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FT-ICR studies of polypyrazolyl-1-yl borates of europium(II) adducts

A. Pires de Matos[a,*], M.A. Freitas[b], A.G. Marshall[c], N. Marques[a], A. Carvalho[a], P.C. Isolani[d], G. Vicentini[d]

[a]*Departamento de Química, ITN, Est. Nacional 10, 2686-953 Sacavém, Portugal*
[b]*The Ohio State University, 100 West 18th Avenue, Columbus, OH 43210, USA*
[c]*National High Magnetic Field Laboratory, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, FL 32310, USA*
[d]*Instituto de Química, University of S. Paulo, C.P. 26077, S. Paulo, SP 05599-970, Brazil*

Abstract

In this work we report the synthesis and characterization of europium(II) hydrotris(pyrazol-1-yl)borate complexes, $Eu(HBPz_3)_2L_2$ (L=bis(pentamethylene)urea, diphenylphosphineamide, 2-azacyclononanone, 2-azacycloheptanone). The characterization of the complexes was accomplished by Fourier transform ion cyclotron resonance mass spectrometry using electrospray ionization. For all the complexes, the $Eu(HBPz_3)_2L_2^+$ ion was observed. To evaluate the relative bond strength of the ligand L to europium polypyrazolylborate, infrared multiphoton dissociation (IRMPD) experiments were performed using a 40-W continuous-wave CO_2 (λ=10.46 μm) laser aligned on-axis with the ion cloud. The parent ion was dissociated to form the daughter ions, $Eu(HBPz_3)_2L^+$ and $Eu(HBPz_3)_2^+$. The kinetics for unimolecular dissociation showed the relative bond strengths of the different adducts of the europium complex to be: diphenylphosphineamide>2-azacyclononanone≈2-azacycloheptanone. Dissociation experiments could not be made for the adduct with bis(pentamethylene)urea due to the weak bond.

Keywords: Europium; FT-ICR/MS; Polypyrazolylborates

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1. Introduction

The polypyrazolyl borate ligands (Tp) provide a versatile coordination environment for a wide range of metal centers including lanthanides (III) and (II) [1,2].

In the course of our studies of lanthanide chemistry with Tp ligands we investigated $Eu(HBpz_3)_2L_2$ complexes [3,4] and we verified that the polypyrazolylborate ligands seemed to provide an interesting antenna effect for the luminescence of the europium compounds. Additional ligands necessary to complete the coordination sphere of the europium poly(pyrazolyl)borate compounds seemed also to influence the luminescent properties of the complexes, with the weaker ligands favouring the luminescent efficiency [4].

In this work we report the synthesis of $Eu(HBPz_3)_2L_2$ (L=diphenylphosphineamide, 2-azacyclononanone, 2-azacycloheptanone) and the evaluation of the relative bond strengths of the different adducts by a gas phase study in a Fourier transform ion cyclotron resonance spectrometer using electrospray ionization.

The ligands used in this study were considered because previous work with Eu(III) complexes have shown that ligands with either carbonyl or phosphoryl groups produce adducts that present satisfactory luminescent properties [5–7].

2. Experimental

The syntheses of all the complexes were carried out under nitrogen using glove box and Schlenk-line techniques by the procedure previously described for $Eu(HBpz_3)_2L_2$ (L=diphenylsulfoxide and bis(pentamethylene)urea) [4].

The MS experiments were carried out on a homebuilt 9.4 T ESI FT-ICR instrument (NHMFL) configured for external ion accumulation [8,9]. Samples were infused into a 50-μm micro-electrospray capillary at a flow rate of 300 nl min^{-1} [10,11]. Ions were accumulated in a linear octapole ion-trap for 3 s and then transferred to the ICR cell. The parent metal ligand complex was mass selected by SWIFT excitation [12,13]. After SWIFT isolation the ions were heated with an on-axis aligned Synrad 40-W CO_2 laser. The beam diameter was expanded and collimated from the factory determined diameter of 3.5–8.75

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*Corresponding author.

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mm using a 2.5X expander collimator obtained from Synrad. Off-axis irradiation resulting from beam misalignment resulted in incomplete dissociation evidenced by non-linear ln (*k*) versus time plots similar to those observed by Dunbar and Zanewski [14]. A Tool command language (Tcl) script that automated the adjustment of time and laser intensity facilitated acquisition of the data. Each stored mass spectrum was the average of four scans.

Dissociation experiments could not be made for the adduct with bis(pentamethylene)urea due to the weak Eu–L bond. The synthesis and characterization by X-ray diffraction analysis of this compound has been reported previously [4].

3. Results and discussion

For all the complexes, the electrospray generated $Eu(HBPz_3)_2L_2^+$ ion was observed along with the $Eu(HBPz_3)_2L^+$ ion. This $Eu(HBPz_3)_2L_2^+$ ion was isolated and fragmented by the use of a CW CO_2 laser with the exception of L=bis(pentamethylene)urea which was so weakly bonded that it was not possible to isolate an appreciable quantity to perform the dissociation studies. Typical mass spectra for the dissociation of the isolated $Eu(HBPz_3)_2L_2^+$ metal complexes are shown in Fig. 1 ($Eu(HBPz_3)_2L_2^+$ *m*/*z* 1013.20, 861.32, 805.27, $Eu(HBPz_3)_2L^+$ 796.16, 720.25, 692.20, for L= diphenylphosphineamide, 2-azacyclononanone and 2-azacycloheptanone, respectively; *m*/*z* for the most abundant peaks correspondent to ^{153}Eu and ^{11}B).

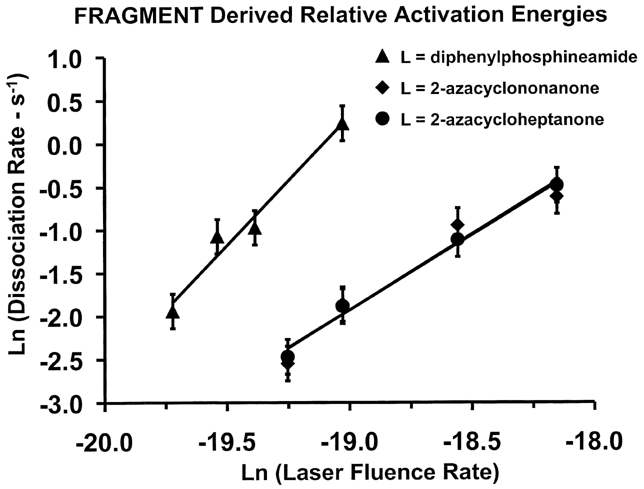

Fig. 2. Plot of the natural logarithm of the unimolecular dissociation rate (s^{-1}) as a function of the natural logarithm of the laser fluence rate. The slope from the resulting line corresponds to the activation energy for dissociation. The species $Eu(HBPz_3)_2L_2^+$ (L=diphenylphosphineamide) has larger slope than the other two species indicating a higher dissociation energy for this metal complex.

Fig. 2 shows the pseudo-Arrhenius plots used in the

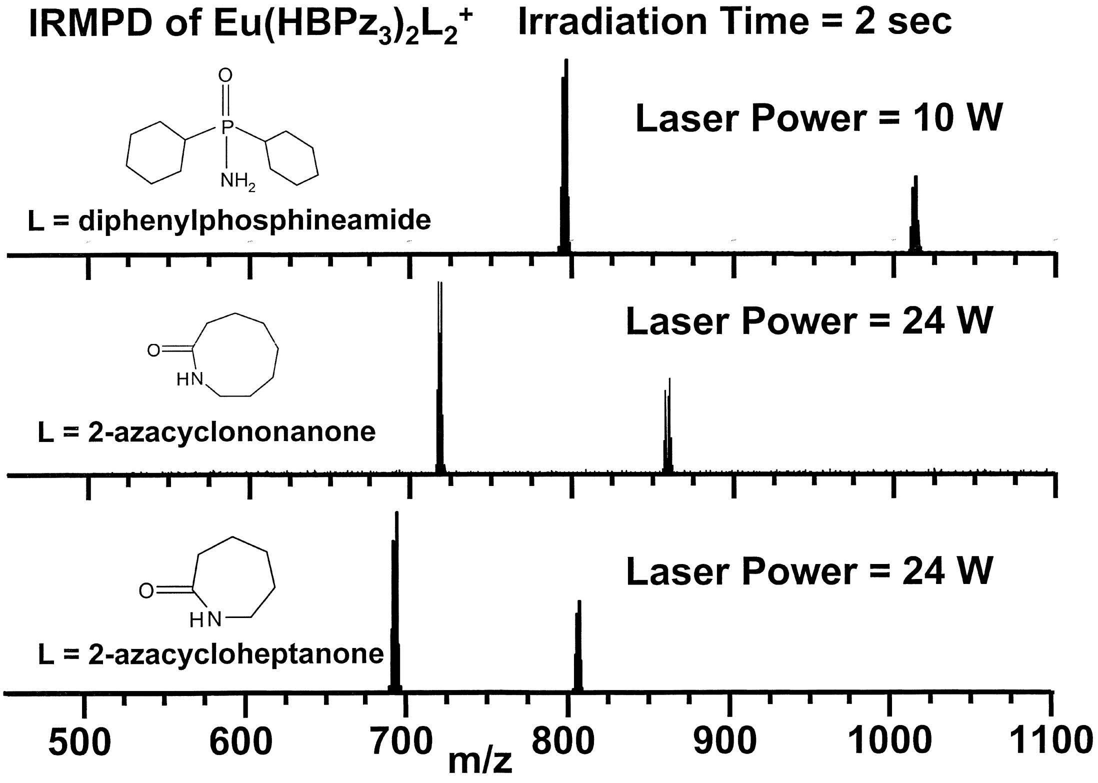

Fig. 1. Infrared multiphoton dissociation (IRMPD) of $Eu(HBPz_3)_2L_2^+$. The fragment ions produced correspond to the loss of a ligand from the metal complex.

determination of the relative activation energy for dissociation of the species $Eu(HBPz_3)_2L_2^+$. The isolated ions were irradiated over a range of laser powers for various time periods and the rate of dissociation recorded. In Fig. 2 a plot of the natural logarithm of the rate of dissociation versus the natural logarithm of the laser fluence rate yields an estimate of the relative activation energy for dissociation as described previously by Freitas and Dunbar [15,16]. In this analysis, the species were all assumed to have the same vibrational spectrum. If we assume that there is no barrier to the reverse reaction, then the relative activation energies can be used to estimate the relative ordering of the bond strengths. From the data in Fig. 2, it is evident that species $Eu(HBPz_3)_2L_2^+$ (L = diphenylphosphineamide) has a higher activation energy than the species with L = 2-azacyclononanone and 2-azacycloheptanone. The slope for complex where L = diphenylphosphineamide is 1.8 times larger than that for L = 2-azacyclononanone and L = 2-azacycloheptanone. This result is counterintuitive considering that in Fig. 1 a lower laser power was required over the same duration to achieve the same amount of dissociation for L = diphenylphosphineamide as compared with L = 2-azacyclononanone and L = 2-azacycloheptanone. This behaviour could be due to the efficiency with which each species absorbs the incoming irradiation (943 cm^{-1}). The complex with the diphenylphosphineamide ligand has strong vibrational mode frequencies at 1040, 1115 and 1170 cm^{-1} which are far from this value. However it has been pointed out that the lack of absorption in the neutral spectra does not necessarily cause the metal containing ions to be transparent as the strong interaction that exists between a metal ion and a ligand can perturb the vibrational frequencies of the ligand in the complex and that several conformations can exist for a complex ion [17,18]; so it is possible to get a resonant frequency close to the incoming radiation.

The data clearly indicate that the ligands, 2-azacyclononanone and 2-azacycloheptanone have virtually the same slope and thus also have similar bond dissociation energy. This result is expected due to the similarities in structure between the two species.

4. Final remarks

In conclusion we showed the relative bond strengths of the different adducts of the europium complex to be: diphenylphosphineamide > 2-azacyclononanone ≈ 2-azacycloheptanone > bis(pentamethylene)urea.

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