Influence of the structure of 2,2’-bipyridyldicarboxamides on stability constants of their complexes with europium and thorium

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INTRODUCTION

Separation of actinide and lanthanide ions is complicated by their similar properties. For modeling the thermodynamics of chemical systems, it is important to accurately determine the stability constants. These thermodynamic equilibrium constants will be used to predict the speciation of metal complexes. We will also have an opportunity to understand the nature of metal-ligand interactions. In this work, we study the complexation reaction between metal nitrate hexahydrates $M(NO_3)_x{\cdot}nH_2O$ (M: Eu^{3+} and Th^{4+}, x=3-4, n=6 or 5) and 2,2'-bipyridine-6,6'-dicarboxamides (R: 2-Me, 2-F, 2-OMe 2,4-diMe) in acetonitrile.

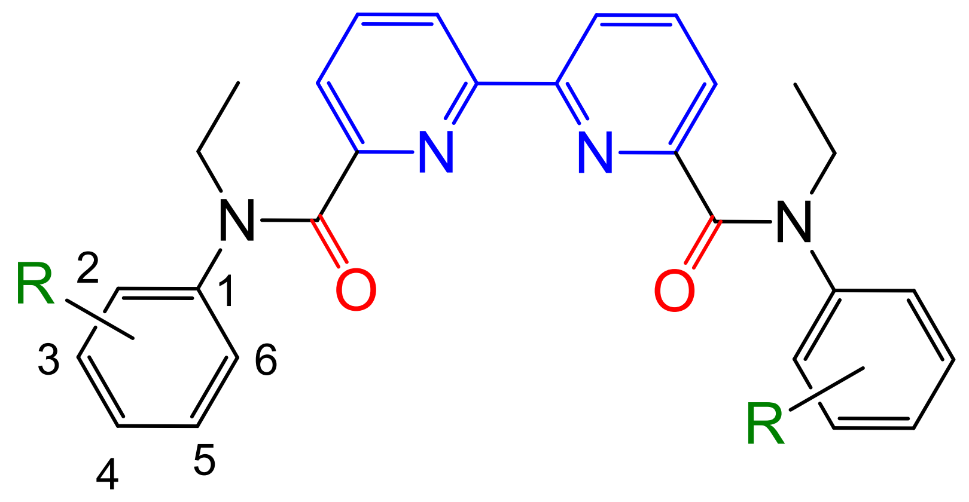

Figure 1. The structure of N^6,$N^{6'}$-diethyl-N^6,$N^{6'}$-bis(***R***phenyl)-[2,2'-bipyridine]-6,6'-dicarboxamide, where radical (**R**): *2-fluoro (2-F), 2 -methoxy (2-OMe), 2-methyl (2-Me), 2,4-dimethyl* (2,4-diMe).

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 cuvete (Hellma). The spectrophotometer was equipped with a cuvete holder attachment that maintained a temperature of 25±0.1°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 20 μM. A solution of the $M(NO_3)_x{\cdot}nH_2O$ 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 $M(NO_3)_x{\cdot}nH_2O$ 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.*

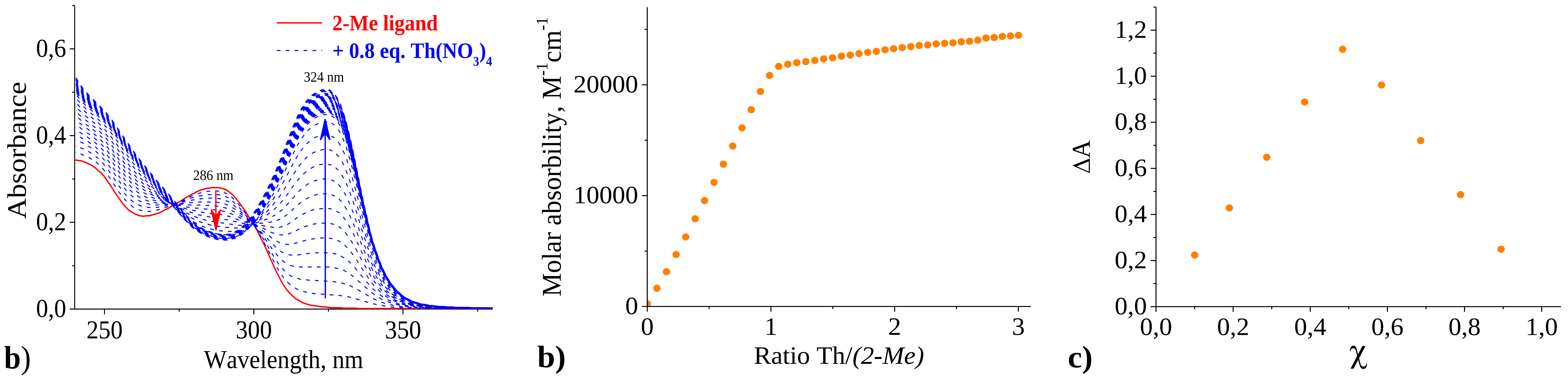

Figure 2. a) spectrophotometric data, where 0.8 equivalents of thorium were added to 2-Me diamide, and titration was carried out to 3 equivalents. Determination of the composition of the 2-Me diamide complex with thorium nitrate by the methods at 324 nm: b - titration curve, c - isomolar series (Job’s plot)

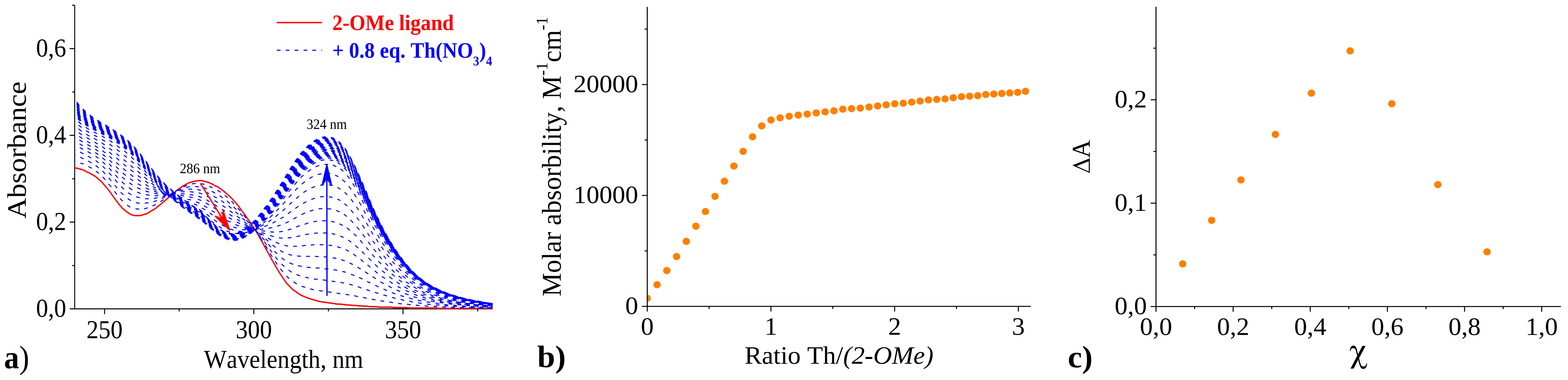

Figure 3. a) spectrophotometric data, where 0.8 equivalents of thorium were added to 2-OMe diamide, and titration was carried out to 3 equivalents. Determination of the composition of the 2-OMe diamide complex with thorium nitrate by the methods at 324 nm: b - titration curve, c - isomolar series (Job’s plot)

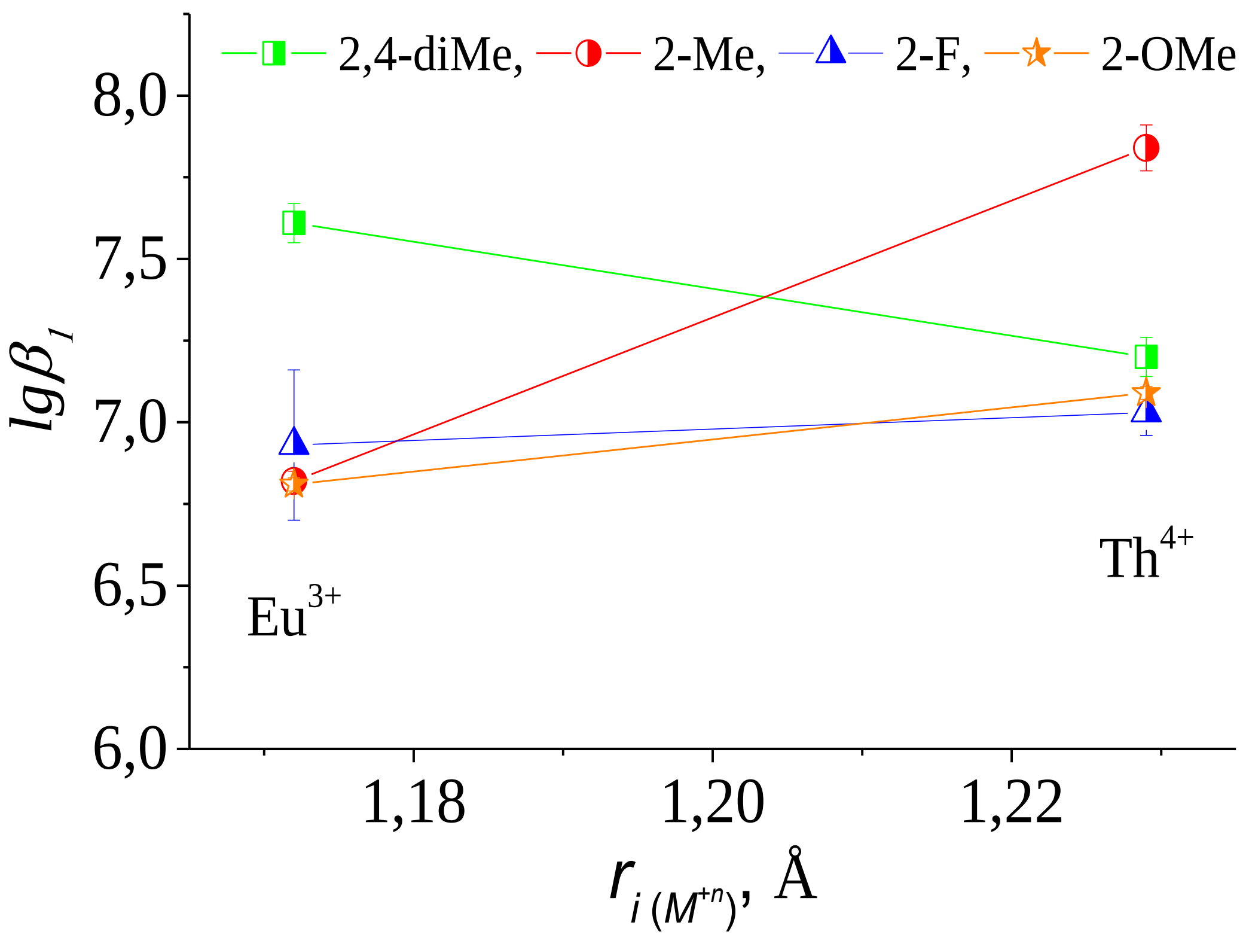

Figure 4. Dependence of the stability constant of complexes on the ionic radius of the metal.

RESULTS AND DISCUSSION

The stability constants of f-element complexes with tetradentate diamides of carboxylic acids were determined using spectrophotometric titration in acetonitrile. The maximum absorbance peaks of the all ligands (2-F, 2-OMe, 2-Me, 2,4-diMe) were at 286 nm. The addition of metal salt to the ligands lead to a 38 shift in the absorption spectra upon formation of the complex (Fig. 2a and Fig. 3a). The composition of the equilibrium solution was studied using the isomolar series method, titrimetric method and factor analysis. The titrimetric method (Fig. 2b and Fig. 3b) shows a sharp bend in the curves at one equivalent of the added metal salt. The composition of the resulting complexes was studied by the isomolar series method (Fig. 2c and Fig. 3c), which showed that for two ions the composition of the complexes is the same and corresponds to a metal-ligand ratio of 1:1. Factor analysis of titration spectra matrices shows the presence of four absorbing particles for each system, corresponding to the free ligand, metal and its complex. The results of spectrophotometric titration was fitted by *HypSpec2014 program* to determine the stability constants of complexes ($lg\beta_1$).

The stability constants of thorium complexes with the 2-Me ligand ($lg\beta_{1:1}$=7.84±0.07) clearly higher compared to other ligands, which are close in their values of stability constants of complexes. The stability constants of europium complexes with the 2,4-diMe ligand ($lg\beta_{1:1}$=7.61±0.06) higher compared to other ligands, which have similar values of the stability constants of the complexes. Therefore, the presence of a donor methyl substituent in the ortho- position increases the stability of the complexes and affects the coordination of the metal ion.

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