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SPIE.

THE INFLUENCE OF THE STRUCTURE OF PHOSPHORUS-BASED LIGANDS ON THE STABILITY OF EUROPIUM COMPLEXES USING SPECTROPHOTOMETRIC TITRATION

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ABSTRACT

The influence of structure of the phosphine oxide ligands on stability of their complexes was studied by spectroscopic techniques. Surprising the electron donating methyl groups at phenyl rings of phosphine oxide groups lead to decrease of the stability of europium complex comparing with ubsubsituted one due to their sterical prevention of conjugation between phenyl rings and P=O-groups.. This unusual behavior was first time demonstrated by spectroscopic titration and Job's plot analysis.

Keywords: absorbance, stability constants; spectroscopy; europium

1. INTRODUCTION

Influence of the structure of the ligand on various properties of their complexes in the focus of modern material sciences. The complexes of lanthanide ions with organic ligands are of most interest due to their high luminescent characteristics and consequent wide usage.[1] For the europium complexes the elucidation of the influence of the ligand type on the optical properties of complexes is extremely important because of lack of precise method of calculations of efficiency of luminescence and stability of complexes in respect to photo bleaching and thermal and chemical decomposition. Here we report the application of spectrophotometric techniques to estimation of the relation between structure of the ligand and chemical stability of their complexes with europium.

2. OBJECTS AND METHODS

2.1 General

6,6′-Bis(diphenylphosphinoyl)-2,2′-bipyridyls (**H** and **MeDPPO**) (Fig.1) was synthesized and characterized by ^{1}H-NMR and HPLC-HRMS techniques earlier[2].

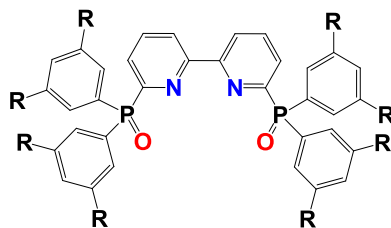Figure 3. Structure 6,6′-bis(diphenylphosphinoyl)-2,2′-bipyridyl: **HDPPO R=H and MeDPPO R=Me**

Acetonitrile (99.95%, HPLC-S Gradient Grade, Biosolve BV) was dried over molecular sieves (zeolite KA, 3 Å, balls, diameter 1.6–2.5 mm, production HKC Corp. Hong Kong) prior to use. Water content was estimated as 40±5 ppm by Karl Fisher titration (Mettler Toledo, C20, coulometric KF titrator). Europium(III) trinitrate $Eu(NO_3)_3 \cdot 6H_2O$ (purity >99%) were stored in a closed container over silica gel balls. The Stock solutions of ligands and metal salt were prepared by weighing the precise amounts of the respective chemicals and dissolving them in acetonitrile.

2.2 Spectrophotometric titration

Ultraviolet–visible (UV-vis) spectra were recorded at ambient temperature (24.5 ± 1.0°C) in the wavelength region 260–500 nm (1 nm interval) on a Hitachi U-1900 spectrophotometer using 10 mm path length quartz cells (Hellma). The implementation of the Beer–Lambert law was determined for DPPO ligand within the range 0.01–0.1 mM.

The binding stoichiometry of one-step complex formation between two different molecules was determined by the method of continuous variation (Job's plot). The solutions of the ligands and metal salt were prepared at a concentration of ≈ 0.1 mM.

For the spectrophotometric titration, a stock solutions of the ligand was prepared (ca. 1–4 mM) and then a ligands working solutions (ca. 10–40 μM) was prepared from the initial solutions. A titrant solutions $Eu(NO_3)_3 \cdot 6H_2O$ (ca. 1–5 mM) was prepared by dissolution of a sample of Eu nitrate hydrate in the working solutions of corresponding ligands. A 2 ml of working solution of each ligand was titrated with 1 μl $Eu(NO_3)_3 \cdot 6H_2O$ solution. The kinetic experiments showed that the complexation reaction is fast and the absorbance becomes stable within 1–2 seconds. The stability constants of the complexes were calculated by nonlinear least-squares regression analysis using the *HypSpec2014* program[3], based on eqn (1) and (2) for the complexes.

$$Eu(NO_3)_3 + DPPO \rightarrow [Eu(NO_3)_3 DPPO], \tag{1}$$

$$\log \beta_1 = \frac{[Eu(NO_3)_3 DPPO]}{[Eu(NO_3)_3] \cdot [DPPO]} \tag{2}$$

3. RESULTS AND DISCUSSION

3.1 Spectral properties of the DPPO based ligands and their complexes with $Eu(NO_3)_3$

The absorbance spectrum of the ligands in acetonitrile is characterized by broad band in the UV range (near 283 nm for both ligands). This band correspond the $\pi \rightarrow \pi^*$ transition of the pyridine rings[4]. The molar absorptivity of two ligands were 15168 for **HDPPO** and 16766 for **MeDPPO** differ about 10% each other with higher value for more electron donating system[4]. Upon additions o europium nitrate solution aliquots a new band (303 nm for **HDPPO** and 305nm for **MeDPPO**) with good isobestic behavior was observed (Figure 1a) similar for both complexes.

3.2 Stochiometry of complexes formation of $Eu(NO_3)_3$ and DPPOs

From the X-Ray data for the complex of $Gd(NO_3)_3$ with **HDPPO**[5] we anticipated formation of complexes with 1:1 stoichiometry in solution. To support this assumption we provide the Job's plot[6] (continuous variation method) for both systems (a Job's plot for Eu-**HDPPO** is placed on Figure 1b as a representative example). The 1:1 binding stoichiometry for both ligands were supported by Job's plots. Moreover, the titration curves (see Figure 1c and later) show smooth grow with marked endpoint for M:L=1:1 which is also supports the formation of the mononuclear complexes with metal-to-ligand composition 1:1 in acetonitrile solution.
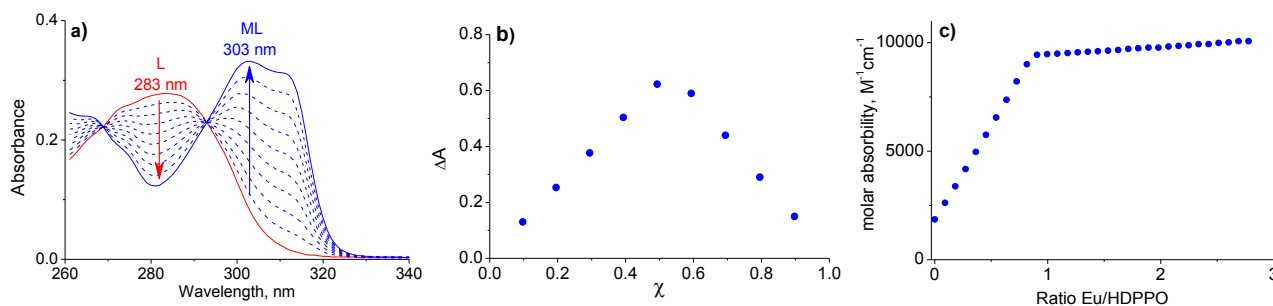

Figure 1. Isobestic behavior (a), corresponding titration plot (b) and Job's plot (c) associated with the interaction of **HDPPO** with $Eu(NO_3)_3 \cdot 6H_2O$ in acetonitrile solution.

3.3 Stability of complexes of DPPOs with Eu

The stability constants of europium complexes with **DPPOs** ligands were studied by using spectrophotometric titration in acetonitrile. During the titration, the pyridine π–π^* absorption band of the ligand was significantly enhanced by metal

solution addition, showing metal coordination with the pyridine rings. For the Eu complex with **HDPPO** ligand, the maximum absorption was at 303 nm, which corresponds to $\pi \rightarrow \pi^*$ transition of pyridine rings in complex. The absorption peak maximum for Eu complex with **MeDPPO** differs only several nm (306 nm), but the molar absorptivity for these two complexes are differ significantly. For the Eu**HDPPO** complex the molar absorbtivity is 9494 M^{-1} cm^{-1} but for Eu**MeDPPO** it is 17865 M^{-1} cm^{-1}. This two fold increase in absorption efficiency can be explained by presence of eight electron donating methyl groups.

For determination of stability constants of europium complexes a series of aliquots of metal solution under a constant ligand concentration were apply. A set of 31–54 spectra were recorded for each titration. In all cases, the slope of linear approximation is close to 1, which confirms the results of the titration. Factor analysis of the absorbance matrix shows the presence of two absorbing species for the each system corresponding to the free ligand and its complex. Upon completion of titration, the water content in the solution was determined to be about 1500 ppm.

The stability constants ($lg\beta_1$) of complexes were calculated using the *HypSpec2014*[3] program. The $lg\beta_1$ results (Table 1) are changing from 6.59 to 7.19 for **HDPPO** and **MeDPPO** ligand correspondingly. This result seems striking keeping in mind the high loadings with donating group for the second ligand, which must enhance the electron density on oxygen atoms of phosphine oxide groups and so increase the stability of the complexes. The decrease of the stability of the complexes with the methylation of the aromatic rings of phosphine oxides can be explained by sterical repulsion which became significant for tetrakis-(3,5-dimethylphenyl)-substituted phosphine oxides and which lead to diminishing the direct polar conjugation between them and P=O group. Thus, in contravention of the electronic nature the donating substituents leads to diminishing the electronic density on oxygen donating atom and so causes to reduce the stability of the complexes with f-elements in acetonitrile.

Table 1. Logs of β_1 and accuracies for binding of the polydentate phosphine oxide ligands with Eu(III) in acetonitrile.

Ligand	HDPPO	MeDPPO
Stability constant ($lg\beta_1$) of their Eu complexes	7.19±0.06	6.59±0.07

4. CONCLUSIONS

For the first time the diminishing the stability of the complexes under high ligand loading with electron-donating groups was shown. This shocking behavior can be related to the sterical repulsion of the methyl groups and subsequent broking of the direct polar conjugation of the phenyl rings with phosphine oxide moiety with lead to diminishing the electron density on oxygen atom of the P=O groups.

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