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ELECTROSPRAY IONIZATION MASS SPECTRAL INVESTIGATIONS ON MULTI-NUCLEAR COMPLEXES OF AN AZACRYPTAND

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Abstract—The electrospray ionization (ES) mass spectrum of a trisodium azacryptate derived from a template reaction of sodium 2,6-diformyl-4-methylphenolate (sdmp) with 2,2′,2″-triaminoethylamine (tren) was investigated and compared with those by fast atom bombardment (FAB), atmospheric pressure chemical ionization (APCI) and electronic ionization (EI) methods. Dinuclear transition metal complexes of this hexaimine macrobicyclic ligand obtained by transmetallation were also studied by ES mass spectra. An $[M_2L]^+$ species has been observed for divalent metal complexes, and an $[MLH]^+$ species for a trivalent metal complex. The possible mechanism of the fragmentation process is discussed.

There have been continuous efforts in the design and preparation of macrocyclic ligands capable of binding two or more metal atoms.[1] Cryptands, especially derived from [2+3] macrocyclic Schiff base condensation, have received much attention for metalloprotein modelling,[2] magnetic exchange,[3] separation and encapsulation processes,[4] and supramolecular chemistry studies.[5] However, no systematic studies have been undertaken on the mass spectra of these macrobicyclic ligands and their complexes. Recently we introduced a sodium template to the preparation of the following cryptand LH_3 and studied the transmetallation of Na_3L by transition metals.[6] Here we mainly report the use of ES mass spectrometry to investigate the fragmentation behaviour of the multi-nuclear metal complexes of the azacryptand.

RESULTS AND DISCUSSION

The mass spectra of Na_3L have been recorded by ES, FAB, APCI and EI-MS methods, respectively. The related abundance of main ligand species and metal-containing fragments and their assignments are presented in Table 1.

As shown in Table 1, the parent molecular ion of Na_3L is observed as a base peak corresponding to $M+1$ only in the APCI mass spectrum. The subsequent fragments of Na_3L are seen in species $[Na_2LH_2]^+$, $[NaLH_3]^+$ and $[LH_4]^+$ in other mass spectra, except EI-MS in which no information was obtained. The commonly used FAB-mass spectrum for studying macrocyclic compounds only gives a base peak of $[NaLH_3]^+$ compared with other techniques for weak ionization. In ES-MS, multi-charged peaks of $[LH_5]^{2+}$ and $[LH_6]^{3+}$ are characteristically observed at *m/z* 339 and 227, with strong intensities different from other spectra. With these

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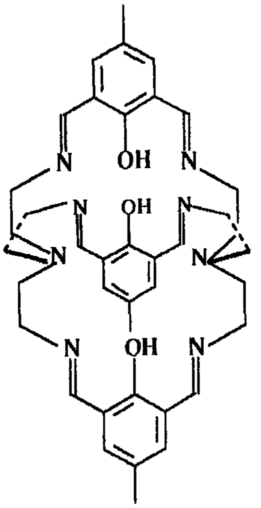
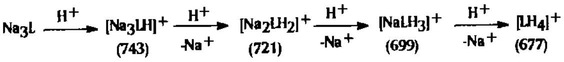
Table 1. Main peaks in the mass spectra of Na_3L by different techniques

Method	Fragment ion	Relative abundance	Assignment
APCI	743 $[M+1]^+$	100	$[Na_3LH]^+$
	721 $[M-22]^+$	23	$[Na_2LH_2]^+$
	677 $[M-65]^+$	19	$[LH_4]^+$
FAB	699 $[M-43]^+$	100	$[NaLH_3]^+$
ES	699 $[M-43]^+$	36	$[NaLH_3]^+$
	677 $[M-65]^+$	27	$[LH_4]^+$
	339 $[M-64]^{2+}/2$	100	$[LH_5]^{2+}$
	227 $[M-63]^{3+}/3$	75	$[LH_6]^{3+}$
EI	No signals observed		



LH_3

spectral data, it is supposed that the initial splitting mode of Na_3L proceeds in the following way (Scheme 1).



$$Na_3L \xrightarrow{H^+} \underset{(743)}{[Na_3LH]^+} \xrightarrow[-Na^+]{H^+} \underset{(721)}{[Na_2LH_2]^+} \xrightarrow[-Na^+]{H^+} \underset{(699)}{[NaLH_3]^+} \xrightarrow[-Na^+]{H^+} \underset{(677)}{[LH_4]^+}$$

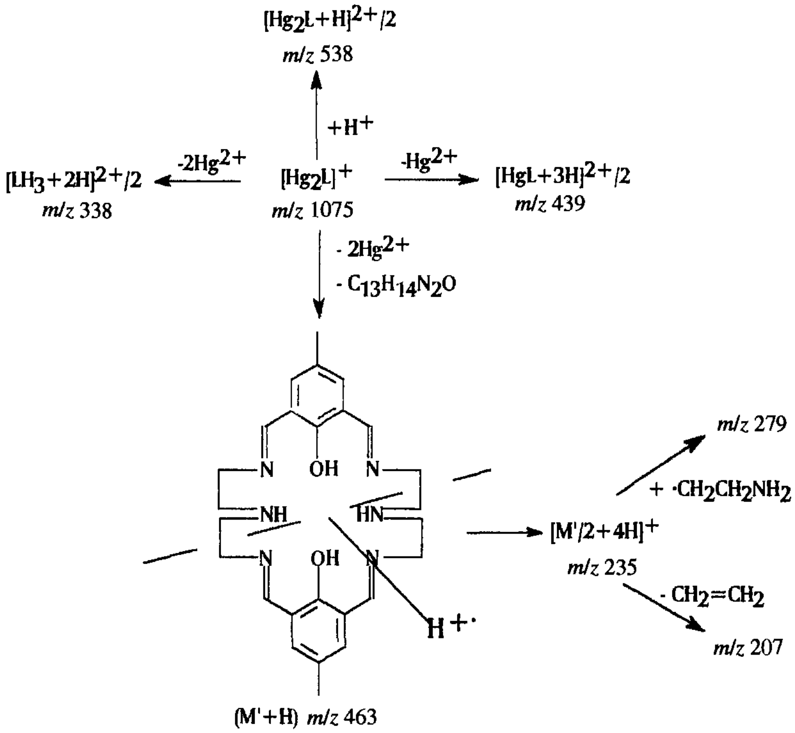
Scheme 1.

It is of significance to note that the loss of each sodium cation from the molecular species would generate a proton, unlocated, to add in among these spectra, similar to the behaviour of reported Na_2L', where L′ is one of the ligands obtained by [2+2] macrocyclic Schiff-base condensation using the same method.[7] In view of the techniques used, ES and APCI mass spectra are found to provide more fragmentation information than FAB- and EI-MS on the study of macrocyclic compounds.

The ES method has been employed to study the mass spectra of the dinuclear transition metal complexes. The main peaks of complexes **1**–**8** are given in Table 2. No molecular ion peaks are observed for all compounds, but peaks corresponding to $[M_2L]^+$ appear in all the mass spectra of divalent metal complexes as base peaks or in certain intensities. The reason is that ES-MS depends upon pre-existing ions in solution and species like $[M_2L]^+$ are formed through ionization of the metal complex in solution. The absence of peaks corresponding to $[M_2L]ClO_4$ are due to the fact that ion pairs between the metal cation and the counterion are not observed in this case. As for $[Fe_2L](ClO_4)_3$, however, one $[FeLH]^+$ species is observed owing to the trivalent metal cation in the macrocyclic anion where a proton is added. As observed in the ES-MS of Na_3L, almost all the complexes show a peak corresponding to $[M_2L+H]^{2+}$ or $[ML+2H]^{2+}$ accompanying the $[M_2L]^+$ or $[MLH]^+$, characteristic of the ES-mass spectra. However, the related $[M_2L+2H]^{3+}$ or $[M_2L+3H]^{3+}$ has not been obviously observed.

Table 2. Principal fragments in the ES-MS of complexes **1**–**8** (*m*/*z*, relative abundance in parentheses)

Ionic species	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
$[M_2L]^+$	783(100)	791(80)	791(20)	801(75)	805(36)	897(100)	1075(100)	730(33) $[MLH]^+$
$[M_2L+H]^{2+}/2$		396(100)	396(85)	401(100)	403(80)		538(45)	366(100) $[ML+2H]^{2+}/2$



Scheme 2.

In order to show the splitting mechanism of complexes, the ES-mass spectrum of $[Hg_2L]ClO_4$, illustrated in Fig. 1, has been interpreted to give a tentative fragmentation pattern in Scheme 2. Under ES conditions, $[Hg_2L]^+$ as a base peak loses two Hg^{2+} ions one by one, and each species is conspicuously observed as the corresponding double-charged peak. The splitting of the macrobicyclic ligand leads to a monocycle, first by losing a bridging phenolic moiety, then to the subsequent open-chain fragments in a mode similar to that of the reported monocycle.[8] It should be noted that the technique

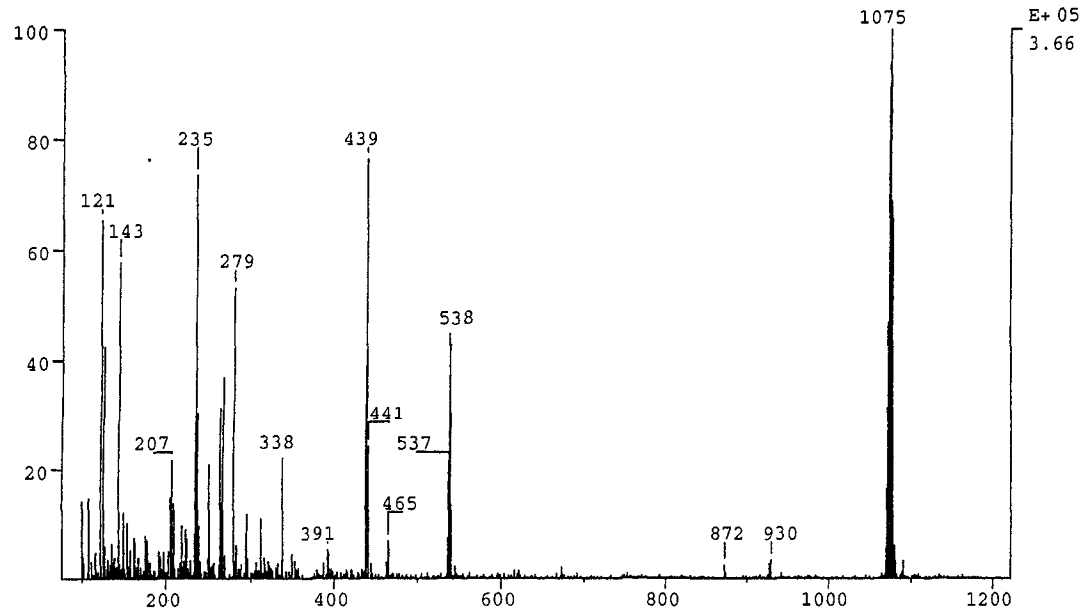


Fig. 1. ES-mass spectrum of $[Hg_2L]ClO_4$.

of electrospray ionization can be used to generate ions (usually singly, doubly and triply protonated ions). In addition, the species containing Hg^{2+} ions such as $[Hg_2L]^+$, $[Hg_2L+H]^{2+}$ and $[HgL+2H]^+$ are observed as groups due to the isotopic peaks of mercury atoms.

EXPERIMENTAL

Synthesis

The preparation of Na_3L by a template reaction of sdmp and tren will be reported elsewhere.[6] The transmetallation of transition metals with Na_3L to obtain $[Mn_2L]ClO_4$ (**1**), $[Co_2L]ClO_4$ (**2**), $[Ni_2L]ClO_4$ (**3**), $[Cu_2L]ClO_4$ (**4**), $[Zn_2L]ClO_4$ (**5**), $[Cd_2L]ClO_4$ (**6**), $[Hg_2L]ClO_4$ (**7**) and $[Fe_2L](ClO_4)_3$ (**8**) was performed by a general method.

An alcoholic solution (10 cm^3) of the corresponding metal acetate or nitrate (0.5 mmol) was added into the suspension of Na_3L (0.2 mmol) in ethanol (20 cm^3). The mixing solution was refluxed and stirred for 30 min, and then was filtered while hot to remove insoluble impurities. To the stirred filtrate $NaClO_4 \cdot H_2O$ (0.7 mmol) in ethanol (10 cm^3) was added. Solids immediately precipitated and were collected by filtration. Recrystallization in CH_3CN–C_2H_5OH (1 : 1) yielded crystalline products. The synthesis of complex **5** was carried out under nitrogen.

Measurements

The ES, APCI and EI-mass spectral measurements were made on a Finnigan MAT SSQ710 mass spectrometer, and the FAB-mass spectrum was recorded on a VG-2AB-HS mass spectrometer with 3-nitrobenzylalcohol (NOBA) as the matrix solvent. The ES-mass spectra were acquired by directly introducing samples into an ES ion source of a SSQ710 mass spectrometer with a low-pressure syringe pump at a flow rate of 0.9 cm^3 min^{-1}. Samples were generally prepared for Na_3L : solvent = 1 : 1 (v/v) CH_3OH/H_2O [mobile phase = 1 : 1 (v/v) CH_3OH/H_2O], and complexes **1**–**8**: solvent = 1 : 1 (v/v) CH_3CN/H_2O [mobile phase = 1 : 1 (v/v) CH_3CN/H_2O].

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