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### The First Heteronuclear Terbium-Zinc Cryptate—An Electrospray Mass Spectrometry Investigation

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## THE FIRST HETERONUCLEAR TERBIUM-ZINC CRYPTATE—AN ELECTROSPRAY MASS SPECTROMETRIC INVESTIGATION

Key words: Heteronuclear Cryptate, Electrospray Mass Spectra (ESMS), Terbium(Tb), Zinc (Zn)

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### ABSTRACT

Electrospray mass spectrometry (ESMS) is described for heteronuclear terbium-zinc cryptate derived from tris(2-aminoethyl)amine (tren) and 2,6-diformyl-4-t-Butyl-phenol. The mass spectral data were compared with those of corresponded mononuclear terbium cryptate to verify the co-existence of zinc in the cryptate through isotope distribution calculation. This is the first heteronuclear cryptate studied by using ESMS.

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## INTRODUCTION

Electrospray mass spectrometry (ESMS) is a valuable means for studying solution species, since it allows pre-existing ions to be transferred to the gas phase with minimal fragmentation<sup>1</sup>. Applications to a number of inorganic and organometallic systems have demonstrated the versatility of the technique<sup>2,3</sup>. The generally recognized view is that the detected ions are pre-formed in solution and electrospray simply transfers them from the solution to the gas phase<sup>4,5</sup>. Hence qualitative agreement should be expected between the species present in solution and those found in ESMS experiment. More recently, ESMS has been used to probe the behaviors of several cryptates in solution<sup>6,7</sup>.

We synthesized heteronuclear terbium-zinc complex by reaction of zinc acetate with mononuclear terbium cryptate derived from tris(2-aminoethyl)amine (tren) and 2,6-di-formyl-4-t-Butyl-phenol (FIG. 1). Elemental analyses, molar conductivity and IR spectra show that the chemical formula of the complex cation is  $[\text{TbZn}(\text{HL})(\text{OAc})]^{2+}$ , which is the first heteronuclear lanthanide-zinc cryptate.

Here we report ESMS investigations of the complex and the corresponding mononuclear cryptate  $[\text{Tb}(\text{HL})(\text{NO}_3)(\text{H}_2\text{O})]^+$  in methanol. To verify the co-existence of zinc in the cryptate, theoretical isotope distribution was calculated and compared with that obtained by ESMS. The ES-induced fragment mechanism was also discussed. To our knowledge, this is the first heteronuclear cryptate studied by using ESMS.

## EXPERIMENTAL

The synthesis of the heteronuclear terbium-zinc cryptate will be reported elsewhere. Positive electrospray mass spectra (ESMS) were obtained with a Finnigan LCQ mass spectrograph using a methanol mobile phase. 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  $\mu\text{l}$ ). Samples for ESMS were prepared by dissolving the cryptate in methanol to archive the concentration of about 0.1  $\text{mmol dm}^{-3}$ . The diluted solutions were electrosprayed at a flow rate of  $2 \times 10^{-4} \text{ dm}^3 \text{ min}^{-1}$ . The needle voltage, temperature of heated capillary, flow rate of sheath gas, flow rate of auxiliary

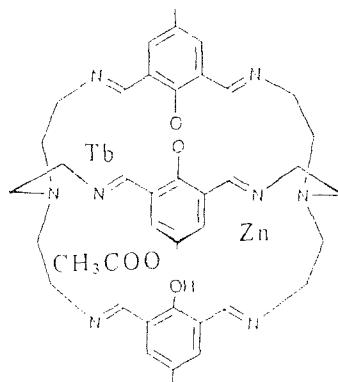


FIG. 1 Chemical formula of  $[\text{TbZn}(\text{HL})(\text{OAc})]^2+$ .

gas and offset of tube lens are 5.0 kV, 200 °C, 50.29 arb, 10.99 arb and + 20.00 V, respectively.

Peaks were assigned from the  $m/Z$  values and from the isotope distribution patterns which were simulated on PC 586 using a modified program of Lee.<sup>8</sup> In the following discussion, the mass spectral patterns are identified by the  $m/Z$  values of the most abundant peak in the isotope distribution.

## RESULTS AND DISCUSSION

The nuclear composition of carbon ( $^{12}\text{C}$ , 98.90 %;  $^{13}\text{C}$ , 1.10 %) and zinc ( $^{64}\text{Zn}$ , 48.6 %;  $^{65}\text{Zn}$ , 27.9 %;  $^{67}\text{Zn}$ , 4.1 %;  $^{68}\text{Zn}$ , 18.8 %;  $^{70}\text{Zn}$ , 0.6 %) result in distinctive isotope signatures of the species in methanol solution of heteronuclear complex. Positive ESMS is depicted in FIG. 2. FIG. 2 is dominated by the peak  $m/Z$  480.5 which is due to complex ion  $[\text{Tb}(\text{H}_2\text{L})]^2+$ . The peak at  $m/Z$  1081.5 is due to  $[\text{TbZnL}(\text{OAc})]^-$ . The chemical formula of  $[\text{TbZnL}(\text{OAc})]^-$  is  $\text{C}_{50}\text{H}_{66}\text{N}_8\text{O}_5\text{ZnTb}$  and the theoretical isotope distribution is shown in FIG. 3 with the observed data for comparison. It shows that good agreement between observed and calculated data was found for the peaks. Both  $m/Z$  values and calculated isotope distribution

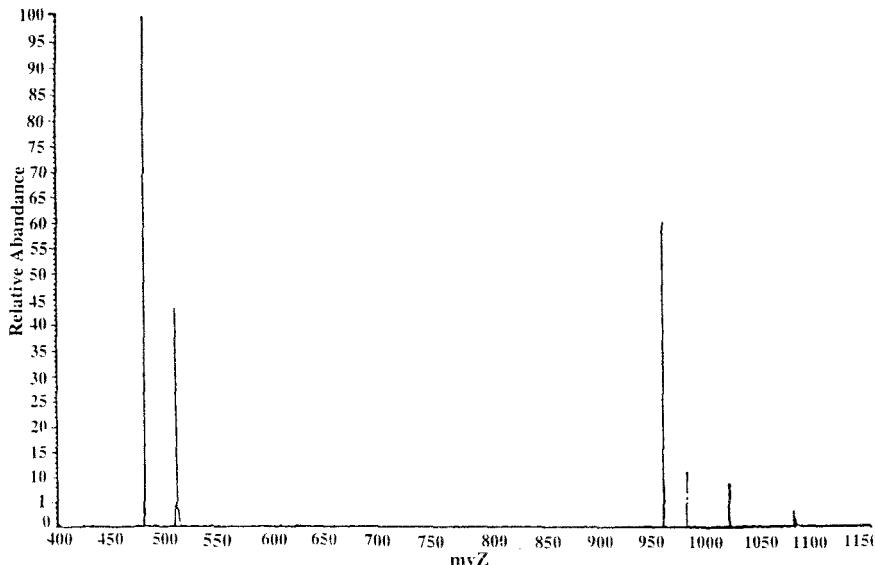


FIG. 2. Positive ESMS of  $[\text{TbZn}(\text{HL})(\text{OAc})]^{2+}$ .

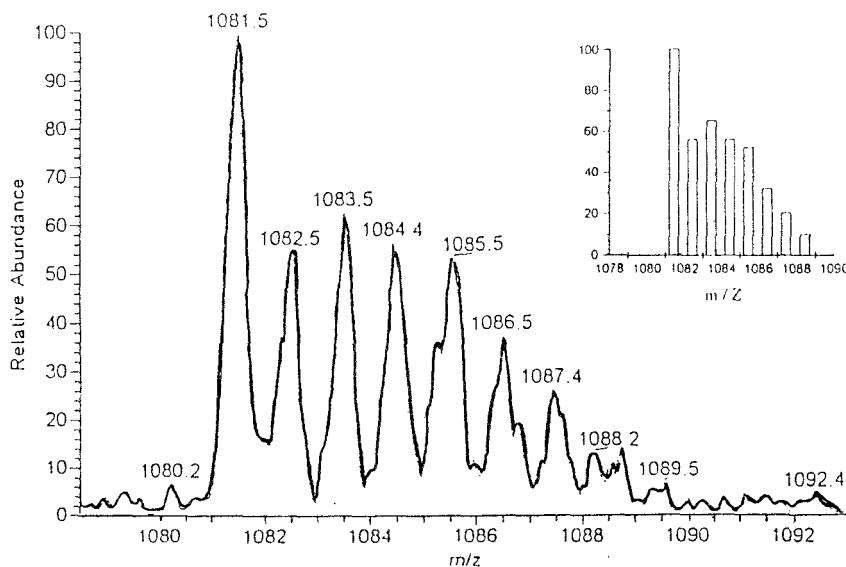


FIG. 3 Experimental isotope distribution pattern of  $[\text{TbZn}(\text{HL})(\text{OAc})]^{+}$  at  $m/z$  1081.5, inset: calculated isotope distribution of the heteronuclear cryptate.

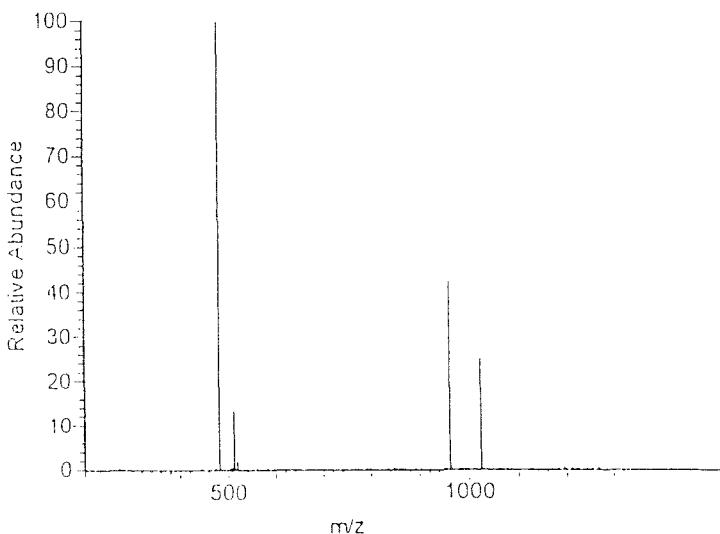


FIG. 4. Positive ESMS of  $[\text{Tb}(\text{HL})(\text{NO}_3)(\text{H}_2\text{O})]^-$ .

patterns are in agreement with experimental data. It is obvious that zinc ion has entered the inner sphere to form heteronuclear complex.

The simplicity of the spectrum is attributed to the thermodynamic and kinetic stability of the cryptates, as well as the low energy of electrospray ionization process. The other main peaks can be assigned to new species formed by protonation of complex cation, loss of acetate ligand, zinc or of t-butyl group. No peaks of cryptate fragment were observed. It shows that the cryptate is rather stable in methanol solution.

Positive ESMS of  $[\text{Tb}(\text{HL})(\text{NO}_3)(\text{H}_2\text{O})]^-$  is shown in FIG. 4 and the ESMS data of the cryptates are listed in TABLE 1. Compared with FIG. 4, FIG. 2 has only an additional peak at  $m/Z$  1081.5 due to the formation of heteronuclear complex ion  $[\text{TbZnL(OAc}])^-$ . ESMS data show that the ES-induced fragment pattern of mononuclear cryptate is very similar to that of heteronuclear cryptate. It implies that the structure of heteronuclear complex has some similarities to that of mononuclear cryptate. This is reasonable because the cryptand ligand has a three-dimensional skeleton which can recognize zinc ions and the obtained two complexes have somewhat similar structures.

TABLE I ESMS data for the cryptates in methanol solutions.

Cryptate	Peaks (m/Z) and assignments
$[\text{Tb}(\text{HL})(\text{NO}_3)(\text{H}_3\text{O})]^+$	1022.2 $[\text{Tb}(\text{H}_2\text{L})(\text{NO}_3)]^+$ , 24% 959.4 $[\text{Tb}(\text{HL})]^+$ , 48% 511.7 $[\text{Tb}(\text{H}_3\text{L})(\text{NO}_3)]^{2+}$ , 14% 480.5 $[\text{Tb}(\text{H}_2\text{L})]^{2+}$ , 100%
$[\text{TbZn}(\text{HL})(\text{OAc})]^{2+}$	1081.5 $[\text{TbZnL}(\text{OAc})]^+$ , 10% 1021.5 $[\text{Tb}(\text{H}_2\text{L})(\text{NO}_3)]^+$ , 12% 981.5 $[\text{Tb}(\text{HL}-\text{C}(\text{CH}_3)_3)(\text{NO}_3) + \text{H}_2\text{O}]^+$ , 15% 959.5 $[\text{Tb}(\text{H}_2\text{L})]^+$ , 60% 510.1 $[\text{Tb}(\text{H}_2\text{L})(\text{OAc})]^{2+}$ , 45% 480.5 $[\text{Tb}(\text{H}_2\text{L})]^{2+}$ , 100%

### CONCLUSION

The co-existence of zinc in the heteronuclear cryptate was confirmed by isotope distribution calculation of ESMS data. The cryptates are very stable in solution. The ES-induced fragment pattern of  $[\text{TbZn}(\text{HL})(\text{OAc})]^{2+}$  is rather similar to that of  $[\text{Tb}(\text{HL})(\text{NO}_3)(\text{H}_3\text{O})]^+$ . It implies that the cryptand is able to recognize zinc ion.

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