Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Matloka, Kornelia , Gelis, Artem , Regalbuto, Monica , Vandegrift, George and Scott, Michael J.(2006) 'C_3-Symmetric Tripodal Thio/Diglycolamide-Based Ligands for Trivalent f-Element Separations', Separation Science and Technology, 41: 10, 2129 — 2146

To link to this Article: DOI: 10.1080/01496390600745727

URL: http://dx.doi.org/10.1080/01496390600745727

Separation Science and Technology, 41: 2129–2146, 2006
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ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600745727

C_3-Symmetric Tripodal Thio/Diglycolamide-Based Ligands for Trivalent f-Element Separations

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Abstract: Three new C_3-symmetric ligands bearing diglycolamide and thiodiglycolamide units on a triphenoxymethane platform have been synthesized and evaluated as trivalent f-element extractants from nitric acid media. Liquid-liquid extraction studies of eleven different lanthanides from 1 M nitric acid into dichloromethane revealed a strong influence of the amidic substituents on the extraction efficiency. A comparison of the ^{1}H NMR spectrum of the Lu(III) complex formed with the tris-DGA ligand and the organic solution after the extraction experiment confirms that all three arms bind the metal during the extraction experiment and form a C_3-symmetric complex. The newly synthesized lipophilic di-n-butyl tris-diglycolamide was found to be a significantly weaker extractant in comparison to the di-isopropyl analogs. The distance separating the metal binding groups from the triphenoxymethane platform had little influence on the selectivity or binding efficiency of the ligands. Experiments with the tris-thiodiglycolamide derivative highlighted the importance of the etheric oxygens for metal binding.

Keywords: Extraction of lanthanides and actinides, nuclear waste separations, diglycolamide, thiodiglycolamide, C_3-symmetric ligand

Received 21 October 2005, Accepted 2 March 2006

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INTRODUCTION

In the view of the ever-increasing use of nuclear power around the world, an accelerated development of effective protocols for waste treatment increasingly becomes imperative. Perhaps, one of the most significant obstacles faced in separation science is partitioning of minor actinides. Decades of work have been dedicated to the development of amidic extractants for the f-element liquid-liquid waste separations (1–13). Recently, a significant interest has been focused on one particular group of amides-diglycolamides (DGA) (14–29). These completely incinerable tridentate, neutral chelates are much more effective in coextraction of lanthanides and minor actinides than commercially operating DIAMEX extractants (11, 30–37). Moreover, unlike other diamide-based compounds, DGAs exhibit significant selectivity within the lanthanide series and track the increase in charge density (19, 21, 22, 26, 27, 29). With this ability to selectively bind metals within the series, DGAs offer many potential applications in analytical chemistry in addition to waste separations. The further refinement of diglycolamide based chelators and careful investigation of their binding potential may help greatly improve efficiency of the lanthanide/actinide coextraction process, and a fundamental understating of the remarkable selectivity of DGA may help in the development of improved methods for partitioning of minor actinides.

Two to four molecules of diglycolamides appear to be involved in the coordination of trivalent f-element ions during the extraction from nitric acid solution (19, 23, 26, 29). Thus, the extraction efficiency could be further improved by the preorganization of several ligating units onto some molecular platform, as it was observed in some cases of carbamoylmethylphosphineoxide (CMPO)-based extracts (38–44).

Recently, a new C_3-symmetric molecule (**1**) was synthesized with three diglycolamide moieties bearing two isopropyl groups attached to each of the terminal amidic nitrogen (tris-DGA)/(45), precisely arranged on a triphenoxymethane platform (46) (Diagram 1). Extraction experiments with this molecule revealed a slowly ascending affinity for trivalent lanthanides typical of the commonly studied DGA derivatives, but a marked increase in binding efficiency was noted. Remarkably, a ten–fold excess of ligand **1** with respect to metal ion afforded a quantitative extraction of the heaviest of lanthanides (Er, Tm, and Yb) from a 1 M nitric acid to the dichloromethane. To achieve similar results typically ~100,000 : 1 DGA to metal ion concentration ratio is required (e.g. 0.1 M N,N'-dimethyl-N,N'-diphenyl-3-oxapenanediamide, 10^{-6} M Ln(III)) (19). Furthermore, at only a 1:1 tris-DGA to metal ratio over two–thirds of Tm(III) and Yb(III) originally held in the 1 M HNO_3 phase was transferred into organic layer.

This article presents the synthesis of three new C_3-symmetric tris-diglycolamide compounds and their evaluation as extractants in f-element separations. The influence of the flexibility and lipophilicity of DGA arms in the

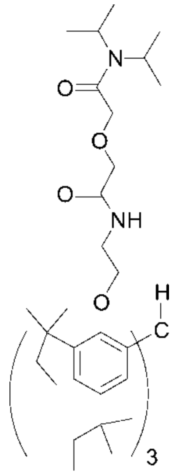

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Diagram 1.

ligand on the extraction profile has been investigated. To verify the contribution of the etheric oxygens to the tris-DGA binding efficiency, a new C_3-symmetric derivative containing a sulfur in the place of the etheric oxygen has been synthesized, and the extraction properties have been tested on a series of eleven lanthanides and ^{152}Eu and ^{241}Am radioisotopes. In addition, the investigation of the metal coordination environment of the solid state Yb(III) and Ce(III) complexes with ligand **1** (45). has been extended over newly synthesized Eu(III) complex with **8,** and the complex properties are presented herein.

EXPERIMENTAL

General Considerations

The lanthanide and actinide salts were used as received. The solutions were prepared from 18MΩ Millipore deionized water, TraceMetal grade HNO_3 (Fisher Scientific), and HPLC grade dichloromethane (Fisher Scientific). A Varian Cary 50 UV/Vis spectrophotometer was used for the Arsenazo(III) assays. Elemental analyses were performed at the in-house facility of Department of Chemistry at University of Florida. The ^{1}H, ^{13}C, and spectra were recorded on a Varian VXR-300 or Mercury-300 spectrometer at 299.95 and 75.4 MHz for the proton and carbon channels respectively. Mass spectrometry samples were analyzed on a Bruker Apex II 4.7T Fourier transform ion cyclotron resonance mass spectrometer.

^{1}H NMR Experiment

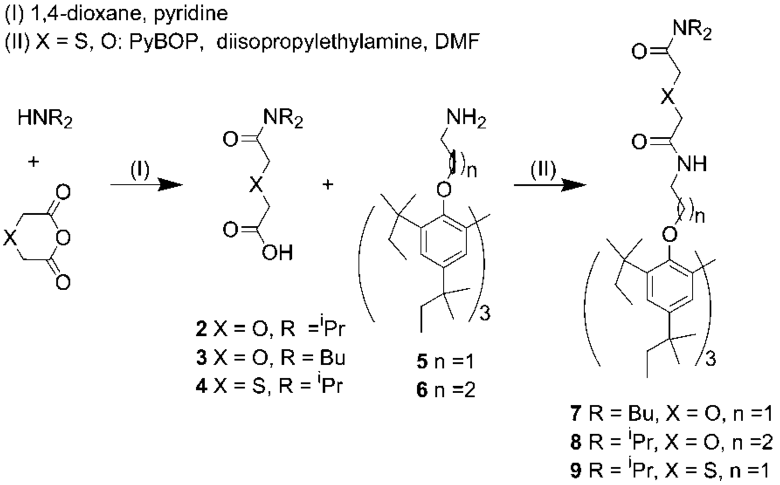
Equal volumes of 10^{-2} M solutions of $Lu(NO_3)_3$ in 1 M nitric acid and Tris-DGA (**1**) in D2-dichloromethane were mixed for 2 h. The second portion of the same 10^{-2} M solution of **1** in D2-dichloromethane was mixed with 1 M nitric acid. After phase separation, the organic layers were analyzed in the ^{1}H NMR experiment. Another NMR sample of the Lu(III) complex with **1** was synthesized directly in the deuterated solvent. The 10^{-5} mol of $Lu(NO_3)_3 \cdot 5H_2O$ salt was stirred with 1 ml of the 10^{-2} M solution of **1** in D2-dichloromethane for 2 h. Even though the complex partially precipitated from the solution, the concentration of the sample was sufficient for the NMR analysis.

Extractions Conditions

The extraction experiments were performed on a series of eleven lanthanides, ^{152}Eu, and ^{241}Am radioisotopes. Solutions of 10^{-4} M metal nitrates in 1 M nitric acid were mixed with equal volumes of 10^{-3} and 10^{-4} M organic solutions for approximately 20 h. The concentration of lanthanide ions in the aqueous phase before and after the extraction were determined spectrophotometrically ($\lambda = 655$ nm)/(40, 45, 47, 48), or in the case of ^{241}Am and ^{152}Eu, concentrations were measured by a Canberra GammaTrac 1185 with Ge(Li) detector and AccuSpec-B multi-channel analyzer (49). Extraction efficiencies were calculated using the formula: $\%E = 100\%(A_1 - A)/(A_1 - A_0)$, where A is the absorbance of the extracted aqueous phase with the Arsenazo(III) indicator, A_1 is the absorbance of the aqueous phase before extraction with the indicator, and A_0 is the absorbance of metal-free 1 M nitric acid and the indicator. The errors, based on the precision of the spectrophotometer and the standard deviation from the mean of at least three measurements, were in most cases no higher than two percent. The extraction percentage was further converted into distribution ratios of the total metal ion concentration in the organic phase against the total metal ion concentration in the aqueous phase ($D = \Sigma[M_{org}]/\Sigma[M_{aq}]$), and in view of the errors associated with the spectrophotometric technique, the maximum value that could be measured for the extraction percentage and distribution ratio was 99.

Synthetic Procedures

The tris-thio/diglycolamides (**7**, **8**, and **9**) have been prepared by the reaction of primary amines **5** or **6** with mono-substituted oxa/thio-pentaneamides (**2**, **3**, or **4**) and with the coupling agent benzotriazole-1-yl-oxy-trispyrrolidinophosphonium hexafluorophosphate (PyBOP) as illustrated in Scheme 1. All final products have been obtained in high yields and purity with relatively small synthetic effort. The synthetic procedures for **1**, **2**, and **3** have been prepared following literature methods (18, 45, 50).



Scheme 1. Synthesis of C_3-symmetric tris-diglycolamides.

N,N-Diisopropyl-2-(2-oxoethylthio)acetamide (4)

The methodology for the preparation of **4** followed the synthetic pathways reported for **2** and **3** (45). A mixture of 3.54 ml (0.025 mol) of diisopropyl amine and 1.00 ml (0.180 mol) of pyridine was slowly added to a solution of 3.00 g (0.023 mol) of 1,4-oxathiane-2,6-dione in 40 ml of 1, 4-dioxane at 0°C. After stirring the reaction mixture for approximately 20 h at room temperature, the solvent was evaporated under reduced pressure, and 3 M hydrochloric acid was added. The organic phase was further extracted with chloroform, dried over magnesium sulfate, and partially evaporated. The product crystallized upon slow evaporation of the solvent to afford 1.50 g (30%) of product ^{1}H NMR ($CDCl_3$): $\delta = 1.12$ (d, $J = 6.7$ Hz, 6H; NCHCH_3), 1.26 (d, $J = 6.9$ Hz, 6H; NCHCH_3), 3.25 (s, 2H; CH_2CON), 3.37 (m, 1H; NCHCH$_3$), 3.42 (s, 2H; CH_2COOH), 3.89 (m, 1H; NCHCH$_3$). ^{13}C NMR ($CDCl_3$): $\delta = 20.1$, 20.4, 33.5, 34.5, 46.4, 50.1 (aliphatic); 168.8, 171.6 (C=O). HR LSIMS $[M+H]^+ = 234.1172$, (Theoretical LSIMS $[M+H]^+ = 234.1143$).

Compound 7

A mixture of mono-substituted amide (**3**) (1.46 g, 5.95 mmol), ethyl-diisopropylamine (1.96 ml, 11.84 mmol), and PyBOP (3.90 g, 7.49 mmol) was stirred in 40 ml of DMF for approximately 30 min. Subsequently, 1.50 g (1.78 mmol) of amine (**5**) was added and stirred for 48 h. Upon treatment with 10% hydrochloric acid, a white solid precipitated from the solution. The solid was extracted with diethyl ether, and the organic solution was further washed with 0.5 M sodium hydroxide, and dried over magnesium sulfate. The solvent was evaporated under reduced pressure to yield 2.00 g (74%) of product. ^{1}H NMR ($CDCl_3$): $\delta = 0.47$ (m, 18H; CH_2CH_3), 0.80–1.70 (signals: 18H, $NCH_2CH_2CH_2CH_3$; 18H + 18H, CCH_3; 12H, $NCH_2CH_2CH_2CH_3$; 12H, $NCH_2CH_2CH_2CH_3$; 6H + 6H, CH_2CH_3), 3.12 (t, $J = 7.4$ Hz, 6H, $NCH_2CH_2CH_2CH_3$), 3.27 (t: $J = 7.2$ Hz, 6H, $NCH_2CH_2CH_2CH_3$), 3.10–3.80 (broad signals: 6H, CH_2CH_2-NH_2; 6H, O—CH_2CH_2), 4.06 (s, 6H; OCH_2), 4.24 (s, 6H; OCH_2), 6.37 (s, 1H; CH), 6.98 (s, 3 H; Ar—H), 7.06 (s, 3 H; Ar—H), 7.86 (t, $J = 5.7$ Hz, 3 H; N-H). ^{13}C NMR ($CDCl_3$): $\delta = 9.3$, 9.7, 13.9, 14.0, 20.2, 20.4, 29.7, 29.9, 31.2, 35.4, 37.0, 37.8, 38.6, 39.2, 39.5 (aliphatic); 45.8, 46.7, 69.8, 70.3 (O—CH_2—CO); 71.4 (O—CH_2); 124.9, 127.8, 137.8, 139.9, 142.8, 153.1 (aromatic), 168.3, 170.0 (C=O). HR LSIMS $[M + H]^+ = 1524.1699$ (Theoretical LSIMS $[M + H]^+ = 1524.1703$). Anal. Calcd for $C_{91}H_{154}N_6O_{12}$: C, 71.71; H, 10.18; N, 5.51. Found: C, 71.99; H, 10.35; N, 5.45

Compound 8

A mixture of mono-substituted amide (**2**) (1.27 g, 5.87 mmol), ethyl-diisopropylamine (1.94 ml, 11.730 mmol), and PyBOP (4.35 g, 6.45 mmol) was stirred in 40 ml of DMF for approximately 30 min. A 1.56 g (1.76 mmol) portion of amine **6** was added and stirred for 48 h. Upon treatment with 10% hydrochloric acid, a yellow solid precipitated from the solution. The solid was extracted with diethyl ether, and the organic solution was further washed with 0.5 M sodium hydroxide, and dried over magnesium sulfate. The solvent was evaporated under reduced pressure leaving 1.90 g (73%) of clean, light yellow product ^{1}H NMR ($CDCl_3$): $\delta = 0.51$ (m, 18H; CH_2CH_3), 1.12 (s, 18H; CCH_3), 1.19 (d, $J = 6.7$ Hz, 18H; $NCHCH_3$), 1.30 (s, 18H; CCH_3), 1.38 (d, $J = 6.7$ Hz, 18H; $NCHCH_3$), 1.67 (q, $J = 7.6$ Hz, 6H; CH_2CH_3), 2,00 (b, 6 H; $CH_2CH_2CH_2$), 3.47 (broad multiplet: 18 H; O—CH_2-CH_2CH_2—NHCO, 3H; $NCHCH_3$), 3.77 (m, 3H; $NCHCH_3$), 4.07 (s, 6H; OCH_2), 4.20 (s, 6H; OCH_2), 6.34 (s, 1H; CH), 6.99 (d, $J = 2.0$ Hz, 3 H; Ar—H), 7.04 (d, $J = 2.0$ Hz, 3 H; Ar—H), 7.84 (bt, 3 H; N—H). ^{13}C NMR ($CDCl_3$): $\delta = 9.2$, 9.7, 20.6, 20.8, 28.7, 29.6, 30.5, 35.2, 36.8, 37.0, 37.7, 38.9, 39.2, 46.1, 47.7, 70.0, 70.9, 71.1 (aliphatic); 124.7, 127.9, 138.0, 139.7, 142.4, 153.4 (aromatic); 167.6, 169.9 (C=O). HR ESI-ICR MS m/z $[M+H+K]^{2+} = 760.5481$, (Theoretical m/z $[M+H+K]^{2+} = 760.5430$). Anal. Calcd for $C_{88}H_{148}N_6O_{12}$: C, 71.31; H, 10.06; N, 5.67. Found: C, 71.68; H, 10.30; N, 5.61.

Compound 9

A mixture of mono-substituted amide **4** (1.79 g, 7.67 mmol), ethyl-diisopropylamine (2.54 ml, 15.37 mmol), and PyBOP (4.40 g, 8.46 mmol) was stirred in 40 ml of DMF for approximately 30 min. Subsequently, 1.95 g (2.31 mmol) of amine (**5**) was added and stirred for 48 h. Upon treatment with 10% hydrochloric acid, a white solid precipitated from the solution. A solid was collected, extracted with diethyl ether, and the organic solution was further washed with 0.5 M sodium hydroxide, and dried over magnesium sulfide. The solvent was evaporated under reduced pressure leaving 2.90 g (84%) of light yellow product. ^{1}H NMR (CDCl$_3$): $\delta = 0.51$ (m, 18H; CH$_2$C*H*$_3$), 1.12 (s, 18H; CC*H*$_3$), 1.21 (d, $J = 6.4$ Hz, 18H; NCHC*H*$_3$), 1.31 (s, 18H; CC*H*$_3$), 1.37 (d, $J = 6.2$ Hz, 18H; NCHC*H*$_3$), 1.20–1.70 (two broad multiplets, 6H + 6H; C*H*$_2$CH$_3$), 3.27–4.10 (signals: 6H, O–C*H*$_2$CH$_2$; 6H, OC*H*$_2$; 6H, OC*H*$_2$; 6H, CH$_2$C*H*$_2$–NH$_2$; 6H, NC*H*CH$_3$), 6.43 (s, 1H; C*H*), 7.01 (s, 3 H; Ar–*H*), 7.07 (s, 3 H; Ar–*H*), 7.94 (bt, 3 H; N–*H*). ^{13}C NMR (CDCl$_3$): $\delta = 9.3$, 9.7, 20.6, 20.9, 28.7, 29.7, 35.3, 35.5, 36.1, 37.0, 38.7, 39.3, 40.2, 46.2, 49, 7, 49, 9 (aliphatic); 70.3 (O–CH$_2$); 125.0, 127.9, 137.8, 140.0, 142.9, 153.2 (aromatic); 167.7, 169.7 (C=O). HR ESI-ICR MS m/z $[M + Na]^+ = 1509.9872$ (Theoretical m/z $[M + Na]^+ = 1509.9893$). Anal. Calcd for $C_{85}H_{142}N_6O_9S_3$: C, 68.60; H, 9.62; N, 5.65, Found: C, 68.94; H, 9.99; N, 5.51.

RESULTS AND DISCUSSION

There are many complex processes that influence the transfer of the metal ion from an acid layer into an organic phase, and in a very simplistic view, the three major factors dominate the extraction event: solubility, steric hindrance presented by a ligand, and the electronic effect (51). The first tris-diglycolamide ligand with two isopropyl groups on the terminal amides (**1**) was found to be a highly effective agent for the extraction of the heaviest lanthanides into dichloromethane (45). With the desire to use more environmentally "friendly" solvents, the extraction profile was examined in 1-octanol and n-dodecane, but during the acidic extraction in n-dodecane, formed complexes quickly precipitated out of the organic solution. In order to increase the lipophilicity of the tris-DGA chelate, and therefore, potentially enhance the solubility of the extracted metal complex in the nonpolar diluents, a new derivative with two n-butyl substituents attached to each of the terminal amidic nitrogens was synthesized (**7**). As expected, the new ligand is highly compatible with nonpolar solvents, but at the same time, the binding ability of **7** relative to **1** is considerably suppressed. A similar trend has been noted in simple diglycolamides (26). In four different diluents: chloroform, toluene, n-hexane, and n-dodecane, the distribution coefficients of the ligands decreased when the length of the alkyl chains was extended.

At a ratio of 10:1 ligand to metal in the dichloromethane/1 M HNO$_3$ system, the extraction efficiency of **7** relative to **1** is reduced by nearly 50%, and in the case of the heaviest lanthanides, the distribution ratio for the extraction with **7** ($D \sim 1$) is significantly lower than the corresponding value for **1** ($D > 99$) (Fig. 1). Even though both ligands exhibit the same general trend for preferential extraction of the heavier lanthanides, the

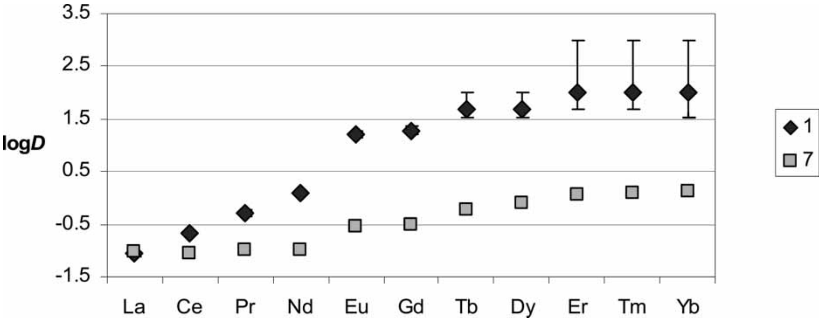


Figure 1. Extraction of 10^{-4} M solutions of trivalent lanthanides in 1 M HNO_3 with dichloromethane solutions containing ligands **1** and **7** at 10^{-3} M. Due to the limitations of the spectrochemical assay, the error bars for *D* are quite large at high extraction efficiency (>98%).

selectivity of the two is notably different. For example, the separation between Yb(III) and La(III) drops from $SF_{Yb/La} = 1138$ for **1**, to $SF_{Yb/La} = 14$ for **7**, while between Yb(III) and Nd(III) the factor decreases from $SF_{Yb/Nd} = 78$ to $SF_{Yb/Nd} = 13$ respectively for **1** and **7** ($SF_{A/B} = D_A/D_B$; the fraction of the individual distribution ratios of two extractable solutes measured under the same conditions). In addition, the extraction efficiency for the four lightest lanthanides is negligible, and the limitations of the spectrophotometric analysis complicate the analysis of this trend. Experiments with **7** in 1-octanol and n-dodecane are underway as are efforts to delineate fully the extraction behavior of the ligands.

In previous work with calix[4]arenes and triphenoxymethane molecule appended with CMPO arms, the extraction efficiency of the constructs was amplified by the increased flexibility of the linker between the CMPO and the base skeleton (40, 49). This trend can be attributed to the enhanced ability of ligand to satisfy the geometrical requirements of the metal center, but often, the improvement in binding affinity comes at the expense of selectivity. In **1,** the DGA groups are tethered to the triphenoxymethane platform by only two carbons, and to test the effect of the length of this arm linker on the extraction ability, a new tri-substituted diglycolamide was synthesized with three carbons linking the DGA arms to the triphenoxymethane base (**8**). Considering the high efficiency of the "more rigid" chelate **1** at the 10:1 ligand to metal proportion, and expected performance enhancement of **8** over **1**, the experiment has been conducted with only 10^{-4} M concentration of **8** in the dichloromethane (1:1 ligand to metal ratio). Interestingly, the new extractant did not appear to be more effective or less selective than its "more rigid" equivalent. In fact, the **8** exhibits the same extraction behavior as compound **1**, suggesting that the binding environment in the two ligands is nearly identical (Fig. 2). Interestingly, the coordination environment of the metal center in the Eu(III) complex of **7** (52) is nearly indistinguishable from

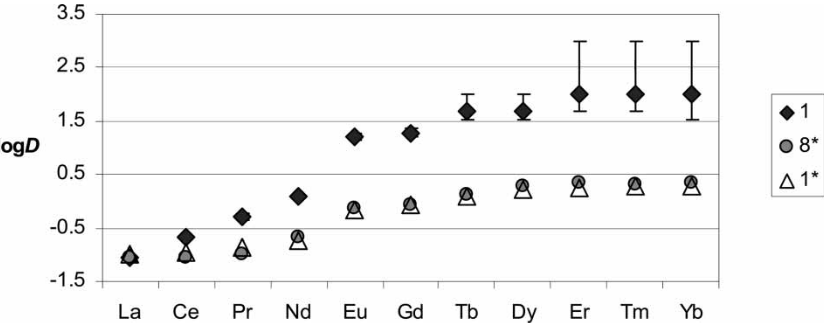


Figure 2. Extraction of 10^{-4} M solutions of trivalent lanthanides in 1 M HNO_3 with dichloromethane solutions containing ligand **1** at 10^{-3} M, and compounds **1** and **8** at 10^{-4} M concentrations (**1***, **8***).

Yb(III) and Ce(III) complexes of **1** (45). Both ligands are perfectly suited to fulfill the coordination requirements of trivalent lanthanides in the organic solution.

In the solid state and in the solution trivalent lanthanides preferentially adopt tricapped trigonal prismatic (TTP) geometry with oxygen donor ligands (Fig. 3) (53–55). The tris-DGA ligand presents lanthanides with nine oxygen donor groups, six of which are relatively hard amide oxygens. The crystal structures of the representatives of the heaviest, lightest, and the middle lanthanides, $Yb(NO_3)_3$ and $Ce(NO_3)_3$ with **1**, and $Eu(NO_3)_3$ with **7**,

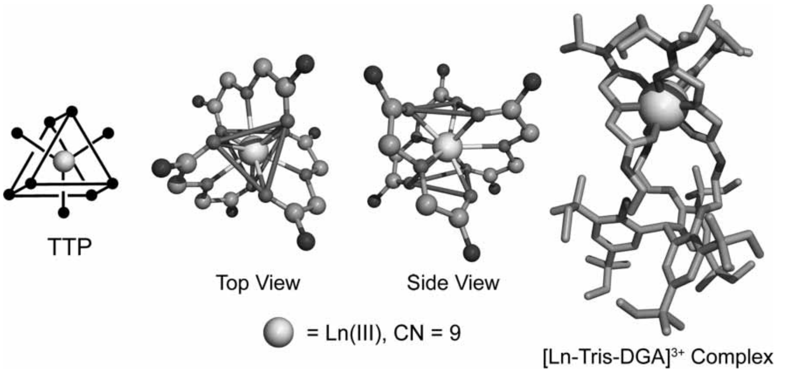


Figure 3. The model of an ideal tricapped trigonal prismatic (TTP) geometry around nine coordinate metal ion (left). The top and side views of a slightly distorted TTP coordination environment of the Yb(III) center in the complex with ligand **1** (nonbonding part of the ligand has been omitted for clarity). The crystal structure of Yb(III) complex with ligand **1** (right).

demonstrate a good match between the size and the tricapped trigonal prismatic coordination requirements of lanthanides and the binding pocket of tris-DGA ligands (45). All three DGA arms are equally involved in the tight metal binding in a tridentate fashion and form a slightly distorted TTP arrangement about the metal center. The ligand fully saturates the coordination sphere of the metal ion leaving no space for nitrates to bind. The two of three charge neutralizing nitrates were found to be bonded to amide hydrogens of ligand via hydrogen bonding interactions in the solid state structure of **1**, and this ability of the amides to hydrogen bond to the nitrates counterions may facilitate the extraction event by providing a suitable environment for the ions in the organic solvent. The bond strength sequence follows the trend in the ionic crystal radius (for $\mathrm{CN} = 9$, $r_{\mathrm{Ce(III)}} = 1.336$ Å, $r_{\mathrm{Eu(III)}} = 1.260$ Å, $r_{\mathrm{Yb(III)}} = 1.182$ Å), and is consistent with an increase in the charge density of metal ions: Ce(III) $<$ Eu(III) $<$ Yb(III) (52, 56). The bond lengths to the carbonyl oxygens (mean distance Ce: Å 2.434(9); Eu: 2.411 (3) Å; Yb: 2.313(3) Å) are shorter than to the etheric oxygens (Ce: 2.566(7) Å; Eu: 2.499(3) Å; Yb: 2.429(2) Å) by approximately 0.1 Å. The rectangular faces of the trigonal prism are caped by the etheric oxygens. The triangular faces are formed by the carbonyl oxygens and are twisted about the three fold axis. Based on the size and similar coordination environment of the newly synthesized complex of **8** with Eu(III), the twist angle about the three fold axis should fall in between the values for Ce(III) and Yb(III) complexes of **1**. As anticipated, the value of the twist angle was found to be 20.0° (15.2°and 21.6° for Yb and Ce respectively). Interestingly, as the coordination geometry distorts away from an ideal TTP in the model complexes the extractant efficiency with **1** in the dichloromethane decreases.

Given the ability of one equivalent of **1** to extract ~70% of the heaviest lanthanides from the acidic layer, the reaction can be easily monitored when deuterated dichloromethane is used for the extraction experiment. Figure 4 presents three superimposed ^{1}H NMR spectra of the ligand **1** equilibrated with 1 M nitric acid, the extracted species generated upon complexation of Lu(III) by ligand **1** in the 1 M nitric acid/D2-dichloromethane extraction system, and the $\mathrm{Lu(NO_3)_3}$ complex with **1** formed directly in D2-dichloromethane. The chemical shifts of protons in the close proximity to the coordination site significantly change upon formation of complex.

Protons that belong to the $\mathrm{C}H_2\mathrm{C}H_2$ tripod-DGA linker become more distinct. Complexation of metal through amidic and etheric oxygens deshields the surrounding protons and results in noticeable downfield change in their chemical shifts. Without a metal, the ^{1}H NMR spectrum of **1** exhibits two sharp singlets for the DGA $\mathrm{C}H_2\mathrm{OC}H_2$ protons and these signals broaden, merge, and shift downfield when a metal is added. The resonances for the protons of secondary amides are the most affected by metal complexation and they shift from a value of 8.15 ppm for **1** to 9.75 ppm for the Lu(III) complex of **1**. From a comparison of the spectrum of the extracted species

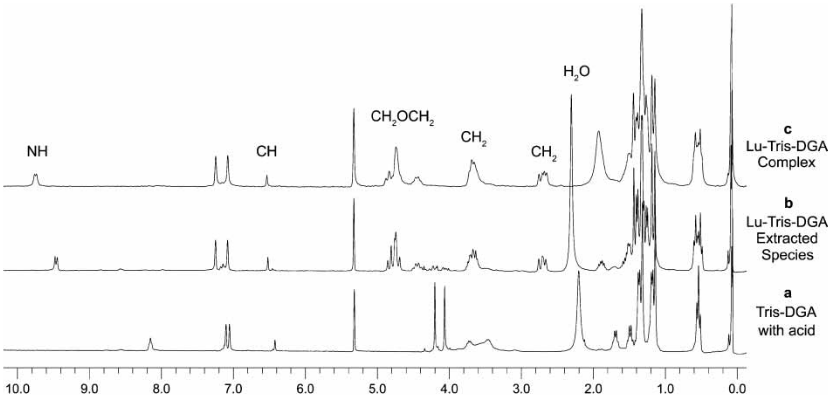


Figure 4. Superimposed ^{1}H NMR spectra of ligand **1** equilibrated with 1 M nitric acid (**a**), Lu(III) extracted by ligand **1** from 1 M nitric acid into the D2-dichloromethane (**b**) and Lu(III) complex with **1** formed in D2-dichloromethane (**c**).

and the isolated Lu(III) complex of **1** (structure completely analogous to the Yb(III) complex presented in Fig. 3), the only significant difference is an upfield shift of the amidic protons in the Lu-tris-DGA species extracted from the acid layer, and the presence of a significant amount of water and acid may influence the chemical shift of these protons causing a less significant change in their position relative to the metal complex formed in dry dichloromethane. Nevertheless, the spectrum demonstrates that a C_3-symmetric complex is formed, and all three arms of the ligand simultaneously bind the metal center during the extraction event. Moreover, the central methine hydrogen (C*H*), aromatic (7.07 and 7.24 ppm) and CH_2OCH_2 regions in the **b** spectrum are completely superimposable with spectrum **c** suggesting the structures of two species are nearly if not completely identical. In agreement with the extraction data at a 1:1 metal to ligand ratio highlighted in Fig. 2, some residual amount of a free ligand is evident in spectrum **b**. This simple experiment highlights that the extraction event involves a single ligand binding to the Lu(III) center, and undoubtedly, the large increase in entropy produced by this process contributes to the high extraction efficiency.

Often, the removal or "stripping" of the metal center from highly efficient extractant molecules is problematic, but in the case of **1**, a single contact with either weak acidic solution or pure water is sufficient to completely remove the metal center from the ligand. When a solution of the Lu(III) extracted complex with **1** (Spectrum **b** in Fig. 4) was shaken with 0.001M HNO_3, all of the metal ions were released from **1** into the aqueous layer. Although this experiment indicates that the metal ions can be easily extracted back from the organic to the aqueous phase using weak acid, the most effective concentration of nitric acid for more practical stripping still needs to be determined.

The properties of an organic solvent strongly influence almost every aspect of the liquid-liquid extraction process, and in our previous studies with **1**, a significant modulation in the extraction pattern was noted when 1-octanol was substituted for dichloromethane as the organic solvent (Fig. 5) (45). From a gradually rising affinity toward heavier lanthanides in dichloromethane, the extractant tends to favor the middle lanthanides in 1-octanol, in particular europium. The heaviest lanthanides are still more readily extracted than the lightest ones, although the separation between Yb(III) and La(III) significantly decreases from $SF_{Yb/La} = 1138$ to $SF_{Yb/La} = 27$. The preference of Eu(III) binding arises apparently from combined effects of the best fit between metal and ligand, and the complex stabilization provided by 1-octanol. Therefore, the origin of selectivity in dichloromethane may not be simply related to the careful recognition of size of the metal ion or an increased charge density on the metal center. The selectivity must be strongly associated with the properties of an organic phase and results from the combined effect of many possible interactions between the ligand, metal and both aqueous and organic solutes.

Most successful extractants for lanthanide(III)/actinide(III) separations contain soft donor atoms for metal binding (17, 27, 57–63), and the central oxygen atom in the DGA ligand can be replaced with a softer sulfur atom producing a thiodiglycolamide (TDGA). Based on a comparison of the extraction ability of TDGA and the related glutalamide (GLA) ligand with a CH_2 group in place of the central oxygen, it appears that the central sulfur atom in TDGA may interact with the Am(III) center in a 1M $NaClO_4$/nitrobenzene extraction system (pH = 3) (27). Since the size and flexibility of the group linking the amide donors is very similar, the groups would form a nearly identical 8-membered chelate with americium if the sulfur atom does not interact with the metal. The much higher extraction efficiency of the TDGA with respect to the GLA suggests otherwise. At pH > 3 and/or in the absence of a synergistic agent (e.g., thenoyltrifluoroacetone) however, the

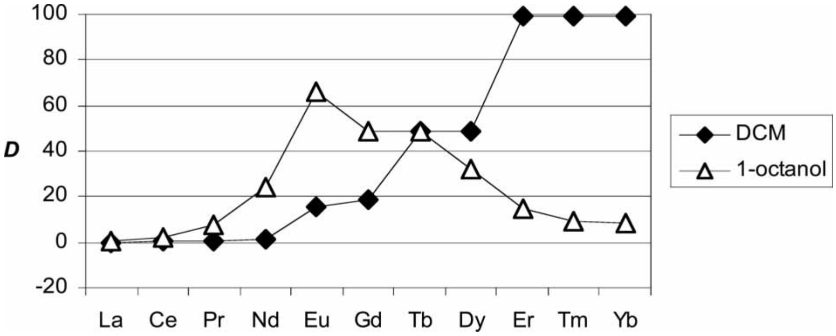


Figure 5. Extraction of 10^{-4} M solutions of trivalent lanthanides in 1 M HNO_3 with dichloromethane (DCM) and 1-octanol solutions containing ligand **1** at 10^{-3} M.

thiodiglycolamides (TDGA) lose their ability to bind efficiently Am(III). Given that the mutual arrangement of ligating TDGA units could enhance binding much like the DGA derivative **1**, a thiodiglycolamide derivative (**9**) was synthesized, and its extraction potential was tested on a series of trivalent lanthanides including ^{152}Eu and actinide ^{241}Am. It was anticipated that the softness of the sulfur as well as the significant difference in the size of sulfur and oxygen (atomic radius: $S = 1.27$ Å, $O = 0.65$ Å) would strongly affect the interactions between the ligand and the metal, and possibly help differentiate trivalent lanthanides and actinides. In spite of the advantageous entropic effect, experiments with the preorganized thiodiglycolamides showed negligibly low distribution coefficients for both lanthanides and americium in 1 M HNO_3 (10^{-3}M of **9** in dichloromethane $D_{Am(III)} < 0.001$) suggesting a fundamental requirement of the etheric oxygen for metal binding under these particular conditions.

The structural studies of N,N'-dimethyl-N,N'-diphenyl-diglycolamide complexes with Ln(III) in solution system via EXAFS (extended X-ray fine structure) spectroscopy revealed participation of the etheric oxygens in the metal binding (21). Consequently, the structure of tris-DGA complexes with lanthanides both in the solid state and in the solution could be very similar. If the etheric oxygen is involved in metal binding in the extracted species, replacing it with much bigger sulfur atom would cause a severe distortion from TTP geometry, and ultimately result in poor metal binding. In view of the crowded environment of the nonadentate ligand **1** and the inability of the ligand arms to rotate once placed on the triphenoxymethane platform, the extracted species would likely interact with several of the donor groups presented by the ligand, and the ether oxygens appear to be very important in this event.

CONCLUSIONS

Three new tripodal chelates bearing three diglycolamide and thiodiglycolamide units precisely arranged on a triphenoxymethane platform have been synthesized to provide for highly efficient extraction of trivalent f-element cations from nitric acid media. Exploiting the preference of the metal center for TPP geometry, the ligand has been designed to completely fill the coordination sphere of the metal and ^{1}H NMR experiments suggest a single ligand binds the smaller lanthanides during the extraction event. The ligand with n-butyl substituents on the diglycolamide arms was found to be a significantly weaker extractant in comparison to the di-isopropyl analogs. The distance separating the metal binding groups from the triphenoxymethane platform had little influence on the selectivity or binding efficiency of the ligands. The tris-thiodiglycolamide derivative proved to be an ineffective chelate for f-elements in the 1 M nitric acid extraction system and demonstrated the importance of the etheric oxygens in the metal binding. Work to improve the solubility and selectivity of the tris-DGA ligands in other solvents such as dodecane is currently underway.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support from the Nuclear Energy Research Initiative (Grant 02–98) of the Department of Energy (DE-FG07-02SF22614). The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

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