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Systematic Modifications of BTP-type Ligands and Effects on the Separation of Trivalent Lanthanides and Actinides

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Abstract

In this study the separation of Am(III) from Eu(III) in nitric acid using two BTP-type N-donor ligands, 2,6-bis(6-ethyl-1,2-diazine-3-yl)pyridine (Et-BDP) and 2,6-bis(4-^{n}propyl-2,3,5,6-tetrazine-1-yl)pyridine (^{n}Pr-tetrazine) is presented. The extraction and separation properties of both ligands are tested by two phase liquid-liquid extraction at different acid concentrations. In contrast to ^{n}Pr-BTP the bisdiazinyl ligand Et-BDP is prone to protonation at nitric acid concentrations of 0.2 M and higher. A separation factor of $SF_{Am/Eu} \approx 5$ is obtained using Et-BDP as extracting ligand and with ^{n}Pr-tetrazine a $SF_{Am/Eu}$ of 9.1 is realized. Hereby 2-bromodecanoic acid as lipophilic anion source is needed.

1. Introduction

Partitioning and transmutation (P&T) is a strategy to reduce the long-term radiotoxicity of waste generated in nuclear power facilities by separating long-lived actinides from fission products. Separation of An(III) from the Ln(III) in the SANEX process is a key step in the partitioning process, because some lanthanides have high neutron cross sections, consequently diminishing the efficiency of the transmutation step.[1] Due to the high

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similarity of actinides and lanthanides in both chemical properties and ionic radius, extremely selective extracting agents are needed to achieve a reasonable separation. Heteroaromatic nitrogen donor compounds derived from a pyridine or a bispyridine backbone have been in the focus of interest for a couple of years now.[2,3,4,5,6,7,8,9] Among these bis(1,2,4-triazin-3-yl)pyridines (BTPs) were the first extractants to achieve separation factors for Am(III) over Eu(III) higher than 100 from acidic solutions.[4,5] Many modifications were carried out on the BTP ligands including change in the substituent ring size[10][11][12][13], the alkylation of the substituents at the molecules periphery[13][14] or the substituents on the pyridine ring[15] in order to optimize the ligands' performance. However the molecular reason for the selectivity of these ligands for An(III) over Ln(III) has not yet been understood.

Within this study the extraction properties of two BTP-type ligands is presented. One ligand (2,6-bis(4-ethyl-pyridazinyl)pyridine, Et-BDP, **1**) with a lower number of nitrogen atoms incorporated in the aromatic ring of the substituents has already been synthesized at University of Reading and tested at CEA-Marcoule. Extraction tests have been performed with alpha-bromocapric acid in 1,1,2,2,-tetrachloroethane as solvent within the EUROPART project. In the present study for a better comparability this ligand is used with a 0.5 M solution of 2-bromodecanoic acid in kerosene as solvent.

The second ligand (2,6-bis(4-^{n}propyl-2,3,5,6-tetrazine-1-yl)pyridine, ^{n}Pr-Tetrazine, **2**) is synthesized as a BTP-type ligand containing a higher number of nitrogen atoms in the lateral rings (see Fig. 1).
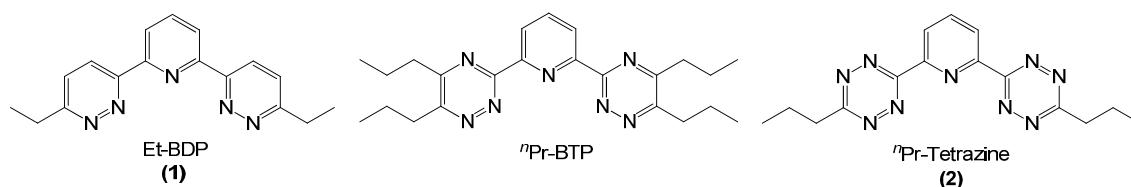

Fig. 1   Molecular structures of Et-BDP (**1**) (left), ^{n}Pr-BTP (middle)[4-6] and ^{n}Pr-Tetrazine (**2**) (right).

Previous complexation studies have shown that both ligands 1 and 2 coordinate with three nitrogen atoms to a lanthanide or actinide metal ion forming nine fold coordinated 1:3-An(III)/Ln(III)-complexes. These 1:3-complexes are also found in two-phase experiments.[16]

2. Liquid-liquid extraction

The impact of changing the number of nitrogen atoms in the aromatic substituents is investigated by liquid-liquid extraction experiments, extracting Am(III) and Eu(III) from nitric acid solutions (Fig. 2).

The aqueous phase consists of ^{241}Am and ^{152}Eu (approx. 1000 Bq/ml each) in nitric acid of different concentration (0.01, 0.1, 0.5, 0.7, 1.0, 1.5, 2.0 M).

Organic phases are solutions of
- Et-BDP, **1** (3.2 mM) in kerosene/0.5 M 2-bromodecanoic acid,
- ^{n}Pr-Tetrazine, **2** (8.8 mM) in 1-octanol, and
- ^{n}Pr-Tetrazine, **2** (6.5 mM) in kerosene/0.5 M 2-bromodecanoic acid, respectively.

500 µl of each phase are brought in contact in 2 ml glass vials. After shaking 30 minutes for experiments with **1** and 60 minutes for experiments with **2** with an orbital shaker (2000 rpm) at T = 20 °C, phases are separated by centrifugation (2 minutes at 6000 rpm). 300 µl of each organic and aqueous phase are taken for analysis on a gamma counter (Packard Cobra Auto Gamma 5003). Distribution ratios are determined from the count rates of both samples.

The liquid-liquid extraction performance of the ligands is determined by measuring the distribution of [241]Am and [152]Eu between the organic phase and the aqueous phase containing nitric acid of varying concentrations. Separation factors are obtained as ratio of the distribution ratios ($SF_{Am/Eu} = D_{Am} / D_{Eu}$).

With Et-BDP, **1** a $SF_{Am/Eu} \approx 5$ for 0.01-0.05 M HNO_3 is found (see Fig. 3a). The separation factor is significantly smaller compared to BTP ligands with hydrophobic substituents where separation factors of over 100 could be realized [4,5]. The separation factor is in good agreement with the data obtained in CEA-Marcoule ($SF_{Am/Eu} = 5$ at $[HNO_3] = 0.01$ M, [Et-BDP] = 30mM, $C_5H_{10}BrCOOH = 1M$). In extraction tests with HNO_3 concentrations of higher than 0.5 M the aqueous phase turns yellow after 30 minutes shaking (see fig. 2a).

Hence, ligand **1** is protonated and becomes soluble in the aqueous phase and consequently, distribution ratios and separation factors at HNO_3 concentrations of higher than 0.5 M can hardly be interpreted.
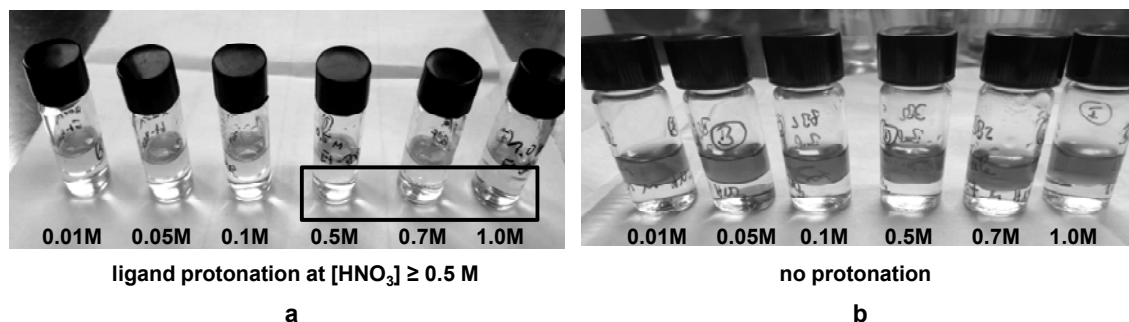

ligand protonation at [HNO₃] ≥ 0.5 M

0.01M 0.05M 0.1M 0.5M 0.7M 1.0M

a

no protonation

0.01M 0.05M 0.1M 0.5M 0.7M 1.0M

b

Fig. 2   Two phase liquid-liquid extraction experiments of Am(III) and Eu(III) using 3.2 mM Et-BDP, **1** (left) and 6.5 mM [n]Pr-Tetrazine, **2** (right) respectively, in kerosene/0.5 M 2-bromodecanoic acid and various concentrations of nitric acid.

Using a shorter phase contact time of 10 minutes distribution ratios and separation factors at low acidity can be excellently reproduced (fig. 3b) showing that an equilibrium is achieved within a time of 10 minutes. However with HNO_3 concentrations exceeding 0.5 M still a color change and hence a dissolution of the ligand in the aqueous phase is observed.
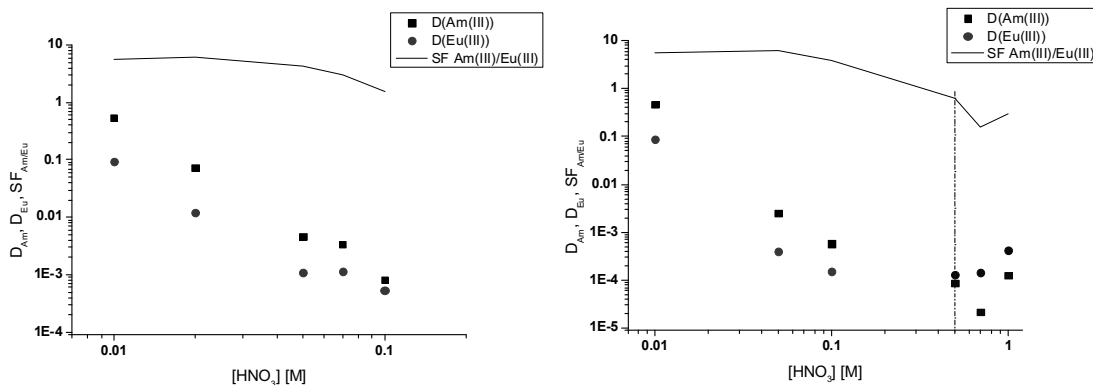

Fig. 3   Liquid-liquid extraction experiments of Am(III) and Eu(III) with 3.2 mM Et-BDP **1** at lower acidity (0.01M-1.0M) and 30 min. shaking time (left) and higher acidity (0.01M-0.1M) and 10 min. shaking time (right). Blue data points represent distribution ratios and separation factors where protonation of the ligand is observed.

With [n]Pr-Tetrazine no extraction of the trivalent metals is observed when using octanol-1 as diluent and hence, this ligand does not extract Am(III) and Eu(III) nitrates (D_{Am}, $D_{Eu} < 10^{-3}$). Yet, it is capable of extracting Am(III) and Eu(III) bromodecanoates. In separation tests with ligand **2** in kerosene containing 0.5 M 2-bromodecanoic

acid it is found that distribution ratios decrease from $D_{Am} = 1.2$ and $D_{Eu} = 0.18$ at an acid concentration of 0.01 M to $D_{Am} = 2.6 \cdot 10^{-3}$ and $D_{Eu} = 2.6 \cdot 10^{-3}$, respectively, at a nitric acid concentration of 1.0 M. At a HNO_3 concentration of 0.05 M a maximum $SF_{Am/Eu}$ of 9 is obtained ($D_{Am} = 3.8 \cdot 10^{-2}$; $D_{Eu} = 4.2 \cdot 10^{-3}$). With a HNO_3 concentration of 0.5 M and higher no separation is observed (see fig. 4).
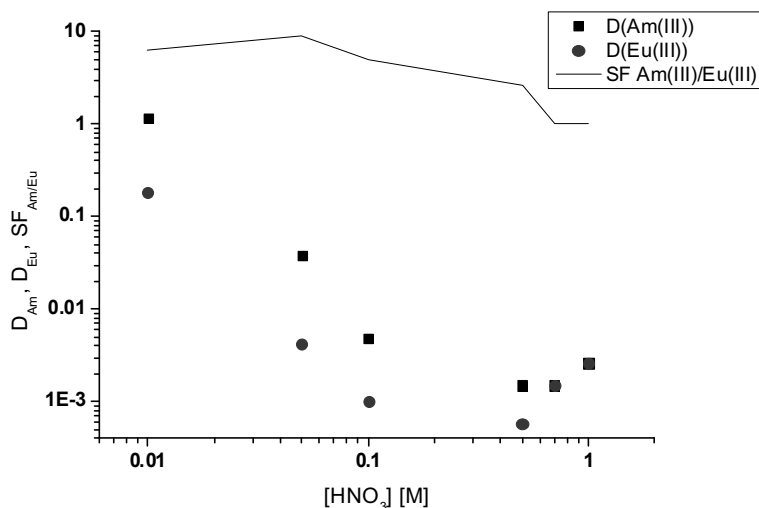

Fig. 4   Liquid-liquid extraction experiments of Am(III) and Eu(III) with 6.5 mM ^{n}Pr-Tetrazine, **2** in kerosene/ 0.5 M 2-bromodecanoic acid.
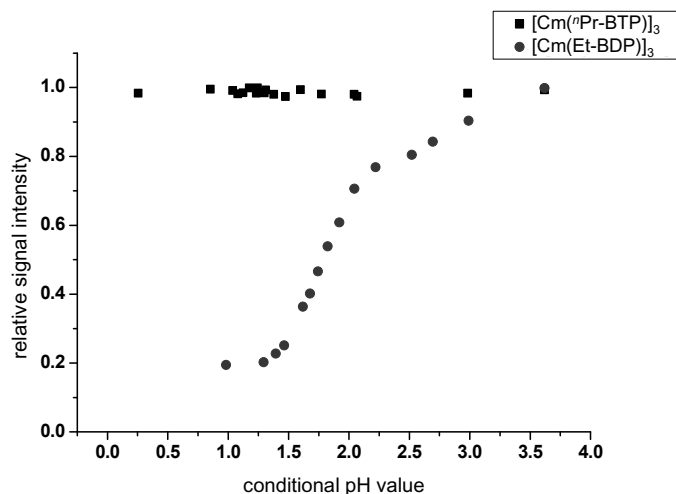

Fig. 5   Relative signal intensity of the nine fold coordinated 1:3-Cm(III) complexes with ^{n}Pr-BTP (black squares) and Et-BDP **1**, (red dots) as a function of the conditional pH.

In contrast to Et-BDP, **1** no color change of the aqueous phase is observed in liquid-liquid extraction experiments using ^{n}Pr-Tetrazine, **2**. Hence, a protonation of ligand **2** seems not to occur in the observed acidity range.

3. Protonation of 1:3-Cm(III)-ligand complexes

For further study of the stability towards increasing acidity the 1:3-Cm(III)-ligand complexes Cm(^{n}Pr-BTP)$_3$ and Cm(Et-BDP)$_3$ are treated with perchloric acid and measured with time-resolved laser fluorescence spectroscopy (TRLFS).[17][18] The 1:3-Cm(III)-ligand complexes are prepared in H$_2$O: ^{i}PrOH 1:1 solution and emission spectra are recorded with increasing HClO$_4$ concentration. Addition of small aliquots of concentrated acid assures that complex and ligand concentrations are not changed significantly. It is observed that at a conditional pH value below 3.6 Et-BDP ligands in the 1:3-Cm(III)-Et-BDP complex are protonated and the relative ratio of the Cm(Et-BDP)$_3$ complex species is reduced to 19% at a conditional pH of 1.0 (see Fig. 5).

In contrast, Cm(^{n}Pr-BTP)$_3$ is not protonated even at low conditional pH values below 0.5. The relative signal intensity of the 1:3-Cm(III) complexes at different conditional pH values are shown in Fig. 5.

4. Summary

The extraction properties of two BTP-type ligands, Et-BDP **1** and ^{n}Pr-tetrazine **2** are examined in liquid-liquid extraction tests. The maximum separation factors of SF$_{Am/Eu} \approx 5$ for Et-BDP and SF$_{Am/Eu} \approx 9$ for ^{n}Pr-tetrazine are significantly lower than it is observed for BTP-ligands. Et-BDP is furthermore protonated and dissolved in the aqueous phase when the nitric acid concentration exceeds 0.2 M. This is confirmed by dissociation of the Cm(Et-BDP)$_3$ complex in one-phase solution experiments.

In liquid-liquid extractions using ^{n}Pr-Tetrazine no protonation is found. Liquid-liquid extractions moreover show that both ligands require a lipophilic anion source to extract trivalent actinides from nitric acid solutions.

Changing the number of nitrogen atoms incorporated in the aromatic ring of the ligands' substituents shows a significant impact on the complexation and extraction properties. By this study it could be shown

that BTP-type ligands containing 1,2,4-triazinyl substituents show the best complexation and separation results among the soft N-donor ligands. This work is a contribution to help optimizing future extracting agents and gaining further knowledge about the molecular reasons of the ligands selectivity.

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