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Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-05-2018-002239.R1
Article Type:	Paper
Date Submitted by the Author:	18-Jul-2018
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Lanthanide Extraction Selectivity of a Tripodal Carbamoylmethylphosphine Oxide Ligand System

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Abstract

Four tripodal carbamoylmethylphosphine oxide (CMPO)-based ligands are reported here and assessed with regard to lanthanide (Ln) coordination chemistry and selective extraction of lanthanide ions from aqueous solution. Inspired by previous liquid-liquid extraction studies that suggested a preference for terbium(III), the current work further probes the extraction behavior of a tris-(2-aminoethyl)amine (TREN) capped, ethoxy substituted CMPO ligand with respect to the entire series of lanthanides. Upon confirmation of Tb^{3+} extraction selectivity versus the whole series, experiments were conducted to assess the effect of increasing the alkyl chain length within the ligand TREN cap, as well as changing the CMPO substituents by replacing the ethoxy groups with more hydrophobic phenyl groups to promote solubility in the organic extraction solvent. Extraction efficiencies remained low for most lanthanides upon increasing the cap size, with %*E* values consistently around 5%, and a complete loss of Tb^{3+} preference was noted with a decrease in %*E* from 18% to 3.5%. For the agent employing the original, smaller TREN cap but with phenyl substituents on the CMPO units, an increase in extraction toward the middle of the row was again observed, albeit modest, with relatively high %*E* values for both Gd^{3+} and Tb^{3+} versus the other lanthanides (13 and 11%, respectively). A more dramatic extraction selectivity for the phenyl substituted ligand was achieved upon modification of the ligand to metal ratio, with a 100:1 ratio resulting in a near linear decrease in %*E* from 41% for La^{3+} to 3.7% for Lu^{3+}. Finally, modification of the TREN capping scaffold by adding an oxygen atom to the central nitrogen led to consistently low %*E* values, revealing the effect of TREN cap oxidation on Ln extraction for this tripodal CMPO ligand system.

Keywords

lanthanide, liquid-liquid extraction, CMPO, NMR, luminescence

Abbreviations

Ln: lanthanide; CMPO: carbamoylmethylphosphine oxide

Introduction

Given their essential and increasing use in a variety of modern applications, the “rare earth” elements (Sc, Y, La – Lu) are widely acknowledged as uniquely important to the development of advanced materials and electronics.[1-4] The magnetic and photophysical properties of several lanthanide (Ln) metals in particular are well documented and have been utilized in medical diagnostic agents,[5,6] luminescent sensors,[7,8] and a variety of smart phones and other modern devices.[9] Recently, Ln-based materials have also shown promise in the area of alternative energy production. For example, terbium (Tb) has been noted as a key component of advanced hybrid car batteries, wind turbines, and potential high-efficiency solar cells, and has been designated by the U.S. Department of Energy as one of the “critical” rare earth elements in the development of such clean-energy technologies.[10,11]

As the breadth of applications of the Lns continues to expand, there exists a growing interest in the efficient extraction of these valuable metals from various sources. While most “rare earth” elements are not exceptionally rare in nature, difficulty in mining and isolating individual Lns in pure form presents a significant challenge due to the complex Ln mixtures within most ground ores as well as the inherent chemical similarities throughout the series. Furthermore, the vast majority of Lns used today (~90%) are mined and exported from just one country.[12] The development of efficient, cost-effective separations technologies for Ln recovery would provide alternative supply chains and remains a worthwhile pursuit. Improved Ln extraction methods may also enable recycling of specific metals from the more than 40 million tons of electronic waste generated annually worldwide,[13] affording yet another viable source of these technologically critical metals with less environmental impact.

Historically, efforts toward the extraction of metals within the *f*-element groups have focused on the separation of the radioactive actinide (An) metals from the lanthanides. Since

Glenn Seaborg's pioneering work in the 1950's utilizing ion-exchange chromatography,[14] substantial progress has been made over the years in An/Ln partitioning. The most common methods, used notably in nuclear waste remediation, involve liquid-liquid extraction processes where an extractant molecule dissolved in an organic solvent is mixed with an acidic aqueous phase to extract the An/Ln ions contained within. For example, the TRansUranic EXtraction (TRUEX) process employs octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (**1**, Figure 1) for extraction primarily of americium and curium from nuclear waste streams.[15,16] Due to appreciable amounts of Lns and other fission products extracted along with the An ions during this process, extractants based on the original carbamoylmethylphosphine oxide (CMPO) ligand have been developed to improve An selectivity.[17-20] While significant progress has been made in terms of An/Ln partitioning, focused efforts toward selective Ln extraction have not been reported to the same extent. This is the case particularly regarding the development of multipodal CMPO-based ligands for use in standard liquid-liquid extraction methods aimed at Ln recovery. Given the current supply chain status of these increasingly important metals as well as recycling possibilities, the selective extraction of Ln ions, ideally using well-established, "industry friendly" methods, remains a worthwhile goal.

This report details our work toward the development of Ln extraction agents for application in selective extraction of specific metals within the series. In other recently published studies, progress has been made toward improving specificity of Ln extraction/recovery via novel approaches that include Ln incorporation into metal-organic frameworks (MOFs),[21] derivatized Fe-based nanoparticles,[22] ionic liquids,[23] and even bacteria possessing metal chelating groups.[24,25] In such studies, enhanced extraction selectivity is noted with regard to separation of one group of Lns from another (typically groups of lighter Lns from the heavier Lns[22-25]). Another recent report aimed at more specific Ln extraction details Ce extraction from a mixture of several other select Lns through a multi-step process involving oxidation from Ce^{3+} to Ce^{4+} followed by sequestration of the ion by an ionic liquid.[26] In similar work aimed at selective Ln extraction, Schelter and co-workers described the separation of Nd and Dy, key components of magnets, based on solubility and self-association equilibria utilizing a tripodal nitroxide ligand.[27] Inspired by these efforts, our group has explored tripodal ligands based on the CMPO chelating unit mentioned above. Specifically, our goal is to achieve selective Ln sequestration using well-established, scalable liquid-liquid extraction conditions by focusing primarily on structural variation of the chelating agent. Through this work, we have found that changing the ligand capping scaffold used to tether three CMPO groups within the extractant can lead to significant differences in general Ln coordination chemistry and An/Ln extraction properties.[28,29] We were particularly encouraged by preliminary results that suggested a tris-(2-aminoethyl)amine (TREN) capped CMPO ligand favored Tb extraction from acidic solution using classic liquid-liquid extraction methods. This potential Tb selectivity was originally demonstrated through extractions of individual Ln solutions and relative to a limited number of Lns included in the study.[28] We report herein a study aimed at exploring the Tb extraction behavior of TREN-CMPO-OEt (**2**, Figure 1), aimed at determining definitive selectivity versus all Lns in the series (except radioactive Pm). Additionally, in an attempt to understand the importance of the ligand capping scaffold in achieving selective extraction with tripodal CMPO agents, a new derivative incorporating a larger, tris-(3-aminopropyl)amine (TRPN) cap was prepared to test structural variation within the cap on extraction behavior (TRPN-CMPO-OEt, **3**). Noting the impact of the ligand cap, a third ligand employing the TREN scaffold with phenyl instead of ethoxy substituents on the CMPO moiety was studied to determine if the more hydrophobic substituents promote higher solubility in the extraction solvent, thereby enhancing Ln sequestration (TREN-CMPO-Ph, **4**). Finally, a fourth derivative similar to **2** but with an additional oxygen atom added to the central nitrogen of the TREN cap was prepared and assessed with regard to Ln extraction (OTREN-CMPO-OEt, **5**).

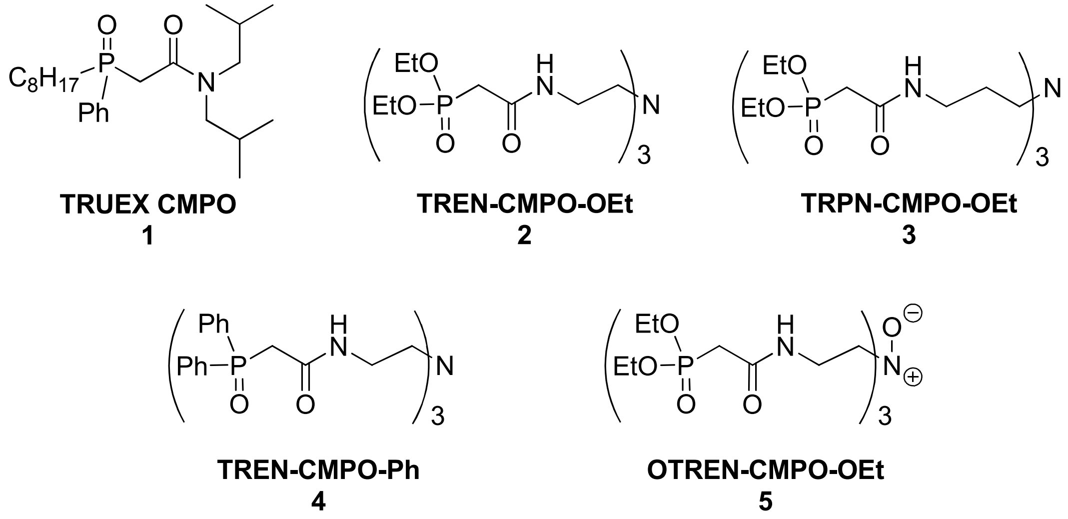


Figure 1. Monopodal CMPO ligand **1** used in the TRUEX process for nuclear waste remediation and the four tripodal CMPO ligands **2-5** studied herein.

Experimental

General considerations

All chemicals were purchased from Sigma-Aldrich, Fisher Scientific, Strem Chemical, or Acros Chemicals and used without further purification. ^{1}H, ^{13}C and ^{31}P NMR spectral data were recorded on either a Jeol Eclipse 300 or a Varian INOVA 400 FTNMR spectrophotometer, as stated. For ^{1}H and ^{13}C NMR spectra, chemical shifts are expressed as parts per million (δ) relative to $SiMe_4$ (TMS, δ = 0), and referenced internally with respect to the protio solvent impurity. For ^{31}P NMR spectra, chemical shifts are expressed as parts per million (δ) relative to H_3PO_4 (δ = 0). Both ^{13}C and ^{31}P NMR spectra were obtained as proton-decoupled data. IR spectra were acquired neat on a Jasco 4100 FT-IR or a Thermo Nicolet Avatar 360 FT-IR spectrometer fitted with the ATR sampling accessory. Elemental (CHN) analyses were performed by Atlantic Microlab Inc., Norcross, GA, and luminescence spectra and lifetimes were measured using a Hitachi F-7000 spectrofluorimeter. Mass spectrometry data were acquired by the Lumigen Instrument Center at Wayne State University. Extracted metal solutions were analyzed with a PerkinElmer Optima 2100 DV ICP-AES spectrophotometer. The synthesis of TREN-CMPO-OEt (**2**) was reported previously.[28]

Synthesis

TRPN-CMPO-OEt (3). Tris(3-aminopropyl)amine (**6**, 250 mg, 1.3 mmol) and 2.5 mL of methanol were added to a 25 mL round bottom flask. The flask was cooled to -78 °C with an EtOAc/LN_2 bath, and 0.73 mL of triethylphosphonoacetate (**7**, 0.83 g, 3.7 mmol) was added dropwise. The solution was allowed to warm to room temperature and stirred for 48 hours. The reaction mixture was concentrated under reduced pressure to give a light pink, viscous oil. The crude product was purified by silica gel chromatography (gradient of 5-10% MeOH in CH_2Cl_2 with 0.1% Et_3N) to give the pure product as a viscous oil. The average percent yield for this reaction was 70%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.59 (broad, 3H, -N*H*), 4.17-4.10 (m, 12H), 3.33-3.29 (m, 6H), 2.88 (d, J_{H-P} = 20 Hz, 6H), 2.58 (broad, 6H), 1.73 (broad, 1.73), 1.33 (t, J = 8.0 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.8, 62.8, 50.7, 37.6, 34.3, 24.8, 16.4; IR (neat) v = ~3275 (N–H), 1652 (C=O), 1236 (P=O) cm^{-1}; ESI-HRMS ($[M-H]^+$, *m/z*): calcd for

$C_{27}H_{58}N_4O_{12}P_3$: 723.3264, found: 723.3239; Anal. Calcd. for $C_{27}H_{57}N_4O_{12}P_3 \cdot 4H_2O$ (found): C, 40.81 (40.86); H, 8.24 (8.05); N, 7.05 (6.72)%.

Tb-TRPN-CMPO-OEt. TRPN-CMPO-OEt (**3**, 80.0 mg, 0.111 mmol) and 1 molar equivalent of $Tb(NO_3)_3 \cdot 6H_2O$ were each dissolved in CH_3CN (5 mL). The ligand solution was then mixed with the $Tb(NO_3)_3$ solution, stirred for 30 minutes at room temperature, and concentrated under reduced pressure. The metal complex precipitated upon addition of cold diethyl ether (10 mL) and the solid light tan product was isolated via vacuum filtration (35.4 mg, 29.9%). IR (neat) v = ~3300 (N–H), 1630 (C=O), 1193 (P=O) cm^{-1}; Anal. Calcd. for $TbC_{27}H_{57}N_7O_{21}P_3 \cdot 7H_2O$ (found): C, 27.17 (26.87); H, 5.99 (5.31); N, 8.21 (8.37)%.

TREN-CMPO-Ph (4). The activated ester *p*-nitrophenyl(diphenylphosphoryl) acetate[17] (**9**, 1.64 g, 4.3 mmol) was dissolved in 75 mL of ethanol-free anhydrous chloroform in a 250 mL round bottom flask. The flask was equipped with a reflux condenser and a N_2 balloon. Tris(2-aminoethyl)amine **8** was added via syringe (0.16 mL, 0.16 g, 1.1 mmol), and the reaction mixture was stirred for three days at 45 °C. The solution was then allowed to cool to room temperature, and 50 mL of water along with 3-4 mL of 40% KOH was added. The reaction was stirred at room temperature for four hours to ensure complete hydrolysis of any remaining *p*-nitrophenyl ester. The organic layer was isolated, washed with water (3 × 50 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give a yellow solid. This crude product was dried overnight on a Schlenk line to remove any residual chloroform. The resulting solid was triturated with alternate volumes of ethyl acetate and diethyl ether (3 × 10-15 mL each), and returned to the Schlenk line to remove residual solvents to give a pale yellow solid as the final product. The average percent yield for this reaction was 78%. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.54 (t, J = 4Hz, 3H, -N*H*), 7.71-7.33 (m, 30H), 3.57 (d, J_{H-P} = 14.4 Hz, 6H), 3.08 (m, 6H), 2.39 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.7 (d, J_{C-P} = 5.5 Hz), 132.2 (d, J_{C-P} = 102.1 Hz), 132.1 (s), 131.2 (d, J_{C-P} = 9.9 Hz), 128.7 (d, J_{C-P} = 12.2 Hz), 53.2 (s), 39.1 (d, J_{C-P} = 62.0 Hz), 37.9 (s); ^{31}P NMR (121 MHz, $CDCl_3$) δ: 30.0; FT-IR v (cm^{-1}): 3222 (N-H), 1661 (C=O), 1174 (P=O); ESI-HRMS ($[M-H]^+$, *m/z*): calcd for $C_{48}H_{52}N_4O_6P_3$: 873.3100, found: 873.3135.

OTREN-CMPO-OEt (5). TREN-CMPO-OEt[28] (**2**, 0.50 g, 0.73 mmol) was added to a 15 mL round bottom flask and dissolved in 1.5 mL of anhydrous THF. The reaction flask was cooled in a water/ice bath, and 0.15 mL of trichloroacetonitrile (0.22 g, 1.5 mmol) was added via syringe. Solid $NaHCO_3$ (31 mg, 0.37 mmol) and 0.15 mL of a 30% (w/w) hydrogen peroxide solution were then added to the reaction flask, and the mixture was stirred for 10 minutes. The reaction mixture was allowed to warm to room temperature and stirred for four hours. The THF was removed under reduced pressure, and acetonitrile (1.5 mL) was added to the solution. The mixture was cooled to 0 °C, at which time the trichloroacetamide byproduct precipitated out as a white solid. This solid was removed by vacuum filtration and rinsed with cold acetonitrile. The volatiles were removed under reduced pressure to give a light-yellow oil as the pure product. The average percent yield for this reaction was 95%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.58 (t, $J = 4.0$ Hz, 3H, -N*H*), 4.12-4.19 (m, 12H), 4.00 (broad m, 6H), 3.82 (broad m, 6H), 2.97 (d, $J_{H-P} = 20$ Hz, 6H), 1.35 (t, $J = 8$ Hz, 18H); ^{13}C ($CDCl_3$, 75 MHz) δ: 165.7 (d, $J_{\text{C-P}} = 5.1$ Hz), 63.6 (s), 63.1 (d, $J_{\text{C-P}} = 6.4$ Hz), 36.1 (d, $J_{\text{C-P}} = 132.4$ Hz), 34.0 (s), 16.4 (d, $J_{\text{C-P}} = 6.2$ Hz); ^{31}P ($CDCl_3$, 162 MHz) δ: 22.3 (s); FT-IR ν (cm^{-1}): 3271 (N-H), 1672 (C=O), 1230 (P=O), 1025 (P-O), 966 (N-O); ESI-HRMS ($[M-H]^+$, *m/z*): calcd for $C_{24}H_{52}N_4O_{13}P_3$: 697.2744, found: 697.2737.

Photophysical studies

Tb^{3+} complexes of **2** and **3** were prepared in MeOH at 2.0×10^{-3} M with 5% ligand excess to ensure full metal ion complexation. Excitation and emission spectra for Tb-**3** were recorded at room temperature with slit widths (ex/em) of 5 nm and a scan rate of 240 nm/min. The excitation spectrum was recorded monitoring emission at 545 nm, and the emission spectrum was recorded exciting the sample at 320 nm. Luminescence decay lifetimes (τ) for Tb-**2** and Tb-**3** were obtained using Phosphorescence Life Time (Short) mode within the Hitachi FL Solutions 2.1 instrument software, again exciting each sample at 320 nm. Resultant decay curves were fit using the standard curve fitting algorithm of the instrument software to yield lifetime values for samples in MeOH and samples with varying relative amounts of MeOH and MeOD; specifically, 1 mL solutions of the complex were prepared in pure MeOH, then 1 mL of MeOD was added to achieve 1:1 MeOH:MeOD, and another to achieve 1:3 MeOH:MeOD. Lifetimes were measured for each combination and used to construct a linear regression to give an extrapolated value for the lifetime in pure MeOD (Supp. Info., Figure S1). The "*m*" values (i.e., the number of metal-bound methanol solvent molecules) were calculated from the average MeOH/MeOD lifetime values obtained in triplicate using the following equation developed by Horrocks and co-workers,[30,31] where k is an emperical constant ($k_{\mathrm{Tb}} = 8.4$), τ is the lifetime, and m is the number of bound solvent molecules.

$$m = k_{Tb}(\tau_{MeOH}^{-1} - \tau_{MeOD}^{-1})$$

Extraction studies

Ligand solutions were prepared at 10^{-3} M in CH_2Cl_2. To achieve a 10:1 ligand to metal ratio for extraction experiments utilizing ligands **2**, **3**, **4**, and **5**, metal solutions were prepared from La(III) and Ln(III) nitrate salts (penta/hexahydrate) for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu at 10^{-4} M in 1 M HNO_3. Extraction experiments with **2** were also performed on the ICP-AES rare earth standard mixture (AccuStandard, Inc.; 100 ppm for each Ln^{3+} ion) with the same ligand concentration. For the 100:1 ratio results obtained for **4**, the same metal ion concentration was used with a ligand concentration of 10^{-2} M in CH_2Cl_2. All extractions were performed in triplicate for each individual metal and for the Ln mixture experiment. For each experiment, a 20 mL scintillation vial was charged with equal volumes (2 or 4 mL) of each ligand and Ln solution. These volumes were measured using volumetric pipets or calibrated pipettors. The combined solutions were stirred vigorously for 20 h at room temperature, then allowed to separate completely. For all individual Ln extraction experiments using ligands **2** and **5**, a 1.0 mL aliquot of each aqueous layer and 2.5 mL of 6.0×10^{-4} M Arsenazo III[32,33] solution in 1M formate buffer (pH 2.8) were then transferred to a 25.00 mL volumetric flask and diluted to the mark with formate buffer. The absorbance of the extracted aqueous layer with Arsenazo III (***A***) was measured at 655 nm. The absorbances of each aqueous metal solution before extraction ($\boldsymbol{A}_1$) and the aqueous solvent (1 M HNO_3) without metal ($\boldsymbol{A}_0$) were also measured following this procedure. Extraction efficiencies were calculated as the percent of Ln removed from the aqueous phase using the following equation:

$$\%E = \frac{(A_1 - A)}{(A_1 - A_0)} \times 100\ \%$$

For analysis of the ICP standard mixture extractions with ligand **2** and for individual Ln extractions using ligands **3** and **4**, from the extraction experiments prepared as outlined above (using 4 mL each of aqueous and organic phase) 2.50 mL aliquots of extracted aqueous metal solutions were diluted to 25 mL in 3% HNO_3 before analysis by ICP-AES. Pre-extraction samples were also prepared by diluting 2.50 mL aliquots of the 10^{-4} M metal solutions and diluting with 3% HNO_3. Calibration samples of the Ln metals were diluted to 1, 4, and 8 ppm from the rare earth standard solution (AccuStandard, Inc.). Wavelengths for ICP emission analysis of each Ln were chosen to minimize interference due to other metal emissions as determined from literature references.[34,35] Concentrations of each Ln were then determined using the best-fit regression line produced from the calibration sample analysis. Percent extraction values were calculated using the following equation:

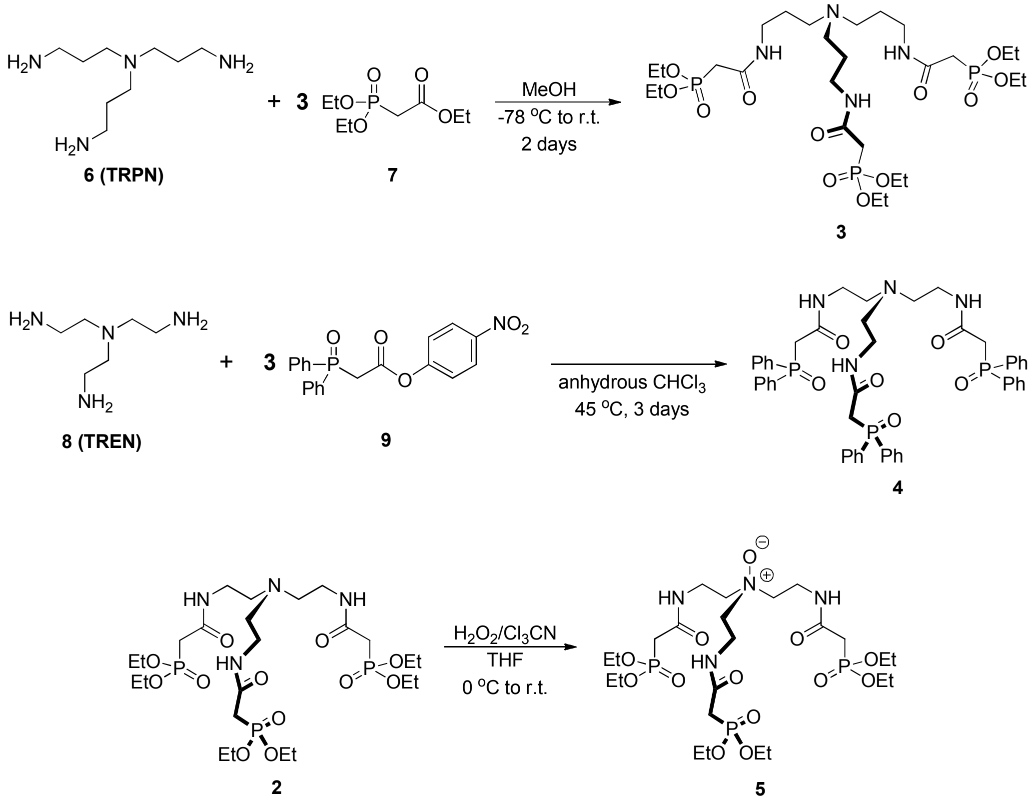
$$\%E = \frac{[Ln_0] - [Ln_{ex}]}{[Ln_0]} \times 100\ \%$$

where Ln_0 and Ln_{ex} represent pre-extraction and extracted Ln metal solution concentrations, respectively.

Results and discussion

Ligand synthesis

The ligand structures relevant to this study are shown in Figure 1, and include the TREN-capped ligand **2** as well as a new, tris(3-aminopropyl)amine (TRPN) capped ligand **3**, and the two additional TREN-based agents **4** and **5**. Ligand **3**, TRPN-CMPO-OEt, is identical to TREN-CMPO-OEt except for the extra methylene group in each "arm" of the tripodal cap which affords a larger, more flexible metal binding cavity for potential Ln complexation. The replacement of TREN with the TRPN cap may give insight into the role of the capping scaffold and the importance of the TREN cap in the context of observed extraction selectivity. The straightforward synthesis of **3** was carried out as shown in Scheme 1 in one step by combining commercially available reagents tris(3-aminopropyl)amine (**6**) and triethylphosphonoacetate (**7**) and subsequent purification with silica column chromatography. Metal complexation with Tb^{3+} was accomplished using the metal nitrate salt under ambient conditions in acetonitrile to yield the solid for structural study via FT-IR. The uncomplexed TRPN ligand **3** exhibits IR stretches for P=O and C=O at 1236 and 1652 cm^{-1}, respectively, which are both close to values seen for **2** and other published CMPO-based ligands.[18,19,28] Upon complexation with Tb^{3+}, the ν(P=O) and C=O bands shift to a smaller wavenumber by 43 and 22 cm^{-1}, respectively, indicating a binding interaction between the phosphine oxide and carbonyl oxygen atoms and the metal cation (Table 1; Figures S2 and S3).



Scheme 1. Synthetic pathways to ligands **3** – **5**.

Further analysis of the FT-IR spectra of the Tb^{3+} complexes of **2** and **3** also reveals the nature of nitrate binding at the metal center, providing additional insight into coordination environment differences induced by ligand cap variation in the solid state. A sharp IR peak was observed for both complexes near ~1400 cm^{-1}, and was attributed to the presence of an outer-sphere, ionic D_{3h} nitrate ion.[36] To assess the binding mode of potential coordinated (inner-sphere) nitrate ions, differences between the apparent ν(N=O) and $\nu_{asym}(NO_2)$ bands at ~1470 cm^{-1} and ~1300 cm^{-1}, respectively, were considered. Larger gaps between ν(N=O) and $\nu_{asym}(NO_2)$ indicate a preference for a bidentate over monodentate binding mode.[36,37] This difference for the Tb-**2** complex was found to be 180 cm^{-1} and is consistent with bidentate nitrate coordination. For the corresponding complex of **3**, the size of this splitting drops to 162 cm^{-1}. While this value appears to be high enough to suggest bidentate binding, the smaller splitting is consistent with a potential mixture of bi- and some monodentate nitrate coordination. As the cap becomes larger upon moving from TREN to TRPN, perhaps a more complete encapsulation of the Ln ion is achieved by **3** leading to greater steric interaction between the chelating oxygens of the ligand and coordinated nitrates. A relatively open coordination sphere afforded by the smaller, more constrained TREN-capped ligand **2** is consistent with a greater preference for bidentate nitrate coordination as suggested by the sold-state IR interpretation.

Table 1. FT-IR absorption bands, reported in units of cm^{-1}, for TREN-CMPO-OEt (**2**) and Tb-**2** (values from reference 28) and TRPN-CMPO-OEt (**3**) and Tb-**3**.

Compound	**ν(C=O)**	**ν(P=O)**	**ν(NH)**	**ν(N=O)**	**$\nu_a(NO_2)$ (ν(N=O) – $\nu_a(NO_2)$)**	**$\nu_s(NO_2)$**	**ν(NO)**	**Ionic NO**
2	1653	1233	3288	-	-	-	-	-
Tb-**2**	1626	1193	3270	1473	1293 (180)	1013	816	1394
3	1652	1236	~3275	-	-	-	-	-
Tb-**3**	1630	1193	~3300	1455	1293 (162)	1024	814	1397

The synthesis of the phenyl substituted ligand, TREN-CMPO-Ph (**4**), was originally reported by Odinets and co-workers.[38] For incorporation into the extraction studies reported here, **4** was synthesized according to the route shown in Scheme 1 through coupling TREN (**8**) to the *p*-nitrophenol activated CMPO precursor (**9**) to yield the desired ligand. To complete the series of tripodal ligands to be assessed in the current work, the *N*-oxide derivative **5** was prepared in one step from the known tripodal ligand **2**[28] using hydrogen peroxide and trichloroacetonitrile.[39] Compounds **2** – **5** were characterized by ^{1}H, ^{13}C and ^{31}P NMR, FT-IR and HR-MS.

Luminescence studies

Luminescence measurements were carried out to probe the Ln coordination chemistry of the TREN and TRPN capped ligands **2** and **3** in the solution state. Previously noting the capability of **2** to sensitive both Eu^{3+} and Tb^{3+} emission in methanol solutions,[28] excitation and emission spectra were obtained for the Tb^{3+} complex of **3** and indicate similar sensitized emission. Shown in Figure 2, the emission spectrum of Tb-**3** was collected upon excitation at 320 nm to match the wavelength where optimal emission is observed in the excitation spectrum (Supp. Info., Figure S4). The emission spectrum reveals the array of expected peaks corresponding to transitions from the $^5D_4$ state of Tb^{3+} to the ^7F_J manifold, as well as some apparent ligand fluorescence centered near 400 nm. These luminescence results provide additional evidence of the ability of **3** to sufficiently bind Ln ions in solution, as the observed sensitization (i.e., the "antenna effect"[8]) would not be possible without sufficient complexation by the CMPO groups.

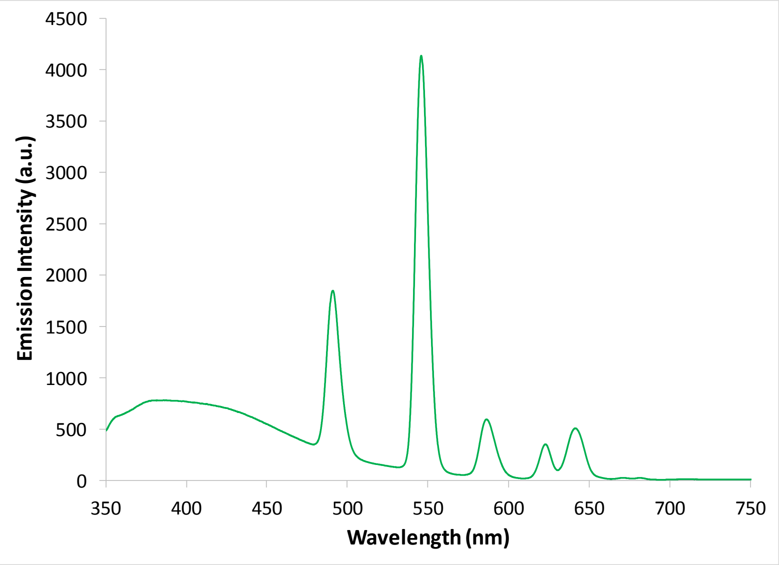


Figure 2. Room temperature emission spectrum of the Tb^{3+} complex of **3** in methanol ([Tb-**3**] = 2.0×10^{-3} M, λ_{ex} = 320 nm).

Excited state decay lifetimes of the Tb^{3+} complex of **2** and **3** were also determined in MeOH and MeOD (Table 2). The lifetime values can be used to estimate the number of metal-bound solvents using the Horrocks method developed for methanol coordination of Tb^{3+}.[30,31] The decay lifetimes for Tb-**2** in MeOH and MeOD yield a bound methanol value of 2.5 ± 0.5 and support the notion of complete complexation by the expected hexadentate chelating motif of the ligand resulting in an overall 8 or 9 coordinate complex (consistent with the expected solution coordination number for Tb^{3+}). If full complexation was not the case, for example due to only a single coordinated CMPO unit in solution, a larger value for bound MeOH molecules would be expected. The lifetime values for Tb-**3** yield a similar bound solvent value of 2.4 ± 0.5, again within range for typical Tb^{3+} coordination and full complexation by all six oxygen donor atoms. Finally, the fractional bound solvent values obtained for both complexes likely indicate a mixture in solution of stable 8- and 9-coordinate states for Tb^{3+}.

Table 2. Luminescence decay lifetime values and calculated bound solvent values for Tb-**2** and Tb-**3** in methanol.

Complex	Lifetime in MeOH (ms)	Lifetime in MeOD (ms)	Number of bound solvent molecules[a]
Tb-**2**	1.282 ± 0.009	2.08 ± 0.03	2.5 ± 0.5
Tb-**3**	1.32 ± 0.04	2.12 ± 0.02	2.4 ± 0.5

[a] Bound solvent molecule values were calculated using the equation developed by W. D. Horrocks, Jr. and co-workers (references 30 and 31).

Extraction studies

Assessment of the Ln extraction capability of ligands **2** and **3** was conducted to further probe the Tb extraction preference noted previously and the significance of the tripodal capping scaffold. These experiments followed the typical liquid-liquid extraction protocols used to explore An/Ln extraction in previous CMPO ligand systems, with solutions of the Ln(III) metal ions dissolved in 1 M nitric acid extracted with solutions of the ligand dissolved in dichloromethane (shown schematically in Figure 3).[17,18] In past studies, following a period of mixing time (typically 12 - 24 h), the two phases were allowed to separate and the aqueous phase was analyzed via an absorption assay requiring an additional Arsenazo III indicator.[32,33] This assay was used to quantify the amount of unextracted Ln ion; the amount extracted by the ligand into the organic phase was then calculated by difference to determine a percent extraction (%*E*) for each Ln studied. In the current study, the aqueous phase after each extraction by the TREN-capped **2** was again analyzed by this method. For subsequent extraction experiments employing **3**, however, ICP-AES was used to quantify metal content of the aqueous, extracted phase. While the Arsenazo III assay has proven to be a reliable method for such experiments, the more direct ICP route requires less sample preparation and does not require an additional indicator for metal ion quantification. In addition, the ICP technique enables additional assessment of Ln mixture experiments, reported below for **2**, that would be impossible using the Arsenazo assay.

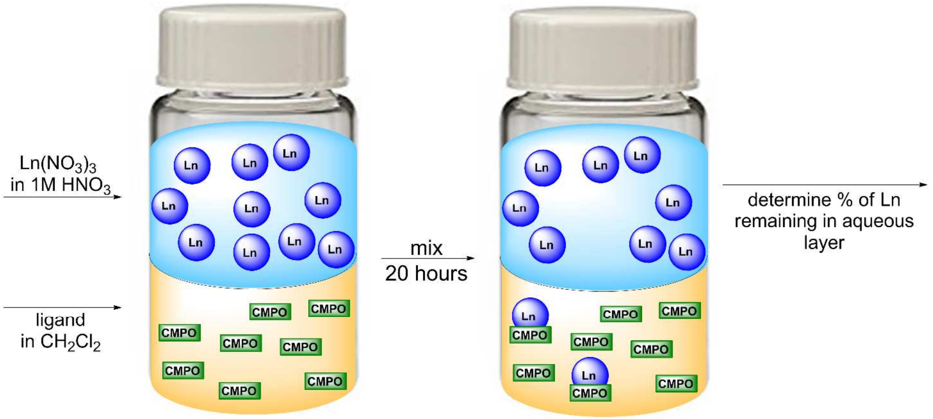


Figure 3. Schematic illustration of liquid-liquid extraction protocol used in this study. Following mixing, the aqueous phase was analyzed by either the traditional Arsenazo III absorption assay, or via ICP-AES to determine Ln ion concentration.

Extraction results for the TREN and the TRPN-capped ligands **2** and **3** are given in Table 3. In this study, extractions of all Lns (except Pm) were carried out with **2**, and the results in Table 3 indicate that the enhanced Tb^{3+} extraction versus the other four Lns included in the original study is maintained relative to the entire series of Lns. It is worth nothing that the overall extraction percentage for Tb^{3+} is not particularly high at 18% (as reported previously[28]) as compared with other systems that achieve extraction efficiencies in excess of 80%.[40-42] While the percent extraction of Tb^{3+} observed for **2** is indeed modest, it is the difference between this value and the values determined for all other Lns that is unique, especially in light of the relatively simple liquid-liquid extraction procedure as used here. With the complete set of data now acquired, TREN-CMPO-OEt (**2**) clearly exhibits an extraction preference for Tb^{3+} under standard liquid-liquid extraction conditions.

Noting this result, the effect of moving to the larger ligand cap of TRPN-CMPO-OEt (**3**) was explored to assess the importance of the ligand scaffold to resultant extraction behavior. While it was predicted that overall Ln extraction efficiency would not be enhanced given the expected decrease in rigidity afforded by the TRPN scaffold relative to TREN, replacement of the ligand cap would help probe the importance of the TREN cap specifically in achieving the observed Tb^{3+} selectivity of **2**. As shown in Table 3, the replacement of TREN with the TRPN scaffold resulted in a complete loss of selectivity, as well as no Ln extraction at an efficiency greater than 6%. As noted above, the larger, more flexible TRPN ligand cap is likely responsible for this marked difference in extraction behavior. Such differences in extraction behavior due to variation of the capping scaffold have been noted before for tripodal CMPO ligands. Our group previously observed that replacement of TREN with a smaller, more rigid phosphine oxide cap appeared to force the CMPO units to splay out, resulting in a preference of accommodating larger Lns (Ce and Pr) as evidenced by the relatively larger extraction efficiencies versus the rest of the series.[29] Taken together, these data indicate how seemingly subtle structural changes to ligand architecture can greatly influence solution behavior within a given system, and, in this case, strongly support the importance of the TREN capping structure in tethering the CMPO chelators such that the enhanced Tb^{3+} extraction of **2** is achieved.

Table 3. Percent extraction (%*E*) of Ln ions for ligands **2** – **5**.[a]

Ln cation	%*E* via TREN-OEt (**2**)	%*E* via TRPN-OEt (**3**)	%*E*, Ln mixture, via **2**[c]	%*E* via TREN-Ph (**4**)	%*E* via OTREN-OEt (**5**)
La^{3+}	5 ± 1[b]	5 ± 1	5.8 ± 0.9	6 ± 2	6 ± 2
Ce^{3+}	4 ± 1[b]	6.0 ± 0.6	6.5 ± 0.6	6 ± 1	3 ± 1
Pr^{3+}	3 ± 1	5 ± 1	7 ± 1	2 ± 2	2 ± 1
Nd^{3+}	3.5 ± 0.8	4.1 ± 0.2	7 ± 1	8 ± 1	2 ± 1
Sm^{3+}	1.2 ± 0.4	4.1 ± 0.1	5.7 ± 0.3	8 ± 2	3 ± 1
Eu^{3+}	8 ± 1[b]	5 ± 1	6.9 ± 0.8	4 ± 2	1 ± 1
Gd^{3+}	1.4 ± 0.1	3 ± 1	7 ± 1	13 ± 3	3 ± 2
Tb^{3+}	18 ± 5[b]	3.5 ± 0.7	10.0 ± 0.3	11.1 ± 0.9	4 ± 1
Dy^{3+}	4.9 ± 0.7	1.6 ± 0.9	6.9 ± 0.8	7.6 ± 0.7	3 ± 3
Ho^{3+}	9 ± 2	5 ± 1	7.0 ± 0.3	7 ± 2	3 ± 1
Er^{3+}	5.5 ± 0.8	3.0 ± 0.7	7.1 ± 0.1	6 ± 2	3 ± 1
Tm^{3+}	7 ± 1	6 ± 1	5.3 ± 0.6	4 ± 1	1 ± 1
Yb^{3+}	6 ± 1[b]	5.2 ± 0.6	6 ± 1	8 ± 3	5 ± 2
Lu^{3+}	2 ± 1	4.0 ± 0.5	7.3 ± 0.9	10 ± 2	8 ± 3

[a] With the exception of the Ln mixture extractions (results shown in third column), all extractions were performed at a 10:1 ligand to metal ratio with each ligand dissolved in CH_2Cl_2 (10^{-3} M) mixed with equal volumes of each individual Ln nitrate solution ($[Ln^{3+}] = 10^{-4}$ M in 1 M HNO_3), stirring for 20 h at room temperature.

[b] From reference 28.

[c] For the Ln mixture extraction with **2**, a 2:1 ligand to metal ratio was used.

Encouraged by the unique Ln extraction behavior shown by **2**, we decided to further test the potential of Tb^{3+} extraction from a mixture of Lns. As noted previously, Lns often are found together in complex mixtures, in both applications of mining from naturally occurring ores or in recycling of consumer products. Additional experiments were thus carried out in which the same concentration of ligand was used in extractions of a mixed Ln metal solution prepared from the ICP calibration standard solution containing all Lns included in this study as well as yttrium, scandium, and the actinides uranium and thorium. Beyond extracting a mixture of metal ions, the only difference between this study and the experiments utilizing individual metal solutions was that the concentration of metal was slightly higher giving a ligand to metal ratio of approximately 2:1 for all Lns (versus 10:1, ligand to metal, as per the traditional method). Despite the complex metal mixture in addition to using slightly less ligand relative to metal within the extraction setup, Tb^{3+} was still extracted at a higher efficiency relative to all other Lns as shown by the $\%E$ values in Table 3. While the selectivity is clearly less than that observed for individual metal extractions, it appears that the terbium preference is maintained to a modest extent.

Noting the importance of the TREN ligand cap in designing tripodal CMPO extractants, further studies of the TREN-capped, phenyl substituted ligand **4** were carried out. Originally reported by Odinets and co-workers and studied as an *f*-element extraction agent under a variety of conditions,[38] we sought to include TREN-CMPO-Ph in the current study with the same extraction protocols used for **2** to enable a direct assessment of the CMPO substituent effect. Given the change from relatively hydrophilic ethoxy groups to phenyl moieties, we initially predicted a greater solubility in the organic extraction solvent and perhaps higher percent extraction values. As seen in Table 3, however, extraction efficiencies remained largely unchanged for most Lns. While overall extraction was not enhanced relative to the results obtained for **2**, noteworthy are the slightly higher $\%E$ values determined for Gd^{3+} and, to a lesser extent, Tb^{3+} relative to the other Lns. While not as significant as the Tb^{3+} result noted for **2**, it appears that for another TREN-capped ligand, a modest extraction preference again arises near the middle of the Ln row. This result, taken with the consistently low extraction efficiencies seen across the entire Ln series for TRPN-CMPO-OEt (**3**), further underscores the importance of the TREN cap in promoting selective extraction of intermediate sized Ln ions.

In addition to modification of the ligand structure, variation of the extraction protocol itself may also lead to significant changes in extraction efficiency. For example, in the previous report on TREN-CMPO-Ph (**4**),[38] it was seen that varying both the nitric acid concentration and using a large excess of ligand (i.e., ligand to metal ratio of 1000:1) yielded a gradual decrease in Ln extraction efficiency moving from La through the series to Lu. Inspired by this result, we looked to test the effect of increasing concentration of **4**, but to a lesser extent of 100:1, ligand to metal, and utilizing dichloromethane as the organic solvent as we have typically used to enable a direct comparison to our 10:1 results for **4** (1,2-dichloroethane used in reference 38). Moving from the typical 10:1 to 100:1 ligand to metal ratio for TREN-CMPO-Ph leads to a dramatic difference in extraction efficiencies across the Ln series, with a %*E* value of 41% for La^{3+} compared to 6% for the 10:1 ratio (Figure 4, Table S1). In addition, a steady, near linear decrease in %*E* across the series was seen and is consistent with the extraction trend resulting from the much higher ligand to metal ratio reported by Odinets.[38]

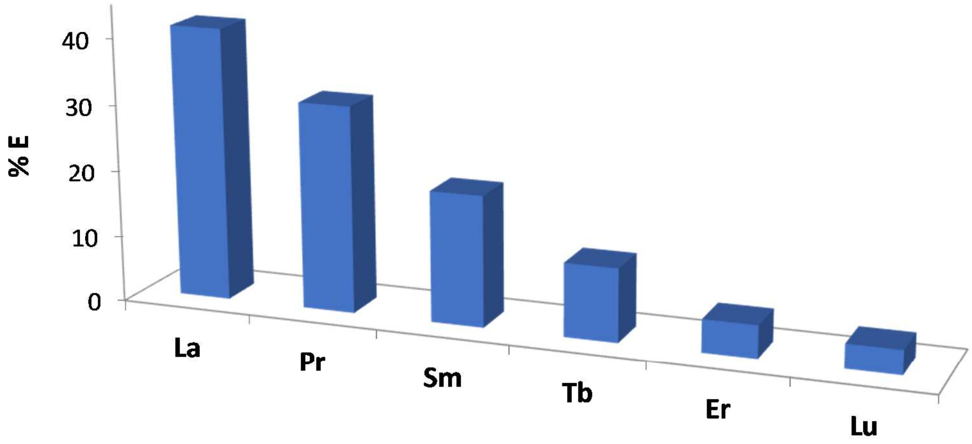


Figure 4. Consistent trend toward decreasing percent extraction for TREN-CMPO-Ph (**4**) through the Ln^{3+} series achieved utilizing a 100:1 ligand to metal ratio (values with standard deviations given in Table S1). Extraction experiments were performed with **4** dissolved in CH_2Cl_2 (10^{-2} M) mixed with equal volumes of each individual Ln nitrate solution ($[Ln^{3+}] = 10^{-4}$ M in 1 M HNO_3), stirring for 20 h at room temperature.

Given the promising extraction results seen for TREN-capped agents within this tripodal CMPO ligand system, OTREN-CMPO-OEt (**5**), was also prepared. Ligand **5** represents an oxidized form of **2**, with an additional oxygen atom attached to the central nitrogen of the TREN cap. It was initially thought that another hard donor atom within the ligand motif may promote stronger Ln ion binding and potentially increase extraction efficiency. The extraction results for **5** show relatively low %*E* values throughout the entire series, however. While the OTREN ligand does not serve to enhance Ln extraction, it does reveal the potential effect of TREN-cap oxidization on resultant Ln extraction behavior. The overall lower %*E* values across the Ln series and loss of any sort of selectivity in comparing **2** with **5** indicate that should the cap become oxidized, the favorable extraction properties of TREN-capped CMPO ligands for intermediate sized Lns is significantly altered.

Conclusions

In closing, we have reported here the unique Tb^{3+} extraction properties of a tripodal CMPO ligand, along with solid- and solution-state characterization and further structural modifications to probe this promising result. Utilizing a well-documented and scalable liquid-liquid extraction method, the TREN-capped ligand **2** shows a preference for Tb^{3+} with regard to extraction from individual metal solutions. In addition, this ligand demonstrates a slight preference for Tb^{3+} from a mixture containing all non-radioactive rare earth ions, thorium, and uranyl. It was also demonstrated that in the case of the tripodal CMPO ligand system discussed herein, it is not enough to simply tether three chelating units to one tripodal scaffold for attaining appreciable Ln extraction. The direct comparison between the TREN and TRPN caps reveals the necessity of the TREN motif and potential impact that the cap can have in influencing extraction behavior and exploiting any differences, as subtle as they may be, moving from one Ln to another. Also, the trend that arises for TREN-CMPO-Ph (**4**) at a relatively large amount of ligand versus metal is noteworthy and shows the dramatic effect that the ligand to Ln ratio may have on extraction results. This result observed for **4** has implications for the separation of lighter Lns from heavier Lns present in naturally occurring sources or in recycling of consumer products. Moving forward, we plan to make additional systematic structural changes to the ligand capping moiety and carry out thorough studies of resultant extraction behavior across the entire series of Lns to develop clearer ligand design parameters for selective Ln extraction. Finally, efforts aimed at varying extraction conditions (e.g., further variation of ligand concentration, temperature, etc.) will be carried out with the goal of developing scalable technologies that meet future needs in the area of rare earth separations.

Conflict of interest

There are no conflicts to declare.

Acknowledgements

We acknowledge financial support from the Department of Chemistry, Biochemistry and Physics (UT), a David Delo Research Professor Grant (UT), and a Dana Foundation Grant (UT). We are also grateful for funding from the UT Office of Undergraduate Research and Inquiry. We thank GVSU's Weldon Fund, CSCE and OURS (S^3 program, K. Tissue; ACF and Student Supplies programs, M. Hudson) as well as the NASA Michigan Space Grant Consortium (M. Hudson) for student support. We are grateful to the National Science Foundation for financial support (CCLI CHE-0087655, 300 MHz JEOL NMR; MRI CHE-1725699, 400 MHz JEOL NMR; REU CHE 1559886) as well as Pfizer, Inc. for the donation of a 400 MHz Varian INOVA NMR spectrometer. Finally, we thank Maya Glander for valuable assistance with manuscript preparation and proofing.

Supplemental information

Electronic supplementary information (ESI) available: Additional luminescence data, FT-IR spectra, and extraction values with errors for ligand **4** are provided. This material is available free of charge via the Internet at www.rsc.org.

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Table of Contents entry

Lanthanide extraction selectivity is attained by variation of the ligand structure and extraction conditions for a series of CMPO-based ligands.