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Ts. Sumyanova, N. Borisova, A. Petukhova, A. Kirsanova,
Chemistry Department, Lomonosov Moscow State University, GSP-1, 1-3 Leninskie Gory,
Moscow, 119991, Russia

ABSTRACT

The effect of a donor methyl groups in the structure of 6,6'-bis(di(3,5-R-phenylphosphinoyl))-2,2'-bipyridyl R = H or Me on the stability constants of lanthanum complexes was studied. Regardless of the presence of a donor substituent in phosphine oxide moiety, the stoichiometry of the complex with lanthanum was 1:1 metal to ligand. The values of the stability constant of the complexes were obtained. The insertion of methyl groups lead to increase in stability of the corresponding complexes with lanthanum which correlates well with enhance in extraction ability of the corresponding compounds towards europium.

Keywords: stability constant of complexes, lanthanum complex, spectrophotometric method

1. INTRODUCTION

Lanthanides find their application as catalysts¹, biomedical labels², optical and luminescent materials³. However, in the nuclear industry, lanthanides acts as neutron scavengers and it's removal required for recycle of the spent nuclear fuel. The similarities in chemical properties of lanthanides(III) and actinides(III) make it difficult to separate them. An urgent problem in nuclear power engineering is the separation of trivalent ions of lanthanides and actinides by liquid extraction. One of the important processes in the extraction separation is the complexation reaction. To study the complexation reaction, it is necessary to establish the compositions of the complexes in solution and the stability constants of complexes. Here we represent our findings in complexation between substituted phosphine oxides – potential actinides(III) extractant⁴ – and lanthanum nitrate.

2. OBJECTS AND METHODS

2.1 General

[2,2'-bipyridine]-6,6'-diylbis-(diphenylphosphine oxide) (DPPO) and [2,2'-bipyridine]-6,6'-diylbis-(bis(3,5-dimethyldiphenyl)phosphine oxide) (3,5-diMe-DPPO) (Fig.1) were synthesized and characterized by ¹H-NMR earlier⁵.

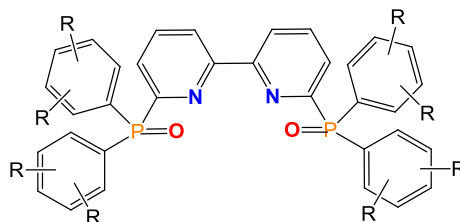


Figure 1. Structure [2,2'-bipyridine]-6,6'-diylbis-R-phosphine oxide (R = H (DPPO), Me (3,5-diMe-DPPO))

Lanthanum (III) nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, purity >99%) was stored in a closed container with silica gel. Before starting the experiment, acetonitrile (99.95%, Biosolve BV) was dried over molecular sieves (zeolite KA, 3 Å, HKC Corp. Hong Kong). The water content in acetonitrile was determined using Karl Fischer titration (C20, coulometric KF titrator, Mettler Toledo). It was found that in the acetonitrile above the sieves, the water content is 40 ± 5 ppm.

Solutions of the ligands and lanthanum nitrate in acetonitrile were prepared by weighing the exact amounts of ligands and lanthanum nitrate.

2.2 Spectrophotometric methods

UV-visible spectra were recorded at room temperature ($24.5 \pm 1.0^\circ\text{C}$) in the wavelength range 200–500 nm with an interval of 1 nm on a Hitachi U-1900 spectrophotometer using quartz cells with a path length of 10 mm (Hellma). The absorption spectra of the **DPPO** and **3.5-diMe-DPPO** ligands were measured at concentrations in the range of 0.01–0.1 mM to check whether the Beer-Lambert law was fulfilled. The method of continuous change (known as the Job's method)⁶ was chosen to study the composition of the complex which is based on determining the ratio of equimolar solutions of reagents corresponding to the maximum yield of the resulting complex compound. For the method of continuous variation, solutions of the ligand and metal salt with a concentration of ≈ 0.1 mM were prepared. For spectrophotometric titration, a ligand solution was prepared approximately 20 μM . A solution of the $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ titrant (about 4–5 mM) was prepared by dissolving a sample of lanthanum nitrate hydrate in a solution of the ligand. 2 ml of the ligand solution was titrated with aliquot of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution. The stability constants of europium complexes ($\lg\beta_1$) were calculated using the *HypSpec2014 program*⁷ based on equations (1) and (2) for the complexes:

$$\text{La}(\text{NO}_3)_3 + X \rightarrow [\text{La}(\text{NO}_3)_3 X] + \log K_1, \text{ where } X = \text{DPPO}, \text{3.5-diMe-DPPO}, \log K_1 = \log \beta_1 \quad (1)$$

$$\log \beta_1 = \frac{[\text{La}(\text{NO}_3)_3 X]}{[\text{La}(\text{NO}_3)_3] \cdot [X]} \quad (2)$$

3. RESULTS AND DISCUSSION

Before starting spectrophotometric titration, it is necessary to establish the analytical wavelengths of the complexation and determine the equilibrium conditions. The absorbance maxima of **DPPO** and **3.5-diMe-DPPO** found at 284 nm and 282 nm respectively. The addition of the lanthanum nitrate salt to the **DPPO** and **3.5-diMe-DPPO** ligands resulted in a bathochromic shift of absorbance maxima on 19 nm and 21 nm, respectively, due to complex formation (Fig. 2). On figure 2(a-b) the analytical wavelengths of the ligands and the complexes were shown, where the maximums of the absorption spectra of the complexes were at 303 nm for La - **DPPO** and 305 nm for La - **3.5-diMe-DPPO** systems. For estimation the rate of the equilibrium reaching during the complexation reaction, the absorbance at the wavelengths of the maxima were monitored depending on time. It was found that the complexation reaction proceeds quickly in 1-3 seconds.

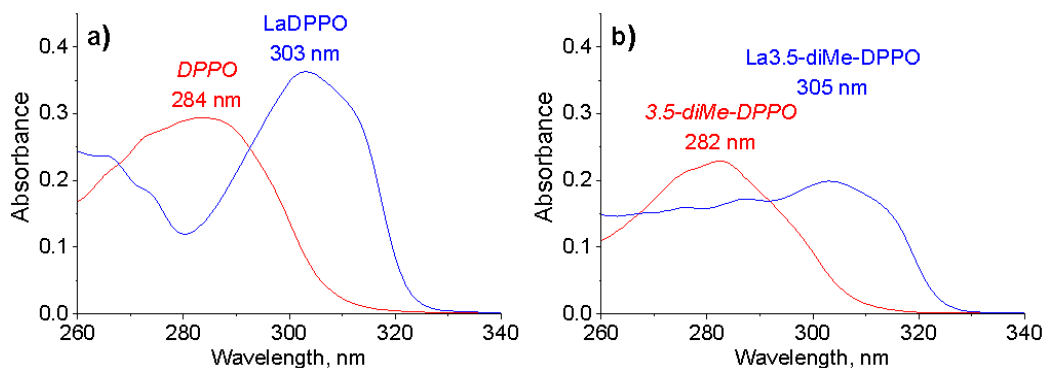


Figure 2. Determination of wavelengths of the maxima for complexation reaction between ligands a) **DPPO** and b) **3.4-diMeDPPO** at concentrations $\sim 1.7 \cdot 10^{-2}$ mM and with lanthanum nitrate.

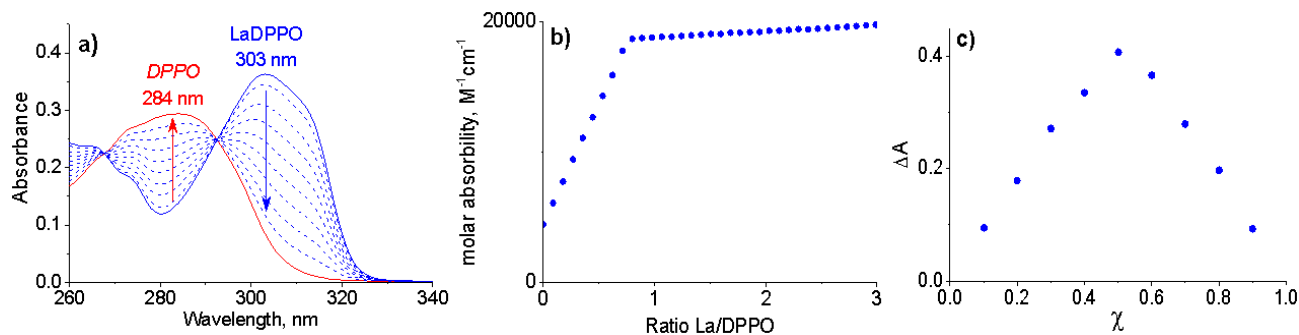


Figure 3. Spectrophotometric titration in CH_3CN solution: 1 μl of 3.57 mM titrant solution $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to 2 ml of $1.94 \cdot 10^{-2}$ mM **DPPO**: a) spectrophotometric data, where red line – **DPPO** spectrum, blue dashed lines – aliquots of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and blue line – complex $[\text{LaDPPO}](\text{NO}_3)_3$; b) titration curve at 303 nm; c) the method of continuous variation for 0,065 mM **DPPO** with 0,091 mM $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at 303 nm.

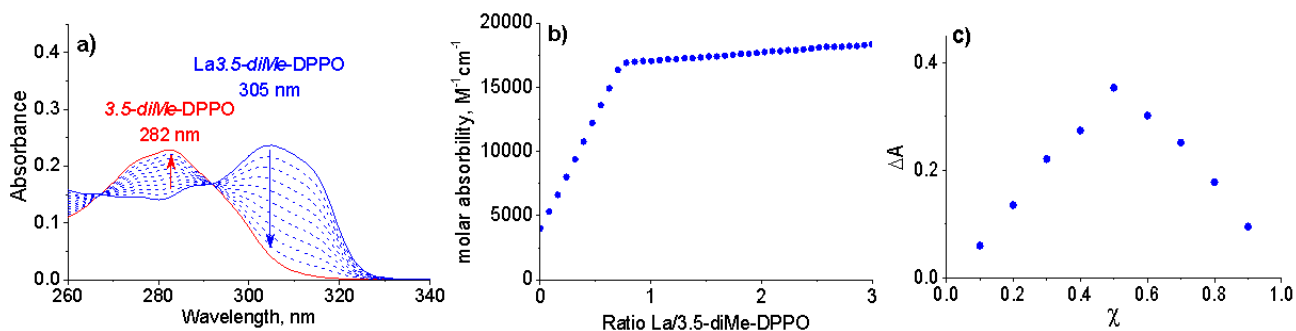


Figure 4. Spectrophotometric titration in CH_3CN solution: 4.2 μl of 4.99 mM titrant solution $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to 2 ml of $1.45 \cdot 10^{-2}$ mM **3.5-diMe-DPPO**: a) spectrophotometric data, where red line – **3.5-diMe-DPPO** spectrum, blue dashed lines – aliquots of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and blue line – complex $[\text{La3.5-diMe-DPPO}](\text{NO}_3)_3$; b) titration curve at 305 nm; c) the method of continuous variation for 0,067 mM **3.5-diMe-DPPO** with 0,047 mM $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at 305 nm.

The stability constants of lanthanum complexes with bipyridine phosphine oxides were determined using spectrophotometric titration in acetonitrile (Fig. 3a and 4a). The method of continuous variations and titration curves (Fig. 3 b-c and Fig. 4 b-c) were show that metal-to-ligand stoichiometry of the complex were 1:1 for both complexes.

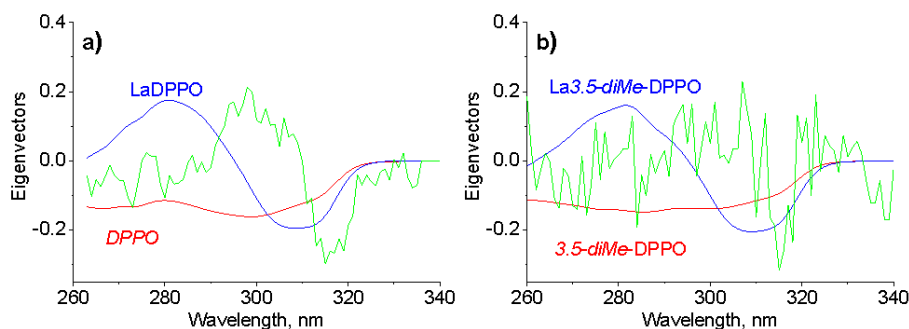


Figure 5. Factor analysis of the complexation reaction between La and ligands (**DPPO** (a) and **3.5-diMe-DPPO** (b)).

On Fig. 5 the results of factor analysis of titration absorbance matrix were represented. For both systems only two absorbing species are present. Figures 5a and 5b evidenced that the third green eigenvector is very noisy, indicating that no more than 2 components are present at equilibrium. It can be assumed that a ligand and a complex are present in the equilibria. The results of spectrophotometric titration were fitted by *HypSpec2014* program to determine the stability constants of complexes ($\lg\beta_1$).

The stability constants of complexes of lanthanum with the **DPPO** ligand ($\lg\beta_1 = 6.82 \pm 0.04$) are lower than for the **3.5-diMe-DPPO** ligand ($\lg\beta_1 = 7.12 \pm 0.04$) since the presence of a substituent in the ligand structure increases the electron density in the aromatic ring.

4. CONCLUSIONS

Regardless of the nature of the substituted phosphine oxide substituent, the stoichiometry of the complex with lanthanum was 1:1 metal to ligand. The introduction of two donor methyl groups into the structure of phosphine oxide leads to an increase in the stability constant of the complexes by 0.3 orders of magnitude. It can be assumed that donor substituents on distant fragments affect the coordination arrangement of the metal in the ligand cavity but not the electronic density on donor atoms.

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