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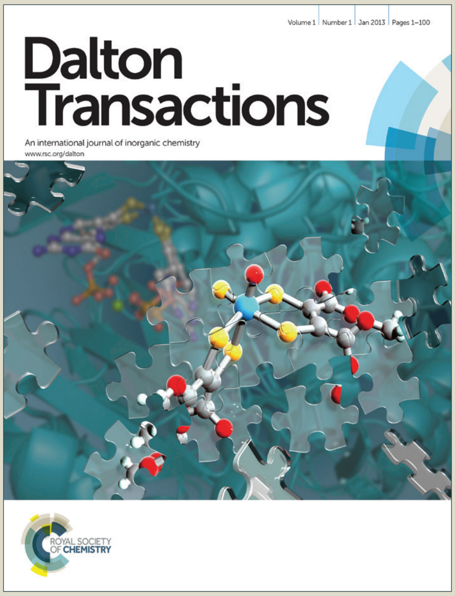

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Theoretical Prediction of Am(III)/Eu(III) Selectivity to Aid the Design of Actinide-Lanthanide Separation Agents

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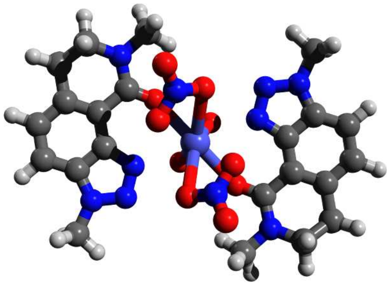


A computational protocol capable of predicting the correct order of Am(III)/Eu(III) selectivity provides a theoretical basis for the design of more selective separation agents

Abstract

Selective extraction of minor actinides from lanthanides is a critical step in the reduction of radiotoxicity of spent nuclear fuels. However, the design of suitable ligands for separating chemically similar 4f- and 5f-block trivalent metal ions poses a significant challenge. First-principles calculations should play an important role in the design of new separation agents, but their ability to predict metal ion selectivity has not been systematically evaluated. In this work, we examine the ability of several density functional theory methods to predict selectivity of Am(III) and Eu(III) with oxygen, mixed oxygen-nitrogen, and sulfur donor ligands. The results establish a computational method capable of predicting the correct order of selectivities obtained from liquid-liquid extraction and aqueous phase complexation studies. To allow reasonably accurate predictions, it was critical to employ sufficiently flexible basis sets and provide proper account of solvation effects. The approach is utilized to estimate the selectivity of novel amide-functionalized diazine and 1,2,3-triazole ligands.

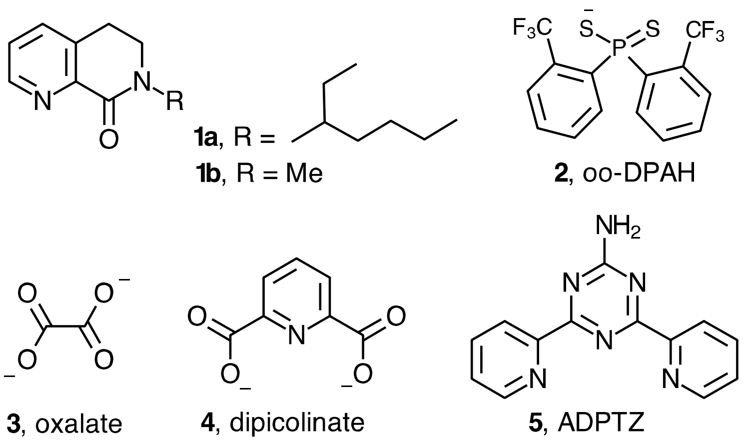
Introduction

One of the challenges faced by the nuclear power industry is a growing concern over the management of irradiated nuclear fuel. Most schemes for used-fuel recycle start with a form of PUREX (Plutonium and URanium EXtraction) processing to recover the reusable uranium and plutonium, which constitute 96% of the mass of the used fuel.[1,2] The liquid waste stream of PUREX process still contains a small fraction (less than 0.1% by mass) of long-term highly radiotoxic Am, requiring the containment of waste in a geological repository for thousands of years. Thus, it is desirable to separate minor actinides (An) from other fission products, such as lanthanides (Ln), to reduce radiotoxicity and thermal emission (storage volume) of post-PUREX nuclear waste.

Separation of chemically similar An(III) and Ln(III) is crucial to closing the nuclear fuel cycle and yet is still not efficiently accomplished.[3,4] Among numerous organic ligands known to extract trivalent metal ions, only those that contain soft donor groups are able to discriminate between An(III) and Ln(III).[5] Important progress has been made to identify organic phase extractants, such as dithiophosphinic acids (e.g., CYANEX-301),[6,7] polyazines (e.g., BTP) used in the SANEX (Selective ActiNide EXtraction) process,[5,8,9] as well as aqueous phase reagents, such as aminopolycarboxylic acids (e.g., DTPA) used in the TALSPEAK (Trivalent Actinide-Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes) process.[10,11] However, such advances are mainly based on trial and error, since the factors governing Ac(III)/Ln(III) separation on a molecular level are still not well understood.[12] Much of the computational efforts have been devoted to evaluating the extent of covalency in the metal-nitrogen or sulfur bond by employing charge, population, and bonding analysis,[13-19] while the ability to predict higher selectivity for Am(III) over Eu(III) has shown only limited success.[19-22]

Given that in most cases the calculated metal-ligand bond strength is higher for Eu(III) over Am(III),[23] one may conclude that perhaps current density functional theory (DFT) methods have not reached a sufficient level accuracy necessary for a reliable prediction of small differences in Am(III)/Eu(III) selectivity.[24] We note, however, that larger ligand binding energies for Eu(III) over Am(III) are reflections of a smaller ionic radius of the former ion.[25] Indeed, results more consistent with experimental observations are reported[19-22] when metal ion hydration free energies are included in the energy balance for trivalent f-block cation separation. Further investigations are required to determine the accuracy of theoretical methods for calculating Am(III)/Eu(III) selectivity. Establishing a reliable computational protocol for predicting the thermodynamic priority for Am(III) and Eu(III) can provide valuable insights into their solution chemistry and open up new opportunities for the use of theory in guiding the design of novel ligands for An(III)/Ln(III) separation.

In what follows, we examine the ability of several DFT methods to predict Am(III)/Eu(III) selectivity with six oxygen, mixed oxygen-nitrogen, and sulfur donor ligands, as observed in liquid-liquid extraction and aqueous phase selective complexation studies (Scheme 1). The results establish a computational method capable of predicting the correct order of selectivities based on the difference in the coordination energy between the extractant/complexant and metal ions. This method is applied to estimate the selectivity of novel mixed oxygen-nitrogen donor ligands formed by covalently linking a nitrogen heterocycle (diazine, triazole) with an amide group (Scheme 2).



Scheme 1. Ligand set used to test the ability of computational methods to predict Am/Eu selectivity.

Computational Details

We used Stuttgart small-core (SSC)[26] relativistic effective core potential (RECP) density functional theory to calculate ligand selectivities for Am(III) and Eu(III) using NWChem 6.3[27] quantum chemistry software. This does not include spin-orbits effects, which we expect not to alter the conclusions of this study. We examined the ability of five density functionals in the spin-unrestricted formalism, including two generalized gradient approximation (GGA) functionals (BPE,[28] BP86[29,30]), one hybrid GGA (B3LYP[29,31]), one local meta-GGA(M06-L[32]), and one hybrid meta-GGA (M06[33]) to predict relative separation abilities of several extractants. The geometries of all complexes were optimized with the standard Stuttgart small-core (SSC) RECP and the corresponding basis sets on Am(III) and Eu(III).[26] High-spin ground state configurations (septet) were employed for all Am(III) and Eu(III) species. Great care was taken to ensure that the lowest energy electronic state was identified via occupied/virtual orbital swaps before geometry optimization in each case.[34] Four different basis sets were considered for B3LYP: 6-31G*, 6311G**, 6-31+G**, and 6-311++G**. Based on the performance, only the 6-

31+G** basis set was employed for the other density functionals. Additional B3LYP calculations were also performed using large-core (LC) RECP of Dolg et al.[35-37] and the related (7s6p5d2f)/[5s4p3d2f] basis sets for Eu[21,35,38] and Am[21,37], and the standard 6-31+G** basis set for the light atoms (denoted B3LYP/LC/6-31+G** hereafter). Gaussian 09 Revision C.01 program[39] was employed for LC RECP calculations on a pseudosinglet state configuration (f-in-core). Including zero-point energies and thermal corrections (T=298.15 K) was reported[20,22] to have a minor contribution to the calculated Am(III)/Eu(III) selectivities (<1.0 kcal/mol). This is consistent with the calculations of the differential Gibbs free energies for reactions given in Table 1. Zero-point and thermal corrections to Am(III)/Eu(III) selectivities obtained at the B3LYP/LC/6-31G* and B3LYP/LC/6-31+G** levels (0.16-0.66 kcal/mol) are less than the uncertainty in our assessment of the Gibbs free energy for each complex (≥ 1.0 kcal/mol) and, therefore, they were not included in the calculations. Further details are provided in the ESI.

Ion solvation is modeled by explicit inclusion of the first coordination shell around metal ion and implicit treatment of the rest of the solvent with a dielectric continuum model (COSMO).[27,35] Although, the explicit treatment of more extended solvent shells is necessary for predicting the absolute binding constants for trivalent metal ions in solution,[41] we expect the predicted trends in complexation energies across An(III) and Ln(III) series to be more reliable. COSMO calculations were carried out with the default values of solvation parameters for water, as implemented in NWChem 6.3.[27] Using the default parameters ensures that the current implementation of the COSMO model in NWChem 6.3 gives the results that are as close as possible to those of the original implementation of Klamt and Schuurmann.[40] The parameters ε = 10.36, 40.25, and 1.8 were used for 1,2-dichloroethane, trifluoromethyl phenyl sulfone, and kerosene, respectively. We note that solvation calculations are not sensitive to the choice of solvation parameters for trifluoromethyl phenyl sulfone, because the difference in the solvation free energies between Am(**2**)$_3$ and Eu(**2**)$_3$ is only 0.01 kcal/mol.

Results and Discussion

In the simplest example of solvent extraction by neutral ligands from aqueous solution containing nitric acid,[3,4] a metal M^{3+} ion coordinates with n neutral ligands and three NO_3^- anions to give an uncharged chelate $M(L)_n(NO_3)_{3(org)}$ soluble in the organic phase[42-45]

$$M^{3+}{}_{(aq)} + nL_{(org)} + 3NO_3^-{}_{(aq)} \rightleftharpoons M(L)_n(NO_3)_{3(org)},\ \Delta G_{ext}(M) \tag{1a}$$

Alternatively, metal ion extraction can proceed via a cation-exchange mechanism[4,22] given by Eq. (1b)

$$M^{3+}{}_{(aq)} + 3HL'_{(org)} \rightleftharpoons M(L')_{3(org)} + 3H^+{}_{(aq)},\ \Delta G_{ext}(M) \tag{1b}$$

The extraction free energies represented by Eqs. 1a and 1b are difficult to predict with quantum chemical methods. On one hand, the association equilibria often show complex dependence on the concentration of counterions and nitric acid, the presence of phase modifiers due to aggregation, precipitation, third-phase formation, etc.[9,20] While the predominant stoichiometry of the extracted species can be deduced from the slope analysis (plotting the distribution coefficient as a function of extractant concentration),[9,20] very little is know about the coordination environment of the metal ion complexes formed upon solvent extraction. On the other hand, the theoretical methods are at best only able to describe the trends in the complexation of multicharged ions.[46,47] For example, when a single coordination shell is employed for metal ions and the remaining solvent effects are described using a dielectric continuum model,[48] the error of calculating the free energy of complexation of three NO_3^- anions to Am^{3+} and Eu^{3+} is > 10 kcal/mol.

Assuming that numerous parameters of the extraction process for both Am^{3+} and Eu^{3+} are equal, the selectivity (relative free energy) for Am(III) over Eu(III) for each neutral extractant can be written as (and similarly extended for cation-exchange extractants)

$$\mathrm{Am[(H_2O)_9]^{3+}_{(aq)} + Eu(L)_n(NO_3)_{3(org)}} \rightleftharpoons$$

$$\rightleftharpoons \mathrm{Am(L)_n(NO_3)_{3(org)} + Eu[(H_2O)]_9{}^{3+}_{(aq)}},\ \ \Delta\Delta G_{ext}(\mathrm{Am/Eu}) \tag{2a}$$

$$\Delta\Delta G_{ext}(\mathrm{Am/Eu}) = \Delta G_{ext}(\mathrm{Am}) - \Delta G_{ext}(\mathrm{Eu}) \tag{2b}$$

For metal ions of similar size and coordination properties[21] some error compensation in calculating $\Delta\Delta G_{ext}$(Am/Eu) is likely and therefore the computational results for $\Delta\Delta G_{ext}$(Am/Eu) are expected to be more reliable than for ΔG_{ext}(M).

For the purpose of predicting relative separation abilities of different extractants, even better cancellation of errors can be expected by considering the competition reaction between the two complexes of Am(III) and Eu(III) with different ligands[22]

$$\mathrm{Am(L_2)_m(NO_3)_{3(org)} + Eu(L_1)_n(NO_3)_{3(org)}} \rightleftharpoons$$

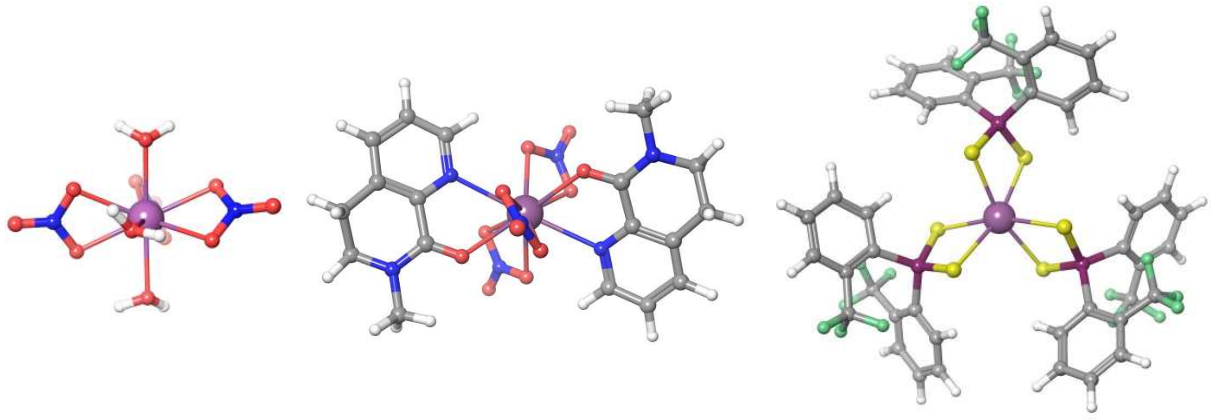
$$\rightleftharpoons \mathrm{Am(L_1)_n(NO_3)_{3(org)} + Eu(L_2)_m(NO_3)_{3(org)}},\ \ \Delta\Delta\Delta G_{ext}(\mathrm{Am/Eu}) \tag{3a}$$

$$\Delta\Delta\Delta G_{ext}(\mathrm{Am/Eu}) = \Delta\Delta G_{1,ext}(\mathrm{Am/Eu}) - \Delta\Delta G_{2,ext}(\mathrm{Am/Eu}) \tag{3b}$$

Indeed, this reaction is devoid of complicated solvation effects for the trivalent metal ions that can potentially introduce large uncertainties into calculations of $\Delta\Delta G_{ext}$(Am/Eu).[22] Moreover, the solvation free energies of neutral complexes show little variance between Am and Eu (<1.0

kcal/mol in all cases), which provides a convenient way for testing the ability of various DFT methods to differentiate between several extractant systems. In what follows, the stoichiometry of the extracted complex was chosen to be consistent with experimental results for the same or related ligands. Since only the first coordination shell was treated explicitly in this study, it was possible to perform a systematic search of low-energy clusters for a given stoichiometry. The results were reported using the lowest-energy clusters.

Table 1 compares the performance of several combinations of density functionals and basis sets in the gas phase for their ability to reproduce the measured selectivity differences between several extractants. The values of $\Delta\Delta\Delta G_{ext}$(Am/Eu) for a cyclic version of picolinamide **1a**[45] and bis-(2-trifluoromethylphenyl)-dithiophosphinate **2**[7] are reported with respect to a $M(H_2O)_4(NO_3)_3$ baseline[49] (Scheme 1). The composition of the extracted species used in the calculations is consistent with the proposed stoichiometry of the organic-phase complexes.[7,45] A composition of the complex with **1a** is 1:2 (metal ion:ligand), in which three nitrate anions can occupy the remaining space in the first coordination shell, and a composition of the complex with **2** is 1:3 (metal ion:ligand). The lowest energy conformations of $M(H_2O)_4(NO_3)_3$ and M(**1a**)$_2$(NO$_3$)$_3$ are obtained by starting from several initial configurations. The most stable geometries are consistent with the structures of the metal ion-nitrate complexes reported in the literature[20,23,48] (Figure 1). The initial geometry of M(**2**)$_3$ was taken from Ref 22. It should be noted that we are unable to treat neutral polyazine ligands on equal footing, because outer sphere coordination of nitrates[3,4] in the extraction complex requires extensive sampling over larger conformation space and thus significantly complicates the theoretical analysis of these systems.



$Am(H_2O)_3(NO_3)_3$ $Am(\mathbf{1b})_2(NO_3)_3$ $Am(\mathbf{2})_3$

Figure 1. Optimized structures of neutral Am(III) complexes.

Table 1. The selectivity of Am (III) over Eu (III) for nitrate ions (reaction 2a, $\Delta\Delta G_{ext}$) and the selectivity difference among several ligands (reaction 3a, $\Delta\Delta\Delta G_{ext}$) calculated in the gas phase using several density functionals and basis sets (kcal/mol)

method	$\Delta\Delta G^g_{ext}$(Am/Eu) $M[(H_2O)_9]^{3+} \rightarrow$ $M(H_2O)_4(NO_3)_3$	$\Delta\Delta\Delta G^g_{ext}$(Am/Eu) $M(\mathbf{1b})_2(NO_3)_3 \rightarrow$ $M(H_2O)_4(NO_3)_3$	$\Delta\Delta\Delta G^g_{ext}$(Am/Eu) $M(\mathbf{2})_3 \rightarrow$ $M(H_2O)_4(NO_3)_3$
$\Delta\Delta\Delta G_{ext}$(Am/Eu), estimated[a]		*-1.53*	*-6.82*
B3LYP/SSC/6-31G*	-1.28	2.59	10.65
B3LYP/SSC/6-311G**	-1.62	2.94	4.46
B3LYP/SSC/6-31+G**	2.94	-1.72	-3.81
B3LYP/SSC/6-311++G^{**b}	3.12	-1.87	-4.27
PBE/SSC/6-31+G**	6.45	-2.18	-4.40
BP86/SSC/6-31+G**	6.39	-2.06	-3.50
M06/SSC/6-31+G**//B3LYP^c	4.85	-3.64	-2.64
M06-L/SSC/6-31+G**//B3LYP^c	7.33	-2.93	-3.14
B3LYP/LC/6-31+G**	5.61	2.87	-4.72

[a]Based on the experimental $\Delta\Delta G_{ext}$(Am/Eu) given in Table 3. [b]A smaller 6-311+G** basis set was employed for M(**2**)$_3$ complexes due to computational limitations. [c]M06 and M06-L density functionals were evaluated for single-point energies at the B3LYP/SSC/6-31+G** geometries.

The results establish that B3LYP, PBE, and BP86 density functionals with the 6-31+G** and 6-311++G** basis sets are capable of correctly predicting the ordering of relative selectivities. We emphasize that augmenting basis sets with diffuse functions is critical to accurately describe ligand affinity for Ln(III) and An(III). A complete reversal of the selectivity order for the studied ligands is obtained with the 6-31G* and 6-311G** basis set. In light of this, it is perhaps not surprising, that most of the previous studies employing basis sets that contain only polarization functions were unable to provide a reliable description of a small difference in the complexation energy between Eu(III) and Am(III). We note that the M06 family of density functionals (M06, M06-L) using B3LYP optimized geometries (see ESI for this choice) performed poorly in predicting the selectivity difference between **1b** and **2**. Finally, a comparison of the B3LYP results using large-core and small-core RECPs indicate that the choice of RECP has a significant impact on the relative binding energy for Am(III)/Eu(III) ions, with f electrons treated in the core resulting in the incorrect prediction of the selectivity difference between **1b** and nitrate anions.

Predicting the absolute Am/Eu selectivity of each extractant using Eq. 2 requires a determination of the difference in the hydration free energies of the two metal ions, $\Delta\Delta G_{hydr}(\text{Am/Eu}) = \Delta G_{hydr}(\text{Am}^{3+}) - \Delta G_{hydr}(\text{Eu}^{3+})$. In modeling solvation effects for multicharged ions, an important question arises as to whether $\Delta\Delta G_{hydr}$(Am/Eu) can be adequately represented by explicit treatment of the first solvation shell and implicit treatment of the rest of the solvent with a dielectric continuum model (COSMO). To address this question, it is instructive to compare the experimentally estimated and computed values of $\Delta\Delta G_{hydr}$(Am/Eu) for the following reaction

$$Am^{3+}_{(g)} + [Eu(H_2O)_n]^{3+}_{(aq)} = [Am(H_2O)_n]^{3+}_{(aq)} + Eu^{3+}_{(g)}, \quad \Delta\Delta G_{hydr}(Am/Eu) \tag{4}$$

The results shown in Table 2 indicate that our computed (B3LYP) values of $\Delta\Delta G_{hydr}$(Am/Eu) (19.9−21.1 kcal/mol) falls between the earlier experimental value from a compilation of Marcus[25] (17.4 kcal/mol) and a recently derived value from semiempirical data provided by David et al[50,51] (22.3 kcal/mol). Furthermore, we find that the degree to which Eu^{3+} is favored in water over Am^{3+} show little variance with the cluster size n and the extension of a basis set from 6-31+G** to 6-311++G**. In contrast, the results obtained with a relatively small 6-31G* basis set are not reliable, thus explaining the failure of the previous study[22] to yield accurate estimates of $\Delta\Delta G_{hydr}$(Am/Eu) from reaction (4).

Table 2. Changes in reaction energies for $Am^{3+}_{(g)} + [Eu(H_2O)_n]^{3+}_{(aq)} = [Am(H_2O)_n]^{3+}_{(aq)} + Eu^{3+}_{(g)}$ calculated (B3LYP) as a function of a basis set size and cluster size n (kcal/mol). Contributions from implicit solvation calculations ($\Delta\Delta G_{COSMO}$) and the sum of the gas phase and solvation contributions ($\Delta\Delta G_{hydr}(Am/Eu) = \Delta\Delta E_g(Am/Eu) + \Delta\Delta G_{COSMO}$) are shown

n	$\Delta\Delta G_{COSMO}$[a]	$\Delta\Delta G_{hydr}$(Am/Eu)			
		6-31G*	6-31+G**	6-311++G**	published data
8	2.10	3.07	20.36	20.43	
9	2.81	3.73	21.05	21.13	
20	0.77	-2.29	19.90	20.02	
Bulk limit estimate					17.4[b]; 22.3[c]

[a]Obtained at the B3LYP/SSC/6-31+G** level using COSMO solvation model. [b]Taken as the difference of the standard Gibbs free energies of hydration of Am^{3+} and Eu^{3+} from a compilation of Marcus[25]. [c]From semiempirical data provided by David et al.[50,51]

Table 3. Calculated and measured selectivities in the separation of Am^{3+} and Eu^{3+} by solvent extraction (kcal/mol). Computed selectivities are obtained as the changes in the free energies for reaction 2a ($\Delta\Delta G_{ext}$(Am/Eu))

complex	calc[a]	expt
$M(H_2O)_4(NO_3)_3$	0.861	~0[b]
M(**1b**)$_2$(NO$_3$)$_3$	-2.23	-1.53[c]
M(**2**)$_3$	-3.97	-6.82[d]

[a]Electronic energies are calculated at the B3LYP/SSC/6-311++G** level. Contributions from implicit solvation calculations for both the aqueous and organic phase are included at the B3LYP/SSC/6-31+G** level. [b]Estimated based on very similar complexation energies of Am^{3+} and Eu^{3+} with one NO_3^- ion in the aqueous phase.[49] [c]Based on a separation factor of 13.2 exhibited by ligand **1a** in 1,2-dichloroethane.[45] [d]Based on a separation factor of ~10^5 in trifluoromethyl phenyl sulfone.[7]

The values of $\Delta\Delta G_{ext}$(Am/Eu) are obtained by combining our best estimates of the gas-phase free energies calculated at the B3LYP/SSC/6-311++G** level (Table 1) with implicit solvent corrections for both the aqueous (Table 2) and organic phase included at the B3LYP/SSC/6-31+G** level. Table 3 shows a comparison of the calculated and experimental values of $\Delta\Delta G_{ext}$(Am/Eu). Overall, our computational protocol is able to reproduce higher affinity of the mixed O,N-donor and S-donor ligands for Am(III) over Eu(III) and rank-order their separation ability. It is important to note that no adjustable parameters were employed in these calculations, showing that ligand selectivity stems directly from the difference in the free energy of complexation. In contrast, a close agreement between the calculated experimental

$\Delta\Delta G_{ext}$(Am/Eu) would not be possible with the PBE and BP86 functionals without shifting the energy by a constant term to compensate for the stronger preference of Eu(III) over Am(III) in the gas phase compared to B3LYP results (by ~3.3 kcal/mol, as follows from the comparison of complexation energies shown in the second column of Table 1). Thus, while PBE and BP86 can still be used to predict relative separation abilities of different extractants (Table 1), only the B3LYP method when combined with the COSMO solvation model is able to predict absolute separation abilities for Am(III) and Eu(III).

Further validation of our theoretical model was carried out by comparison of the predicted and measured relative complexation energies of Am^{3+} and Eu^{3+} in the aqueous phase. Ligands with O- (oxalate, **3**[49]), mixed O, N- (dipicolinate, **4**[52]) , and N-donor (ADPTZ, **5**[53]) atoms were included in the analysis (Scheme 1). A competitive complexation of Am^{3+} and Eu^{3+} ions with these ligands was modeled according to reaction (5)

$$[Am(H_2O)_9]^{3+} + [Eu(ligand)(H_2O)_n]^{m+} = [Am(ligand)(H_2O)_n]^{m+} + [Eu(H_2O)_9]^{3+} \qquad (5)$$

Several initial geometries were built by substituting two and three water molecules in $[M(H_2O)_9]^{3+}$ by the corresponding bidentate and tridentate ligands, respectively. Geometry optimization revealed that in case of dianionic ligands, **3** and **4,** one or two water molecules were displaced from the first to the second coordination sphere to complex with the negatively charged O donor atoms (Figure S1 of ESI). Furthermore, it was noted that the oxalate ligand in $[Eu(\mathbf{3})(H_2O)_7]^+$ had a partially broken C−C bond (2.14 Å), a clear artifact of the gas-phase optimization. Adding two additional water molecules to solvate dianionic ligands was sufficient to remove calculation artifacts and stabilize each cluster in the nine-coordinate geometry (Figure 2). With these considerations, the results, Table 4, demonstrate that our theoretical prediction of aqueous complexation agrees closely with experimental measurements,[49,52,53] reproducing the selectivity of 'hard' O-donor ligands for Eu^{3+} and 'softer' polyazine ligands for Am^{3+}.

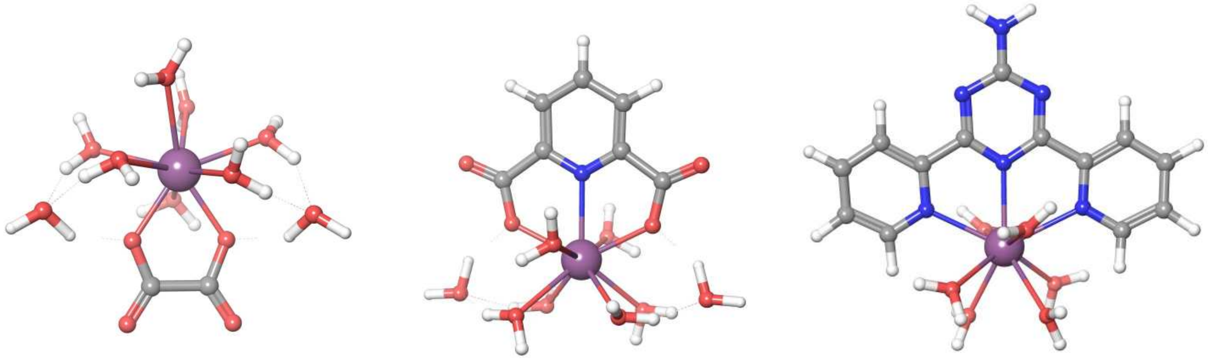

$[Am(oxalate)(H_2O)_9]^+$ $[Am(dipicolinate)(H_2O)_8]^+$ $[Am(ADPTZ)(H_2O)_5]^+$

Figure 2. Optimized structures for aqueous 1:1 metal ion-ligand complexes stabilized in the nine-coordinate geometry.

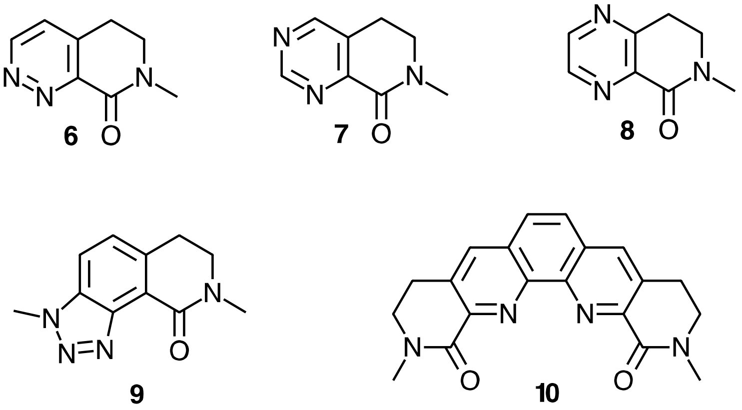
Table 4. Predicted and experimental differences in complexation free energies of O- and N-donor ligands with Am^{3+} and Eu^{3+} ions in aqueous solution (kcal/mol). Computed selectivities are obtained as the changes in the free energies for $[Am(H_2O)_9]^{3+}$ + $[Eu(ligand)(H_2O)_n]^{m+}$ = $[Am(ligand)(H_2O)_n]^{m+}$ + $[Eu(H_2O)_9]^{3+}$

ligand	$\Delta\Delta E^g_{compl}$(Am/Eu)	$\Delta\Delta G_{hydr}$(Am/Eu)	$\Delta\Delta G_{compl}$(Am/Eu)	
			calc[a]	expt
3, oxalate	4.30	-2.70	1.60	0.20[b]
4, dipicolinate	3.25	-2.36	0.89	0.0[b]
5, ADPTZ	0.47	-2.38	-1.91	-1.72[c]

[a] Calculated as the sum of the complexation energy differences ($\Delta\Delta E^g_{compl}$(Am/Eu)) and implicit solvent corrections ($\Delta\Delta G_{hydr}$(Am/Eu)) for the reaction. The number of water molecules n in the ligated complexes is 9, 8, and 6 for ligands **3**, **4**, and **5**, respectively (this choice is discussed in the text). [b] Measured in 1.0 M $NaClO_4$ in water.[49,52] [c] Measured in 1.0 M $NaClO_4$ in 75/25 vol % methanol/water.[53]

Having developed a computational method capable of interpretation of observed Am(III)/Eu(III) separation factors, we can now begin to examine the trends in selectivity for potential actinide-lanthanide separation agents. Compared to polyazine N-donor ligands,[3-5] mixed N,O-donor ligands formed by the addition of amide groups to N-heteroaromatic compounds offer potential advantages because the amide oxygen donor provides an increased metal binding affinity and allows application at lower pH by lowering the basicity of N-heteroatoms.[5,42-45] It was recently demonstrated that preorganization of prototype mixed-donor ligand, picolinamide, to give **1** resulted in a dramatic increase (~10^8-fold) in the strength of extraction of trivalent f-block metal ions while retaining a moderate selectivity for Am(III) over Eu(III).[45]

In a study of the factors controlling selectivity exhibited by polyazine extractants, it was shown that the average hardness of the azine donor groups correlated with observed selectivity trends.[24] This observation suggests the possibility of improving selectivity in preorganized N,O-extractants through variation of the N-heterocycle, a concept that can now be explored. The results of calculations of extractabilities ($\Delta G_{ext}(M)$) and selectivities ($\Delta\Delta G_{ext}(AM/Eu)$) for a series of mixed-donor ligands, **6-8**, with fused diazine and N-alkyl δ-lactam rings (Scheme 2) are shown in Table 5. The results predict that one of these derivatives, **6** (the softest diazine) would give a higher selectivity than **1**, although it is predicted to be a weaker extractant despite the fact that its intrinsic affinity (gas phase binding energy for 1:1 complex[24]) with La^{3+} is comparable to that of **1** (see Table S1 of ESI). After further screening of a number of amide-functionalized polyazine- and polyazole-based ligands, one candidate, consisting of fused 1,2,3-triazole, benzene, and δ-lactam rings, **9**, stood out as having the highest intrinsic metal-ion affinity. Computations for the 1:2 metal ion-extractant complex with counterions indicated that the extractability of **9** was similar to that of **1**, but more importantly, the selectivity for Am^{3+} over Eu^{3+} was significantly higher (Table 5). Additional improvements in the selectivity are expected through the use of higher denticity structures[54,55] that are preorganized for f-block metal ions, for example, **10**.



Scheme 2. Mixed O,N-donor ligands evaluated for Am/Eu separation using theoretical methods

Table 5. Calculated extraction energies represented by reaction 1b (ΔG_{ext}) and predicted selectivities of ligands **6**–**10** in the separation of Am^{3+} and Eu^{3+} ($\Delta\Delta G_{ext}$(Am/Eu)) by solvent extraction into kerosene (kcal/mol)

complex	ΔG_{ext}[a]		$\Delta\Delta G_{ext}$(Am/Eu)
	Am	Eu	
M(**1b**)$_2$(NO$_3$)$_3$	-23.66	-21.77	-1.89
M(**6**)$_2$(NO$_3$)$_3$	-16.60	-14.47	-2.14
M(**7**)$_2$(NO$_3$)$_3$	-18.39	-16.84	-1.55
M(**8**)$_2$(NO$_3$)$_3$	-19.62	-18.10	-1.53
M(**9**)$_2$(NO$_3$)$_3$	-21.36	-18.92	-2.44
M(**10**)(NO$_3$)$_3$	-22.23	-20.53	-1.70

[a] Calculated as the sum of the electronic energy differences (ΔE^{g}_{ext}) and implicit solvation corrections ($\Delta\Delta G_{hydr}$) for reaction 1a, where the hydrated metal ion is represented as $[M(H_2O)_9]^{3+}$.

Conclusions

At present, experimental research programs aimed at improving the performance of separation processes for minor actinide recovery are mostly empirical in nature. Although several ligand descriptors are proposed in the literature to correlate with the observed An/Ln selectivity (polarizability, the energy of the highest occupied molecular orbital, hardness), the range of applicability of these parameters is unknown. Another approach invokes different bonding analysis descriptors to rationalize small differences in binding of Eu^{3+} and Am^{3+}. However, no clear consensus has emerged from these studies and different tools often yield conflicting results. In this work, we took a more straightforward approach to calculate An(III)/Ln(III) selectivities as the differences in complexation energies between the extractants and metals. Examination of several DFT methods established a computational protocol capable of predicting the correct order of selectivities for six oxygen, mixed oxygen-nitrogen, and sulfur donor ligands obtained from liquid-liquid extraction and aqueous phase complexation studies. To allow reasonably accurate predictions, it was critical to employ sufficiently flexible basis sets and provide proper account of solvation effects. The results have important practical consequences for effective An(III)/Ln(III) separation, providing a theoretical basis for detailed understanding of ligand selectivity and targeting the design of more efficient and selective extractants. Computational screening of several mixed-donor extractants formed by covalently linking several aromatic nitrogen heterocycles with an amide group allowed the identification of a new ligand, **9**, that can potentially have one of the highest separation efficiencies among bidentate mixed-donor extractants.

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Electronic Supplementary Information (ESI) Available: Complete reference 39, additional computational details, calculated bond distances to Am^{3+} and Eu^{3+}, gas-phase interaction energies with La^{3+}, structures of the selected optimized complexes, optimized geometries and absolute energies (in Hartrees) for all metal-ion complexes obtained at the B3LYP level.

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