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A Molecular Basis to Rare Earth Separations for Recycling: Tuning TriNOx Ligand Properties for Improved Performance

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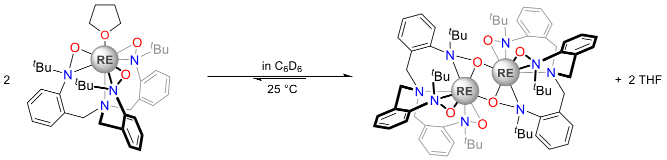
The methoxy-substituted tripodal hydroxylamine ligand, H_3TriNOx^{OMe}, was synthesized and coordinated to rare earth cations for separations purposes. Metrics of the resulting complexes were investigated and compared to their parent TriNOx^{3-} counterparts for determination of the molecular basis for the described rare earth separations system. Addition of the electron donating group to the aryl backbone resulted in a more electron rich ligand that increased the equilibrium constant for complex dimerization five-fold. The new separation system yielded efficient Nd/Dy separations in toluene rather than benzene.

The rare earth elements (RE), La-Lu, Y, and Sc, are critical materials found in clean energy technologies including permanent magnets, phosphors, and electric vehicle batteries.[1-4] Neodymium iron boron permanent magnets doped with dysprosium are pervasive in modern technologies. They are used in applications ranging from wind turbine generators and electric vehicle motors to magnetic resonance imaging (MRI) and magnetic refrigeration.[1] While electronic and magnetic applications require individual pure RE or binary mixtures these elements are found in nature as mixtures in their ores.[5, 6] Separation of individual rare earth elements is accomplished by counter-current solvent extraction processes requiring large amounts of energy and solvents.[7] Ion exchange resins have also been used to purify rare earths.[8-12] Recently, several alternative separation techniques involving selective crystallization,[13-15] photo- or kinetic-redox processes,[16-18] biosorption,[19, 20] bio-inspired mineralization,[21] or functionalized mesoporous materials[22-25] have been demonstrated. A molecular-based approach to RE separations is desirable to probe how subtle changes in RE interactions with organic molecules affect separation efficiencies. As such, we have targeted a tunable system in an effort to accomplish rational RE separations.



$$K_{dimer} = \frac{[[RE(TriNOx)]_2][THF_{free}]^2}{[RE(TriNOx)(THF)]^2}$$

Scheme 1 Dimerization equilibrium for early RE(TriNOx) complexes.

Previously, we described the RE(TriNOx) separation system, in which early/late RE combinations were separated with a single leaching step from benzene solutions due to the formation of monomeric or dimeric complexes, depending upon the identity of the RE cation (Scheme 1).[26, 27] However, the use of benzene as the separations medium was a limitation to the system. Benzene is a carcinogenic and volatile compound, and substitution of this component with a greener solvent would benefit potential application of the described separations process.[28, 29] Solvent selection guides from Pfizer, Astra Zeneca, GlaxoSmithKline, and others suggest the substitution of benzene with toluene in industrial processes.[30-32] Additionally, evaluation of the “greenness” of solvents with the “EHS Excel Tool” identifies toluene as a greener alternative to benzene due to lower air hazard and toxicity values (See SI for details).[33, 34] The TriNOx system represented an opportunity to directly correlate molecular design principles with performance of a RE separations system. In other previous work by our group, we established that modification of sterics and electronics of pyridyl-hydroxylamine ligands imparted a structural change to the hydroxylamine moiety in the resulting complexes.[35] These results together suggested that similar modification of the TriNOx ligand would influence the size of the molecular aperture responsible for RE separations selectivity. We hypothesized that addition of an electron donating group in this context would to lead to pyramidalization of the hydroxylamine arms of H_3TriNOx, resulting in a smaller molecular aperture around the RE cation. Perturbation of the ligand geometry was expected to alter the dimerization constant of the resulting

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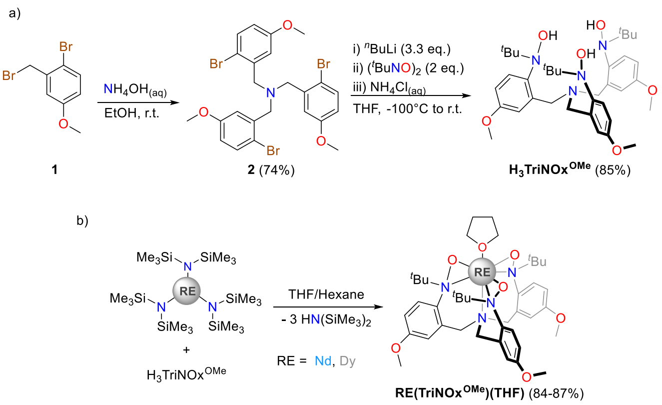


Scheme 2 Synthesis of a) $H_3TriNOx^{OMe}$ and b) $RE(TriNOx^{OMe})(THF)$ complexes.

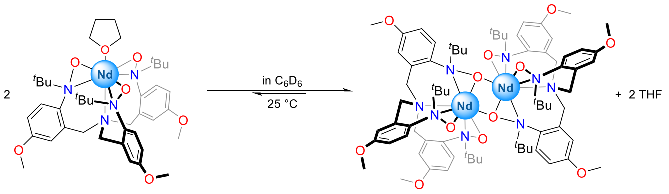
complexes, to improve separation and/or operating conditions. We report herein a new TriNOx ligand with methoxy substituents, whose solubility properties enabled comparable early/late RE separations in toluene, compared to carcinogenic benzene that was used previously.

The new tris(hydroxylamine) ligand, *tris*(2-tert-butylhydroxylaminato-5-methoxy)benzylamine ($H_3TriNOx^{OMe}$), was synthesized by a procedure similar to that of the parent $H_3TriNOx$.[26] 2-bromo-5-methoxybenzylbromide (**1**) was converted to *tris*(2-bromo-5-methoxy)benzylamine (**2**) by alkylation of aqueous ammonia (Scheme 2).[36] Intermediate **2** was lithiated and subsequently reacted with $(^tBuNO)_2$. Strict control of the temperature of the lithium-halogen exchange was critical for product formation; the best results were obtained by conducting the reaction at –100 °C. Aqueous work-up provided the targeted product in 85 % yield.

Synthesis of isostructural $RE(TriNOx^{OMe})(THF)$ compounds, RE = Nd, Dy, was accomplished by protonolysis reaction of $H_3TriNOx^{OMe}$ and the corresponding $RE[N(SiMe_3)_2]_3$ starting materials. We have also demonstrated that $RE(TriNOx^{OMe})(THF)$, similar to the parent RE(TriNOx)(THF) complexes, can be prepared from $RE(OTf)_3$ and $RECl_3$ sources (See SI). However, these reactions included the generation of salt byproducts that complicated the evaluation of recovery and separation values. As such, separation experiments included below were conducted with $RE[N(SiMe_3)_2]_3$ as the rare earth source to establish the baseline separations characteristics. Samples suitable for X-ray analysis were obtained by layering a THF solution of the compound with hexanes (See SI, Figure S11). Desolvation was observed upon the removal of individual crystals from the mother liquor at room temperature, so the samples were handled over dry ice while mounting crystals on the diffractometer. The structures exhibited similar coordination environments to the parent RE(TriNOx)(THF) compounds, with each hydroxylamine arm coordinated η^2-(*N*,*O*) to a rare earth cation, forming a C_3-symmetric coordination environment with the apical positions occupied by a THF molecule. Comparison of the bond metrics of $RE(TriNOx^{OMe})(THF)$ and analogous parent RE(TriNOx)(THF) complexes revealed similar features (See SI, Table S2). The average N-O bond lengths in $RE(TriNOx^{OMe})(THF)$ (1.441(3) and 1.445(5) Å for RE = Nd and Dy, respectively) were slightly longer than in RE(TriNOx)(THF) (1.420(4) and 1.424(4) Å for RE = Nd and Dy, respectively). A similar phenomenon was observed in an isostructural series of substituted pyridyl-hydroxylamine cerium complexes, where $Ce[2\text{-}(^tBuNO)\text{-}3\text{-}(OMe)py]_4$ had an N-O bond length of 1.410(6) Å, while $Ce[2\text{-}(^tBuNO)py]_4$ had an N-O bond length of 1.375(2) Å.[35] Also of note, the $RE\text{-}O_{THF}$ bond lengths in $RE(TriNOx^{OMe})(THF)$ complexes (2.625(2) and 2.551(3) Å for RE = Nd and Dy, respectively) were significantly longer than in the RE(TriNOx)(THF) complexes (2.546(9) and 2.487(10) Å for RE = Nd and Dy, respectively). Elongation of the RE-THF interaction in $RE(TriNOx^{OMe})(THF)$ complexes suggested that the size of the $(N,O)_3$ molecular aperture formed around the RE^{3+} cation was reduced by addition of a methoxy group to the ligand backbone as hypothesized, prompting further analysis of the solid state structures.

In previous work, we established that the percent buried volume ($\%V_{bur}$) of RE(TriNOx)(THF) complexes served as a suitable metric to describe the degree of exposure of the rare earth cation at the $(N,O)_3$ molecular aperture.[37] A small increase was observed in the $\%V_{bur}$ of the $RE(TriNOx^{OMe})(THF)$ compounds compared to the parent RE(TriNOx)(THF) compounds (79.9% to 80.1% for Nd and 81.3% to 81.7% for Dy).[26] The increase of 0.2 – 0.4 % is on the same order as that observed between adjacent rare earth cations in the previously reported series (ex. 79.6% Pr versus 79.9% Nd).[27] Thermogravimetric analysis (TGA) was also conducted to probe the strength of the RE-THF interactions in the $RE(TriNOx^{OMe})(THF)$ compounds, as we expected this measurement would be an indication of the closure of the molecular aperture (see SI for experimental details). A weight loss corresponding to 1 equiv THF was observed at 148 °C for $Nd(TriNOx^{OMe})(THF)$, indicating a similar RE-THF interaction as in the parent complex Nd(TriNOx)(THF) (153 °C).[27] However, no weight loss was observed before decomposition for $Dy(TriNOx^{OMe})(THF)$, indicating that upon isolation of the solid sample, dissociation of THF in the apical coordination site of the complex occurred readily under ambient conditions. Thermogravimetric analysis of both $RE(TriNOx^{OMe})(THF)$ (RE = Nd, Dy) complexes were performed in triplicate, and there was no evidence for THF dissociation found in any of the $Dy(TriNOx^{OMe})(THF)$ samples. Clearly, there is a weaker RE-THF interaction in $Dy(TriNOx^{OMe})(THF)$ than in the parent TriNOx compound, suggesting that the molecular aperture was indeed reduced in size with the addition of an electron-donating group to the ligand backbone.

Similar to the previously reported RE(TriNOx)(THF) compounds,[26, 27] evidence for a self-association equilibrium was observed in the ^1H NMR of Nd(TriNOx)(THF) in C_6D_6 (Scheme 3). The $[Nd(TriNOx^{OMe})]_2$ dimeric compound was synthesized by dissolving $Nd(TriNOx^{OMe})(THF)$ in toluene followed by removal of solvents under reduced pressure to yield a blue solid in 83% yield. Single crystals of $[Nd(TriNOx^{OMe})]_2$ were grown from toluene/hexanes solution. X-ray diffraction studies revealed similar bond metrics for $[Nd(TriNOx^{OMe})]_2$ compared to the parent $[Nd(TriNOx)]_2$ structure.[26] Notably, a shorter $Nd\text{-}O_{bridge}$ average bond length was observed for $Nd(TriNOx^{OMe})]_2$ (2.5037(17) Å vs. 2.5413(17) Å), which may be described by a



$$K_{dimer} = \frac{[[Nd(TriNOx^{OMe})]_2][THF_{free}]^2}{[Nd(TriNOx^{OMe})(THF)]^2}$$

Scheme 3 Dimerization equilibrium between Nd(TriNOx^{OMe})(THF) and [Nd(TriNOx^{OMe})]$_2$.

more electron-rich hydroxylamine having a stronger interaction with the neodymium cation during self-association.

The value of the self-association equilibrium constant (K_{dimer}) was evaluated for Nd(TriNOx^{OMe})(THF) by titrating a C_6D_6 solution of [Nd(TriNOx^{OMe})]$_2$ with THF in the presence of a ferrocene internal standard and measuring relative concentrations using ^{1}H NMR spectroscopy. Equilibrium concentrations of Nd(TriNOx^{OMe})(THF) and [Nd(TriNOx^{OMe})]$_2$ were calculated at each titration point to determine the self-association equilibrium constant of 11.7 ± 0.5 for Nd(TriNOx^{OMe})(THF). This value is about one order of magnitude larger than that of Nd(TriNOx)(THF) (2.4 ± 0.2), suggesting that dimerization is more favorable for the H$_3$TriNOx^{OMe} system, consistent with a more electron-rich hydroxylamine moiety.[26]

We expected Nd(TriNOx^{OMe})(THF) to have a higher solubility than the parent, due to its larger self-association equilibrium constant and subsequent higher propensity towards formation of the soluble dimeric complex in solution. The solubilities of the RE(TriNOx^{OMe}) complexes in C_6D_6 were determined by ^{1}H NMR spectroscopy, comparing saturated solutions against an internal ferrocene standard. Solubility values of 120 mmol L^{-1} and 1.7 mmol L^{-1} were determined for Nd(TriNOx^{OMe})(THF) and Dy(TriNOx^{OMe}), respectively. These results indicate that Nd(TriNOx^{OMe})(THF) was more soluble in C_6D_6 than the parent system, while the Dy species remains largely insoluble (60 mmol L^{-1} and 1.2 mmol L^{-1} for the parent system complexes, respectively).[26] These observed solubility differences prompted us to investigate the separations of the new RE(TriNOx^{OMe}) system in benzene, for direct comparison with the parent system, and other solvents. All separations experiments described herein were performed in triplicate.

In order to make the most straightforward set of comparisons for separations performance, a standardized separations procedure was established with the original RE(TriNOx)(THF) system (See SI, Scheme S2). A solid-solution of a 50:50 mixture of Nd/Dy(TriNOx)(THF) was prepared by addition of a THF solution of H$_3$TriNOx to a homogeneous solution of 1:1 Nd[N(SiMe$_3$)$_2$]$_3$ and Dy[N(SiMe$_3$)$_2$]$_3$ in THF. After stirring 2 hours, solids were removed by filtration and washed with THF, followed by drying under reduced pressure for 1 hour. The resulting solid mixture was stirred in a fixed amount of the leaching solvent (4 mL for 320 mmol of RE(TriNOx) species) for 30 minutes followed by filtration and rinsing. Subsequent drying of both portions yielded a solid portion enriched in dysprosium and a filtrate portion enriched in neodymium.

To compare the original separations system to the new RE(TriNOx^{OMe}) system, a similar procedure was conducted with H$_3$TriNOx^{OMe}. A hot THF solution of H$_3$TriNOx^{OMe} was added to a homogeneous solution of 1:1 Nd[N(SiMe$_3$)$_2$]$_3$ and Dy[N(SiMe$_3$)$_2$]$_3$ in THF. After 2 hours of stirring, solvents were removed from the reaction mixture under reduced pressure. Due to the solubility of RE(TriNOx^{OMe}) compounds in THF, the solid was suspended in pentane for 10 minutes before filtration and drying for 1 hour. Leaching was performed in a variety of solvents following the aforementioned procedure. For all separation experiments, the molar ratio of Nd- and Dy-containing species in the solid (η_{Dy}/η_{Nd}) and filtrate (η_{Nd}/η_{Dy}) portions was estimated by ^{1}H NMR (See SI, Table S3) and determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) to evaluate the enrichment factor (D_{solid} and $D_{filtrate}$, respectively), which were then used to calculate the separation factor, $S_{Nd/Dy}$, according to the equation $S_{Nd/Dy} = D_{solid} \cdot D_{filtrate}$. Separation experiments were performed in triplicate, and the results were recorded in Table 1.

Efficient Nd/Dy separations were achieved in benzene with both the TriNOx- and TriNOx^{OMe}-based procedures, with separation factors of 303 and 299, respectively, comparable, in the case of the parent, to our previously reported results. Comparison of the filtrate and solid enrichment factors (D) for each of these separations indicated that TriNOx^{OMe}-based separations in C_6H_6 led to solid portions with higher purity, at the expense of lower purity filtrate portions, compared to TriNOx-based separations in C_6H_6. The efficiency of TriNOx^{OMe}-based Nd/Dy separations in toluene was also comparable to those in benzene (254 versus 299, respectively), offering a less carcinogenic solvent in which to conduct RE separations. TriNOx^{OMe}-based Nd/Dy separations conducted in other solvents led to diminished separation factors, indicating that exploitable differences in solubility were not retained in different solvent types.

We have demonstrated that substitution of the H$_3$TriNOx aryl backbone with a methoxy group caused pyramidalization of the

Table 1 Enrichment (D) and Separation Factors (S) for TriNOx and TriNOx^{OMe} systems in various solvents by ICP-OES (wavelengths monitored for Nd (430.358 nm) and Dy (365.540 nm)). All experiments were performed in triplicate and values reported with the standard error of the mean.

Ligand	Solvent	ICP-OES Results			Avg. % Distribution/Purity		% Recovery	
		$D_{Filtrate}$	D_{Solid}	$S_{Nd/Dy}$	Filtrate (% Nd)	Solid (% Dy)	% Nd Rec.	% Dy Rec.
TriNOx	C_6H_6	17 ± 2	18 ± 2	303 ± 19	94.3 ± 0.5%	94.7 ± 0.5%	77 ± 2%	48 ± 2%
TriNOx	Toluene	15.4 ± 0.7	1.9 ± 0.1	30 ± 2	93.9 ± 0.3%	66.0 ± 0.8%	50 ± 2%	51 ± 1%
TriNOx^{OMe}	C_6H_6	9.8 ± 0.4	29 ± 3	299 ± 35	90.9 ± 0.3%	96.7 ± 0.3%	84 ± 7%	66 ± 4%
TriNOx^{OMe}	Toluene	12 ± 2	22 ± 4	254 ± 10	93.3 ± 0.1%	94.8 ± 0.3%	79 ± 3%	63 ± 5%
TriNOx^{OMe}	DME	3.5 ± 0.2	11.6 ± 0.5	41 ± 4	77.9 ± 0.9%	92.0 ± 0.3%	71 ± 2%	54 ± 2%
TriNOx^{OMe}	Et_2O	7.2 ± 0.3	1.2 ± 0.1	8.4 ± 0.6	87.8 ± 0.5%	54 ± 2%	17 ± 1%	72 ± 2%

hydroxylamine nitrogen atoms, which induced a subtle closing of the molecular aperture in RE(TriNOx^{OMe}) complexes. The nature of the molecular aperture was described and compared to that of the parent complexes. Analysis of structural metrics revealed that RE(TriNOx^{OMe})(THF) complexes contained longer hydroxylamine N-O bonds and RE-O$_{THF}$ interactions than the parent RE(TriNOx)(THF) complexes, indicative of more electron-rich hydroxylamine arms and weaker RE-THF interactions. RE(TriNOx^{OMe})(THF) complexes exhibited slightly higher %V$_{bur}$, suggesting that the RE cation is less exposed in the methoxy-substituted complexes. Thermogravimetric analyses indicated that the RE-O$_{THF}$ interaction in Dy(TriNOx^{OMe})(THF) was much weaker than in the parent complex, and evaluation of the self-association equilibrium constant of Nd(TriNOx^{OMe})(THF) indicated that dimerization was more favorable by one order of magnitude, consistent with more electron-rich hydroxylamine groups at the molecular aperture. These phenomena all contribute to an increased solubility of [Nd(TriNOx^{OMe})]$_2$, allowing for efficient Nd/Dy separations in a greener solvent (toluene) that was previously unavailable in the parent separations system. This work demonstrates that substitution of H$_3$TriNOx impacts the RE(TriNOx) separations system and its underlying processes, enabling new separations conditions through modifications to RE(TriNOx) coordination chemistry.

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Conflicts of interest

Intellectual property pertaining to the technology described in this article is covered by International Patent Application no. PCT/US2015/042703.

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