



Synthesis and characterization of new unsymmetrical diglycolamide extractants for lanthanide ion partitioning: part one—straight-chain alkyl derivatives

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Abstract

Six novel unsymmetrical diglycolamide (UDGA) ligands have been synthesized and evaluated as solvent extraction reagents for the partitioning of lanthanide (Ln) ions from nitrate media. The partitioning of europium between aqueous phases of varying nitric acid concentrations and a UDGA organic phase has been characterized radiometrically. The stoichiometry and phase-transfer equilibrium constants of the Eu-UDGA complexes extracted into the organic phase have been reported. Luminescence spectroscopy investigations have established the relative stability and stoichiometry of the complexes in acetonitrile. These UDGA ligands have displayed enhanced interfacial activity, which has decreased the necessary equilibration time while maintaining high Ln distribution ratios.

Keywords Unsymmetrical diglycolamide · Solvent extraction · Lanthanide partitioning · Nuclear fuel reprocessing · Ligand synthesis

Introduction

Diglycolamide (DGA) ligands are diamide analogs of the water-soluble complexant, diglycolic acid, which bind to metal cations (in this investigation, trivalent neodymium and europium) in a tridentate configuration through two amidic carbonyl oxygen atoms and a bridging etheric oxygen atom. The aqueous chemistry of trivalent f-element metal ions with diglycolic acid has been extensively investigated [1]. Diglycolamide compounds were initially developed by Stephan et al. in the early 1990s as simpler alternatives to expensive macrocyclic compounds (e.g., crown ethers and cryptands) for the extraction of divalent strontium from various aqueous media [2]. In the late 1990s, Sasaki et al. synthesized a series of symmetrical diglycolamide extractants for the

partitioning of both trivalent lanthanides (Ln) and actinides (An) from highly acidic media [3, 4]. The ligand *N,N,N',N'*-tetraoctyldiglycolamide (TODGA, Fig. 1) exhibits reasonable solubility in aliphatic diluents (e.g., *n*-dodecane) and has been shown to quantitatively extract both actinides and lanthanides from acidic nitrate solutions (e.g., 1 M HNO₃) [5]. Numerous derivatives of the basic diglycolamide ligand have been reported and advanced nuclear waste partitioning methods have been developed based on this class of complexant [6].

Unfortunately, organic phases containing 0.1 M TODGA in *n*-dodecane tend to form a problematic third (heavy organic) phase when in contact with highly acidic nitrate aqueous phases (e.g., > 3 M HNO₃) or with higher concentrations of lanthanide ions (e.g., > 14 mM Nd in 1 M HNO₃) [7, 8]. Nave et al. posited that the third phase formation is caused by the self-aggregation of the polar TODGA cores into reverse micelles [7]. The addition of the phase modifier tributyl phosphate (TBP) increases the metal loading capacity of the extractant; this adjustment inhibits third phase formation but increases the complexity of the solvent and introduces phosphorus into the waste stream [9]. Phosphorus-based extractants leave behind phosphate residues in the solid waste stream, which complicates waste management [10]. The diglycolamide ligands are composed of only

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carbon, hydrogen, oxygen, and nitrogen, which makes them completely incinerable [11].

A series of TODGA analogs were synthesized by Iqbal et al. in the late 2000s. The methylated version of TODGA (Me-TODGA, Fig. 2) exhibited similar distribution ratios for Am(III) and Eu(III) to TODGA at high nitric acid concentrations (i.e., 3–4 M HNO_3) while having significantly lower distribution ratios (ca. two orders of magnitude difference) for Am(III) and Eu(III) than TODGA at low nitric acid concentrations (i.e., 0.01–0.1 M HNO_3). Lower distribution ratios for Am(III) and Eu(III) at lower nitric acid concentrations is potentially beneficial in the back-extraction process [12]. Wilden et al. confirmed this reduction in An(III) and Ln(III) extraction efficiency for Me-TODGA compared to TODGA by using time-resolved laser fluorescence spectroscopy (TRLFS) in a monophasic ethanol media to determine conditional complex formation constants [13].

In the early 2010s, Ravi et al. developed a series of unsymmetrical diglycolamide extractants (octyl chains on one amide and hexyl to dodecyl on the other amide). The bulkiest ligand *N,N*-didodecyl-*N',N'*-dioctyldiglycolamide (D^3DODGA , Fig. 3) exhibited no third phase formation upon contact with 3–4 M HNO_3 containing up to 600 mM Nd and an extractant concentration of 0.1 M D^3DODGA in *n*-dodecane. Unfortunately, D^3DODGA also displayed considerably lower distribution ratios for the extraction of Am(III) and Eu(III) compared to TODGA and the shorter chain ligands [14].

The overall objective of this work was to design and synthesize a version of diglycolamide extractants that would improve on previous ligand performance by adjusting the amphiphilicity of the diglycolamide moiety. The newly synthesized ligands incorporated the diglycolamide backbone

by creating diamides with lipophilic and hydrophilic directionalities superimposed on opposite sides of the DGA cation binding pocket. The work reported here focuses on introducing polar/nonpolar asymmetry with one end of the molecule being a five- or six-membered cyclic amide or amide-ether ring and the opposite end being populated by dihexyl- or dioctyl- amide groups. The dihexyl group was chosen because of previous work showing that *N,N,N',N'*-tetrahexyldiglycolamide (THDGA) showed increased Ln(III) complexation compared to longer alkyl chains (e.g., octyl, decyl, dodecyl). The dioctyl group was chosen to mimic the aliphatic alkyl chains in the TODGA ligand. The cyclic amides (pyrrolidinyl, piperidinyl, and morpholinyl) were chosen instead of previously studied methyl, ethyl, and propyl amide groups because the ring structures are less likely to interfere with metal complexation in the nearby cation binding pocket due to the reduced molecular footprint of the cyclic amides [5, 15]. In this exploration of size-property relationships of this class of extractants, novel unsymmetrical diglycolamide ligands were synthesized and characterized using NMR and IR spectroscopy. The purpose of this study was to determine whether the more compact geometry provided by the asymmetric alkyl groups might favorably impact the phase transfer/compatibility properties of this type of reagent.

Experimental

Materials

The diglycolic anhydride starting material was obtained from Alfa Aesar (97%) and used without further

Fig. 1 Structure of *N,N,N',N'*-tetraoctyldiglycolamide (TODGA)

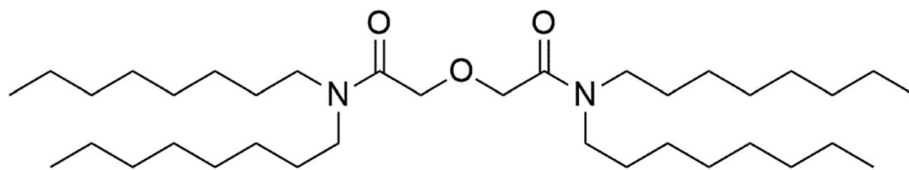


Fig. 2 Structure of methyl-*N,N,N',N'*-tetraoctyldiglycolamide (Me-TODGA)

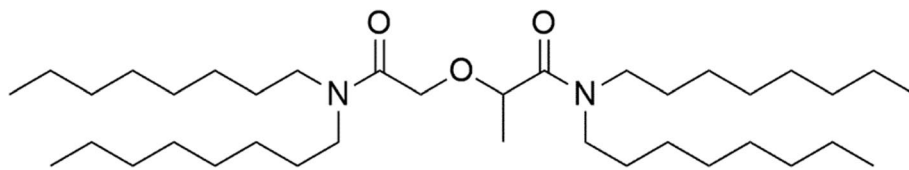
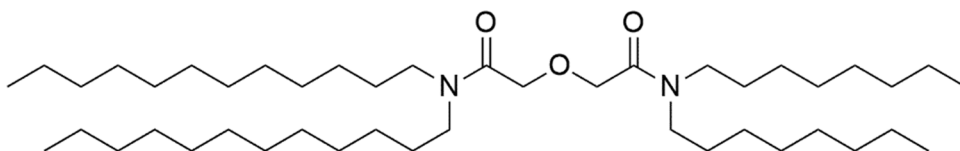


Fig. 3 Structure of *N,N*-didodecyl-*N',N'*-dioctyldiglycolamide (D^3DODGA)



purification. All amines were obtained from Sigma-Aldrich (reagent grade) and distilled out of calcium hydride before use to remove any absorbed water. All other synthesis reagents were obtained from Sigma-Aldrich (reagent grade) and used without further purification. All nitric acid solutions were titrated with sodium hydroxide to determine accurate concentrations using a Mettler Toledo DL50 titrator. The radiotracer europium-152/154 was produced by neutron activation of Eu_2O_3 (Arris International Corp., 99.999%) in the 1 MW Teaching Research Isotopes General Atomics (TRIGA) nuclear reactor at the Washington State University Nuclear Science Center (WSUNSC). A cold europium nitrate stock solution was prepared by the dissolution of Eu_2O_3 (Arris International Corp., 99.999%) in concentrated nitric acid. The resulting stock solution was standardized by complexometric titration using Arsenazo III as a colorimetric indicator. Organic diluents *n*-octane, 1-octanol, *n*-dodecane, and acetonitrile were obtained from Acros Organics (99%), Sigma-Aldrich (99%), Alfa Aesar (99%), and Fisher Scientific (HPLC grade), respectively, and used without further purification. Synthesized unsymmetrical diglycolamide ligands were purified by Kugelrohr distillation (Büchi) or flash chromatography (Teledyne Isco CombiFlash®) and were characterized using infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and high-resolution mass spectrometry (HRMS). All IR, NMR, and HRMS data and spectra can be found in the supporting information. All synthesized ligands were determined to be > 97% pure through the combined use of ^1H NMR spectroscopy integration and HRMS. The symmetrical diglycolamide *N,N,N',N'*-tetraoctyldiglycolamide (TODGA, > 99% purity) was generously donated by Dr. Yuji Sasaki from the Japan Atomic Energy Research Institute in Tokai, Ibaraki, Japan.

Synthesis of UDGA extractants

The amidation of diglycolic anhydride has been adapted from previous work by Ramírez [16]. The methylation of the diglycolamic acid has been adapted from a fundamental work by Stodola [17]. The amidation of the diglycolamic acid methyl ester has been adapted from a review on amide bond formation by Montalbetti and Falque [18]. All steps have been performed under ambient atmospheric conditions. The overall reaction scheme for the synthesis of *N,N*-dihexyl-*N'*-pyrrolidinyl diglycolamide (DHpyrDGA) is shown in Fig. 4.

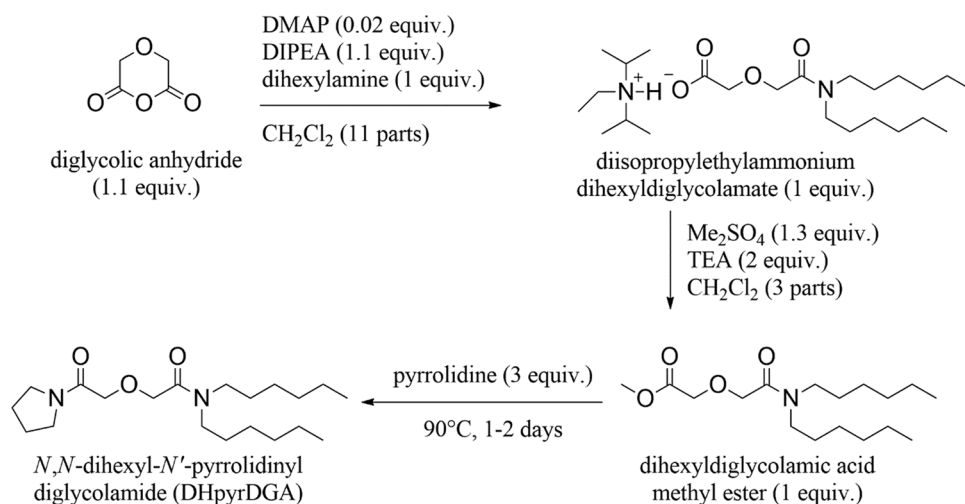
The structures of all six newly synthesized unsymmetrical diglycolamide extractants are shown in Fig. 5.

Data for the ligand DHpyrDGA(1) are given as follows (data and spectra for all ligands can be found in the supplementary information): ^1H -NMR (400 MHz, CDCl_3 , δ): 4.32 (s, 2H), 4.26 (s, 2H), 3.49 (t, $J = 6.9$ Hz, 2H), 3.41 (t, $J = 6.8$ Hz, 2H), 3.29 (m, 2H), 3.19 (m, 2H), 1.94 (p, $J = 6.8$ Hz, 2H), 1.83 (p, $J = 6.5$ Hz, 2H), 1.51 (br m, 4H), 1.27 (br m, 12H), 0.87 (br m, 6H). ^{13}C -NMR (101 MHz, CDCl_3 , δ): 168.46, 167.81, 69.94, 69.33, 47.10, 46.01, 45.93, 45.70, 31.73, 31.67, 29.04, 27.68, 26.84, 26.64, 26.32, 24.05, 22.73, 22.71, 14.17, 14.12. IR (NaCl, film) ν_{max} (cm^{-1}): 2955 (s, CH, aliphatic), 2928 (s, CH, aliphatic), 2869 (s, CH, aliphatic), 2857 (s, CH, aliphatic), 1651 (s, C=O), 1451 (m, C–N), 1431 (m, C–N), 1131 (m, C–O). HRMS-MALDI TOF/TOF (m/z): $[\text{M} + \text{H}]^+(\text{calc.}) = 355.29614$; $[\text{M} + \text{H}]^+(\text{exp.}) = 355.29568$. Overall yield = 79%.

Liquid–liquid solvent extraction

All solvent extraction experiments have been conducted at room temperature (22 ± 1 °C) unless otherwise indicated. All organic solutions have been prepared by mass for both the ligand and the diluent. Mixed organic diluents (e.g.,

Fig. 4 Synthesis of the new unsymmetrical diglycolamide extractant, *N,N*-dihexyl-*N'*-pyrrolidinyl diglycolamide (DHpyrDGA)



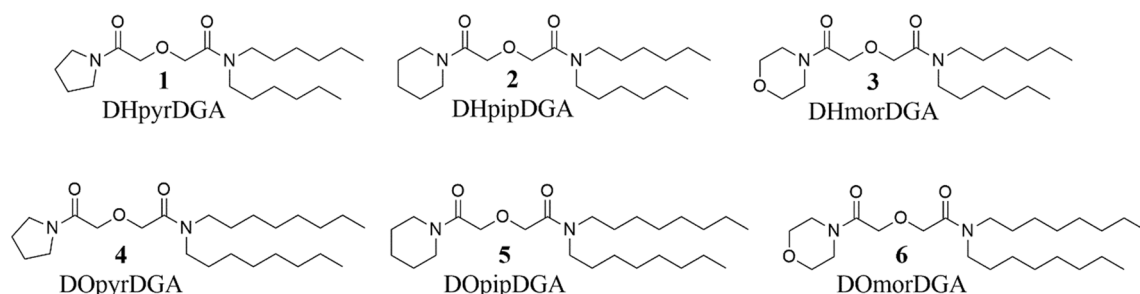


Fig. 5 Structures of newly synthesized unsymmetrical diglycolamides (1–6) with acronyms provided (DH = dihexyl, DO = dioctyl, pyr = pyrrolidinyl, pip = piperidinyl, mor = morpholinyl, DGA = diglycolamide)

5.0 or 10.0% v/v 1-octanol in *n*-dodecane) were made in large batches (i.e., 1 L) to maintain consistency in the diluent makeup. Aqueous nitric acid solutions were prepared using EMD Millipore OmniTrace[®] nitric acid (67–70%) and 18 MΩ cm deionized water. All nitric acid solutions were titrated with sodium hydroxide to determine accurate concentrations (less than 1% error) using a Mettler Toledo DL50 titrator. The organic phase (2000 μL) was pre-equilibrated with a metal-free aqueous phase (2000 μL) for 30 min in a 4 mL screw-cap glass vial using a Fisher Scientific[™] Analog Vortex Mixer on level 9 (ca. 2850 rpm). The samples were then centrifuged for 5 min to achieve complete phase separation. Three aliquots (500 μL) of fresh aqueous phase were pipetted into three different 2 mL glass, screw-cap vials. Three aliquots (500 μL) of the pre-equilibrated organic phase were taken and transferred to the same 2 mL screw-cap glass vials. For radiotracer experiments, a 5.0 μL aliquot of radiotracer europium-152/154 (total activity varying from 20,000 to 30,000 cpm) was spiked into each 2 mL vial containing both phases. The spiked phases were then contacted for at least 30 min using a Vortex mixer. The samples were centrifuged again to separate the two phases completely prior to sampling. A 200 μL sample was taken from the organic and aqueous phases of each vial and deposited in a polyethylene tube for gamma counting. Residual organic phase was removed from the vial before sampling the aqueous phase to avoid cross contamination. The counts per minute (cpm) in each phase represent the partitioning of the europium metal from the aqueous phase into the organic phase. The distribution ratio (D_{Eu}) was determined by the relationship in Eq. (1).

$$D_{Eu} = \frac{[Eu]_{org}}{[Eu]_{aq}} = \frac{\text{cpm (organic phase)} - \text{cpm (background)}}{\text{cpm (aqueous phase)} - \text{cpm (background)}} \quad (1)$$

The total cpm of the ^{152,154}Eu(III) spike were counted separately and compared to the total cpm found in both phases. This method accounted for all of the cpm in the sample and confirmed the absence of a metal-rich third phase. The uncertainty associated with each distribution ratio

was a combination of the standard deviation of three data points and the propagated counting error. The vast majority of reported distribution ratios exhibit less than $\pm 10\%$ uncertainty.

Luminescence spectroscopy

All luminescence spectroscopy titrations have been performed at room temperature (22 ± 1 °C). Both the titrand and titrant were dissolved in acetonitrile (MeCN) to allow for mutual solubility of both the free europium metal and the UDGA ligand in a single phase. The titrand for these experiments was a solution of 0.5 mM Eu(NO₃)₃ in 0.3 mM HNO₃/0.2 M H₂O/99.7% MeCN. Identical samples of the same titrand solution were used for each of the seven titrations (ligands 1–6 and TODGA). The titrant solution was created fresh for each experiment (UDGA in MeCN) for each component (purified UDGA or TODGA ligand, MeCN ($d = 0.781$ g cm⁻³), 0.096 M HNO₃ ($d = 1.004$ g cm⁻³)). The ligand concentrations varied from 5 to 8 mM UDGA in 0.3 mM HNO₃/0.2 M H₂O/99.7% MeCN. The titrand (1000 μL of 0.5 mM Eu(NO₃)₃ in 0.3 mM HNO₃/0.2 M H₂O/99.7% MeCN) was pipetted into an open top, 1.4 mL Spectrocell Semi-Micro Fluorimeter FUV cell (quartz) with a PTFE lid and five polished windows (path length = 4×10 mm, spectral range = 170–2200 nm). The titrant was added in 10.0 μL aliquots using a 5–50 μL Finnpiptette[®] that was calibrated every week according to the manufacturer's instructions. The solution was equilibrated for 1 min before each emission spectrum was acquired. A lifetime measurement was taken of the original titrand and after the final 10.0 μL aliquot addition. The number of 10.0 μL aliquots needed to reach the end of the titration (defined as a 5:1 ligand-to-metal ratio) was determined by the concentration of the titrant solution.

Luminescence spectroscopy emission experiments were completed on a HORIBA Jobin–Yvon FluoroMax[®]-4 spectrofluorometer. The excitation source for the emission experiments was an ozone-free, continuous output 150 W xenon lamp with an excitation wavelength range of 220–600 nm. An excitation wavelength of 393 nm (excitation slit

width = 3 nm) was used to excite the 4f electrons in the Eu^{3+} cation. The excitation source was coupled to a Czerny–Turner monochromator with 1200 grooves/mm gratings. A second monochromator was set up at a 90° angle from the excitation source to avoid reflected light and collimate the emission. The emission slit width was set to 1 nm. Emission spectra were obtained using the FluorEssenceTM software (HORIBA Scientific, version 3.5 for Windows[®]). The emission spectra were recorded in the range of 550–650 nm at increments of 0.25 nm and an integration time of 1 s.

Results and discussion

Liquid–liquid solvent extraction

Ligand solubility

All ligands were highly soluble in the aliphatic diluents *n*-octane and *n*-dodecane. Solubility limits have not been calculated due to limited ligand stocks but known solubilities ranged from 35 to 43 g UDGA/L *n*-octane or *n*-dodecane. The ligand solubility in *n*-octane and *n*-dodecane decreased, however, when the organic phase was contacted with an aqueous phase containing nitric acid and Eu(III). A solubility experiment has been performed using 0.099 M DHpyrDGA in *n*-octane in contact with 10.0 mM $\text{Eu}(\text{NO}_3)_3$ in 1.0 M HNO_3 . When the two phases were mixed, a third phase appeared between the two layers. The phase modifier, 1-octanol, was added to the biphasic system, which immediately reverted back to two clear phases. Various percentages of 1-octanol have been tested and 5% 1-octanol has been selected due to the avoidance of a third phase while maintaining reasonable high distribution ratios (D_{Eu}).

Equilibration time

The unsymmetrical diglycolamide (UDGA) ligand 1 (*N,N*-dihexyl-*N'*-pyrrolidinyldiglycolamide, DHpyrDGA) has been used to determine the contact time required for the dihexyl derivatives (1–3) to reach thermodynamic equilibrium. This experiment monitored the distribution ratio (D_{Eu}) with increasing equilibration time (Fig. 6). This first experiment also used a millimolar concentration of Eu(III) to ensure that ensuing radiotracer Eu(III) studies were accurate surrogates for higher Ln(III) concentration solvent extraction systems.

Compared to TODGA, the new unsymmetrical dihexyl diglycolamide ligands have shorter alkyl chains and thus less steric bulk around the binding pocket. It was expected that the required equilibration times would be shorter than those needed for TODGA (i.e., 15–20 min) [12, 13, 19]. The results in Fig. 6 are consistent with this expectation.

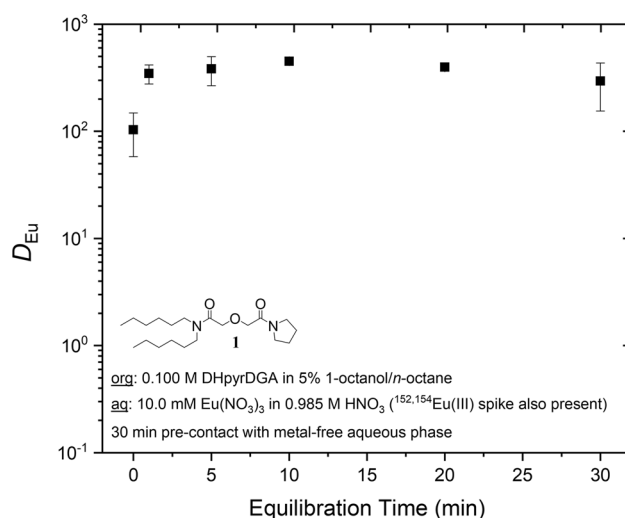


Fig. 6 The extraction of Eu(III) from 0.985 M HNO_3 by *N,N*-dihexyl-*N'*-pyrrolidinyldiglycolamide (DHpyrDGA) in 5% v/v 1-octanol/*n*-octane with varying equilibration times. Organic phases were pre-equilibrated with metal-free aqueous phase for 30 min

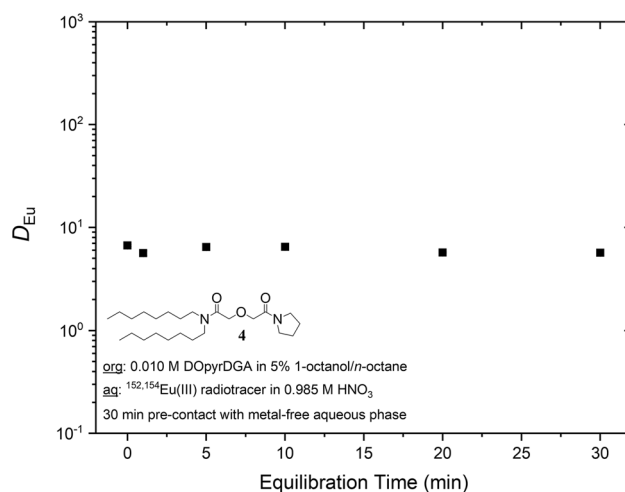


Fig. 7 The extraction of Eu(III) from 0.985 M HNO_3 by *N,N*-dioctyl-*N'*-pyrrolidinyldiglycolamide (DOPyrDGA) in 5% v/v 1-octanol/*n*-octane with varying equilibration times. Organic phases were pre-equilibrated with metal-free aqueous phase for 30 min

The distribution ratio (D_{Eu}) quickly came to equilibrium and levelled off after only 2 min of equilibration on a Vortex mixer. The unsymmetrical diglycolamide (UDGA) ligand 4 (*N,N*-dioctyl-*N'*-pyrrolidinyldiglycolamide, DOPyrDGA) has been used to determine the contact time required for the dioctyl derivatives (4–6) to reach thermodynamic equilibrium. This experiment monitored the distribution ratio (D_{Eu}) with increasing equilibration time (Fig. 7).

The new unsymmetrical dioctyl diglycolamide ligands (4–6) have amidic rings on one end of the molecule, which

could be responsible for the nearly instantaneous equilibrium achieved in Fig. 7. As such, all subsequent solvent extraction experiments used a 30-min contact time unless otherwise stated.

Nitric acid dependence

In solvent extraction systems based on “solvating” extractants like the DGAs, cation extraction is favored at high concentrations of nitric acid (more specifically, nitrate anion) and back-extraction, or stripping, of the cation is achieved by contacting the loaded organic phase with dilute nitric acid. At low concentrations of HNO_3 (e.g., 0.01 M), solvating extractants lack sufficient NO_3^- counter anions to drive the extraction of trivalent metal cations and the metal cations are strongly solvated by water molecules. At high concentrations of HNO_3 (e.g., 1 M), there is a large excess of available NO_3^- anion to drive the extraction of the neutral metal–ligand complex and the metal cations are more weakly hydrated due to the decrease in free water molecules (salting-out effect) [20].

The extraction of Eu(III) by the dihexyl derivatives (DHmorDGA, DHpyrDGA, and DHpipDGA) has been stronger than expected, but these systems have also shown a greater tendency toward phase incompatibility, exhibiting a notable trend toward forming a triphasic system at 3.0 M HNO_3 . Though triphasic systems offer interesting challenges in describing solvent–solute interactions, they are less interesting than a biphasic system within the scope of this study. Partitioning data for these derivatives at 0.05 M extractant concentration (in 5% v/v 1-octanol/*n*-octane) from 0.01 M, 0.1 M, and 1.0 M nitric acid are summarized in Table 1.

None of the dihexyl derivatives have exhibited much promise for use in a solvent extraction system, at least under the conditions investigated in this study. The shorter C_6 alkyl chains (relative to the standard TODGA) may ultimately reduce the solubility of the metal–ligand complexes in the bulk *n*-dodecane, which results in a more polar and denser third phase enriched with metal and ligand at 3.0 M HNO_3 . Moreover, under the conditions of the experiments, the D_{Eu}

Table 1 Distribution ratios (D_{Eu}) for the partitioning of $^{152,154}\text{Eu(III)}$ by three different asymmetric dihexyl diglycolamide ligands (1–3) from varying nitric acid aqueous phases

$[\text{HNO}_3]$ (M)	D_{Eu} (DHpyrDGA)	D_{Eu} (DHpipDGA)	D_{Eu} (DHmorDGA)
0.01	0.94 ± 0.01	1.02 ± 0.08	0.04 ± 0.02
0.1	16 ± 2	2.53 ± 0.06	6.1 ± 0.5
1.0	1000 ± 600	150 ± 10	2000 ± 1000

Organic phase: 0.05 M dihexyl diglycolamide in 5% v/v 1-octanol/*n*-dodecane. Error reported is $\pm 1\sigma$

is about 1 for both DHpyrDGA and DHpipDGA at 0.01 M HNO_3 , which means that only 50% of the Eu(III) would end up in the aqueous phase during the back-extraction step of the operation, i.e., Eu(III) is poorly stripped from the loaded organic phase under these conditions.

The corresponding dioctyl derivatives (Fig. 8, 4–6) contain two of the octyl groups that are considered to be optimal for use in the symmetrical diglycolamides (i.e., TODGA) [5]. The straight chain C_8 groups increase the lipophilicity of the aliphatic extractant tails relative to the C_6 groups and exhibit improved solubility in aliphatic diluents such as *n*-octane and *n*-dodecane. Extractants 4–6 achieve D_{Eu} greater than 1000 at 3.0 M HNO_3 and less than 1 at 0.01 M HNO_3 thus demonstrating the desired ability of the ligands to extract Ln(III) at high acidity (e.g., 3 M HNO_3) and to allow quantitative stripping of the metal at low acidity (e.g., 0.01 M HNO_3).

DOpyrDGA exhibits a consistently linear nitric acid dependence (slope = 1.9 ± 0.1). The relatively constant slope over a moderate range of acidity (0.01–1.0 M HNO_3) is unusual for diglycolamide extractants [21] and is only seen here with the pyrrolidinyl ligand. It is proposed that the smaller, five-membered amide ring does not promote nitric acid extraction and leads to a more linear trend in metal extraction with increasing nitric acid concentration. DOpipDGA and DOMorDGA derivatives both have nitrate dependence slopes of less than 1 at low acidity (0.01–0.1 M HNO_3) and much steeper slopes at higher acidity (0.5–1.9 M HNO_3). This result suggests a nitric acid-induced structural change in the extractant (aggregation) may be occurring as $[\text{HNO}_3]$ increases. DOMorDGA achieves the first observed hyperstoichiometric nitric acid dependence (slope = 5.9 ± 0.7)

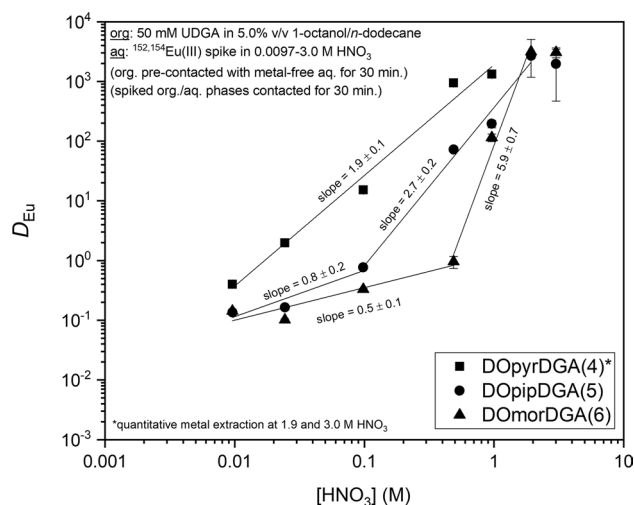
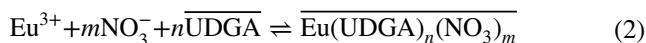


Fig. 8 The extraction of $^{152,154}\text{Eu(III)}$ by the dioctyl derivatives (4–6) from varying initial concentrations of nitric acid. The asterisk (*) signifies quantitative metal extraction at 1.9 and 3.0 M HNO_3 . Error in the $[\text{HNO}_3]$ was less than 1%

from 0.5 to 1.9 M HNO₃. This stoichiometry would require a reorganization of the Eu(NO₃)₃·(HNO₃)_x·(DOMorDGA)_n complex into a supramolecular aggregate containing as many as three molecules of nitric acid. In a recent study of nitric acid extraction by the symmetrical diglycolamide *N,N,N',N'*-tetra-2-ethylhexyldiglycolamide (T2EHDGA), Campbell and coworkers reported that one or two molecules of HNO₃ were associated with each T2EHDGA molecule in a similar organic phase [22]. It is possible that the comparatively more polar morpholinyl group promotes the extraction of a third molecule of nitric acid into the organic phase. The most promising candidate for the extraction of Ln(III) and An(III) from used nuclear fuel of these first two sets of ligands is DOPipDGA because it has two distinct regions of nitric acid dependence at low and high acidity (metal stripping region: slope₁ = 0.8 ± 0.2; metal extraction region: slope₂ = 2.7 ± 0.2) and does not form a third phase at high nitric acid concentrations.

Metal–ligand complex stoichiometry

The UDGA ligands 1–6 synthesized in this work are amphiphilic molecules that are not designed to readily form crystalline materials. Thus, an alternative method (to radiometric slope analysis) for determining ligand-to-metal complex stoichiometry was necessary. Solvent extraction experiments can offer a representation of the coordination complex in a realistic organic phase (e.g., 5.0% v/v 1-octanol/*n*-dodecane). The generic extraction of Eu(III) by a UDGA is represented by the reaction shown in Eq. 2; in principle, the Eu:NO₃[−] stoichiometric ratio in the extracted complexes must be 1:3 if the requirement of charge neutralization is to be respected. The extraction of water and nitric acid has been neglected in this representation, though literature reports indicate that the extraction of Eu(III) by TODGA from nitric acid media is characterized by a complex and variable stoichiometry [23]. The overlined species are in the organic phase.



The conditional extraction equilibrium constant for this extraction reaction can then be written as Eq. 3,

$$K_{\text{ex}} = \frac{[\overline{\text{Eu}(\text{UDGA})_n(\text{NO}_3)_m}]}{[\text{Eu}^{3+}][\text{NO}_3^-]^m[\overline{\text{UDGA}}]^n} \quad (3)$$

Absent the effects of nitric acid extraction, the Eu³⁺:NO₃[−] stoichiometry should be 1:3 to satisfy the requirements of electroneutrality in the extractant phase, hence *m* should ideally be three. The idealized distribution ratio expression for Eu(III) can be expressed as Eq. 4,

$$D_{\text{Eu}} = \frac{[\overline{\text{Eu}(\text{UDGA})_n(\text{NO}_3)_m}]}{[\text{Eu}^{3+}]} \quad (4)$$

Substituting Eq. 4 into Eq. 3 and converting to the logarithmic form gives Eq. 5,

$$\log(D_{\text{Eu}}) = n \cdot \log[\overline{\text{UDGA}}] + \log K_{\text{ex}} + m \cdot \log[\text{NO}_3^-] \quad (5)$$

Equation 5 can then be represented by the equation for a straight line (*y* = *mx* + *b*) where *y* = log(*D*_{Eu}), *m* = *n* (the average number of extractant molecules associated with each metal center), *x* = log[$\overline{\text{UDGA}}$], and *b* = log *K*_{ex} + *m*·log[NO₃[−]]. This mathematical relationship can help to obtain both the ligand-to-metal ratio (*n*) in the organic phase and the conditional extraction equilibrium constant (log *K*_{ex}).

A series of solvent extraction experiments have been run in which the concentration of the UDGA ligand has been varied while the [HNO₃] has been held constant at 1 M. The metal partitioning has been measured radiometrically by introducing a ^{152,154}Eu(III) spike (10^{−5} M total Eu) into the biphasic system and measuring the counts per minute (cpm) in each separated phase. The mixed diluent 5.0% v/v 1-octanol/*n*-dodecane was used throughout to prevent third phase formation and allow for clean phase disengagement. Both morpholinyl ligands (DHmorDGA and DOMorDGA) have exhibited third phase formation with the 5.0% v/v 1-octanol/*n*-dodecane diluent so the experiments were repeated with 10.0% v/v 1-octanol/*n*-dodecane. The concentration range for each UDGA ligand varied depending on metal extraction strength (e.g., 5.0, 10.0, 20.0, and 40.0 mM DHpyrDGA) and used at least four triplicate data points for the linear fitting in OriginPro®. The concentration of UDGA ligand has been plotted versus the Eu(III) distribution ratios on a logarithmic scale to utilize Eq. 5. An example of the graphed data for DHpyrDGA is shown in Fig. 9 (see supplementary information for graphs of the other ligands 2–6 and TODGA).

The slope (*n*) of the line fit through all twelve graphed points was 3.10 ± 0.02, which represents a 3:1 ligand to metal center ratio. Sasaki et al. also have performed identical ligand concentration dependence experiments with TODGA in various diluents [5]. They have reported that the numbers of ligands associated with each metal center in the organic phase increased with the decreasing dielectric constant of the diluent used. Table 2 shows the conditional extraction equilibrium constants (log *K*_{ex}) and metal–ligand complex stoichiometry (*n*) for unsymmetrical diglycolamide ligands (1–6) and TODGA with Eu(III).

The ligand to metal ratios (*n*) for the Eu-UDGA complexes fall in between the Sasaki et al. literature values for

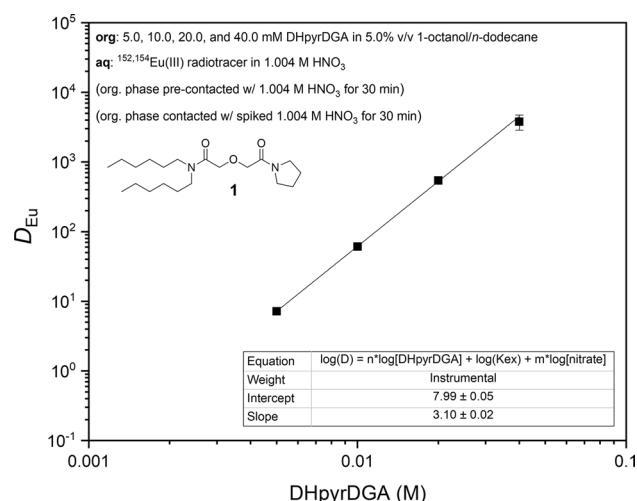


Fig. 9 The partitioning of Eu(III) metal between 1.004 M HNO₃ and varying [DHpyrDGA] in 5.0% v/v 1-octanol/*n*-dodecane

Table 2 Conditional extraction equilibrium constants ($\log K_{\text{ex}}$) and metal–ligand complex stoichiometry (n) for unsymmetrical diglycolamide ligands (1–6) and TODGA in 5.0 or 10.0% v/v 1-octanol/*n*-dodecane in contact with radiotracer $^{152,154}\text{Eu(III)}$ in 1.004 M HNO₃

#	Diglycolamide ligand	$\log K_{\text{ex}}$ (Eu)	n (ligand: metal)
<i>5% 1-octanol/n-dodecane</i>			
1	DHpyrDGA	7.99 ± 0.05	3.10 ± 0.02
2	DHpipDGA	7.51 ± 0.07	3.36 ± 0.04
4	DOpyrDGA	8.06 ± 0.27	3.21 ± 0.13
5	DOpipDGA	6.71 ± 0.12	3.04 ± 0.07
–	TODGA	6.26 ± 0.02	2.93 ± 0.01
<i>10% 1-octanol/n-dodecane</i>			
3	DHmorDGA	6.44 ± 0.14	3.13 ± 0.08
6	DOmorDGA	6.85 ± 0.23	3.34 ± 0.13

Error reported is $\pm 1\sigma$

Eu-TODGA (4.10 ± 0.05 in *n*-dodecane and 2.48 ± 0.07 in 1-octanol) [24]. The combination of *n*-dodecane with 5 or 10% 1-octanol phase modifier brings the ligand-to-metal ratio to an average of about 3:1 in this investigation. An experiment was run using TODGA in 5.0% v/v 1-octanol/*n*-dodecane to confirm these results and the 3:1 stoichiometry was verified. The conditional extraction equilibrium constants ($\log K_{\text{ex}}$) also agree with the general trend of extraction strength between ligands seen in other solvent extraction experiments: decreasing in strength from pyrrolidinyl to piperidinyl to morpholinyl derivatives. Figure 10 reports the results for the extraction of Eu(III) from 1.0 M HNO₃ by ligands 1–6 and TODGA in 5.0% v/v 1-octanol/*n*-dodecane.

The dihexyl UDGA extractants (squares, 1–3) behave quite similarly to the dioctyl group (circles, 4–6) with a slight decrease in distribution ratios from the analogous dihexyl

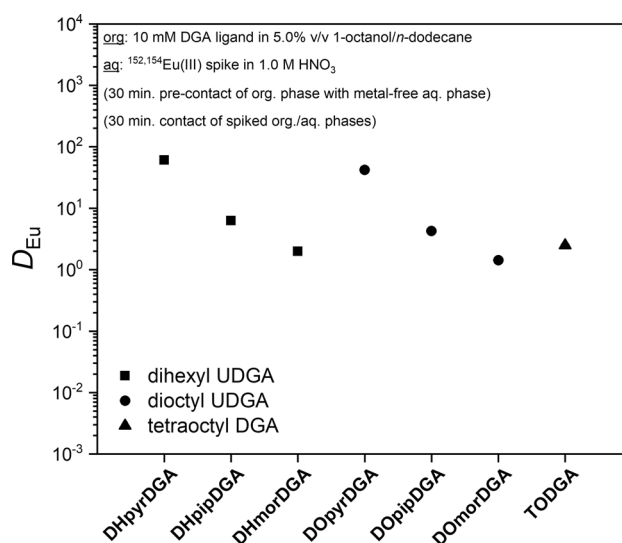


Fig. 10 The distribution ratios (D_{Eu}) for radiotracer $^{152,154}\text{Eu(III)}$ between a 10 mM diglycolamide (ligands 1–6 and TODGA) in 5.0% v/v 1-octanol/*n*-dodecane organic phase and a 1.0 M HNO₃ aqueous phase

to dioctyl derivatives. This decrease in Eu(III) extraction with increasing alkyl chain length follows the assertion by Sasaki et al. that longer alkyl chains tend to interfere with metal–ligand complexation [5]. Within the dihexyl and dioctyl families, Eu(III) extraction decreases by an order of magnitude between the 5-membered pyrrolidinyl ring derivative ($-\text{NC}_4\text{H}_8$) and the analogous 6-membered piperidinyl ring ($-\text{NC}_5\text{H}_{10}$). The orientation of the 5-membered pyrrolidinyl ring is slightly staggered while the 6-membered piperidinyl ring likely adopts a chair configuration. This puts the third carbon on the piperidinyl ring out-of-plane with the amide, which results in the metal binding site being more sterically hindered than the mostly in-plane pyrrolidinyl ring. The 6-membered morpholinyl ring ($-\text{NC}_4\text{H}_8\text{O}$) replaces the third carbon in the piperidinyl ring with an oxygen atom, which should be less sterically hindered and lead to an increase in metal complexation strength. The opposite trend is seen to occur in the data, however, and there is a small decrease in metal extraction from the piperidinyl (2 and 5) to the morpholinyl (3 and 6) derivatives. The morpholinyl derivatives have been observed to more readily form a third organic phase during the pre-equilibration step with a metal-free aqueous phase. The Lewis base oxygen atom in the morpholinyl ring could hydrogen bond with the proton in a nitric acid molecule, leading to an increase in nitric acid extraction. It is possible that the morpholinyl ligands are extracting greater stoichiometric amounts of nitric acid. This would lead to a decrease in free ligand concentration and could suppress metal distribution ratios.

Overall, under the conditions used in this investigation, the pyrrolidinyl (1 and 4) and piperidinyl (2 and 5)

derivatives are stronger extractants than TODGA, while the morpholinyl ligands (3 and 6) are slightly weaker. Based on a steric bulk argument, TODGA should be a much weaker extractant than the more compact unsymmetrical diglycolamide ligands. The four, long straight-chain alkyl groups (C_8) off the diglycolamide backbone are theoretically long enough and have enough rotational freedom to interfere with metal complexation in the tridentate (three oxygen) binding pocket. The unsymmetrical diglycolamide ligands have similar straight-chain alkyl groups (C_6 or C_8) on one end of the molecule, but unlike TODGA they have smaller and rotationally restricted rings on the other end of the molecule. These amide rings should decrease the overall steric hindrance around the binding pocket and increase the strength of the metal–ligand complexes. On the other hand, the four, long straight-chain alkyl groups (C_8) on both sides of the TODGA molecule may serve to decrease nitric acid extraction while not completely blocking metal complexation. Further experiments to determine nitric acid extraction are necessary for a more complete interpretation of metal partitioning results between the various ligands.

Luminescence spectroscopy

A solution of Eu(III) in the polar organic solvent acetonitrile (MeCN) was titrated with the unsymmetrical diglycolamides (also dissolved in MeCN) and spectral changes were monitored using luminescence spectroscopy. Changes in the hypersensitive peak around 615 nm and the magnetic dipole peak at 592 nm represented changes in the metal–ligand complex speciation. In each ligand system, the titrations were run until the ligand-to-metal ratio was greater than five or to the point at which there were no additional spectral changes. The spectra from a representative titration using DHmorDGA are shown in Fig. 11 (see supplementary information for emission spectra of the other five UDGA ligands and TODGA).

In every ligand system, the majority of the spectral changes occur at the hypersensitive peak (ca. 615 nm), which eventually splits into two peaks at ca. 613 and 617 nm (see inset in Fig. 11). The magnetic dipole transition peak at 592 nm remains at the same wavelength throughout the titration but does steadily increase in magnitude until levelling off at the end of the titration. The relatively weak electric dipole transition at 578 nm experiences a small redshift to 578.5 nm during the titration, but the peak intensity was too small for data fitting purposes.

The other UDGA ligands generated spectral peaks nearly identical to those seen in Fig. 11.

The spectral shapes for each metal–ligand species and Eu(III) have been deconvoluted by the HypSpec fitting program. The spectra for the 1:1 through 1:4 Eu-DHmorDGA complexes are shown in Fig. 12. Similar spectra were

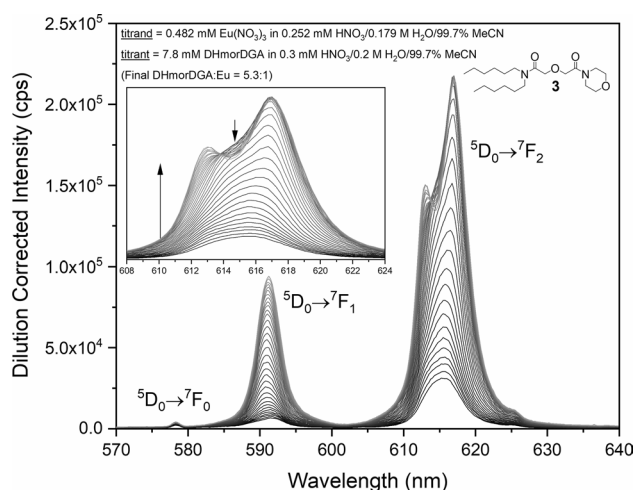


Fig. 11 Emission spectra of Eu(III) with increasing concentration of the ligand *N,N*-dihexyl-*N'*-morpholinyl diglycolamide (DHmorDGA) in acetonitrile. Inset of 608–624 nm included to show the peak splitting toward the end of the titration (black line = beginning; gray line = end)

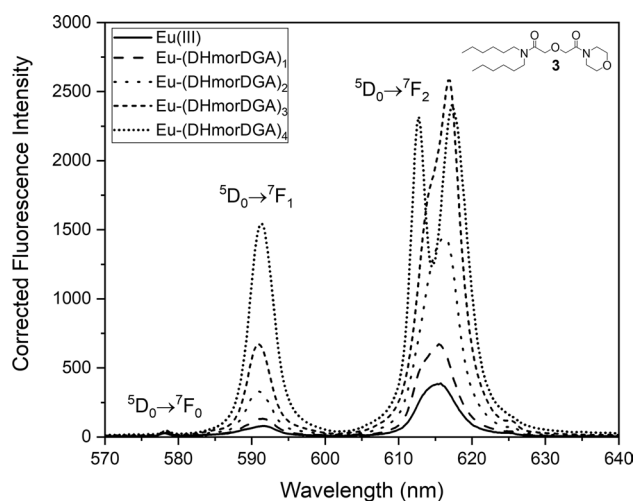


Fig. 12 Deconvoluted spectra for 1:1 through 1:4 Eu(III)-DHmorDGA complexes in 0.3 mM HNO_3 /0.2 M H_2O /99.7% MeCN

resolved for each system that converged on an internally consistent model in the HypSpec program.

The deconvoluted spectra show changes in both peak intensity and wavelength. The intensity of the 592 nm peak increases exponentially from the beginning to the end of the titration while the wavelength remains static. The largest spectral changes occur at the hypersensitive peak around 615 nm where the development of a second blue-shifted peak adds a shoulder to the 1:1, 1:2, and 1:3 complexes. The blue-shifted peak (613 nm) is almost resolved from the red-shifted peak (617 nm) in the 1:4 complex spectrum and the relative intensity of the 613 nm peak becomes almost

equal to the 617 nm peak with the formation of the terminal complex, Eu-(DHmorDGA)₄.

HypSpec was also used to resolve conditional stability constants (β_{MHL}) for the four metal–ligand species using non-linear least-squares regression analysis [25]. The equilibrium expressions used to fit each β_{MHL} are shown in Eqs. 6–9. The nitrate concentration was held constant during the titration and has thus been ignored in the equilibrium expressions. Any protonated (H) metal–ligand species have also been ignored in these calculations because these titrations took place in the polar organic solvent, acetonitrile, which does not allow for cationic species.

$$\beta_{101} = [\text{Eu}(\text{UDGA})]/[\text{Eu}][\text{UDGA}] \quad (6)$$

$$\beta_{102} = [\text{Eu}(\text{UDGA})_2]/[\text{Eu}][\text{UDGA}]^2 \quad (7)$$

$$\beta_{103} = [\text{Eu}(\text{UDGA})_3]/[\text{Eu}][\text{UDGA}]^3 \quad (8)$$

$$\beta_{104} = [\text{Eu}(\text{UDGA})_4]/[\text{Eu}][\text{UDGA}]^4 \quad (9)$$

The β_{MHL} values were very large so a logarithmic operator was applied to simplify the reporting. The model was tested starting with the 1:1 metal–ligand complex ($\log \beta_{101}$) and new fits were attempted after the addition of each new species (e.g., $\log \beta_{102}$, $\log \beta_{103}$, $\log \beta_{104}$). Different sets of stability constants were obtained for the two, three, and four species systems, but the four species system was accepted as the most accurate due to the final experimental metal–ligand ratios and the factor analysis in HypSpec.

Most of the full data sets did not successfully converge on stability constant values immediately. Series of data points were graphed near important wavelengths (e.g., 592, 613, and 617 nm) and observed for discontinuities or aberrations in the curve. The data sets were then truncated near the theoretical 1:4 metal–ligand ratio and the model was tested as before. This process was repeated until stability constants converged with reasonable values and low error ($\leq 3\%$). The quality of the fit was tested by entering much lower initial values (e.g., $\log \beta_{101} = 4$) and confirming the convergence to the same higher value (e.g., $\log \beta_{101}$ (DOpyrDGA) = 7.9). The titrations and data fitting routines were repeated for all six unsymmetrical diglycolamide ligands and TODGA. The conditional stability constants are reported in Table 3. The uncertainties in the conditional stability constants ($\log \beta_{\text{MHL}}$) were calculated in HypSpec and are reported at $\pm 2\sigma$. Spectral data describing europium complexes with the first two UDGA ligands (DHpyrDGA and DHpipDGA) failed to converge on stability constant values. The luminescence spectra for DHpyrDGA and DHpipDGA were nearly identical to the other ligands so the inability to converge on $\log \beta_{\text{MHL}}$ values is probably a failure in the Newton–Raphson fitting method

Table 3 Conditional overall stability constants ($\log \beta_{\text{MHL}}$) for Eu(III)-UDGA and Eu(III)-TODGA complexes in 0.3 mM HNO₃/0.2 M H₂O/99.7% MeCN

Ligand	$\log \beta_{101}$	$\log \beta_{102}$	$\log \beta_{103}$	$\log \beta_{104}$
DHmorDGA	7.83 \pm 0.08	14.4 \pm 0.1	19.6 \pm 0.1	22.7 \pm 0.1
DOpyrDGA	7.9 \pm 0.2	15.1 \pm 0.3	20.9 \pm 0.4	23.5 \pm 0.4
DOpipDGA	7.3 \pm 0.2	14.5 \pm 0.3	20.0 \pm 0.4	22.8 \pm 0.8
DOmorDGA	6.8 \pm 0.2	12.6 \pm 0.3	18.1 \pm 0.3	22.4 \pm 0.4
TODGA	6.28 \pm 0.02	11.69 \pm 0.02	17.03 \pm 0.02	21.55 \pm 0.02

Error reported is $\pm 2\sigma$

due to discontinuities in the data sets and not an indication of different coordination complexes.

The step-wise stability constants ($\log K_{\text{MHL}}$) can also be calculated by evaluating the difference between each successive $\log \beta_{\text{MHL}}$ value. For example, the step-wise stability constants for DHmorDGA are $\log K_{101} = 7.83$, $\log K_{102} = 6.57$, $\log K_{103} = 5.2$, and $\log K_{104} = 3.1$. This steady decrease in step-wise stability constants is expected due to an increase in steric crowding around the metal center as more ligands coordinate. The conditional $\log \beta_{\text{MHL}}$ values are validated by the low error, reproducibility of the fit, and the correct trend in step-wise stability constants.

For the successive 1:1 through 1:4 complexes the Eu-UDGA complexes are 10–1000 times stronger than the Eu-TODGA complexes. The dioctyl (DO) derivatives have decreasing $\log \beta_{\text{MHL}}$ values from DOpyrDGA to DOpipDGA to DOMorDGA. The same trends in complex stability have been seen in earlier experiments using liquid–liquid solvent extraction ($\log K_{\text{ex}}$ values) wherein all the UDGA ligands have been found to be stronger Eu(III) extractants than TODGA. The evident predominance of the terminal 1:4 metal-UDGA complex in the luminescence titrations, assuming a tridentate ligand, would suggest a Eu(III) metal center with a coordination number of 12. Although possible, 12-coordinate complexes with Eu(III) are rare and usually involve small multidentate ligands that take up very little space in the coordination sphere (e.g., nitrate) [26]. Alternatively, it is also possible that the presumed tridentate UDGA ligands are functioning as bidentate ligands in which both of the amidic carbonyl oxygens are binding to the metal but the central etheric oxygen is not. This would give a more probable 8-coordinate Eu-UDGA complex that does not rely upon the presence of other ligands like nitrate.

Conclusions

Six new unsymmetrical diglycolamide extractant ligands were synthesized using a three-step organic synthesis. The trivalent lanthanide metal extraction behavior of the

unsymmetrical diglycolamides (1–6) was studied using radiotracer $^{152,154}\text{Eu(III)}$. DHpyrDGA and DOPyrDGA in 5.0% v/v 1-octanol/*n*-octane were contacted with $^{152,154}\text{Eu(III)}$ in 0.985 M HNO_3 for varying amounts of time and were both found to reach equilibrium in less than 2 min. The conditional metal extraction equilibrium constants ($\log K_{\text{ex}}$) were determined using a ligand dependence slope analysis experiment and the UDGA ligands were found to be comparable or stronger Eu(III) extractants than the symmetrical diglycolamide, TODGA. The same slope analysis experiment also determined the metal–ligand complex stoichiometry (in 5.0% v/v 1-octanol/*n*-dodecane) to be approximately 1:3 for the UDGA ligands and TODGA.

The change in Eu(III) extraction with varying concentrations of HNO_3 was determined radiometrically and compared across the UDGA ligand series. The dihexyl derivatives (1–3) dissolved in 5.0% v/v 1-octanol/*n*-dodecane were the strongest extractants for Eu(III) but formed a dense third phase when contacted with 1.9 or 3.0 M HNO_3 , which is undesirable for a biphasic liquid–liquid solvent extraction process. The dioctyl derivatives (4–6) had slightly lower distribution ratios (D_{Eu}) for Eu(III) but did not form a third phase at 1.9 and 3.0 M HNO_3 . The best extractant candidate, DOPipDGA, was shown to quantitatively extract Eu(III) at higher acidity (> 1 M HNO_3) and allowed for metal stripping at lower acidity (< 0.1 M HNO_3).

Luminescence spectroscopy titrations were performed and resulted in the formation of 1:1 through 1:4 metal–ligand complexes for all six UDGA ligands and TODGA in the polar organic solvent acetonitrile. The UDGA ligands were shown to form complexes with Eu(III) 10–1000 times stronger than those reported for TODGA under these conditions.

The most promising ligands identified in this study were the longer alkyl chain dioctyl derivatives. The logical path forward with this research is to move to longer alkyl chains (e.g., didecyl or didodecyl) or increase the branching on the same base alkyl chains (e.g., di-2-ethylhexyl or 3,7-dimethyloctyl). Future work will focus on the synthesis of these more massive unsymmetrical diglycolamide ligands with the hope of increasing solubility in the organic phase while maintaining high lanthanide metal extraction efficiency.

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