

Lanthanide Extraction and Luminescence Properties of Multipodal CMPO Ligands

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ABSTRACT

Toxic waste streams containing lanthanide (Ln) and actinide (An) metals are byproducts of nuclear power generation. While these metals are considered waste by nuclear energy manufacturers, they may serve many purposes if selectively extracted. Liquid-liquid separation of these metals can be readily achieved using carbamoylmethylphosphine oxide (CMPO) ligand derivatives dissolved in organic solvents and mixed with aqueous waste streams. While An selectivity is currently achieved by CMPO-based ligands, efficient extraction of the valuable Ln ions presents a challenge. Therefore, new ligands are being investigated in attempts to successfully target selective Ln extraction. In this study, the tripodal TREN-CMPO-OEt ligand was explored for its efficiency in Ln ion extraction. By way of ICP-AES analysis, an extraction percentage of 23.0% was determined for Tb(III), an unprecedented four to five times greater than that of any other Ln ion in the study. Further, a fluorimetric study conducted to probe the effect of solvent on luminescence showed a strong correlation between acetonitrile and increased metal-centered emissions of Tb(III) or Eu(III) ions when complexed with an uncapped CMPO-diOEt ligand.

1 INTRODUCTION

The harnessing of nuclear reactions to yield sustainable energy can be considered a revolutionary human accomplishment. However, further improvements must be made in order to ensure the environmental responsibility of nuclear power processing. In the process of producing energy, nuclear reactors create toxic waste byproducts as spent fuels. Spent nuclear reactor fuels are essentially streams of aqueous wastes containing primarily lanthanide (Ln) and radioactive actinide (An) ions. These wastes are then stored in depositories world-wide (Mertz et al., 2013; Wang & Hirsch, 2006). In the United States alone, approximately 1.9 million gallons of hazardous waste is stored. The waste contains radioactive nuclides, with half-lives ranging from 30 to 50,000 years (Wang & Hirsch, 2006). While most Ln ions are not radioactive, separation of the resultant f-elements must be achieved so that proper processing of the harmful radioactive An ions can occur (Sartain et al., 2015). Currently, extractions of An metals utilize the TRUEX (TRAnsuranic EXtraction) process which employs the carbamoylmethylphosphine oxide (CMPO) ligand shown in Figure 1 (Sartain et al., 2015). Bonding observed in An-CMPO complexes is primarily covalent in nature, making for strong bonds, thus facilitating their separation. Removal of the less reactive Ln metals, however, requires deeper investigation and refinement of ligand

design and extraction techniques. In subsequent applications, the Ln ions boast various medical and materials applications (Sartain et al., 2015). For example, Gd(III)-ligand complexes are well known for their use as MRI contrast agents, and other Lns exhibit unique luminescence properties which may find use in biosensor applications (Bünzli, 2010). The selective recovery of such valuable metals therefore encourages the development of novel ligands aimed at selective Ln extraction, as well as fundamental studies of the solution coordination chemistry of resultant complexes. Within our study of Ln-ligand extraction, novel multipodal CMPO ligand complexes were prepared and analyzed. The tripodal ligand examined in this study was designed to facilitate a 3:1 CMPO ligand-to-metal ratio which provides the strongest binding (Peters et al., 2002). These complexes incorporate the well-known tris(2-aminoethyl)amine (TREN) central capping scaffold, attached to three CMPO derivatives. This affords the multipodal ligand TREN-CMPO-OEt Figure 1 (Sartain et al., 2015), a higher denticity chelating ligand relative to the bidentate mono-CMPO derivative used in the TRUEX process. Assuming coordination of all six oxygen donors, this hexadentate ligand motif should favor stronger complexation. Subsequent studies of luminescence properties were also performed to probe the effect of solvent on relative emission intensities for complexes of a simpler, uncapped bis-CMPO ligand CMPO-diOEt, Figure 1 (Stoscup et al., 2014). O—H bonds in close proximity to the Ln center are known to quench the intensity of Ln-ligand complex luminescence (Bünzli, 2010). Various solvents were chosen to investigate this phenomenon. Considering the antenna effect, the diOEt CMPO ligand studied is an ideal outlet for amplified emissions, by way of its incorporated pi bonds (Bünzli, 2010). Pi bonds have recently been known promote the antenna effect, which describes energy absorption and transfer from a ligand excited state to the Ln metal emissive state, thus enhancing metal-centered luminescence (Bünzli, 2010).

2 EXPERIMENTAL

All extracted metal solutions were analyzed by a PerkinElmer Optima 2100 DV ICP-AES spectrophotometer. Luminescence spectra were collected on a Hitachi F-7000 fluorescence spectrophotometer. ICP-AES standard solutions were obtained from AccuStandard; all other solvents and reagents were purchased from Sigma-Aldrich or Fisher Scientific and used without further purification. The TREN-CMPO-OEt (Sartain et al., 2015) and CMPO-diOEt (Stoscup et al. 2014) ligands were synthesized by Dr. Shannon Biros of Grand Valley State University.

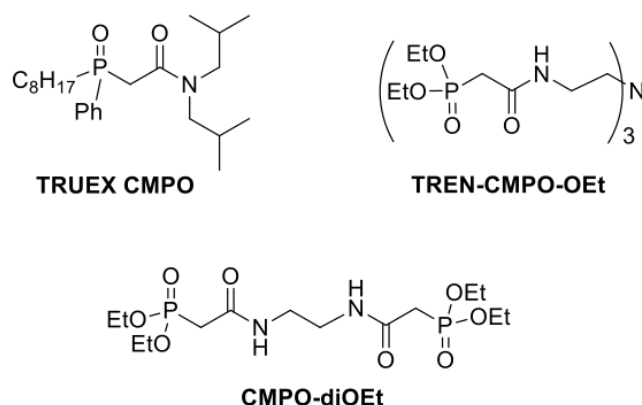


Fig. 1: Chemical structures of CMPO-based ligands

Extraction Studies

Ln nitrate salt solutions (10^{-4} M) were prepared in 1 M HNO₃. Ligand solutions (10^{-3} M) were prepared in CH₂Cl₂. Equivalent volumes of each were then mixed and stirred for 24 hours. Aliquots (0.5 mL or 2.5 mL) of the extracted aqueous phase were then diluted to 25 mL in 3% HNO₃ for metal analysis by ICP-AES. Calibration standards were also prepared (0.2, 0.4, 0.6 ppm). ICP-AES spectrophotometry was used to quantify Ln concentrations.

Luminescence Studies

Luminescence spectra were recorded for Tb(III) and Eu(III) complexes of CMPO-diOEt. These solutions were diluted to 10^{-4} M in respective solvents in a 1:1.05 Ln to ligand ratio. Optimal excitation wavelengths were found by monitoring emission in the excitation spectra. Eu(III) complexes were excited at a wavelength of 278 nm, while Tb(III) complexes were excited at a wavelength of 275 nm. The slit width of the fluorimeter was held constant at 5 nm for all measurements. Solvents investigated include acetonitrile, DMSO, DMF, THF, methanol, and ethanol. Qualitative overlays of target metal emission peaks were compiled to show the relative intensities of emission.

3 RESULTS AND DISCUSSION

Extraction Studies

Extractions of Ln metal ions dissolved in aqueous acid solutions (1 M HNO₃) were performed to mimic acidic nuclear waste conditions (Peters et al., 2002). Post-extraction metal solutions were analyzed in acidic aqueous conditions (3% HNO₃) using an ICP-AES spectrophotometer to yield the data shown here. Noteworthy is the use of ICP-AES versus the more traditional, absorption based Arsenazo III assay frequently reported for such analyses. The ICP method used in the current study requires less sample preparation, does not require an additional indicator reagent to quantify metal concentration, and is less susceptible to interference by other metals. Table 1 shows the percent metal extracted from the aqueous phase into the organic phase by the TREN-CMPO-OEt ligand.

Percent extraction values for Dy(III) and Tm(III) were not recorded. An exceptional selectivity was seen for Tb(III) extraction

Table 1. ICP-AES extraction results for TREN-CMPO-OEt

Ln Ion	Percent Extraction TREN-CMPO-OEt
La ³⁺	5 ± 1
Nd ³⁺	1.7 ± 0.6
Sm ³⁺	3 ± 1
Eu ³⁺	6.0 ± 0.4
Gd ³⁺	3 ± 2
Tb ³⁺	23.0 ± 0.8
Er ³⁺	5.3 ± 0.5
Yb ³⁺	7 ± 1

when compared to other Ln metals. At 23.0%, this result was much more favorable than any other Ln-TREN-CMPO-OEt complex, by more than 15%. This result is unique in comparison with extraction values for previously reported CMPO ligands and may have implications in the separation of Tb from mixtures of Ln ions in nuclear waste or other naturally occurring ores from which these valuable metals are derived. Additionally, when compared to the previously used Arsenazo III extraction assay, the assay commonly used and reported for such analyses (Arnaud-neu et al., 1996; Peters et al., 2002), the new ICP-AES analysis yielded a comparable result. Beyond confirming the use of ICP in generating results consistent with past extraction studies, implementation of this method affords a procedure with less solution preparation (as noted above) and inherently lower detection limits as compared with the Arsenazo absorption based technique.

Table 2. ICP-AES (obtained in this study) vs. Arsenazo III assay (previously obtained by Sartain et al. 2015) percent extraction data.

Ln Ion	Arsenazo III Assay	ICP-AES
La ³⁺	5 ± 1	5 ± 1
Eu ³⁺	8 ± 1	6.0 ± 0.4
Tb ³⁺	18 ± 5	23.0 ± 0.8
Yb ³⁺	6 ± 1	7 ± 1

Luminescence Studies

Luminescence data was collected for Eu(III) and Tb(III) complexes of the uncapped CMPO-diOEt ligand to probe the dependence of Ln-centered luminescence on solvent. This analysis explored potential sensitization of Ln metal luminescence when complexed with CMPO ligand derivatives, a topic not often documented in the literature. According to recent theory, CMPO derivatives may work well to promote Ln luminescence, but further analysis must be done to probe the photophysical properties of such systems (Bünzli, 2010). Luminescence emission spectra overlays were collected as shown in Figures 2 and 3. An additional overlay displaying emissions exclusive to acetonitrile for both complexes is also shown in Figure 4.

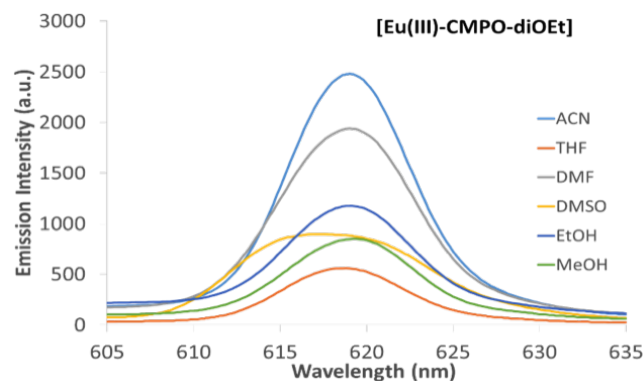


Fig. 2: Emission spectra of Eu-CMPO-diOEt (10^{-4} M) in various solvents. Complexes were excited at a wavelength of 278 nm with slit width of 5 nm.

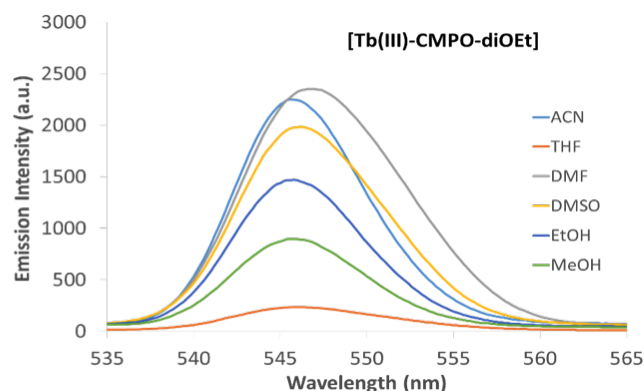


Fig. 3: Emission spectra of Tb-CMPO-diOEt (10^{-4} M) in various solvents. Complexes were excited at a wavelength of 275 nm with slit width of 5 nm.

Among the solvents studied, acetonitrile appeared to provide the best environment for amplified Ln emission. This was consistent with quenching theory, as acetonitrile is devoid of oxygen-hydrogen bonds which lead to quenching (Bünzli, 2010). Complex solutions in MeOH and EtOH both exhibited relatively weak emissions, as a result of O—H bond vibrations coupled to the metal ion emissive states. THF, however, showed a more quenched emission than both alcohols, contrary to theory. Further studies aimed at understanding this effect will be conducted for CMPO-diOEt as well as other ligand motifs.

4 CONCLUSIONS

A successful study of two novel CMPO ligand derivatives was conducted, providing further insight into the extraction and photophysical properties of CMPO-based ligands and Ln complexes. ICP-AES data provided evidence of a unique selectivity for Tb(III), 23.0%, by the novel TREN-CMPO-OEt ligand and confirmed previous results obtained using an independent

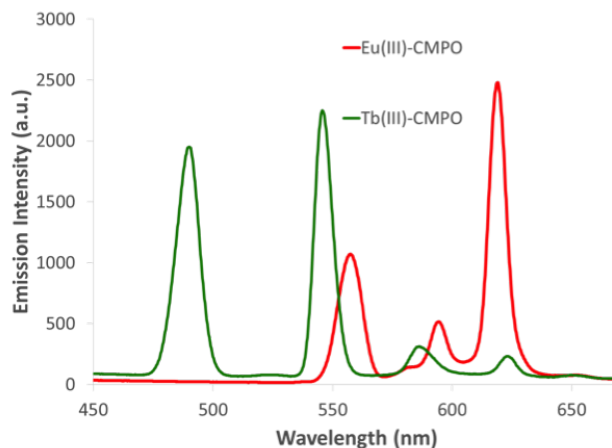


Fig. 4: Emission spectra of Eu(III) and Tb(III) complexes of CMPO-diOEt in acetonitrile. All parameters match those stated in Figures 2 and 3. The large peaks at ~ 550 nm and ~ 620 nm are metal-centered emissions, those of Tb(III) and Eu(III), respectively.

absorption based method. This was seen to be an unprecedented four to five times more selective than any other Ln ion. More extractions and studies will need to be performed to determine what factors govern this selectivity. During the solvent analysis, an uncapped CMPO-diOEt ligand was studied for luminescence character. However, the quenched emissions seen in THF solvent for both Eu(III) and Tb(III) complexes were perplexing and further solvent analysis will be conducted to probe this unexpected result. In future work, other novel CMPO derivatives will be investigated for extraction and luminescence potential. The novel CMPO ligands used in this experiment will also be analyzed for extraction selectivity of aqueous actinide metal ions. Future research will also investigate the absence or presence of aromatic structures on CMPO ligands and the subsequent effect on luminescence. Finally, polyoxometalate ligands will also be considered for their reductive capacity when complexed with Eu(III), perhaps opening new directions in utilizing the redox properties of select Ln ions to facilitate separation.

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