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Publisher *Taylor & Francis*

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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 Feng, Chang-Jian , Jiang, Li-Jian , Pan, Zhi-Quan , Mei, Yu-Hua and Luo, Qin-Hui(2000) 'A Study on Some Europium(III) Supramolecules by Electrospray Mass Spectrometry', *Spectroscopy Letters*, 33: 3, 399 — 406

To link to this Article: DOI: 10.1080/00387010009350086

URL: <http://dx.doi.org/10.1080/00387010009350086>

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A STUDY ON SOME EUROPIUM(III) SUPRAMOLECULES BY ELECTROSPRAY MASS SPECTROMETRY

Key words: Europium(III), Supramolecule, Electrospray Mass Spectra

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ABSTRACT

Electrospray mass spectrometry (ESMS) of a series of europium(III) supramolecules derived from tris(2-aminoethyl)amine (tren) and 2,6-diformyl-4-R-phenol (R = F, Cl, t-Butyl) is described. The peaks were assigned by both m / Z values and the isotope distributions. The ESMS are largely affected by the nature of the cryptates.

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INTRODUCTION

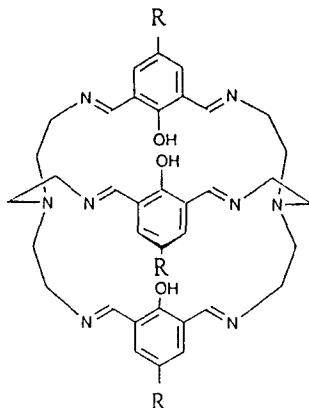
Particular interests have developed in three-dimensional macrocycles and their lanthanide complexes, owing to their importance in basic and applied chemistry¹. We synthesized a series of cryptands H_3L (FIG. 1) by (2+3) Schiff base condensation of tris(2-aminoethyl)amine (tren) with 2,6-diformyl-4-R-phenol in the presence of Eu^{III}, among which H_3L^1 , H_3L^2 and H_3L^3 denote the cryptand with R = Cl, F, and t-Butyl, respectively. Elemental analyses, molar conductivity and X-ray structural determination show that the complexes are the asymmetric mononuclear cryptates and the complex cations have similarities similar structures, i.e. $[Eu(HL)(NO_3)(H_3O)]^+$. They are the first lanthanide supramolecules in which the guest oxonium ions are encapsulated by hydrogen bonds consisting of uncoordinated imino nitrogens².

Electrospray mass spectrometry (ESMS) is a soft ionization technique based on the ion-evaporation process. It is particularly suitable for characterizing preformed ions in solution³. More recently, it has been used to probe the coordination behavior of several macrocycles toward a variety of ions in solutions^{4, 5}. The successful application demonstrated the ability of ESMS to study noncovalent interaction systems in the case of supramolecules, as well as molecular recognition⁶, which are unable to be studied by other mass spectrometry methods. We reported the effects of experimental conditions on the electrospray ionization process of lanthanide supramolecule⁷.

Based upon the gentle nature of ESMS, we used it for characterization of the europium cryptates in solutions to verify the existence of oxonium ion. The peaks were assigned by isotope distribution calculation. The pattern of ESMS are greatly affected by the properties of cryptates.

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 μ l). Samples for ESMS were prepared by dissolving the cryptate in methanol to archive the concentration of about 10^{-4} mol dm^{-3} . The diluted solutions were electrosprayed at a flow rate of 2×10^{-4} $dm^3 min^{-1}$. The mobile phase is methanol. The needle voltage, temperature of heated capillary, flow rate of sheath gas, flow rate of

FIG. 1 Chemical formulae of ligand H₃L.

auxiliary gas, and offset of tube lens are 5.0 kV, 200 °C, 50.29 arb, 10.99 arb and + 20.00 V, respectively. The isotope distributions were calculated on PC 586 by the modified program of Lee⁸.

RESULTS AND DISCUSSION

General Characteristic of ESMS

Typical ESMS is depicted in FIG. 2 which is the positive ESMS of $[\text{Eu}(\text{HL}^1)(\text{NO}_3)(\text{H}_3\text{O})]^+$. The simplicity of the spectra is attributed to the thermodynamic and kinetic stability of the cryptates, as well as the relatively low energy of electrospray ionization process. FIG. 2 is dominated by the peak at m/Z 887.4 which is due to $[\text{Eu}(\text{HL}^1)]^+$. Its experimental isotope distribution is in agreement with the calculated pattern, as shown in FIG. 3. The peak at m/Z 969.3 is due to $[\text{Eu}(\text{HL}^1)(\text{NO}_3)(\text{H}_3\text{O})]^+$ in which the oxonium ion exists in the inner sphere. 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. No peaks of cryptate fragment were observed. It shows that the cryptate is very stable in methanol solution.

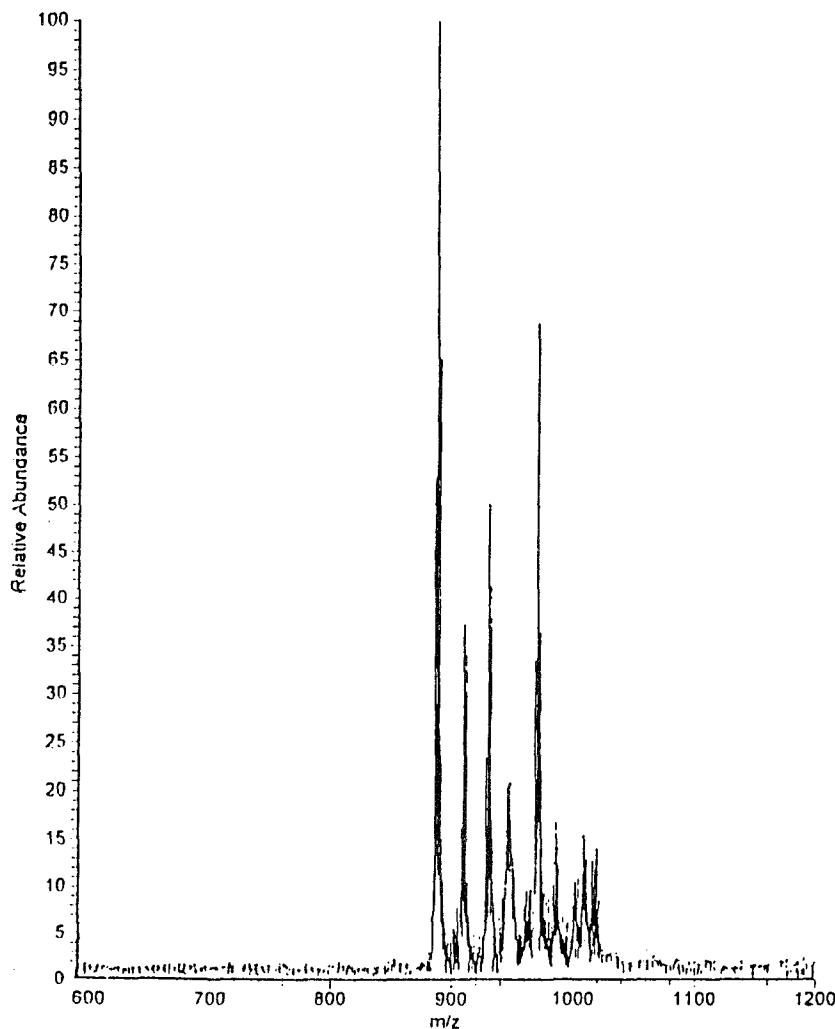


FIG. 2. Positive ESMS of $[\text{Eu}(\text{HL}^1)(\text{NO}_3)(\text{H}_3\text{O})]^+$.

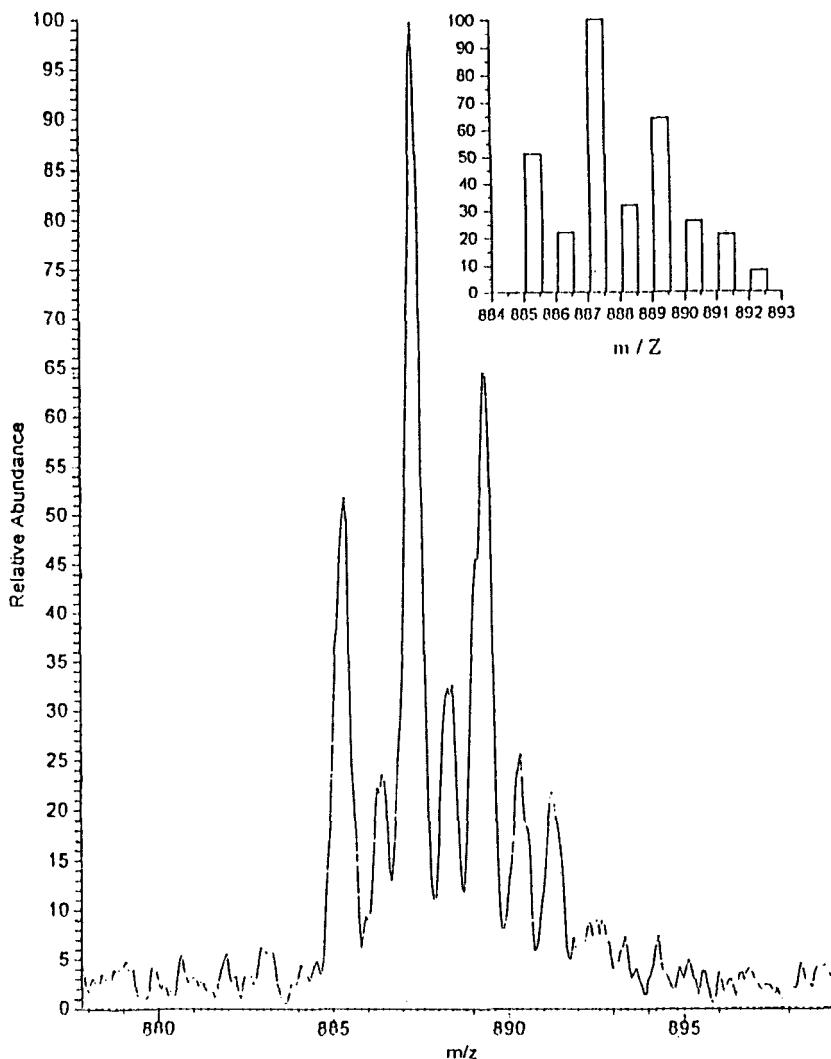


FIG. 3 Experimental calculated isotope distribution of $[\text{Eu}(\text{HL}^1)]^+$ at m / Z 887.4, inset: calculated isotope distribution.

TABLE 1 ESMS spectral data for the europium cryptates in methanol solutions.

Cryptate	Peaks (m/Z) and assignments
$[\text{Eu}(\text{HL}^1)(\text{NO}_3)(\text{H}_3\text{O})]^+$	969.5 $[\text{Eu}(\text{HL}^1)(\text{NO}_3)(\text{H}_3\text{O})+\text{H}^+]^+$, 60% 929.5 $[\text{Eu}(\text{HL}^1-2\text{Cl})(\text{NO}_3)(\text{H}_3\text{O})+\text{MeOH}]^+$, 55% 947.5 $[\text{Eu}(\text{HL}^1-2\text{Cl})(\text{NO}_3)(\text{H}_3\text{O})+\text{MeOH}+\text{H}_2\text{O}]^+$, 25% 887.5 $[\text{Eu}(\text{HL}^1)]^+$, 100% 474.3 $[\text{Eu}(\text{HL}^1-2\text{Cl})(\text{NO}_3)(\text{H}_3\text{O})+\text{MeOH}+\text{H}_2\text{O}+\text{H}^+]^+$, 33% 444.3 $[\text{Eu}(\text{HL}^1)+\text{H}^+]^{2+}$, 100%
$[\text{Eu}(\text{HL}^2)(\text{NO}_3)(\text{H}_3\text{O})]^+$	938.2 $[\text{Eu}(\text{HL}^2)(\text{NO}_3)(\text{H}_3\text{O})+\text{H}_2\text{O}]^+$, 32% 920.2 $[\text{Eu}(\text{HL}^2)(\text{NO}_3)(\text{H}_3\text{O})]^+$, 36% 915.2 $[\text{Eu}(\text{H}_2\text{L}^2-\text{F})(\text{NO}_3)+\text{MeOH}]^+$, 42% 902.2 $[\text{Eu}(\text{H}_2\text{L}^2)(\text{NO}_3)+\text{H}_2\text{O}]^+$, 38% 883.2 $[\text{Eu}(\text{H}_2\text{L}^2-\text{F})(\text{NO}_3)]^+$, 35% 862.2 $[\text{Eu}(\text{HL}^2-3\text{F})(\text{NO}_3)(\text{H}_2\text{O})]^+$, 70% 839.2 $[\text{Eu}(\text{HL}^2)]^+$, 100%
$[\text{Eu}(\text{HL}^3)(\text{NO}_3)(\text{H}_3\text{O})]^+$	976.2 $[\text{Eu}(\text{L}^3-\text{C}(\text{CH}_3)_3)(\text{NO}_3)(\text{H}_3\text{O})]^+$, 45% 953.6 $[\text{Eu}(\text{HL}^3)]^+$, 100% 477.2 $[\text{Eu}(\text{H}_2\text{L}^3)]^{2+}$, 30%

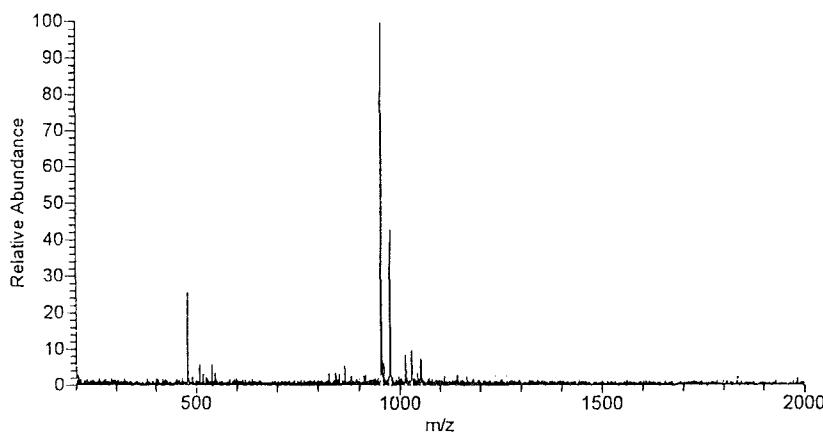


FIG. 4. Positive ESMS of $[\text{Eu}(\text{HL}^3)(\text{NO}_3)(\text{H}_3\text{O})]^+$.

ESMS of Cryptates with Different Substitute

The assignment of peaks are listed in TABLE 1 for comparison. The data shows that the pattern of ESMS are greatly affected by the properties of the cryptates. When R = F and Cl, the ESMS of the cryptates have some similarities, while the ESMS of $[\text{Eu}(\text{HL}^3)(\text{NO}_3)(\text{H}_3\text{O})]^+$ with R = t-Butyl (FIG. 4) differs from the former two spectra to a large extent, which are due to the different properties of the cryptates. This is reasonable because F and Cl have analogous effects on the aromatic ring which is different from t-Butyl. It shows that ESMS is able to indicate the property of the compounds.

CONCLUSION

The results show that ESMS is useful for characterization of the lanthanide supramolecules. The existence of guest oxonium ion in the europium cryptates was confirmed by ESMS. The cryptates are very stable in solution. The pattern of ESMS depends on the properties of the cryptates.

ACKNOWLEDGMENTS

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

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Date Received: October 27, 1998

Date Accepted: August 20, 1999