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N,N′-Dialkyl-N,N′-diaryl-1,10-phenanthroline-2,9-dicarboxamides as donor ligands for separation of rare earth elements with a high and unusual selectivity. DFT computational and experimental studies.

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N,N′-Dialkyl-N,N′-diaryl-1,10-phenanthroline-2,9-dicarboxamides (IV) were predicted (DFT simulation) and then were proved experimentally to be the efficient donor ligands with high and unusual selectivity for the extraction separation of lanthanides. Distribution coefficients *D* of lanthinide cations in two-phase aqueous solution – polar organic solvent decrease with increasing Ln^{3+}atomic number. The selectivity factors $SF_{Ln1/Ln2}$ for adjacent lanthanide ions were found to be about 3.

Rare earth elements (REE) have strategic importance for the world economic development. Especially, the demand for high-purity individual lanthanide compounds increases very rapidly. Currently, the main method of REE separation is liquid-liquid extraction in two-phase aqueous solution–organic solvent systems using lipophilic neutral or anionic donor ligands as extractants. The most important characteristics of these ligands are distribution coefficients of Ln^{3+} ions between organic and aqueous phases ***D*** and the separation factors $SF_{Ln1/Ln2}$ which are the ratio of coefficients ***D*** for two adjacent metals. The $SF_{Ln1/Ln2}$ values for the majority of extractants currently used on industrial scale are less than 2. The search of extractants with a higher selectivity is a challenging goal. The state of the art of the problems given in reviews[1-6].

The promising strategy to create selective extractants for REE and actinides separation is the design of polydentate ligands with a rigid geometry, which inner cavity could be accurately tuned to the size of a target cation. Among such ligands are heterocyclic compounds containing "soft" (heterocyclic nitrogen) and "hard" (amide oxygen) donor centers. Shimada et al.[7] found that the coefficients ***D*** increase with increasing the atomic number of Ln^{3+} when studied the extraction of lanthanides with N,N′-dialkyl-N,N′-diaryl-2,2'pyridine-2,6-dicarboxyamides (**I**). This trend was confirmed and supplemented with quantitative data by Babain *et al*.[8, 10], Kobayashi *et al*.[9], Paulenova *et al*.[11], and Bubeníková *et al*.[12]. When studying the extraction of lanthanides with N,N′-dialkyl-N,N′-diaryl-2,2'-bipyridyl-6,6'-dicarboxamides (**II**) having larger coordination cavity, Alyapyshev *et al*.[13] showed that for these ligands coefficients ***D*** decrease with increasing the atomic number of Ln^{3+} but this trend is not very clear. The complexation of Ln^{3+} with 1,10-phenantroline-2,9-dicarboximide (**III**) having no alkyl or aryl groups at the amide nitrogens in 0,1 M $NaClO_4$ water solution have been studied by Hancock *at al*.[14,15]. It was found that $\log K_1$ values for its 1 : 1 lanthanide complexes show only small changes from La^{3+} to Lu^{3+} (both have $\log K_1$ = 3,80).

Complexation constants of lanthanides with polydentate ligands and $SF_{Ln1/Ln2}$ depend very strongly not only on the cavity size but as well on the substituents in the molecule and on the other neutral or anionic ligands in the cation coordination sphere. Having this in mind we turned to N,N′-dialkyl-N,N′-diaryl-1,10-phenanthroline-2,9-dicarboxamides (**IV**) which previously have been successfully used as the ligands for the separation of minor actinides (Am, Np, Cm) and lanthanides in the reprocessing of spent nuclear fuel[16-19]. We assumed that diamides **IV** should possess higher affinity for the light

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lanthanides having larger ionic radii, and have to exhibit higher selectivity than diamides **II** due to the more rigid geometry.

The rapid development of quantum chemistry techniques coupled with the fast improvement in the computer technologies opened an opportunity to perform calculations of the structure and properties of molecular systems containing hundreds of atoms and to obtain reliable data with an accuracy allowing direct comparison with the experimental ones. This approach was already successfully used in the quantum chemical simulation of the structures of N-heterocyclic ligands and their actinide and lanthanide complexes[20–28]. In particular, we performed the DFT study of Eu^{3+} and Am^{3+} complexes with several diamides **I** in ref.[28].

To test above-mentioned assumption we decided as a first step to perform DFT calculations of metal-to-ligand binding energies in the lanthanides complexes with several ligands **IV** using first-principles DFT (GGA PBE), scalar-relativistic theory[29] and large relativistic full-electron basis sets[30] (see ESI for calculation details). All calculations were performed at the MBC-100к Cluster of the Joint Supercomputer Center (JSCC, Moscow) using the PRIRODA program[31].

N,N′-Diethyl-N,N′-diphenyl-4,7-dichloro-1,10-phenanthroline-2,9-dicarboxamide (**V**) was chosen as a starting ligand because subsequent replacement of the chlorine atoms in further experiments allows us to tune its extractive properties by varying substituents in the aromatic rings. Previous extraction experiments have shown[8-13] that diamides **I** and **II** form mainly 1 : 1 complexes with lanthanides. That is why the 1 : 1 complexes **[(V)Ln(NO$_3$)$_3$]** were chosen for theoretical study in our case.

The geometries of ligand **V** and its complexes **[(V)Ln(NO$_3$)$_3$]** were completely optimized for the gas phase conditions. The non-planar twisted conformation of **V**, where the amide oxygen atoms separated from each other, corresponds to the global minimum on PES (see ESI for the structure). This ligand in the complexes binds the metal ions through two phenanthroline nitrogens and two amide oxygens. The nitrate counter-anions act as bidentate ligands. The structure of Gd complex shown in Fig. 1 as an example (see ESI for Cartesian coordinates).

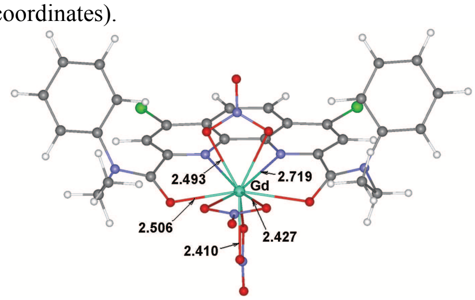


Fig. 1. Calculated structure of **[(V)Gd(NO$_3$)$_3$]** complex.

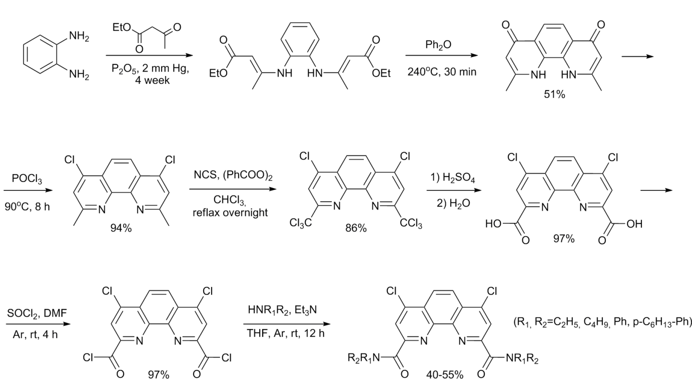
The metal-to-ligand binding energies in the complexes **[(V)Ln(NO$_3$)$_3$]** were calculated as the differences between the total energies (or free energies) of **[(V)Ln(NO$_3$)$_3$]** complexes and the corresponding energies of anhydrous nitrates **Ln(NO$_3$)$_3$**, calculated as described in ref. [28]. The calculations were performed for the gas phase conditions, *i.e.* taking no account for the medium effects, which can be quite significant. Therefore, these results should be used to estimate the general trend of changes in the binding energy along the lanthanide series on the qualitative level only. Data given in table 1 show clearly the general trend, *i.e.* the significant decrease in the binding energies with increasing the atomic number of lanthanide. Thus the calculation data confirmed our assumption that diamide (**V**) should possess higher affinity for the light lanthanides.

Table 1. Metal-to-ligand binding energies in **[(V)Ln(NO$_3$)$_3$]**

M	E^b, (G^b) kcal/mol	ΔE_{Ce-M}* (ΔG_{Ce-M})** kcal/mol	**M**	E^b, (G^b)* kcal/mol	ΔE_{Ce-M}* (ΔG_{Ce-M})** kcal/mol
Ce	63.2 (43.8)	0.0	Tb	55.4 (35.2)	7.8 (8.6)
Pr	56.9 (38.5)	6.3 (5.3)	Dy	54.0 (33.8)	9.2 (10.0)
Nd	55.3 (35.7)	7.9 (8.1)	Ho	53.1 (33.1)	10.1 (10.7)
Pm	55.2 (35.6)	8.0 (8.2)	Er	54.2 (34.0)	9.0 (9.8)
Sm	54.3 (35.4)	8.9 (8.4)	Tm	51.1 (31.3)	12.2 (12.5)
Eu	56.1 (36.6)	7.1 (7.2)	Yb	50.7 (31.2)	12.5 (12.6)
Gd	56.4 (36.2)	6.8 (7.6)	Lu	51.8 (29.7)	11.4 (14.1)

*) Total binding energies difference in comparison with the Ce complex.**) Free binding energies difference in comparison with the Ce complex.

This result convinced us to synthesize several ligands **IV** with different substituents at the amide nitrogens and to study their extraction properties. These ligands were synthesized in 4 steps[e] (scheme 1) and their structures were confirmed by NMR, IR, MS and elemental analysis data.



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Scheme 1. Synthesis of diamides **IV.**

N,N′-Diethyl-N,N′-di(4-n.hexylphenyl)-4,7-dichloro-1,10-phenanthroline-2,9-dicarboxamide (**VI**) was selected for the extraction experiments. It differs from diamide **V** which was used for the theoretical simulation only by the presence of two n.hexyl-substituents in the remote 4-positions of phenyl radicals at the amide nitrogens. Due to that it is much more soluble in *m*-nitro(trifluoromethyl)benzene (F-3) which was used as organic phase.

The distribution coefficients ***D*** at different concentrations of nitric acid and various concentrations of ligand **VI** have been determined at 25^{0}C (see ESI for extraction experiments details). The dependence of ***D*** on the ligand concentration allowed us to calculate the metal to ligand **VI** ratios in the complexes to be extracted (solvation numbers), which are given in Table 2. It follows from these data that the cerium-subgroup lanthanides form 1 : 1 and 1 : 2 complexes with **VI**, while the yttrium-group lanthanides produce the 1 : 1 complexes exclusively.

Table 2. Lanthanides solvation numbers in extracted complexes with **VI**

Metal	Solvation number	Metal	Solvation number
La	1.96	Gd	1.11
Ce	1.81	Tb	1.20
Pr	1.63	Dy	1.07
Nd	1.55	Ho	1.03
Sm	1.33	Er	0.88
Eu	1.24	Tm	0.98
Gd	1.11	Yb	0.97
Tb	1.20	Lu	0.95

Figure 2 shows the ***D*** values for the extraction of lanthanide ions from 3M nitric acid into F-3 when the extractants were *N,N'*-diethyl-*N,N'*-di(*o*-tolyl)pyridine-2,6-dicarboxamide (data from ref.[12]) , *N,N'*-diethyl-*N,N'*-di(4-n.hexylphenyl)-2,2'-bipyridyl-6,6'-dicarboxamide (data from ref.[13]), and diamide **VI**.

Our experimental data show several important regularities:

- In accordance with the results of theoretical simulation, **VI** exhibits high affinity for the light lanthanides. The distribution coefficients ***D*** from lanthanum to lutetium decrease sharply with increasing atomic number of Ln^{3+} for each concentration of nitric acid. This abnormal relationship was noted previously only for functionalized aza-crownethers[32-34] which, however, cannot extract the Ln^{3+} from strongly acidic media and, therefore, are not suitable for extraction and separation of lanthanides on industrial scale.
- The selectivity factors $SF_{Ln1/Ln2}$ for separation of pairs of adjacent lanthanides upon extraction of La^{3+} ions with **VI** from 1M HNO_3 are significantly higher than those for other extractants under similar conditions.
- The distribution coefficients ***D*** for **VI** throughout the HNO_3 concentration range under study increase with increasing the acid concentration. This fact agrees well with the extraction mechanism proposed by us in ref.[28], according to which the formation of metal complexes proceeds at the water/organic interface, where the hydroxonium ion within the ligand cavity is replaced with the metal cation.

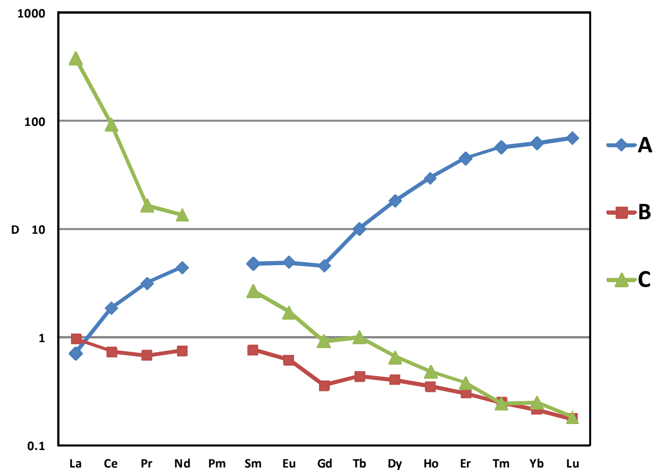

Fig. 2. Distribution ratios ***D*** for the extraction of Ln^{3+} in the system 3 M HNO_3 – F-3 (three different extractants): (**A**) – 0.2 M N,N'-diethyl-N,N'-di(*o*-tolyl)-pyridine-2,6-dicarboxamide[12]; (**B**) – 0.1 M N,N'-diethyl-N,N'-diphenyl-2,2'-bipyridyl-6,6'-dicarboxamide[13]; (**C**) – 0.05 M **VI**. Different concentrations of extractants were used to obtain close distribution ratios for easy comparison.

Dramatic differences in the extraction properties of *N*-heterocyclic dicarboxylic acids diamides **I**, **II** and **VI** can be explained quite clearly in view of experimental and calculation data. As one can expect diamides (**I**) with a small coordination cavity bind preferentially small heavy lanthanide ions. The distance between donor centers in 2,2'-bipyridyl-6,6'-dicarboxamides (**II**) increases significantly, but the ligand has conformational flexibility due to the almost free rotation around the C_2–$C_{2'}$ bond. Therefore, they can bind both small and large Ln^{3+} cations. Diamides **VI** are much more rigid and not capable to bind strongly the cations having small ionic radii.

Conclusions

In the present work, N,N′-dialkyl-N,N′-diaryl-1,10-phenanthroline-2,9-dicarboxamides (**IV**) were shown to be highly efficient and selective ligands for lanthanides separation. Unusual trend in the variations of metal-to-ligand binding energies (energy

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decrease with increasing Ln^{3+} atomic number) found by theoretical simulation was confirmed in extraction experiments.

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Notes and references

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Electronic Supplementary Information (ESI) available: calculation details; Cartesian coordinates for ligand **V** and **[(V)Gd(NO_3)$_3$]** complex; extraction procedure.