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Piperidine- and 2-(*p*-tolyl)piperidine-derived DAPhen ligands: the aryl substituent unexpectedly suppresses the extraction efficiency

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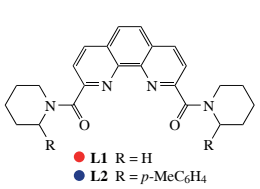
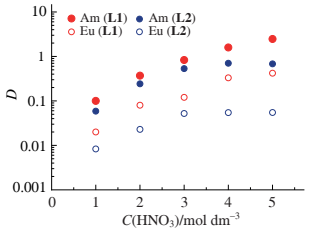
New piperidine- and 2-(*p*-tolyl)piperidine-derived phenanthroline diamides were synthesized, and their extraction efficiency toward Eu/Am pair was studied. The introduction of aryl substituent suppresses the extraction efficiency of such ligands from acidic solutions. The experimental results are in good agreement with DFT calculations.





Keywords: phenanthroline, N,O-donor ligand, americium, europium, solvent extraction, quantum-chemical calculations.

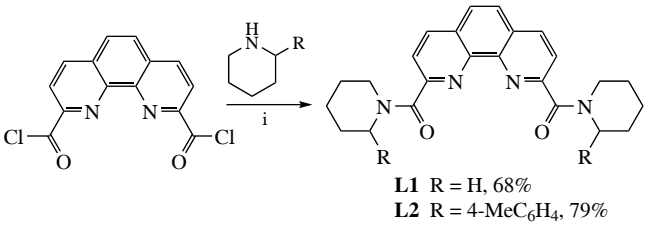
Reprocessing of spent nuclear fuels is an important part of the nuclear fuel cycle both for economic and environmental reasons. However, an obvious and still unresolved problem is the need to process high-level radioactive wastes that arise after the extraction of uranium and plutonium-239 from spent nuclear fuel solutions in 3 M nitric acid using PUREX technology.[1] To reduce the radiotoxicity of high-level radioactive wastes, minor actinides (mAn = Am, Cm, Np) have to be extracted and then transmutated into shorter-lived radionuclides in fast neutron reactors or using Am as a part of MOX fuel.[2,3] Before the transmutation, mAn must be separated from lanthanides (Ln) since Ln are neutron poisons.[4] So far, the separation of mAn from Ln is a difficult hydrometallurgical task due to similarity in chemical properties of these elements.[5–7] Solvent extraction, as one of the most common methods for *f*-elements separation, requires the use of effective and selective ligands. 1,10-Phenanthroline-2,9-dicarboxamides (DAPhen)[8,9] are promising class of ligands with a wide range of potential applications, including solvent extraction.[10–14] These *N*,*N*′,*O*,*O*′-tetradentate ligands have both 'hard' carbonyl oxygen atoms and 'soft' heterocyclic nitrogen atoms. They exhibit high selectivity in the separation of minor actinides and lanthanides, have high radiation and hydrolytic stability and relatively low Brønsted basicity. This allows them to bind f-element cations in highly acidic media and form stable complexes soluble in polar organic solvents, such as 3-nitrobenzotrifluoride (F-3).[15]

In our previous works, we studied the DAPhen ligands with alicyclic $(CH_2)_nNC(O)$ (n = 4–6) amide fragments.[16–19] It was shown that an increase in the ring size reduced the extraction capacity of the ligand. Introducing CF_3-groups at the position 2 to the nitrogen in pyrrolidine derivatives (n = 4) almost completely suppressed the extraction,[17] while the introduction of methyl[18] or phenyl groups improved it. The record extraction efficiency and Am/Ln selectivity was achieved for ligands bearing phenyl groups in pyrrolidine fragment.[19]

In this work, we decided to investigate the piperidine-derived ligands **L1** and **L2** (Scheme 1) to compare their properties with the corresponding pyrrolidine derivatives. These new ligands were prepared from the corresponding diacid dichloride by the reaction with piperidine and 2-arylpiperidine. Ligand **L2** has two asymmetric carbon atoms and was obtained as a mixture of *meso*- and *rac*-diastereomers.

Next, the extraction properties of compounds **L1**, **L2** were studied. The separation of a pair of Am^{III} and Eu^{III} is a common test to evaluate the extraction properties of organic ligands (Figure 1). It was found that the introduction of an aryl substituent suppressed the extraction capacity of the ligand **L2** for Am^{III} and Eu^{III} in comparison to **L1**. For **L1** ligand, the distribution ratios D increased over the entire range of nitric acid concentrations, while for **L2** the maximum of extraction was observed at 4 M HNO_3. The separation factors SF(Am/Eu) range from 5 to 7 for **L1** and from 7 to 13 for **L2**. Previously, we have shown that incorporation of phenyl group into pyrrolidine-derived DAPhen ligands **L3** and **L4** was highly beneficial in terms of extraction properties. In contrast, 2-(*p*-tolyl)piperidine-derived ligand **L2** demonstrated lower distribution ratios and separation factor for Am/Eu pair.

To complement the experimental data and to gain further insight into the extraction process, we performed DFT calculations to assess the energetics of Am and Eu complex formation.[20,21] The formation of complexes $L \cdot M(NO_3)_3$ was calculated using equation (1) (Table 1). It is important to note that compounds **L2** and **L4** consist of a mixture of diastereomers.



Scheme 1 *Reagents and conditions*: i, Et_3N, CH_2Cl_2, –10 °C to room temperature.

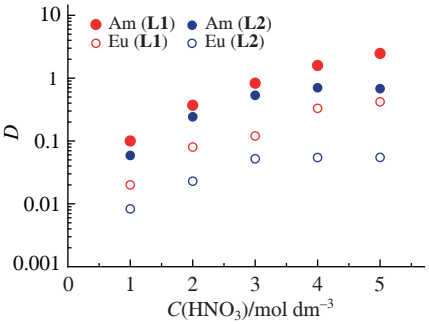


Figure 1 The dependence of D_{Am} and D_{Eu} on the HNO_3 concentration in the equilibrium aqueous phase during the extraction with 0.05 mol dm^{-3} solutions of **L1** and **L2** into F-3 (3-nitrobenzotrifluoride). Aqueous phase: 1–5 mol dm^{-3} HNO_3 + ^{241}Am and ^{152}Eu radiotracers.

Table 1 ΔG values for reaction (1), kcal mol^{-1}.

Ligand	$Eu(NO_3)_3$	$Am(NO_3)_3$
L1	–3.9	–7.1
$\mathbf{L2}_{rac}$	–4.4	–7.6
$\mathbf{L2}_{meso}$	–5.4	–8.8
L3	–3.2	–6.8
$\mathbf{L4}_{rac}$ [a]	–4.3	–7.9
$\mathbf{L4}_{meso}$ [a]	–5.7	–9.3

[a] Data from ref. 19.

$$M(NO_3)_3(H_2O)_6 + \mathbf{L} = \mathbf{L}\cdot M(NO_3)_3 + 6H_2O \quad (1)$$

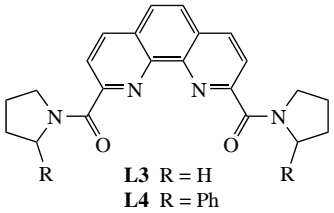
The computational results reveal that the presence of aryl substituent increases the thermodynamic stability of the complexes in both pyrrolidine- and piperidine-derived ligands. However, these findings do not align with the experimental extraction trends which show a clear preference for **L1** over **L2** suggesting that additional factors may influence the extraction process. Therefore, we decided to take into account the formation of complexes of ligands **L1** and **L2** with hydroxonium ion since the extraction is carried out from nitric acid media. We have demonstrated recently that the basicity of such ligands could be modulated significantly by substituents.[22] Next, we calculated the relative Gibbs free energies $\Delta\Delta G$ during the exchange reaction of hydroxonium ion in $[L\cdot H_3O]^+$ complexes to form complexes with Am^{III} and Eu^{III} nitrates according to reaction (2) (Table 2). The absolute values of the free energies ΔG for all diastereomeric forms of **L2**, as well as the optimized structures of ligands and complexes, are given in Online Supplementary Materials (Table S1 and Figures S9–S26).

$$[\mathbf{L}\cdot H_3O]^+ + M(NO_3)_3(H_2O)_6 = \mathbf{L}\cdot M(NO_3)_3 + [(H_3O)(H_2O)_6]^+ \quad (2)$$

The data presented in Table 2 show good agreement with the experimental extraction results. The ΔG values for **L2** are higher than for **L1** by 1.7–2 kcal mol^{-1}, confirming the reliability of the proposed model with formation of $[L\cdot H_3O]^+$ complexes. To further validate the model, we also calculated the relative Gibbs free energies $\Delta\Delta G$ for reaction (2) with ligands **L3** and **L4** (see Table 2). The absolute values of the free energies ΔG for **L3** and all diastereomeric forms of **L4**, as well as the optimized structures

Table 2 $\Delta\Delta G$ values for reaction (2), kcal mol^{-1}.

Ligand	$Eu(NO_3)_3$	$Am(NO_3)_3$
L1	0	–1.5
$\mathbf{L2}_{rac}$	2.0	0.2
$\mathbf{L2}_{meso}$	2.0	0.4
L3	0	–3.6
$\mathbf{L4}_{rac}$	–0.3	–3.7
$\mathbf{L4}_{meso}$	–0.6	–4.2



L3 R = H
L4 R = Ph

of ligands and complexes, are given in Online Supplementary Materials (Table S2 and Figures S9–S26).

As expected, the selected model is consistent with the extraction data for pyrrolidine-derived ligands. The lower ΔG values for **L4** compared to **L3** indicate higher extraction efficiency for this ligand. Therefore, when extraction from acidic media takes place the formation of intermediate complexes with hydroxonium ion should be taken into account.

To summarize, new piperidine- and 2-(*p*-tolyl)piperidine-derived phenanthroline diamides **L1** and **L2** were synthesized. It was shown that the introduction of an aryl substituent into the 2-position of piperidine leads to decline of the extraction efficiency in contrast to pyrrolidine derived ligands. The quantum chemical calculations demonstrated importance of binding to hydroxonium ion by these tetradentate ligands in acidic media.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7728.

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