Unprecedented Inversion of Selectivity and Extraordinary Difference in the Complexation of Trivalent *f* Elements by Diastereomers of a Methylated Diglycolamide

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Abstract: When considering *f* elements, solvent extraction is primarily used for the removal of lanthanides from ore and their recycling, as well as for the separation of actinides from used nuclear fuel. Understanding the complexation mechanism of metal ions with organic extractants, particularly the influence of their molecular structure on complex formation is of fundamental importance. Herein, we report an extraordinary (up to two orders of magnitude) change in the extraction efficiency of *f* elements with two diastereomers of dimethyl tetraoctyl diglycolamide (Me_2-TODGA), which only differ in the orientation of a single methyl group. Solvent extraction techniques, extended X-ray absorption fine structure (EXAFS) measurements, and density functional theory (DFT) based ab initio calculations were used to understand their complex structures and to explain their complexation mechanism. We show that the huge differences observed in extraction selectivity results from a small change in the complexation of nitrate counter-ions caused by the different orientation of one methyl group in the backbone of the extractant. The obtained results give a significant new insight into metal–ligand complexation mechanisms, which will promote the development of more efficient separation techniques.

Introduction

New solvent extraction techniques for the separation of highly radiotoxic nuclides from used nuclear fuel or contaminated wastewater from sites of nuclear accidents are intensively studied worldwide.[1] The separation of trivalent actinides from lanthanides is one of the most challenging tasks, due to the chemical similarity of these two groups of elements. The separation of Am^{3+} from Cm^{3+} is in equal measure very difficult owing to the similar ionic radii. Nevertheless, Am/Cm separation has gained tremendous interest, as the separation and recycling of Am (without Cm) in advanced nuclear fuel cycles was shown to have a major impact on the size (volume and footprint) and cost of a geological disposal facility for high level nuclear waste.[2] Furthermore, the recycling of lanthanides from end-of-life products is very important to reach a sustainable economy.[3] Consequently, different types of ligands have been developed for the selective complexation of actinides and lanthanides.[4] For this purpose we have focused on diglycolamides both as individual ligands[5] and as pre-organized species on a molecular platform.[6]

Diglycolamides are widely used in solvent extraction for the separation of trivalent lanthanides and actinides from used nuclear fuel solutions.[4c] One of the most prominent members of the class of diglycolamides used for this purpose is TODGA (*N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide).[7] A large number of derivatives has been studied to date, with main focus on derivatization of the amidic side chains.[4c] Additionally, we are interested in understanding the influence of modifications in the central backbone of the diglycolamides. In particular, methylated derivatives were found to be suitable ligands for solvent extraction processes, as they show lower co-extraction of unwanted metal ions (especially Sr^{2+})[5a,b] and higher loading capacity for

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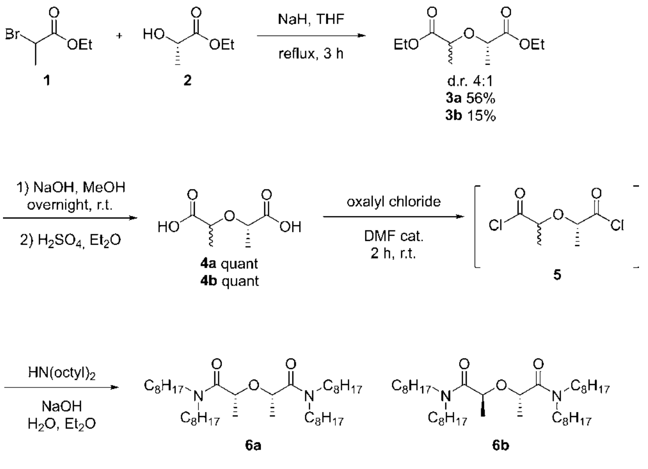
example, towards Pu loading. Consequently, the development of new processes for grouped actinide extraction utilizing methylated diglycolamide ligands has become quite topical.[8]

A paucity of information exists regarding the complexation behavior of individual diastereomeric ligands. In the case of two diastereomers of 1,4,7-triazacyclononane-1,4,7-tris-(glutaric acid) no difference was found in the complexation reaction with $^{67}GaCl_3$ and the affinity for $\alpha_v\beta_3$ integrin.[9] Similar conclusions were reached by Sun et al. in the case of diastereomerically pure bifunctional chelators for copper radiopharmaceuticals.[10] Ishimori et al. described the extraction of Am^{3+} and Eu^{3+} with different diastereomers of a tripodal pyridine ligand and observed differences in metal extraction of a factor of 2–3.[11] Yamada et al. studied the lanthanide complexation and luminescence behavior of un-, mono-, and disubstituted tripodal pyridine ligands and found that their complexation behavior was “rarely influenced by ligand chirality” with an enhancement in Tb luminescence of approximately three times for one diastereomer over the other.[12] Crown ether compounds are known to show very high selectivity for metal ions with ionic radii fitted to the cavity size of the crown compound. Differences in the extraction with the *cis-syn-cis* and *cis-anti-cis* isomers of dicyclohexano-18-crown-6 (DCH18C6) were found for the extraction of Ca^{2+}, Sr^{2+} Ba^{2+}, Ra^{2+}, and K^{+}, [13] and Pu^{IV}[14] ranging between a factor of 2–3. Bond et al. studied the extraction of Ca^{2+}, Sr^{2+}, and Ba^{2+} in a synergistic system of four stereoisomers of DCH18C6 with di-*n*-octylphosphoric acid (HDOP). Due to the combination of the high selectivity of HDOP and the crown compounds, differences in the extraction of up to a factor of ca. 100 were observed. However, no explanation for the observed differences were provided in any of the cases.

We report an extraordinary difference in the extraction efficiency of trivalent *f* elements and even a reverse in selectivity for trivalent actinide (i.e., Am^{3+}, Cm^{3+}) extraction for two diastereomers of dimethyl tetraoctyl diglycolamide (Me_2-TODGA), a derivative of the well-known TODGA, differing only in the orientation of a single methyl group. We investigate the origin of this phenomenon by a combination of solvent extraction techniques, EXAFS analysis, and quantum chemical calculations.

Results and Discussion

We previously reported the synthesis of Me_2-TODGA **6** as a mixture of diastereomers.[5a] The major diastereomer was isolated and its behavior and complex stoichiometry towards trivalent lanthanide and actinide extraction was studied.[5a,b] In the current study, the individual diastereomers were prepared *via* a slightly modified procedure from 2-bromopropionate (**1**) and ethyl (*S*)-lactate (**2**) (Scheme 1). Compound **1** was reacted with **2** to give the diesters **3** in a diastereomeric ratio of 4:1, which were isolated by flash chromatography. Apparently, lactate **2** reacts faster with one of the enantiomers of **1** as opposed to the other. The unreacted lactate **2** undergoes racemization, which is known to occur for α-bromo esters in the presence of Br^-.[15] Saponification of the ester groups in **3a**,**b** afforded the dicarboxylic acids **4a**,**b**. Using the recently developed approach involving Schotten–Baumann conditions,[16] **4a**,**b** were converted into the target ligands **6a** and **6b** *via* the in situ prepared diacyl dichlorides, in 50 % and 68 % yield, respectively.



Scheme 1. Synthesis of the Me_2 TODGA ligands **6a** and **6b**.

Both diastereomers **6a** and **6b** are symmetrical, which is reflected in their ^1H NMR spectra (Figure 1 a,b), although they are not easily distinguishable because of their free rotation. However, upon addition of lanthanum(III) triflate ($La^{III}(OTf)_3$), the corresponding complexes were formed, locking the ligands and preventing rotation. In the case of the La^{3+}-complex of **6a**, the symmetry in the ^1H NMR spectrum is broken, whereas that of the La^{3+}-complex of **6b** is maintained (Figure 1 c,d). Subsequently, we conclude that **6a** and **6b** have C_s and C_2 symmetry, with *RS*- and *SS*-configuration, respectively. Complexation of the ligands with La^{3+} *via* the amide carbonyl groups induces a change in their geometry. In the case of **6a**, steric hindrance of the two central methyl groups will force the molecule in a twisted position upon complexation, resulting in the loss of symmetry. Upon complexation of **6b**, the methyl groups will only move further apart, whilst maintaining the symmetry.

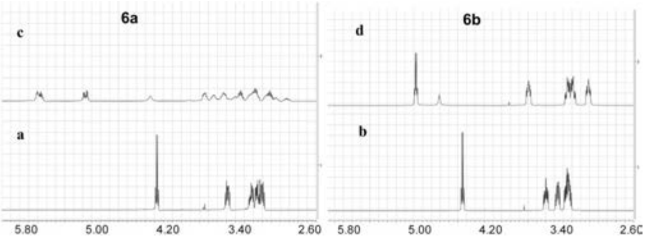


Figure 1. 600 MHz ^1H NMR spectra in $CDCl_3$ of a, b) the free ligands **6a** and **6b** and c, d) upon addition of excess $La^{III}(OTf)_3$.

Both diastereomers **6a** and **6b** were tested as extractants in solvent extraction experiments dissolved in TPH (hydrogenated tetrapropene) for the extraction of $^{241}Am^{3+}$, $^{244}Cm^{3+}$, and $^{152}Eu^{3+}$, as well as 10^{-5} mol L^{-1} of each lanthanide (w/o Pm, incl. Y + La) from HNO_3 solution. Me_2-TODGA is a relatively weak extractant in comparison to the parent molecule TODGA[7a,17] and the mono-methylated analogue Me-TODG-

A.[5a,b] Significant distribution ratios (the ratio of activity or concentration of a metal ion in the organic phase versus that in the aqueous phase) for the studied metal ions are only reached at relatively high HNO_3 concentrations of $\geq 2\ \text{mol L}^{-1}$.

Figure 2 shows the distribution ratios of Am, Cm, Y, La and other lanthanides (w/o Pm) as a function of the inverse ionic radius for nine-fold coordination[18] for the extraction from $4.3\ \text{mol L}^{-1}$ HNO_3 using $0.1\ \text{mol L}^{-1}$ **6a** (blue) and **6b** (red) in TPH. Figure 2 shows that the distribution ratios mostly increase with decreasing ionic radius of the extracted metal ion. This behavior is generally observed for diglycolamides used in solvent extraction and has also been observed before for the methylated TODGA analogues.[5b] Diastereomers **6a** and **6b** show a maximum in the distribution ratios for Ho, similar to previous observations.[5b] We already reported on a shift of the maximum of distribution ratios by successive introduction of additional methyl groups into the TODGA backbone.[5b]

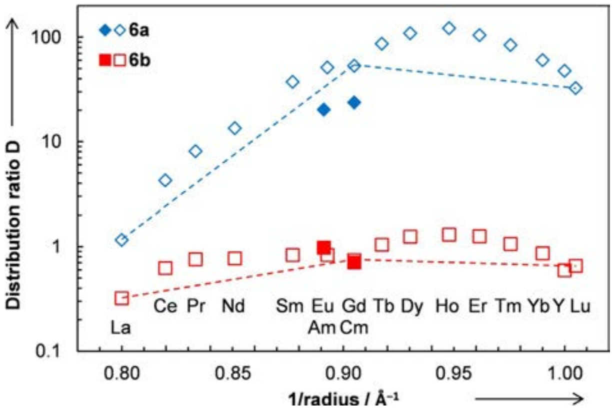


Figure 2. Distribution ratios of Am, Cm (filled symbols), Y, La, and other lanthanides (w/o Pm, open symbols) as a function of the inverse ionic radius for the extraction from $4.3\ \text{mol L}^{-1}$ HNO_3 using $0.1\ \text{mol L}^{-1}$ **6a** (blue) and **6b** (red) in TPH.

When the extraction efficiencies of the two diastereomers, **6a** and **6b**, are compared, a large and, to our knowledge, unprecedented difference is observed. **6a** shows much higher distribution ratios than **6b**, with the largest difference a factor of 94 greater observed for Ho. Furthermore, the variation in distribution ratios for the lanthanides examined with **6a** and **6b** is far greater for the former diastereomer.

Diastereomer **6a** shows a preference for the extraction of Cm^{3+} over Am^{3+} with a separation factor $SF_{Cm/Am}$ of 1.4. To our knowledge, a preference for Cm^{3+} complexation was always observed for related diglycolamides (even water-soluble ones).[4c,7a,19] As such, this is the first report on a diglycolamide (diastereomer **6b**) showing a preference for Am^{3+} over Cm^{3+}.

As the two diastereomers **6a** and **6b** only differ in the orientation of a single methyl group, the significant variation in extraction performance is apparently a consequence of this subtle structural difference. Based on our previous findings, we postulate that diastereomers **6a** and **6b** both form 1:3 metal/ligand complexes in the organic phase, with the central metal ions bound through the three oxygen donor atoms of each ligand, resulting in an overall nine-fold coordination.[5b] Nitrate ions, required for charge compensation, are presumably located in the outer shell of the complexes, as no direct nitrate coordination was found by spectroscopic methods or single-crystal structure analyses in the inner-sphere of comparable complexes.[20] Consequently, we argue that the specific interaction of the metal-ligand complex with the nitrate anions is controlled by the orientation of the additional methyl groups in Me_2-TODGA complexes bound with *f* elements, which causes the observed differences in extraction performance. Additional to this, the Gd break and tetrad effects[21] further influence the complexation process of the lanthanides with diastereomers **6a** and **6b**. The dashed lines in Figure 2 illustrate these effects and contributions to the distribution ratio. The Gd break is explained by the half-filled electron shell for Gd and the tetrad effect is related to observations that certain liquid-liquid extraction systems show discontinuities grouping the lanthanide behavior in four tetrads.[21] The observed inversion of Am/Cm selectivity could therefore be caused by the combined effects of complexation with **6a** or **6b** and the Gd break and tetrad effects.

To further understand the extraction mechanism, the molecular structure of the extracted complexes, and the observed differences in the extraction efficiency with **6a** and **6b**, we conducted EXAFS measurements and DFT-based ab initio calculations to gain better insight into structures and thermodynamics parameters of the metal–ligand complexation.

EXAFS measurements were conducted on organic solution samples of metal complexes (La^{3+}, Eu^{3+}, Er^{3+}, and $^{243}Am^{3+}$) with **6a** and **6b**, which were prepared by solvent extraction to give sample compositions as representative for separation process application as possible. The sample preparation procedure and EXAFS measurements are described in the Supporting Information. The structural models required to evaluate the EXAFS data were built from the complex structures resulting from the DFT calculations (see below). They represent the final relaxed structures of the 1:3 metal–ligand complexes. To obtain a good description of the complex structures, we applied PBEsol exchange-correlation functional,[22] which by design results in better predicted molecular structures than other standard DFT functionals, including PBE.[23] These structural models gave very good fits to the experimental EXAFS data (Figures S1, S2, and Table S1). The obtained number of scattering atoms and bond lengths agree well with the theoretical results. Figure 3 shows the bond distances between the central metal ions and the first coordination shell oxygen atoms for **6a** and **6b**. For both ligand diastereomers, a decrease in M–O bond distance is observed as a function of the inverse ionic radius of the central metal ion. This is a result of the lanthanide contraction. Ligand **6a** yields lower bond distances compared with **6b**, reflecting the stronger complexation of **6a**. Ligand **6b** exhibits a slightly steeper dependency of the M–O bond distance as a function of the inverse ionic radius of the central metal ion. The average M–O distances of ligands **6a** and **6b** are slightly larger than related distances reported for TODGA complexes.[20b] This reflects a significantly

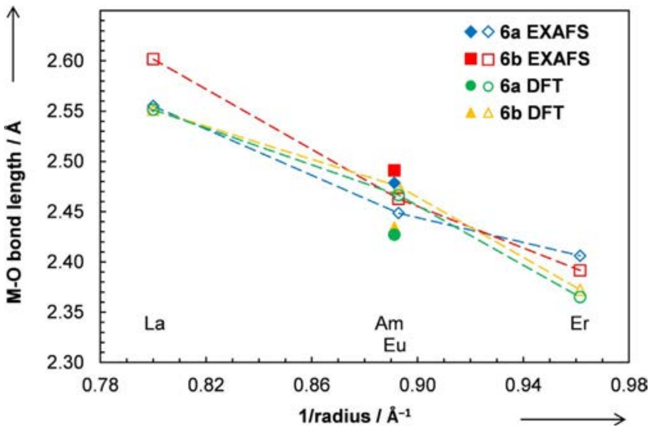


Figure 3. Bond lengths between central metal ion and first coordination shell oxygen atoms (mean values) of ligands **6 a** (blue/green) and **6 b** (red/yellow), as determined by EXAFS measurements and DFT calculations for Am (filled symbols), La, Eu, and Er (open symbols) as a function of the inverse ionic radius. A tabular representation is given in Table S2.

larger steric demand of ligands **6 a** and **6 b**, due to the additional methyl groups.

Based on the good agreement between EXAFS structures and the DFT-based calculations, we conclude that 1:3 metal–ligand complexes are formed in organic solution with diastereomers **6 a** and **6 b**. Furthermore, these results support our previous argument that the difference in orientation of the methyl groups in the ligands is the key structural feature behind the observed differences in affinity and selectivity for the extraction of trivalent actinide and lanthanide ions with diastereomers **6 a** and **6 b**.

We attempted to understand the underlying mechanisms causing the difference in the extraction performance of the two diastereomers using systematic DFT calculations (PBE functional[23]) of the metal-ion complexes and the related compounds.

First, we computed the enthalpies of the extraction reaction [Eq. (1)]:

$$[\mathrm{M(H_2O)_9}]^{3+}_{aq} + 3\mathrm{Me_2} \quad \mathrm{TODGA} + 3\mathrm{NO_3^-} \rightarrow [\mathrm{M[Me_2\text{-}TODGA)_3(NO_3)_3}]_{\mathrm{org}} + 9\mathrm{H_2O} \tag{1}$$

and the difference between the cases with the two diastereomers, given by Equation (2):

$$\mathrm{E([M(\mathbf{6\,a})_3(NO_3)_3])} \quad \mathrm{E([M(\mathbf{6\,b})_3(NO_3)_3])} \quad 3\cdot(\mathrm{E_{\mathbf{6\,a}}} \quad \mathrm{E_{\mathbf{6\,b}}}) \tag{2}$$

The results are given in Figure 4. For both diastereomers, the computed reaction enthalpies decrease along the lanthanide series. However, the reaction enthalpies in the case of **6 a** are lower, which indicates a higher stability of M ($\mathbf{6\,a}$-$\mathrm{NO_3^-}$)$_3$ complexes and a higher extraction ability, which is observed experimentally. Since the difference between the diastereomers **6 a** and **6 b** in the reaction [Eq. (1)] is just the orientation of methyl groups, we assume a negligible reaction entropy difference for the two cases and conclude that the difference in the reaction Gibbs free energies can be estimated by the difference in the reaction enthalpies. The computed $\Delta\Delta H$ (difference of ΔH values for complexes with diastereomers **6 a** and **6 b**) is ca. 10 kJ mol^{-1}. This should correspond to a factor of ca. 50 difference in the distribution ratios with diastereomers **6 a** and **6 b** (applying Boltzman distribution assuming ambient conditions (kT ≈ 2.5 kJ mol^{-1}) (Eq. (3)):

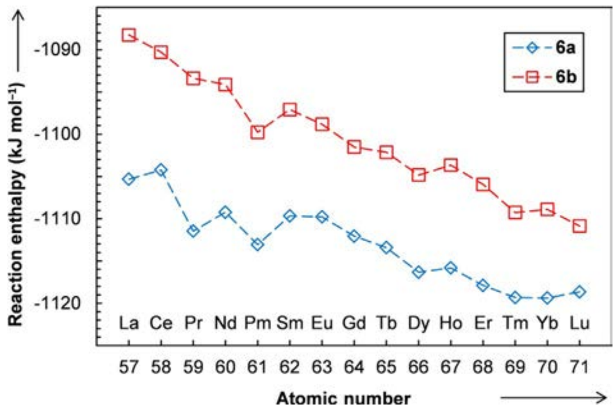


Figure 4. Computed enthalpy of reaction [Eq. (1)] with diastereomers **6 a** (blue) and **6 b** (red).

$$\frac{\mathrm{D_{M,6a}}}{\mathrm{D_{M,6b}}} = e^{\frac{10}{2\,5}} \approx 50 \tag{3}$$

This is consistent with the average ratio of the distribution ratios measured for diastereomers **6 a** and **6 b** for Sm Lu (values between 44–94) and shows that DFT can capture the considered reaction also on the quantitative level. However, we note that our DFT studies cannot explain the subtle differences observed between the extraction results for the lighter lanthanides La Nd (values between 4–17). This could potentially be attributed to a different number of co-extracted water molecules for the heavier lanthanides, as described recently by Baldwin et al.[24] The effect of co-extracted water is not accounted for in our DFT calculations, as the water content was not assessed during the solvent extraction experiments.

The DFT data presented in Figure 4 do not show the experimentally observed slight decrease of the distribution ratios around Gd and Lu. However, these effects likely result from the tetrad effect[21] and probably have their origin in the subtle differences in the electronic structure, especially of *f* electrons, which is not taken into account by the standard DFT methods. The effect of *f* electrons is minimal for La^{3+}, Gd^{3+}, and Lu^{3+}, because these elements in the trivalent state have either no *f* electrons, half-, or fully-filled *f* shells, respectively.[25] This also explains the observed inversion of selectivity in the extraction of Am^{3+} and Cm^{3+}. Given that Cm^{3+} has a half-filled 5*f* shell, the *f*-electron effect is zero, leading to a lower extraction with **6 b** compared to Am^{3+}. With **6 a**, however, the steeper increase in the extraction of La^{3+} Gd^{3+}, as shown by the dashed lines in Figure 2, leads to a higher extraction of Cm^{3+} compared with Am^{3+}, despite of the tetrad effect.

The electrostatic interaction between the metal cation and the extractant is one of the factors influencing the selectivity. If this would be the only factor, we should expect to see a linearly increasing trend in the measured distribution ratios along the lanthanide series. However, experimental studies of the extraction of trivalent lanthanides with diglycolamides (especially TODGA) show an increase of the distribution ratios for light lanthanides and nearly constant ones for heavier ones.[24] This is also clearly visible in our data using diastereomers **6a** and **6b** (Figure 2). Recently, it was shown by Baldwin et al. and Ellis et al. that this trend in distribution ratios is determined by interactions of water and nitrate in the outer-sphere. They called this effect "aqueous phase selectivity".[24,26] Consistent with the previous findings,[24] these values increase along the lanthanide series, resulting in an increased selectivity towards the heavier lanthanides (details are described in the Supporting Information).

Other factors known to influence the performance of organic extractants are the HOMO-LUMO levels and their related parameters.[27] We thus computed the electronic structures and HOMO-LUMO energies of the two diastereomers, **6a** and **6b**, and the metal-ligand complexes. These are given in Tables S3 and S4. Interestingly, the HOMO-LUMO parameters of the diastereomers themselves are nearly identical; showing that there is no difference in the absolute electronegativity and hardness that could lead to a possible explanation of the different performance of the two diastereomers.[27a] The only significant difference involves the energy of the HOMO levels and the band gap of the M (Me$_2$-TODGA-NO$_3$)$_3$ complexes. While these parameters do not vary significantly between different metal ions, they are significantly different for the two diastereomers. For diastereomer **6a**, the average HOMO and HOMO-LUMO gap are 4.3 and 2.9 eV, respectively, whereas for diastereomer **6b** they are 3.9 and 2.2 eV, respectively. These values already indicate the enhanced stability of M (Me$_2$-TODGA-NO$_3$)$_3$ complexes with diastereomer **6a**. This may result from slightly shorter metal oxygen bond lengths (steric effect). As shown in Figure S5, DFT calculations showed only a slight difference in the M O_{in} bond lengths for **6a** and **6b** complexes, whereas a slightly higher difference in the EXAFS measurements (Figure 3) was observed with **6a** complexes, yielding slightly shorter M O_{in} bond lengths. Thus, the coordination of metal cation alone cannot be responsible for the differences in the HOMO-LUMO levels.

To understand the difference in the HOMO levels of the considered metal–ligand complexes, we studied the origin of the HOMO state. The HOMO state of the La (**6a**-NO$_3$)$_3$ complex is plotted in Figure 5, where it is composed only of *p*-orbitals of outer oxygen atoms belonging to the NO$_3^-$ groups. It is clearly visible in the plots of the DOS (Figure S4) that the only contributors to the HOMO level are the O_{out} atoms. This indicates that the arrangement of nitrates in the complexes and interaction of the outmost parts of the complexes with the organic solution is a main effect driving the stability of the metal–ligand complexes. Notably, calculations of the La (**6a**)$_3^{3+}$ and La (**6b**)$_3^{3+}$ complexes without nitrate groups resulted in La (**6b**)$_3^{3+}$ being significantly more stable. This suggests that the nitrate anions have a significant influence on the relative stability of the considered M-ligand complexes. Comparison of the relaxed structures of the La (**6a**)$_3^{3+}$ and La (**6b**)$_3^{3+}$ with the La (**6a**-NO$_3$)$_3$ and La (**6b**-NO$_3$)$_3$ complexes showed that the orientation of the backbone methyl groups caused a structural change in the nitrate coordination. In the case of diastereomer **6b**, the steric interaction between the methyl and nitrate groups is increased, which apparently causes the reduced complexation strength observed experimentally and in the DFT calculations. This also explains why diastereomer **6a** yields stronger complexes, although the NMR study of La^{III}(OTf)$_3$ complexes (Figure 1) suggests a higher stability of complexes with diastereomer **6b**.

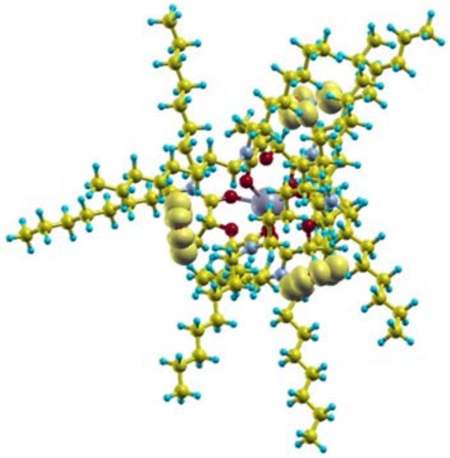


Figure 5. HOMO state in the La (**6a** NO$_3$)$_3$ complex. The only contributors are the *p* states of oxygen atoms from nitrates.

Our results are fully in line with the conclusions of a recent theoretical investigation on the complexation of metal ions with *N*,*N*,*N′*,*N′*-tetraethyl diglycolamide (TEDGA) ligands by Baldwin et al.[24] They state that the M NO$_3^-$ distance is an important indicator of the extraction selectivity.[24] Therefore, we plotted the average M N(NO$_3^-$) distances in Figure 6. Interestingly, we observe a larger variation in the M N_{out} distance values for **6a** complexes than for **6b** complexes, which is consistent with the larger variation of the distribution ratios for **6a** (ca. 100) than for **6b** (ca. 10). For **6a**, the average M N_{out} bond

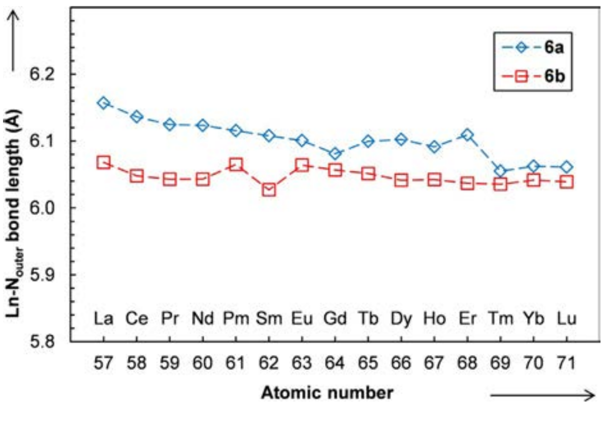


Figure 6. Computed average Ln N_{out} bond length between lanthanide cation and three outer nitrate groups.

lengths vary from 6.15 Å (La) to 6.06 Å (Lu). For **6 b**, they are roughly constant, but consistently smaller than for **6 a**. This also causes large differences in the solvation energy of the metal ion complexes with **6 a** and **6 b** (Figure S6). Apparently, the additional methyl groups in the backbone of the extractants partly hinder the approach of nitrate counter ions to the metal ions. This effect is more pronounced for diastereomer **6 a**. Furthermore, the distance between the closest methyl groups and nitrate anions is much shorter for diastereomer **6 b**, resulting in steric repulsion between methyl group and nitrate anion, and consequently in the lower complexation strength. This finding is consistent with the shorter $M-N_{NO3}$ distances of ca. 5.3–5.4 Å reported by Baldwin et al. for unsubstituted TEDGA complexes[24] and Reilly et al. for a $Pu^{IV}(TMDGA)_3(NO_3)_4$ complex crystal structure.[20e]

We also have searched for any substantial differences in the ion structure of the complexes. For this purpose, we computed the Löwdin charges on each atom,[28] showing no significant differences between diastereomers **6 a** and **6 b**. However, the small variation of the charge on the metal ions (observed for both **6 a** and **6 b**), and shown in Figure S7, indicates an enhanced stability of the complex going along the lanthanide series.

Theoretical investigations demonstrate the importance of the NO_3^- anions and the interaction of the complex with the organic medium for the stability of the M-Me_2-TODGA complexes. We note that the complex–organic medium interaction in our calculations (model) is approximated by interaction of the complex with the continuum, polarizable medium. Such a simple approximation may be missing some additional factors that could lead to the measured variation of the extraction along the lanthanide series. Baldwin et al. have shown the importance of the interaction of the complex with H_2O molecules, which leads to different amounts of co-extracted water.[24] This effect, however, is difficult to model accurately on the DFT level and is not in the scope of this paper. Its omission does not affect the results or conclusions of this paper.

Conclusion

Our study shows a large difference in extraction efficiency of trivalent actinides and lanthanides by two diastereomers of Me_2-TODGA, which only differ in the stereochemical orientation of a single methyl group. In the case of Am/Cm there is an inversion in selectivity, which we explained by a combination of Gd break and tetrad effect. From a combination of EXAFS analysis and DFT-based *ab initio* calculations, we conclude that the observed difference in complexation is caused by a change in the complexation of nitrate ions that is induced by the different orientation of the methyl groups in the backbone of the ligands. To our knowledge, the herein reported large difference in complexation and extraction behavior of two diastereomers is unprecedented and will have a wide impact on the design of better organic extractants and will promote the development of more efficient separation techniques. The impact of a change in the counter ion from nitrate to, for example, ClO_4^- would be of strong interest for further investigation.

Experimental Section

Details of the synthesis of diastereomers **6 a** and **6 b**, experimental procedures and analytical details, as well as details of the DFT calculations are described in the Supporting Information.

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Conflict of interest

The authors declare no conflict of interest.

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