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Complexation Reactions between N,N'-Diethyl-N,N'-Difluorophenyl-2,2'-Bipyridyl-6,6-Dicarboxamides with Europium in Ethanol: Spectrophotometric and Isothermal Titration Calorimetry Studies

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Abstract—In this work, we studied the thermodynamic parameters of the complexation reaction between europium and *N*,*N*'-diethyl-*N*,*N*'-difluorophenyl-2,2'-bipyridyl-6,6'-dicarboxamides in ethanol. The complexation reaction for the studied metal—ligand pair lead to one complex particle with 1 : 1 metal : ligand composition. Spectrophotometric and calorimetric titration methods were used for determination of the stability of complexes. According to our data, the *meta*-position of the fluorine atom in the ligand ($\log K = 3.59$) increases the stability of complexes, enthalpy and entropy compared with the *para*-position ($\log K = 3.26$). Comparison of two parameters $\Delta_r H$ and $T\Delta_r S$ for the 3-F ligand (–8.6 and 14.15 kJ/mol, respectively) shows that they are lower than that of for the 4-F ligand (–15.5 and 10.19 kJ/mol, respectively).

Keywords: complexation, stability of complexes, enthalpy, entropy, europium, 2,2'-bipyridine, ethanol

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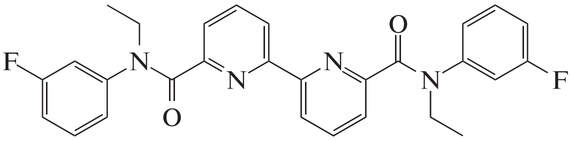
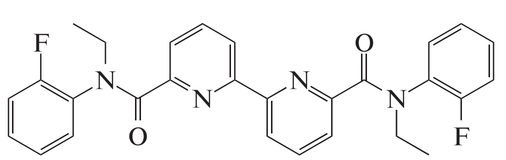
INTRODUCTION

Lanthanide complexes are interesting as luminescent materials [1], laser dyes [2], organic light-emitted diodes [3] and fluorescent probes [4]. Not only lanthanide complexes are of interest but also the *f*-elements themselves for nuclear technology applications. Generation of liquid radioactive wastes during spent nuclear fuel reprocessing raise the question of safely dispose of them. One of treatment methods is their fractionation with the separation of long-lived radiotoxic nuclides and their vitrification in accordance with their half-lives and chemical properties. The most complex process in fractionation technology is the separation of trivalent ions of actinides (minor actinides) and lanthanides since their properties are very close. Therefore, it is necessary to study the effect of the structure of the potential extractant on the thermodynamic parameters of their complexes (the stability, enthalpy, and entropy of complexing reaction) in order to understand how to design the structure of the extractant to obtain the required properties of lanthanide complexes. One of the widely used extractant is polyamides [5]. The complexation between of lanthanide(III) ions and polyamides are studied in nonaqueous solution due to absence of hydrolysis of the metal ions or ligand protonation [6]. So the aim of the work is to determine the thermodynamic parameters of the complexation reaction between the europium ion and *N*,*N*'-diethyl-*N*,*N*'-difluorophenyl-2,2'-bi[yridyl-6,6-dicarboxamides **3-F** and **4-F** in ethanol:



N_6,N_6'-diethyl-N_6,N_6'-di(**3-F-phenyl**)-[2,2'-bipyridine]-6,6'-dicarboxamide (**3-F**)



N_6,N_6'-diethyl-N_6,N_6'-di(**4-F-phenyl**)-[2,2'-bipyridine]-6,6'-dicarboxamid (**4-F**)

Table 1. Thermodynamic parameters of [EuL] complex formation reaction (lg K, Δ_rH, Δ_rG, $T\Delta_rS$) at $T = 298.15$ K

Ligande	lg K	$-\Delta_rH$, kJ mol^{-1}	$-\Delta_rG$, kJ mol^{-1}	$T\Delta_rS$, kJ mol^{-1}
3-F in EtOH	3.51 ± 1.5[a]	9.2 ± 1.2	19.9	30.29
	3.59 ± 0.02[b]	8.6 ± 0.06	20.5	14.15
4-F in EtOH	3.7 ± 1.6[a]	12.0 ± 0.09	20.75	27.12
	3.26 ± 0.02[b]	15.5 ± 0.09	18.58	10.19
ADPTZ in 75% MeOH [11]	4.5 ± 0.1[b]	20.4 ± 0.7	25.7 ± 0.6	18 ± 0.2
TPTZ in 75% MeOH [12]	3.60 ± 5[b]	18.6	20.6	4

[a] All values log$K$, $-\Delta_rH$, $-\Delta_rG$ and $T\Delta_rS$ determined by ITC.

[b] The value log$K$ is taken from spectrophotometric data and is taken as a fixed value and the values are calculated by the calorimetric method.

MATERIALS AND METHODS

Materials

The compounds **3-F** and **4-F** were synthesized as described earlier [5]. Quantitative and qualitative chemical analysis of diamides was recorded using an Agilent 1100 chromatograph (HPLC/MS). Ethanol (Sigma-Aldrich, 99.8%), where water content in ethanol was estimated as 2.0 ± 0.5% by Karl Fisher titration. Europium nitrate hexahydrate ($Eu(NO_3)_3 \cdot 6H_2O$, fluorimetrically pure, purity >99%) was stored in a closed container over silica gel balls. The stock solutions of ligands and europium salts were prepared by weighing the amounts of the respective chemicals and dissolving them in ethanol.

Methods

Spectrophotometric titration. UV–Vis spectra were recorded at ambient temperature (24.5 ± 1.0°C) in the wavelength region 260–500 nm (1 nm interval) on Hitachi U-1900 spectrophotometer using by quartz cells (10 mm path length). The implementation of the Beer–Lambert law was determined for ligand within the range 0.01–0.1 mM. The method of continuous variation (called as Job's plot [7]) was determined the binding stoichiometry of one-step complex formation between two different molecules, that corresponds to the scheme:

$$[L] + Eu(NO_3)_3 \leftrightarrow [EuL](NO_3)_3.$$

The solutions of ligand (3-F, 4-F) and europium nitrate hexahydrate were prepared at a concentration of ≈0.1 mM. For the spectrophotometric titration were prepared solution of ligand (ca. 10 μM) and a titrant solution $Eu(NO_3)_3 \cdot 6H_2O$ (ca. 2 mM) in ethanol. A 2 mL of solution of ligand was titrated with 8 μL $Eu(NO_3)_3 \cdot 6H_2O$ solution.

Isothermal titration calorimetry (ITC). The thermodynamic parameters of the reactions between ligand (3-F, 4-F) and europium nitrate in ethanol at 25°C were obtained from calorimetric experiments using the TAM III (TA Instruments) calorimetric titration system provided with a titration cell of 20 mL. TAM III calorimeter system was calibrated electrically. In addition, a chemical calibration by the binding reaction between Ba^{2+} and 18C6 in water at 298.15 K has been provided [8].

A standard titration procedure was applied. A ligand solution with an initial concentration of 1–4 mmol/L in EtOH was placed in the cell. In the syringe was a solution of $Eu(NO_3)_3 \cdot 6H_2O$ with an initial concentration of 30 mmol/L in EtOH. Fresh solutions of reagents were prepared before measurements. In each titration series, 8 titrant additives of 125 μL were added to the cell, and a parallel experiment was carried out by adding 250 μL. Titration was completed on 3–3.5 stoichiometric ratio.

RESULTS AND DISCUSSION

UV–Vis Titration

The UV-spectra of the free ligands showed a broad band near 280 nm, corresponding to the $\pi \rightarrow \pi^*$ conversion at pyridine rings. After adding a metal salt, a new peak at 324 nm with good isobestic behavior was appear (Fig. 1a). We found that only one complex particle was formed. By the method of continuous change, we discovered only one type of complex with composition of Eu_1L_1 (L = 3-F, 4-F) for both studied pairs (Fig. 1b), this composition was also supported by the titration method (Fig. 1c). Factor analysis also showed the presence of two absorbing particles corresponding to the free ligand and the complex.

The stability constants (log$K$) of europium complexes were calculated using the HypSpec2014 program [9]. The titration was repeated twice and the results were within the confidence interval. The values log$K$ of europium(III) complexes with **3-F** and **4-F** diamides were 3.59 ± 0.01 and 3.26 ± 0.02 respectively (Table 1). Thus, the *meta*-position of the fluorine atom increases the stability of complex than the *para*-position in the phenyl fragment of diamide.

A similar effect of the *meta*-position in the dimethyl-substituted diamides of bipyridine-dicar-

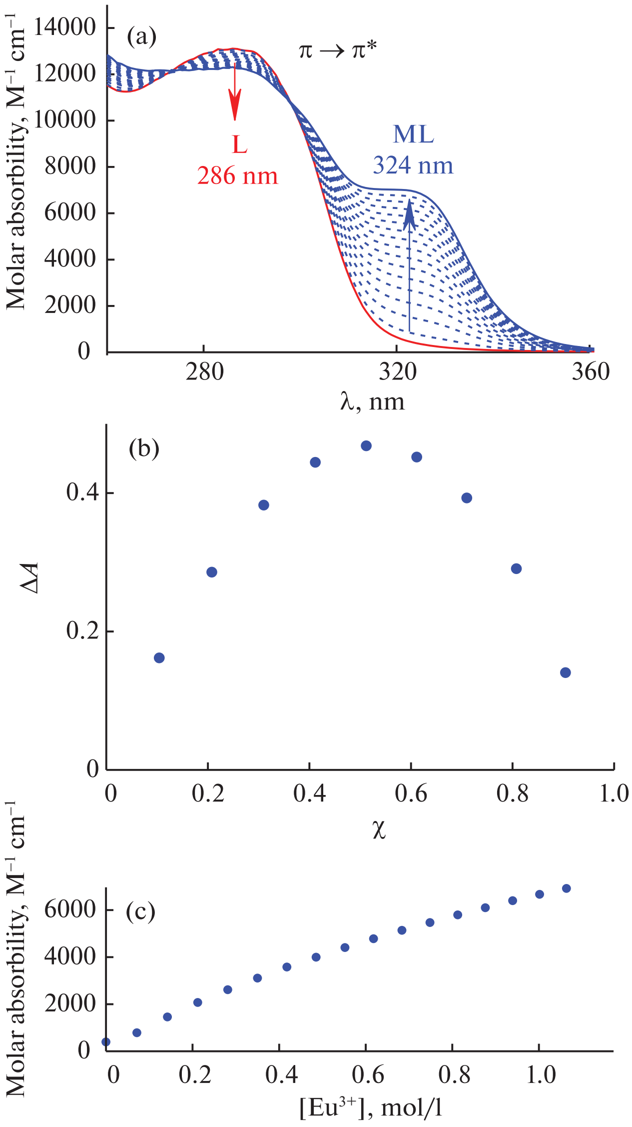


Fig. 1. Spectrophotometric titration of 4-F with $Eu(NO_3)_3 \cdot 6H_2O$ in ethanol, where 8 μL of 28.9 mM titrant solution $Eu(NO_3)_3 \cdot 6H_2O$ were added to 2 mL of 2.01 mM 4-F (0–3.0 equiv.); (a) UV-vis titration of 4-F observed upon the addition of 0–1.0 equiv. of $Eu(NO_3)_3 \cdot 6H_2O$ at 25°C; (b) the Job's plot at 324 nm and (c) titration curve at 324 nm.

boxylic acids in acetonitrile was described in the work [10], for the complexes with coordination of metal ions to nitrogen atoms of the pyridine rings and oxygen atoms of the carboxyl groups.

Thermodynamics of Complex Formation in Water–Ethanol Solvent

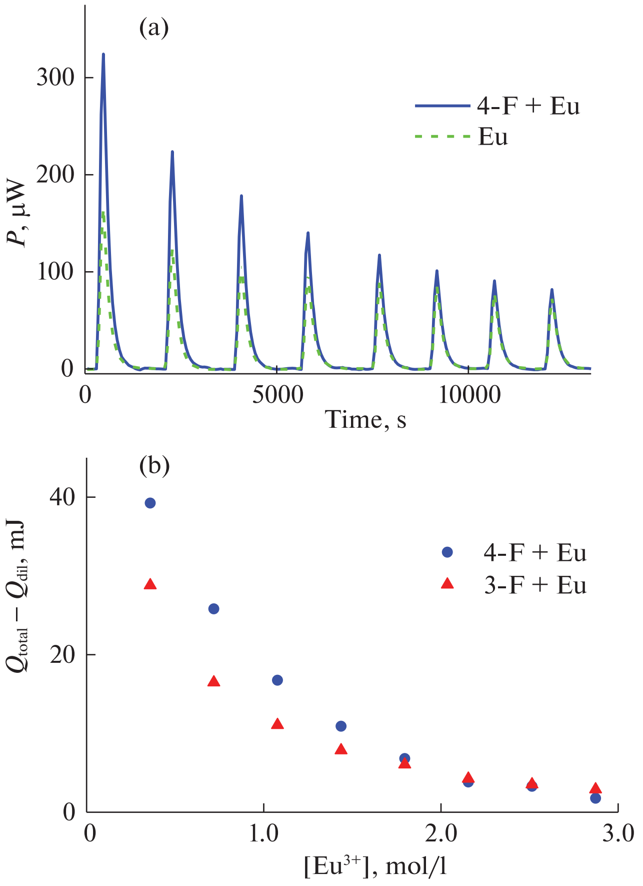


Fig. 2. Calorimetric titration of 10 mL of 1 mM ligand by addition of 8 × 125 μL of 30 mM $Eu(NO_3)_3 \cdot 6H_2O$ in ethanol at 25°C ($\Delta t = 30$ min between two injections): (a) calorimetric data; (b) corrected heat measured ($Q_{\text{total}} - Q_{\text{dil}}$).

The example of heat effects determined by ITC is shown in Fig. 2. After each addition of a titrant, the observed heat Q was recorded, which corresponds to the sum of the heat of formation of the EuL complex (Q_{complex}) and the heat of dilution (Q_{dil}) of metal salt solution in ethanol (Fig. 2a). The sett up of dilution experiments were the same as for experiments of mixing between ligand and Eu (III) solutions.

The ITC results for experiments with **4-F** and **3-F** ligands depending on the concentration of europium ion is shown in Fig. 2b. The complexation enthalpy for the formation of the EuL 1 : 1 complex is directly related to heat, adjusted for dilution, by the following ratio:

$$Q_{\text{complex}} = Q - Q_{\text{dil}}.$$

TAM Assistant software was used to calculate the thermodynamic parameters of complexation reactions (K; $\Delta_r H°$; $T\Delta_r S$) from calorimetric data (Table 1). The stability constants of the complexes obtained by both methods are in satisfactory agreement with each other. The calculation of all parameters of complex formation was complicated by large contribution of the heat of dilution since diamides possess low solubility in ethanol. So, they limit the precision of the calculated both K and $\Delta_r H°$ values [11]. To improve the quality of the thermodynamic parameters the stability constants from the independent spectrophotometry titration can be applied to calculations. The diminishing of independent parameters significantly enhances the precision of the data.

Comparing enthalpy ($\Delta_r H°$) and entropy ($T\Delta_r S°$) contributions the 3-F ligand (−8.6 ± 0.6 and 14.15 kJ/mol, respectively) possesses twice less enthalpy of complex formation than the 4-F ligand (−15.5 ± 0.9 and 10.19 kJ/mol, respectively), but complexation of metal ions with 3-F is entropy driven process. This can be connected with electron withdrawing nature of the fluorine atom, so the receding of it from the coordinating oxygen atoms of amide groups lead to better enthalpy of complex formation. From the other hand the *metha*-position of substituent in the resulting complex provide them a large number of position isomers of rotationally rigid complex, comparing with *para*-substituted one.

Comparing 3-F and 4-F diamides with well known thermochemically characterized extractants as 2-amino-4,6-di-(pyridin-2-yl)-1,3,5-triazine (ADPTZ) and 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ) we found that the enthalpy of complexing is lower and the entropy – is larger for both of diamides. The TPTZ ligand ($\log K$=3.60 ± 0.5, $\Delta_r H°$ = −18.6 kJ/mol and $T\Delta_r S°$ = 4 kJ/mol [12]) possesses the stability of complexes of the same order of magnitude relative the diamides. But the enthalpy of complex formation is three times larger than for **3-F** with a significantly lower enthropy. The same is observed for ADPTZ ligand ($\log K$ = 4.5 ± 0.1, $\Delta_r H°$ = −20.4 kJ/mol and $T\Delta_r S°$ = 18 kJ/mol [11]). The difference in the thermodynamics of complexation between europium and polyaminocarboxylate ligands is a change in the effective number of chelated nitrogen atoms depending on the donor-acceptor ability of the europium ion [13], since the entropy contribution prevails over the enthalpy.

CONCLUSIONS

Using spectrophotometric and calorimetric methods, it was found that one complex particle (Eu_1L_1) is formed in the solution for both ligands. The stability of complexes of diamides with Eu(III) were in the range lg K = 3.26–3.59. It was found that the *meta*-position of the fluorine atom in the anilide increases the stability of the complex compared with the *para*-position. Stoichiometric composition of L_1Eu_1 complexes were determined by continuous variation method. Apparently the complexing process include two aspects desolvation of the Eu^{3+} ion and metal–ligand interaction. For strong metal–ligand interactions, negative complexation enthalpies and positive entropy values were expected, which is consistent with inner sphere coordination with displacement of solvent molecules from the hydration sphere of the metal ion.

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