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INTRODUCTION

One of the approaches for solving the global energy crisis is nuclear energy. Nuclear energy is considered now as a sustainable green source of energy. The main advantages of which are high energy intensity and low levels of greenhouse gas emissions. Its disadvantages include the possibility of radioactive contamination and the problem of radioactive waste storage. Thorium fuel is receiving increasing attention due to the continued consumption of uranium resources, since ^{232}Th can be converted to ^{233}U by absorbing slow neutrons. Extraction and separation of lanthanides and thorium is necessary both for isolation of thorium from ore sources and the disposal of high-level wastes. To study the extraction separation of thorium and lanthanides, we need knowledge of the stability constants of f-elements. In this work, the effect of complexation between hydrates of metal nitrates (M : La^{3+} , Nd^{3+} , Eu^{3+} , Lu^{3+} and Th^{4+}) and organic reagents based on [2,2'-bipyridine]-6,6'-diylbis(phosphonate) and 1,10-phenanthroline-2,9-diylbis(phosphonate) was studied by spectrophotometric titration on a Hitachi U-1900 spectrophotometer at a constant temperature of 25°C .

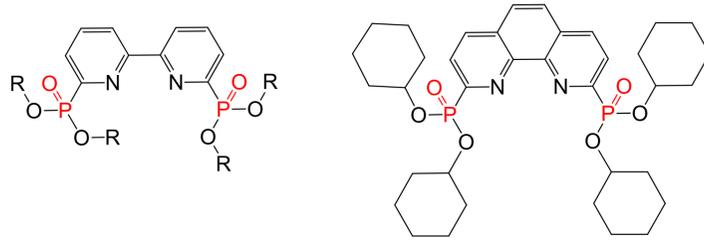


Figure 1. The structure on the left is tetra- R [2,2'-bipyridine]-6,6'-diylbis(phosphonate), where the radical (R) is (a) isopropyl (*iPr*), (b) cyclohexyl (*cHex*). The structure on the right is (c) tetracyclohexyl-1,10-phenanthroline-2,9-diylbis(phosphonate). The abbreviations for the structure of 1,10-phenanthroline are phen and [2,2'-bipyridine] are bipy and then, respectively, (a) *bipy-PO-(OiPr)*₄, (b) *bipy-PO-(OchHex)*₄ and (c) *phen-PO-(OchHex)*₄.

METHODS

UV-visible spectra were recorded in the wavelength range of 200–500 nm (with an interval of 1 nm) using a Hitachi U-1900 spectrophotometer in a 10 mm quartz cuvette (Hellma). The spectrophotometer was equipped with a cuvette holder attachment that maintained a temperature of $25 \pm 0.1^\circ\text{C}$ using a heating/cooling circulating water bath (VWR Scientific 1162). To verify the fulfillment of the Beer-Lambert law, the absorption spectra of the studied ligands were measured in the concentration range of 0.01–0.1 mM. For spectrophotometric titration, a ligand solution was prepared approximately 15 μM . A solution of the $\text{M}(\text{NO}_3)_x \cdot n\text{H}_2\text{O}$ (M : La^{3+} , Nd^{3+} , Eu^{3+} , Lu^{3+} , Th^{4+} ; x : 3 or 4; n : 4, 5, 6) titrant (about 0.5 mM) was prepared by dissolving a sample of M^{x+} nitrate hydrate in a solution of the ligand. 3 ml of the ligand solution was titrated with aliquot of $\text{M}(\text{NO}_3)_x \cdot n\text{H}_2\text{O}$ solution. It was found that for all metal-ligand pairs in the solution, only one complex particle of the metal-ligand composition 1:1 is present in acetonitrile (with a water content of 40 ± 5 ppm). The stability constants of complexes with f-elements were determined by spectrophotometric titration. The stability constants of uranyl complexes ($\lg\beta_1$) were calculated using the *HypSpec2014* program.

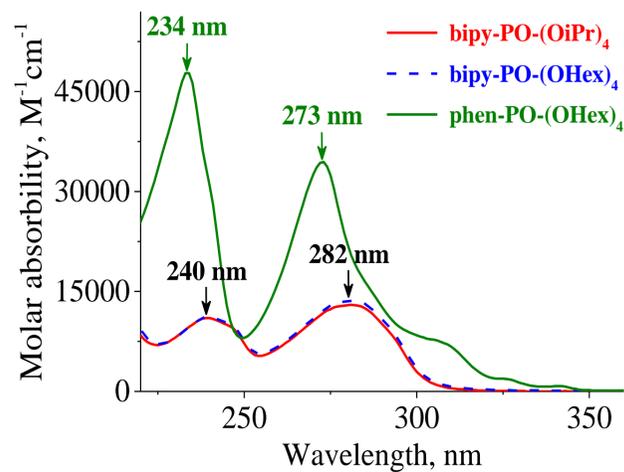


Figure 2. Absorption spectra of phosphonates, where the green dotted line indicates the spectrum of the *bipy-PO-(OiPr)*₄ ligand, the red line indicates *bipy-PO-(OHex)*₄, and the blue line indicates *phen-PO-(OHex)*₄.

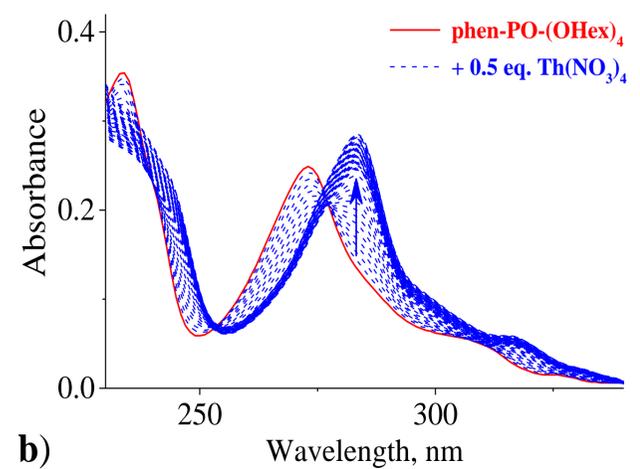
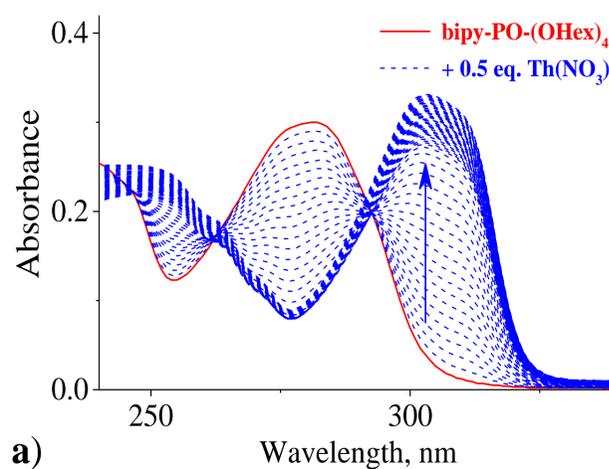


Figure 4. Spectrophotometric data where 0.5 equivalents of thorium were added to the phosphonate and titration was carried out to 3 equivalents. a – *bipy-PO-(OHex)*₄ и b – *phen-PO-(OHex)*₄.

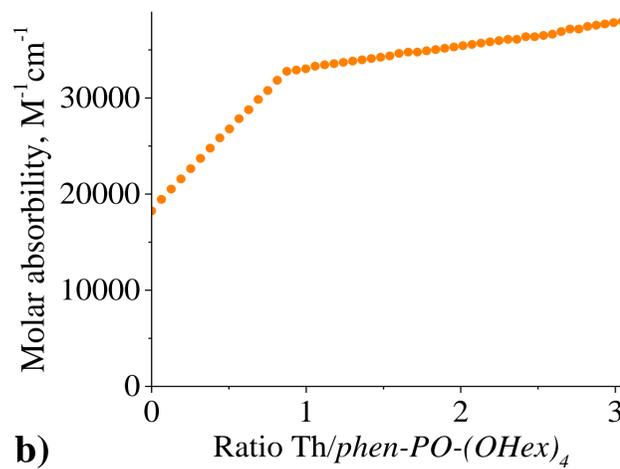
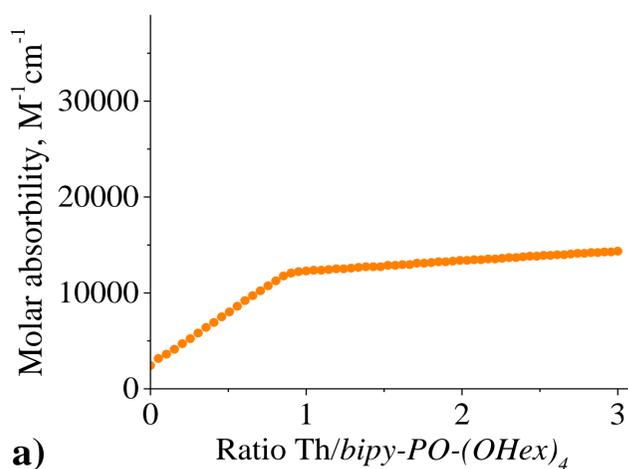


Figure 5. Titration curves of ligands with thorium nitrate at 300 nm for *bipy-PO-(OHex)*₄ ligand (a) and at 286 nm for *phen-PO-(OHex)*₄ ligand (b).

RESULTS AND DISCUSSION

The stability constants of f-element complexes with tetradentate phosphonate esters were determined using spectrophotometric titration in acetonitrile. The maximum absorbance peaks of the *bipy-PO-(OiPr)*₄ and *bipy-PO-(OHex)*₄ ligands were at 282 nm. The maximum absorbance peaks of the *phen-PO-(OHex)*₄ ligand was at 273 nm. The addition of a metal salt to the *bipy* ligands results in a shift of 18 nm and for the *phen* ligand a shift of 17 nm in the absorption spectra of the complex formation (Fig. 4a and 4b). The titrimetric method (Fig. 5a and 5b) shows a sharp bend in the curves at one equivalent of the added metal salt. The composition of the obtained complexes was studied by titrimetric method (Fig. 5a and 5b), which showed that one complex particle is formed and the composition of the complexes is the same and corresponds to a metal-ligand ratio of 1:1. The results of spectrophotometric titration was fitted by *HypSpec2014* program to determine the stability constants of complexes ($\lg\beta_{1:1}$).

Thus, the presence of a phenolic fragment in the ligand structure leads to the formation of a maximum value of the stability constants of complexes on the europium ion in the series of f-elements with an increase in the ionic radius of the metal. It can also be concluded that the presence of a less volumetric effect in the remote phenyl fragment leads to a decrease in the stability of the complexes. At the same time, the presence of a volumetric effect as a result of the bipyridine ligand leads to almost close values of the stability of the complexes.

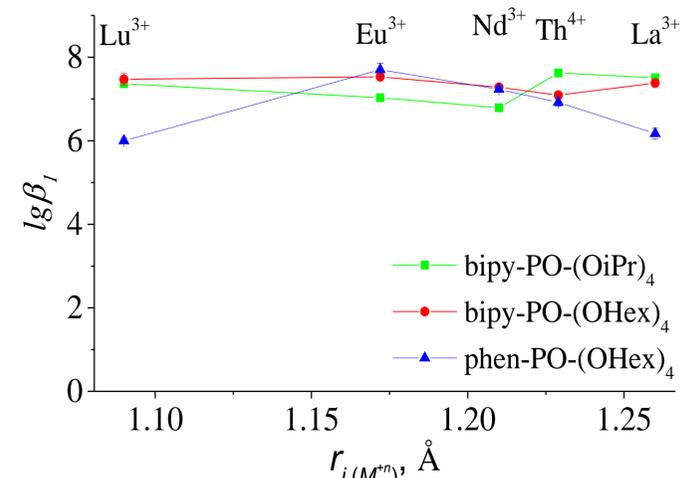


Figure 6. Dependence of the stability constant of complexes on the ionic radius of the metal.