two complexes that the 'temperature' of volatilisation for the two complexes is approximately the same. Peak intensities are thus directly proportional to the concentrations of the tdoha and crown ether complexes. A dilution study showed a good correlation of complex concentration and ion intensity.

Mixing various crown ethers, alkali-metal chlorides, and tdoha in a 1:1:1 mole ratio and then subjecting the samples to f.a.b.m.s. gave an interesting insight into the relative 'strength' of the crown ether and tdoha complexes. In the case of the potassium cation, when mixed with 18-crown-6 and tdoha the majority of the potassium was found to be co-ordinated to the crown ether because of the optimum size of its cavity for this cation (Table 3). With 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) a greater percentage of the potassium was complexed to the tdoha because of the smaller size of the crown-ether cavity. Using 12-crown-4 (1,4,7,10-tetraoxacyclododecane) all the potassium was complexed by the tdoha and none by the crown ether, as determined by f.a.b.m.s.

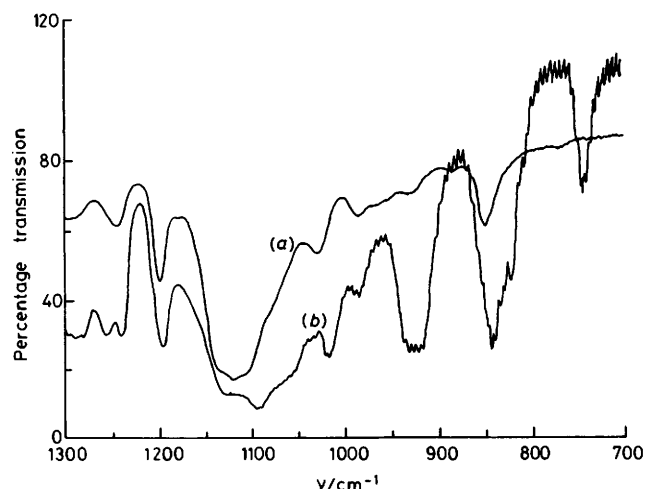
Using sodium chloride, tdoha, and the same range of crown ethers a similar series was obtained which may be rationalised in terms of the relative size of the crown ether cavities, the size of the sodium ion, and the affinity of tdoha for sodium (see Table 3).

With lithium chloride, 18-crown-6, and tdoha 77% of the lithium was bound to tdoha and 23% to the crown ether. Decreasing the crown ether cavity size resulted in a greater percentage of the lithium being complexed to it. In the case of 15-crown-5, 35% of the observed lithium was complexed to the crown ether because of the better fit with its cavity. With 12-

Table 3. F.a.b.m.s. of crown ether–tdoha–alkali chloride solution

Crown ether	Cation	Crown cavity radius (Å)	Cation radius (Å)	Crown ether complex *	tdoha complex *
18-crown-6	K ⁺	1.3–1.6	1.33	88	12
15-crown-5	K ⁺	0.8–1.1	1.33	55	45
12-crown-4	K ⁺	0.6–0.7	1.33	0	100
18-crown-6	Na ⁺	1.3–1.6	0.98	100	0
15-crown-5	Na ⁺	0.8–1.1	0.98	40	60
12-crown-4	Na ⁺	0.6–0.7	0.98	0	100
18-crown-6	Li ⁺	1.3–1.6	0.78	23	77
15-crown-5	Li ⁺	0.8–1.1	0.78	35	65
12-crown-4	Li ⁺	0.6–0.7	0.78	3	97

* Percentage of total metal-containing ions.

**Figure 2.** Infrared spectra of (a) tdoha and (b) NaI–tdoha saturated solution

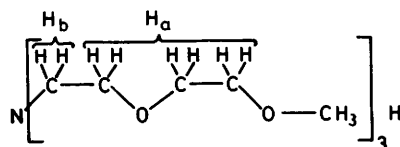
crown-4, tdoha, and lithium 97% of the lithium observed was found to be bound to tdoha.

Addition of an excess of water to the crown ether, tdoha, and alkali chloride systems produced crystals in some cases. I.r. and f.a.b.m.s. analysis of these crystals showed them to be crown ether hydrates with no complexed cation in each case. The f.a.b.m.s. spectra of the samples in which no crystals were produced showed in most cases that the equilibria between the crown ether metal and the tdoha–metal complexes were unchanged. When a shift in the position of the equilibrium was observed it resulted in a decrease in the crown ether complex concentration relative to that of the tdoha complex.

Systems that showed alkali-metal tdoha complexation by f.a.b.m.s. also showed distinct changes in their i.r. solution spectra consistent with complex formation implying that the f.a.b.m.s. was indeed monitoring solution behaviour. On complex formation new bands were observed in the i.r. spectrum, notably at *ca.* 930 and 750 cm^{-1} . The C–O–C asymmetric stretching vibration at 1120 cm^{-1} in tdoha was also perturbed on complexation as might be expected, being shifted to lower wavenumber depending on the cation and also significantly broadened (Figure 2). The frequency change of the C–O–C asymmetric vibration appears to parallel the strength of the complex the shift being 33, 26, 26, and 0 cm^{-1} for LiI, NaI, KI, and CsI respectively. (The exact frequency differences are difficult to measure accurately since the width of the bands increases.) The intensity of the new bands observed at 930 and

Table 4. F.a.b.m.s. of the crude solid NaI–tdoha complex in glycerol

<i>m/z</i>	Percentage of base peak	Assignment
346	100.0	[Na(tdoha)] ⁺
324	16.4	[tdoha + H] ⁺
322	14.1	[tdoha – H] ⁺
234	31.6	[C ₁₁ H ₂₄ NO ₄] ⁺
154	16.3	[C ₆ H ₁₃ NO ₂ Na] ⁺
59	85.2	[C ₃ H ₇ O] ⁺
23	10.9	[Na] ⁺

**Figure 3.** Hydrogen labelling in tris(3,6-dioxaheptyl)amine (tdoha)

750 cm^{-1} was also found to be dependent upon the degree of complex formation, but not on the cation. The anomalous behaviour of CsF and RbF seen by f.a.b.m.s., in that some complexation to tdoha was observed, was confirmed by both the i.r. and ¹⁹F n.m.r. spectra of the solutions; the shift in the C–O–C asymmetric stretching vibration for CsF and RbF being 10 cm^{-1} . Other caesium salts showed no complex formation by f.a.b.m.s. or i.r. Solution ¹⁹F n.m.r. spectra showed that the CsF–tdoha complex contained substantial amounts of HF₂[−] and the i.r. spectrum showed the presence of water because of the very hygroscopic nature of this salt. This was also found to be the case for RbF.

The i.r. solution spectra were run as thin films between KBr discs and some complexation between tdoha and the potassium from the disc was observed in the time taken to record the spectrum (*ca.* 2 min), but not enough as to affect the spectrum. This was demonstrated by rerunning the spectra using an attenuated total reflectance accessory with a zinc selenide crystal.

The ¹H n.m.r. spectra of the tdoha complexes showed few significant changes compared to that of tdoha itself even when strong complexes with Li were formed; more significant changes were observed in the isolated solid NaI–tdoha complex. The ¹⁹F n.m.r. spectra of LiF, NaF, KF, RbF, and CsF were also in good agreement with the f.a.b.m.s. results of those systems. In the case of LiF and NaF no cation–tdoha complex was seen by f.a.b.m.s. and no signal was seen in the ¹⁹F n.m.r. spectrum demonstrating that none of the salt had dissolved. KF, RbF, and CsF, which gave weak cation–tdoha complexes by f.a.b.m.s. (1.5, 1.4, and 1.0% of the base peak respectively), showed the presence of F[−] in the ¹⁹F n.m.r. spectrum. The chemical shifts were between −98 and −111 p.p.m. (CFCl₃) which is typical for the fluoride ion, although the signals were unusually broad, that of CsF–tdoha having a linewidth at half peak height of 740 Hz. This is analogous to the linewidths observed with crown ethers and alkali-metal fluoride complexes⁷ for which the possibility of reversed micelles was postulated. Addition of excess water to the CsF–tdoha system resulted in the formation of HF₂[−] ion and a fluoride ion signal of width 39 Hz at half peak height at −117 p.p.m. (CFCl₃).

We were also able to isolate a solid NaI–tdoha complex, but were unable to prepare solid complexes of either lithium or potassium by the same method. The i.r. spectrum of the crude solid NaI–tdoha complex as a Nujol mull was virtually identical to that of the saturated solution of NaI in tdoha. The ¹H n.m.r.

spectrum of the isolated NaI–tdoha complex showed slight changes when compared to tdoha itself in [$^2\text{H}_6$]dmsO (dimethyl sulphoxide) solution. The complex resonance from protons H_a (Figure 3) were observed to shift to 0.15 p.p.m. higher field on complex formation, consistent with an ion dipole interaction between the oxygen atoms of tdoha and the sodium ion. The triplet resonance from protons H_b and the singlet resonance from protons H_c were unchanged on complexation having chemical shifts of 2.63 p.p.m. and 3.23 p.p.m. respectively. The f.a.b.m.s. spectrum of the crude solid NaI–tdoha complex is described in Table 4.

In conclusion the ability of tdoha to complex a range of alkali-metal halides has been investigated by f.a.b.m.s. It has been found that the lithium cation was the most strongly bound followed by potassium and sodium. Larger cations such as rubidium and caesium were observed to bind only very weakly. Evidence in support of the ability of f.a.b.m.s. to monitor solution behaviour has been obtained since both i.r. and n.m.r. spectra were in excellent agreement with those obtained by f.a.b.m.s. Our results substantiate claims that tdoha, unlike crown ethers, is able to complex cations of a wide range of sizes.

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