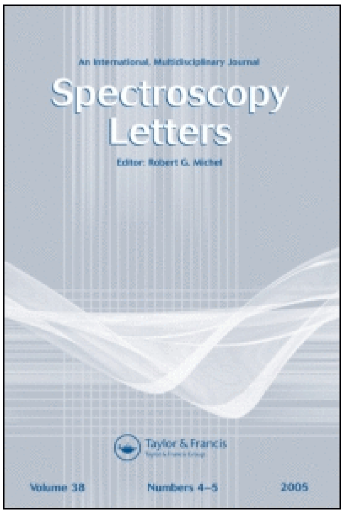

Spectroscopy Letters

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Chang-Jinn, Feng , Zhi-Lin, Wang , Yu-Hua, Mei , Li-Jinn, Jiang and Qin-Hui, Luo(1998) 'A Study on an Europium(III) Cryptate by Electrospray Mass Spectrometry', Spectroscopy Letters, 31: 7, 1441 — 1449

To link to this Article: DOI: 10.1080/00387019808001651

URL: http://dx.doi.org/10.1080/00387019808001651

SPECTROSCOPY LETTERS, 31(7), 1441-1449 (1998)

A STUDY ON AN EUROPIUM(III) CRYPTATE BY ELECTROSPRAY MASS SPECTROMETRY

Key words: Europium Cryptate, Electrospray Mass Spectra

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ABSTRACT

Electrospray mass spectrometry (ESMS) of an europium(III) cryptate derived from tris(2-aminoethyl)amine (tren) and 2,6-diformyl-4-chloro-phenol (dcp) is described. The effect of mobile phase, needle voltage and temperature of heated capillary on the ESI process are studied to get the best experimental parameters. The ES-induced fragmentation mechanism is discussed.

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INTRODUCTION

Electrospray mass spectrometry (ESMS) is a near atmosphere-pressure ionization technique base on the ion-evaporation process where the ions are formed outside the vacuum region. It is particularly suitable for characterizing preformed ions in solution [1]. Under appropriate conditions, ESMS may give a clear direct picture of the species in the solution under thermodynamic equilibrium [2, 3]. More recently, it has been used to probe the coordination behavior of several macrocycles toward a variety of ions in solution [4, 5]. The successful application demonstrated the ability of ESMS to study noncovalent interaction system in the case of supramolecules as well as molecular recognition [6], which are unable to be studied by other mass spectrometry method.

Although the electrospray process has been discussed qualitatively in detail [7, 8], the electrospray ionization (ESI) process remains speculative for larger ions. R. S. Smith showed that, the loss of noncovalent associations during ESI process depend upon the location and number of charges remaining on each of the associated species (i.e. due to Coulumbic force), the solvent's role in the noncovalent association, and the extent of complex activation in the interface [9, 10]. Due to complexity, it is not enough to make blanket statement from fundamental consideration. At present, experiments is the best way to find the best parameters for various systems.

We synthesized cryptand H_3L (FIG. 1) by (2+3) Schiff base condensation of tris(2-aminoethyl)amine (tren) with 2,6-diformyl-4-chloro-phenol (dcp) in the presence of Ln^{III} ($Ln^{III} = Eu^{III}$, Nd^{III}). Elemental analyses, molar conductivity and X-ray structural determination show that the complexes are asymmetric mononuclear cryptate and the structures of the complex cations have some similarities, i.e. $[Eu(HL)(NO_3)(H_3O)]^+$, which are the first lanthanide cryptates acting as host molecular to encapsulate guest oxonium ions [11]. Here, basing upon the gentle nature of ESMS, we use it for characterization of the europium cryptate in solution to verify the existence of oxonium ion. To obtain the best experimental conditions, we study the effect of mobile phase, needle voltage and temperature of heated capillary respectively on the ESI process of $[Eu(HL)(NO_3)(H_3O)]^+$. The peaks were assigned and the ES-induced fragmentation mechanism was discussed.

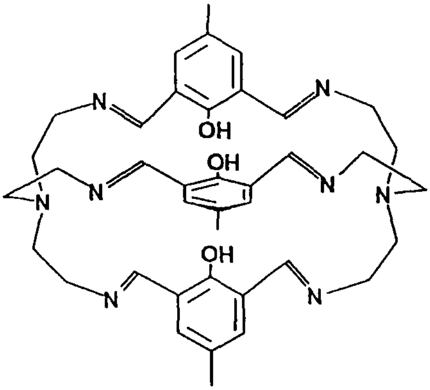

FIG. 1 Chemical formulae of ligand H_3L.

EXPERIMENTAL

Electrospray mass spectra (ESMS) were obtained in positive mode with a Finnigan LCQ mass spectrograph. Scanning was performed from m /Z 200 to 1200. Sample solutions were introduced into the mass spectrometer source with a syringe in constant volume (1 μl). Samples for ESMS were prepared by dissolving the cryptate in methanol to archieve the concentration of about 10^{-4} mol dm^{-3}. The diluted solutions were electrosprayed at a flow rate of 2 × 10^{-4} dm^3min^{-1}. Unless additional statement, the mobile phase is an aqueous solution of methanol (1:1) and the needle voltage, temperature of heated capillary, flow rate of sheath gas, flow rate of auxilary gas and offset of tube lens are 5.0 kV, 200 °C, 50.29 arb, 10.99 arb and + 20.00 V, respectively.

RESULTS AND DISCUSSION

Effect of Experimental Conditions on ESI Process

FIG. 2 illustrates the obvious effect of variation in mobile phase. The effect of mobile phase may be due to the surface tension of droplet. The surface tension of water is larger than that of methanol, which prevents the singly charged ions from good electrospray, thus decreased the relative intensity of them. However, under

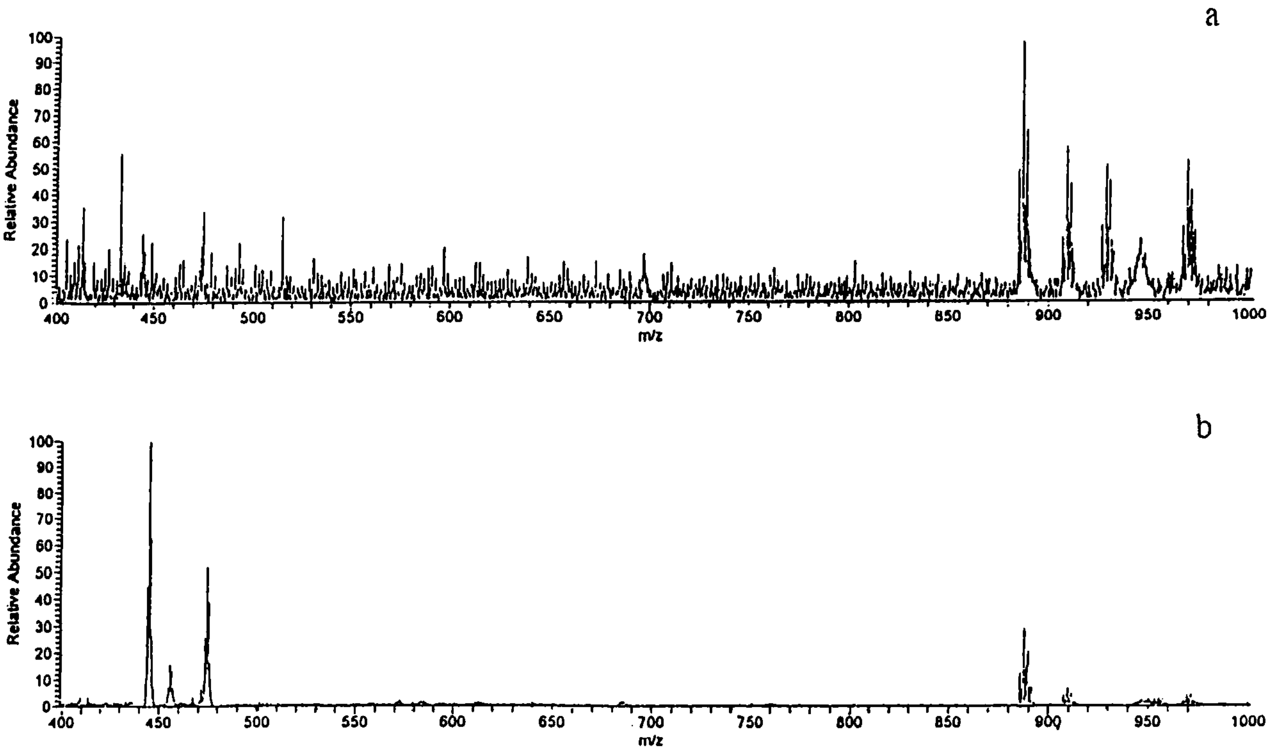

FIG. 2. Positive ESMS of $[Eu(HL)(NO_3)(H_3O)]^+$ (a) flow phase MeOH, (b) flow phase MeOH–H_2O (1:1).

methanol–water (1:1 v /v) mobile phase, the intensity of the doubly charged ions increased, compared to that of them when methanol is used as mobile phase. The results above suggested that during the ESI process, the formation of ions is affected synthetically by liquid surface tension, solvation strength and surface charge.

When the needle voltage is 3.5, 5.0 and 8.0 kV respectively, the obtained ESMS is shown in FIG. 3. When the voltage is 5.0 kV, the overall signal is most intense and minimum fragmentation occurred. Upon further increase of the needle voltage, the ions dissociate. The needle voltage is vital to obtain good quality of ESMS because the surface charge density is determined directly by it.

Controlled heating of the capillary assists the evaporation of solvent from the droplet and in the desolvation of solvent analyse ions [12]. The effect of temperature of heated capillary is illustrated in FIG. 4. When the temperature is 200 °C, the spectrum give the most intense signal and minimum fragmentation. When the temperature is 150 °C, the desolvation effect is weak, thus the ESI efficiency is reduced. While the temperature is 250 °C, further fragmentation occurred. The effect of capillary temperature varies with different ions, especially to the ions at m /Z 887.5 and 969.5, corresponding to $[Eu(HL)]^+$ and $[Eu(HL)(NO_3)(H_3O) + H_2O + MeOH]^+$. As the fine control of temperature of heated capillary can tune the desolvation condition at molecular level, its effect differs with various ions, which is influenced by the nature of ions, such as surface charge and ion solvation strength.

The results presented above show that the selection of suitable experiment parameters is of great importance toward the quality and pattern of ESMS of $[Eu(HL)(NO_3)(H_3O)]^+$. The best configuration for the cryptate is as follows: mobile phase methanol–H_2O (1:1), needle voltage 5.0 kV and temperature of heated capillary 200 °C. Under the best conditions, the obtained ESMS of $[Eu(HL)(NO_3)(H_3O)]^+$ is depicted in FIG. 5. The peak assignments are also displayed in FIG. 5.

Peak Assignment of ESMS

The simplicity of the spectra is attributed to the thermodynamic and kinetic stability of the cryptate, as well as the relatively low energy of ESI process. FIG. 5 is dominated by the peak at m /Z 444.4 which is due to $[Eu(HL) + H^+]^{2+}$. The other main peaks can be assigned to new species formed by solvation or protonation of complex cation, loss of nitrate ligand, chloro radical or of phenolic proton. The

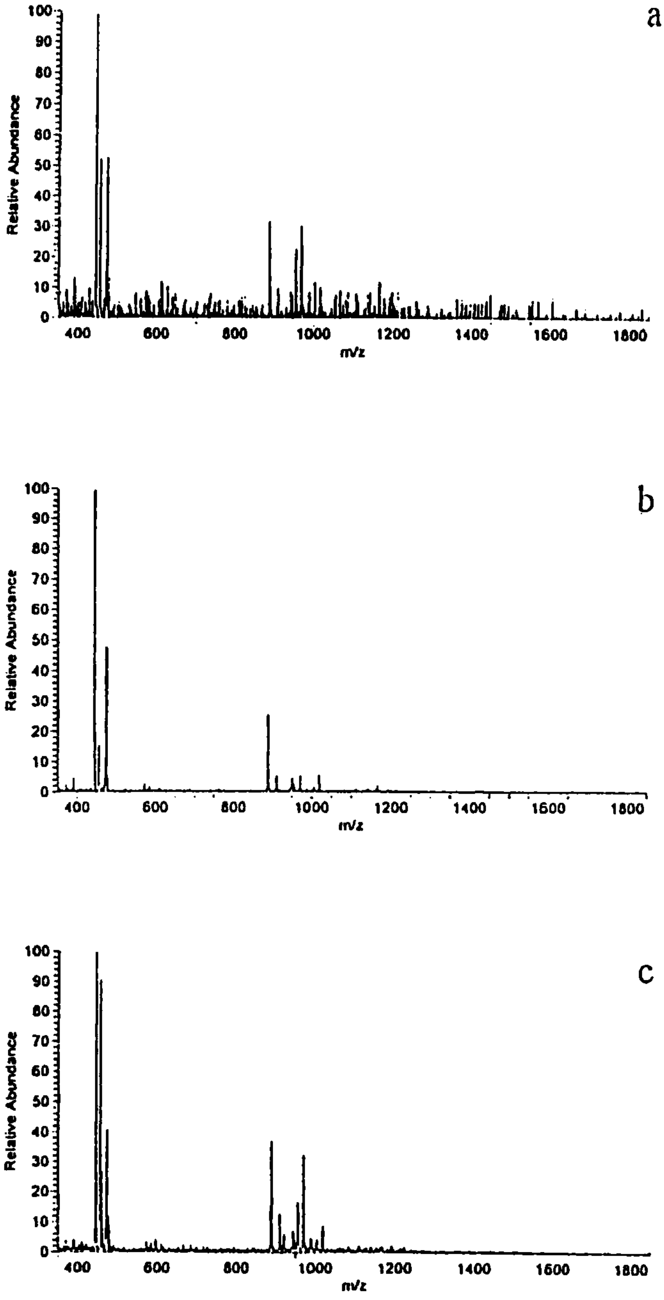

FIG. 3. Positive ESMS of $[Eu(HL)(NO_3)(H_3O)]^+$ at spray capillary voltage (a) 3.0, (b) 5.0, (c) 8.0 kV (flow phase $MeOH-H_2O$ 1:1)

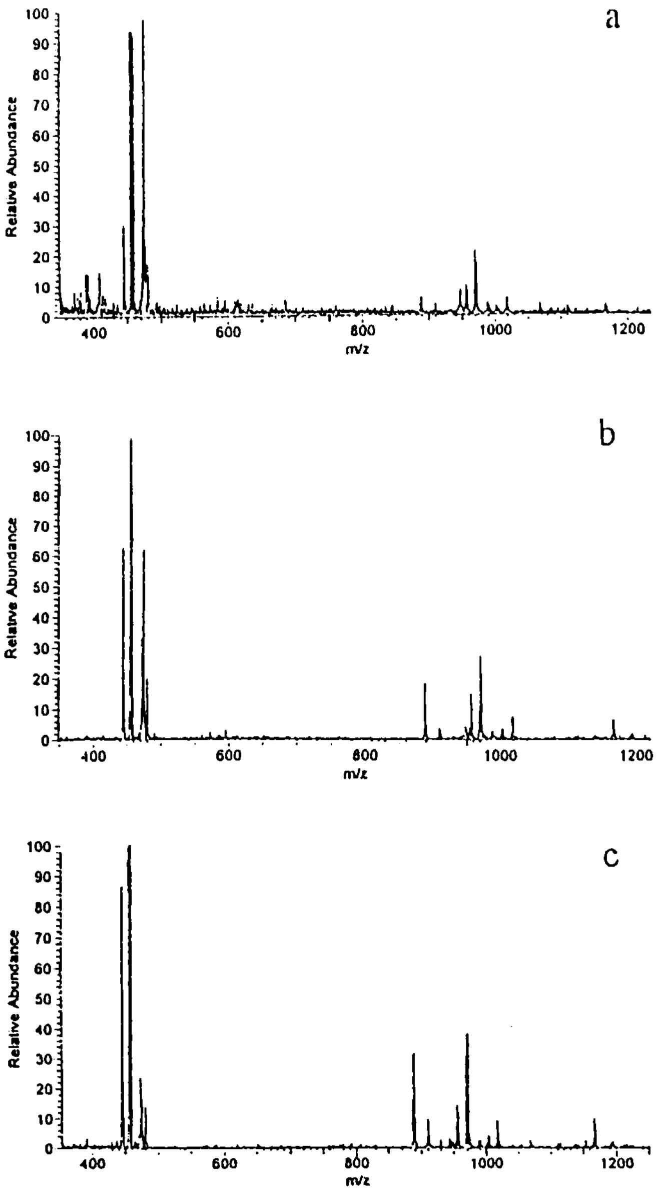

FIG. 4. Positive ESMS of $[Eu(HL)(NO_3)(H_3O)]^+$ at heated capillary temperature (a) 150, (b) 200, (c) 225 °C (flow phase $MeOH-H_2O$ 1:1).

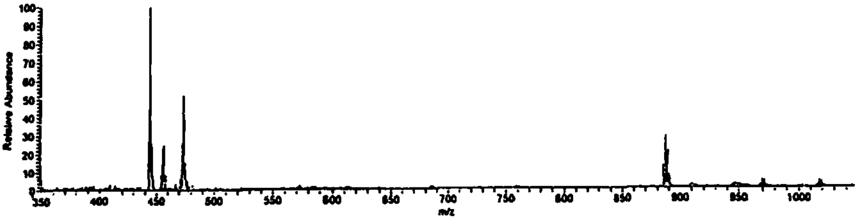

FIG. 5. Positive ES-MS of $[Eu(HL)(NO_3)(H_3O)]^+$ at heated capillary temperature 200 °C, flow phase $MeOH\text{-}H_2O$ (1:1) and spray capillary voltage 5.0 kV. Peak assignments (m/Z values given in parentheses): $[Eu(HL)(NO_3)(H_3O) + H_2O + MeOH]^+$ (1017.5), $[Eu(HL)(NO_3)(H_3O) + H^+]^+$ (969.5), $[Eu(HL-2Cl)(NO_3)(H_3O) + MeOH + H_2O]^+$ (947.5), $[Eu(HL-2Cl)(NO_3)(H_3O) + MeOH]^+$ (929.5), $[Eu(L-2Cl)(NO_3)]^+$ (909.5), $[Eu(HL)]^+$ (887.5), $[Eu(HL-2Cl)(NO_3)(H_3O) + MeOH + H_2O + H^+]^{2+}$(474.3), $[Eu(L-2Cl)(NO_3) + H^+]^{2+}$ (455.5), $[Eu(HL) + H^+]^{2+}$ (444.3).

spectrum shows that the cryptate is able to recognize not only oxonium ion, but also other small molecules such as methanol. The hydrogen bonds are the key to the molecular recognition. No peaks of cryptate fragment were observed. It shows that the cryptate is well stable in methanol solution.

CONCLUSION

The existence of guest oxonium ion in the europium cryptate was confirmed by ESMS. The cryptate was well stable in solution. Except oxonium ion, the host molecule can encapsulate other small molecules by hydrogen bonds. The pattern of ESMS depend on special experimental conditions which were selected by comparative study.

ACKNOWLEDGMENTS

This project was supported by Natural Science Fundation of China and State Key Lab of Rare Earth Materials Chemistry and Applications, Beijing University.

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Date Received: April 9, 1998
Date Accepted: June 29, 1998