

On Altering the Lanthanide Chelate Formation Constant Sequence To Improve Am^{3+} - Ln^{3+} Separations in Cation-Exchange Elutions

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The philosophy of resolving actinon-lanthanon mixtures via cation-exchange elution with selective chelating agents is considered in view of the lanthanon chelate formation constant sequences obtained with various ligands derived from polyamino polycarboxylic acid analogues of bis(2-aminoethyl) ether N,N,N',N' -tetraacetic acid. Stability constant data and other characteristics are reported for a newly synthesized variant, bis(2-aminoethyl) ether N,N,N' -triacetic acid N' -(3-propanoic acid). Synthetic details for preparing the reagent are reported.

Introduction

In 1982, we published our first account¹ of attempts to develop a method for isolating actinide nuclides from fission-produced lanthanide mixtures via cation-exchange elution. In that paper, bis(2-aminoethyl) ether N,N,N',N' -tetraacetate (EEDTA) was cited as the leading candidate to accomplish the task, exhibiting an established separation factor for all individual Am^{3+} - Ln^{3+} separations in excess of 1.7. The minimum separation factor of 1.7 occurred in the case of Am^{3+} and Eu^{3+} (or Tb^{3+}) because a maximum in the Ln^{3+} -EEDTA formation constant sequence is apparent at Eu (or Tb).

Because the radius of Am^{3+} is approximately the same as that of Nd^{3+} and the separation factor for Am^{3+} and Nd^{3+} with EEDTA as the eluant was discerned as ca 7.5, it was perceived that a factor approaching this magnitude could represent a hypothetical minimum Am^{3+} - Ln^{3+} separation factor in an optimal case (i.e., with a ligand exhibiting overall affinities similar to those of EEDTA, with the maximum Ln^{3+} affinity occurring at Nd rather than at Eu (or Tb)). The problem then is to find a means of achieving an earlier downturn in the formation constant sequence without too much attenuation in the affinity of the ligand for Nd^{3+} (and An^{3+} and Ln^{3+} cations in general). Decreasing the overall metal-ligand affinity diminishes the Am - Nd separation factor to be had and negates the gains that could be exploited by achieving an earlier downturn.

The effect of variations in the ligand's backbone (the chain between N and N' atoms of diamino tetraacetate analogues) on its ability to bond to Ln^{3+} cations of decreasing radius has been examined in subsequent studies.²⁻⁴ The first study² considered a homologue of EEDTA in which the ethylene segments of the backbone were extended by one CH_2 unit each, $\text{O}[\text{CH}_2\text{CH}_2\text{C}(\text{H}_2\text{N}(\text{CH}_2\text{COO}^-))_2]_2$ (BPETA). A second study³ dealt with replacing the centrally located O donor atom by CH_2 , S, and N (with either a phenyl or an ethyl substituent to alter the basicity of the N).

$\text{O}[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COO}^-)_2]_2$	EEDTA
$\text{CH}_2[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COO}^-)_2]_2$	PMDTA
$\text{S}[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COO}^-)_2]_2$	TEDTA
$\text{C}_6\text{H}_5\text{N}[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COO}^-)_2]_2$	BEATA
$\text{CH}_3\text{CH}_2\text{N}[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COO}^-)_2]_2$	DEATA
$-\text{OOCCH}_2\text{N}[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COO}^-)_2]_2$	DTPA

From stability constant sequences, elution coincidences, and computed separation factors, we have been able to substantiate that the most significant separation factor (Am^{3+} - Nd^{3+}) increases from about 3 to ca. 16 as the NdL formation constant increases from the order of 10^{10} to the order of 10^{22} (PMDTA to DTPA).^{1,5} At our point of reference, EEDTA, the Am^{3+} - Nd^{3+} factor projected is approximately 7.5.¹

Replacement of O by NCH_2CH_3 (converting EEDTA to DEATA) had little effect on either the position of the maximum in the LnL stability sequence or the overall magnitudes of the individual stabilities. Substituting a phenyl group for the ethyl of DEATA (yielding BEATA) merely attenuated the ligand's affinity for all Ln^{3+} species (by a factor of ca. 220 compared to the affinity of ethyl analogue). In view of the electron-withdrawing proclivity of the phenyl group, this was not unexpected. The measured Am^{3+} - Eu^{3+} (minimum Am^{3+} - Ln^{3+}) separation factor dropped from 1.7 for EEDTA to only 1.16 in the case of BEATA.

When the O of EEDTA was replaced by S (see TEDTA), Ln-ligand affinities dropped some 5000-fold, and the Am^{3+} - Eu^{3+} separation factor dropped to 1.00. No shift in the position of the stability constant maximum was observed.

With the above background, a new approach was considered ... that of weakening the grip of one of the four carboxyl O atoms on the host cations so that its hold on the host might fail earlier with decreasing radius of the La^{3+} - Lu^{3+} sequence. The terminal O's grip at a coordination site presumably could be weakened in several ways: (1) by replacing a H atom on the acetate α -carbon by an electron-withdrawing group such as the phenyl radical; (2) by introducing a bulky substituent on the α -carbon that would introduce an adverse steric effect; (3) by increasing the tentacle length by one CH_2 unit, so that the chelate ring that could form would be 6-membered instead of 5-membered (the optimum size from a steric viewpoint).

Preparing an α -phenyl-substituted EEDTA analogue in any substantial yield proved to be beyond our collective expertise at this writing, thus efforts have been concentrated upon the more straightforward preparation of bis(2-aminoethyl) ether N,N,N' -triacetic acid N' -(3-propanoic acid) (DETAP) and a study of its anion's properties as a ligand for rare-earth-metal cations.

Experimental Section

Bis(2-aminoethyl) Ether N,N,N' -Triacetic Acid N' -(3-Propanoic Acid). The starting point of our synthesis was bis(2-aminoethyl) ether dihydrochloride, prepared from Aldrich Chemical bis(2-chloroethyl) ether via a standard Gabriel (potassium phthalimide) primary amine synthesis. Sixty grams (0.338 mol) of the dihydrochloride in 30 mL of H_2O (neutralized below 10 °C with 67.3 mL (0.673 mol) of 10 M NaOH) was treated dropwise with a solution prepared below 10 °C from 36.7 g (0.338 mol) of Aldrich Chemical 3-chloropropanoic acid, 30 mL of H_2O , and 33.8 mL of 10 M NaOH. After the reactants were combined at 25 °C, the temperature of the mixture was raised to 60 °C while the pH was kept at 10 by adding 10 M NaOH, dropwise. The mixture was finally stirred overnight at 60 °C.

After the pH was dropped to 5 by adding 12 M HCl, the mixture was diluted to 2 L and passed through one 2 in. \times 4 ft bed of -40+50 mesh, H^+ -form, Dowex 50W-X8 cation-exchange resin. After a deionized water rinse, an additional 1 in. \times 4 ft bed of the same cation-exchange resin was coupled to the 2 in. bed and the system was eluted with 0.2 M aqueous NH_3 (first at 60 mL/min, and finally at 15 mL/min, as the discernible (30 cm long) band of sorbed amino acid proceeded down the smaller diameter column). As the lighter colored band passed off the system, the effluent solution was collected in a series of 138-mL fractions.

Titrations of small aliquots of the solutions in the presence of Cu^{2+} ion revealed that most of the bis(2-aminoethyl) ether had undergone coupling to but one 3-propanoic acid, as had been intended. Decoupled material amounted to less than 5% of the whole and was confined to the

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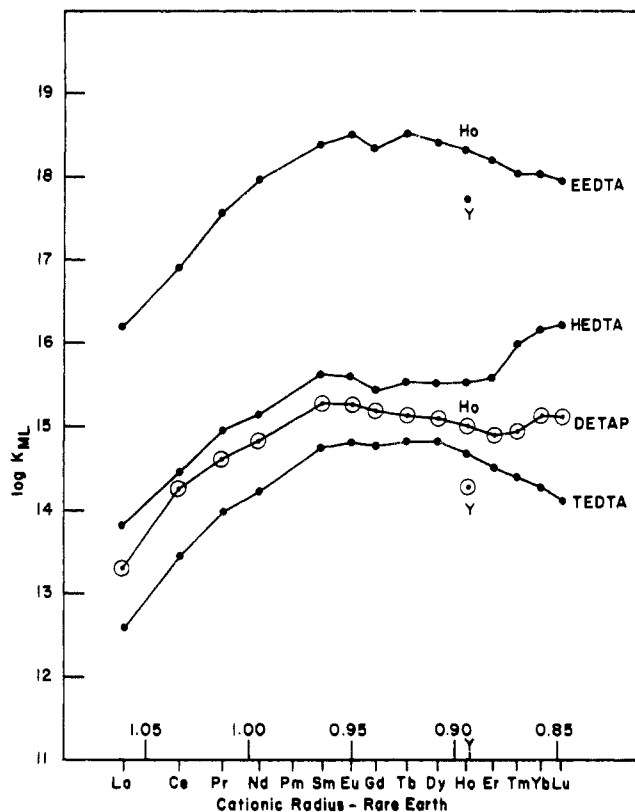


Figure 1. Logarithms of formation constants of rare-earth-metal chelates.

first few fractions collected after breakthrough of the visible band. Samples 29–36, containing an estimated 0.17 mol of bis(2-aminoethyl) ether *N*-(3-propanoic acid), were combined and evaporated under vacuum to about 50 mL and treated with 7 mL of 10 M NaOH. This solution was combined with a solution prepared below 10 °C from 94.5 g (1 mol) of chloroacetic acid, 100 mL of H₂O, and 95 mL of 10 M NaOH. The reaction mixture was maintained at 40 °C for 8 h, while its pH was maintained at 10 by periodic additions of NaOH.

The reacted mixture was next diluted to 1 L and washed with water through a pair of 1 in. × 4¹/₂ ft cation-exchange beds connected in sequence. The sorbed material was then eluted down and off the system, by 0.10 M aqueous NH₃, and collected in a series of 138-mL fractions. The middle 15 fractions (pH 2.48–2.50) were combined and evaporated to a glassy consistency under vacuum. The product acid was finally recovered as a fine white powder (solvent by methanol) by crystallization from boiling methanol (in which it is sparingly soluble). In all, 25.1 g of bis(2-aminoethyl) ether *N,N,N'*-triacetic acid *N'*-(3 propanoic acid)-methanol were recovered (39% yield). Titration with standard base indicated a molecular weight of 385, which corresponded closely to the composition C₁₃H₂₂N₂O₉CH₃OH (fw 382.34). Anal. Calcd: C, 43.9, H, 6.85, N, 7.33; O, 41.85. Found: C, 43.73; H, 6.70; N, 7.41; O, 42.16. The material softened at about 60 °C and decomposed at about 100 °C giving off a very disagreeable odor.

DETAP Anion Protonation Constants. The DETAP anion's sequential protonation constants were obtained from p*H*_c measurements on series of prepared chelating-agent solutions in two different pH ranges. *K*₁ and *K*₂ were obtained simultaneously in the p*H*_c range 8–10 and *K*₃ and *K*₄ were obtained in the p*H*_c range 2–5. *K*₅ and *K*₆ representing formation of H₅L⁺ and H₆L²⁺ were not determined, although such species are known to exist at high H⁺ concentrations and were utilized in the reagent purification by cation-exchange elution. A knowledge of the latter two constants was not needed in subsequent metal chelate stability constant measurements due to the restricted pH range employed (3.0–4.5). Such constants play a significant role only below pH 2. All buffer solutions used in these studies were adjusted to an ionic strength of 0.100 by appropriate incorporations of KNO₃, and the p*H*_c measurements were made at 25.00 ± 0.05 °C, by using a Corning pH Meter 130 calibrated vs. known HNO₃ concentrations at *I* = 0.100 (KNO₃) rather than H₃O⁺ activities.

Chelate Formation Constants of Ln-DETAP Species. The stability constants for ML⁻ and MHL species (*K*_{ML} = [ML⁻]/[M³⁺][L⁴⁻] and *K*_{MHL} = [MHL]/[M³⁺][HL³⁻]) formed by our new reagent (dubbed DETAP) with yttrium and the lanthanide rare-earth metals (except Pm) were calculated from p*H*_c values of buffer solutions measured in the pH

Table I. Protonation Constants of DETAP at 25.0 °C and *I* = 0.100

<i>n</i>	<i>K</i> _{<i>n</i>}	log <i>K</i> _{<i>n</i>}	α _{<i>n</i>}	log α _{<i>n</i>}
1	3.55 × 10 ⁹	9.55	3.55 × 10 ⁹	9.55
2	9.55 × 10 ⁸	8.98	3.39 × 10 ¹⁸	18.53
3	7.26 × 10 ³	3.86	2.46 × 10 ²²	22.39
4	4.31 × 10 ²	2.63	1.06 × 10 ²⁵	25.02

Table II. Logarithms of Formation Constants of Rare-Earth-Metal DETAP-Protonated (MHL) and DETAP-Unprotonated (ML⁻) Species at 25.0 °C and *I* = 0.100 (KNO₃)^a

cation	at. no.	radius, Å	log <i>K</i> _{MHL}	log <i>K</i> _{ML}
Y ³⁺	37	0.893	8.77	14.28
La ³⁺	57	1.061	8.36	13.31
Ce ³⁺	58	1.34	8.89	14.26
Pr ³⁺	59	1.013	9.21	14.61
Nd ³⁺	60	0.995	9.40	14.80
Pm ³⁺	61	0.979	(9.5)	(15.1)
Sm ³⁺	62	0.964	9.59	15.29
Eu ³⁺	63	0.950	9.50	15.28
Gd ³⁺	64	0.938	9.32	15.21
Tb ³⁺	65	0.923	9.43	15.16
Dy ³⁺	66	0.908	9.31	15.11
Ho ³⁺	67	0.894	9.06	15.01
Er ³⁺	68	0.881	9.24	14.90
Tm ³⁺	69	0.869	9.29	14.97
Yb ³⁺	70	0.858	9.38	15.17
Lu ³⁺	71	0.848	9.40	15.14

^a Values in parentheses are interpolated values.

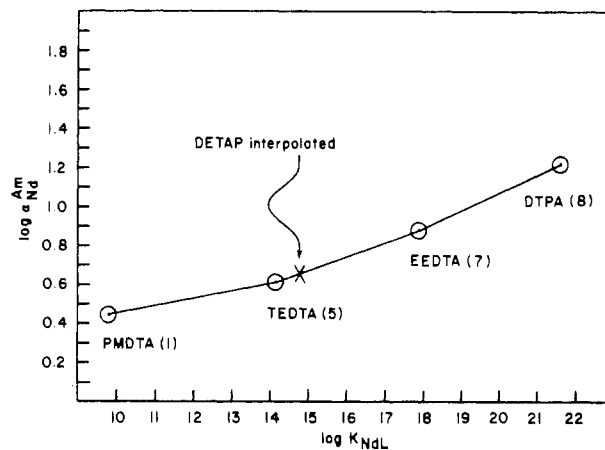


Figure 2. Am³⁺-Nd³⁺ separation factors as a function of affinity.

3–4.5, at 25.00 °C and *I* = 0.100 (KNO₃). The nonlinear calculation method that was employed in the computations has been described in detail elsewhere.⁵ Our results reported as log *K*_{MHL} and log *K*_{ML} are estimated to be reliable to ±0.05 log units.

The results of our protonation and metal chelate formation constants are summarized in Tables I and II, respectively. log *K*_{ML} values for DETAP have been compared graphically with those for EEDTA, HEDTA, and TEDTA in Figure 1 vs. decreasing atomic radius. The reader should recall that Δ log *K*_{ML} represents a close approximation of the logarithm of the cation-exchange-elution separation factor for lanthanide elements.⁶

Discussion

The first point of interest in these data is that the maximum in the DETAP stability constant sequence (Figure 1) has shifted toward the lighter (larger radius) end of the lanthanide series. The maximum occurs in this case at Sm–Eu, rather than at Eu–Tb. Although the stability trends move upward again after a decline from Eu through Er, it is apparent that the radius-related attenuation in affinity is greater in the case of DETAP than in the case of TEDTA (at least from Eu through Er). Y³⁺, a nonlanthanide rare-earth-metal cation having a radius akin to that

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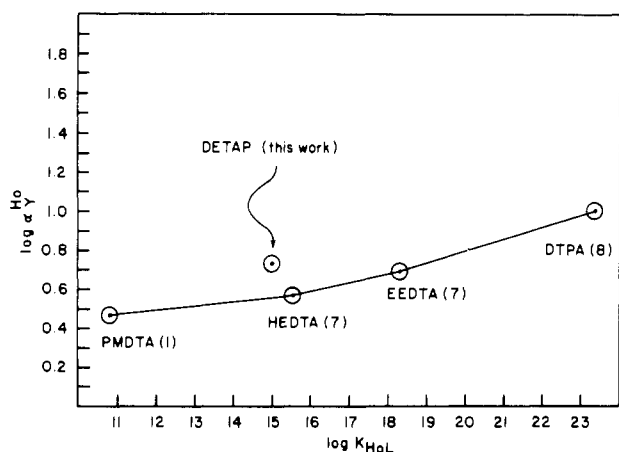


Figure 3. Ho^{3+} - Y^{3+} separation factors as a function of affinity.

of Ho^{3+} , exhibits a ligand affinity depressed to the point that it appears that Y^{3+} would elute nearly in coincidence with the light lanthanon Ce^{3+} ($\log K_{YL} = 14.28$; $\log K_{CeL} = 14.26$). This is a position later in the elution sequence than Y^{3+} has ever been observed to elute. Yttrium elutes between Tb and Dy when EDTA is the eluant and nearly (but not quite) in coincidence with Nd when either EEDTA or HEDTA is the eluant. If one first removed Ce, e.g. via solvent extraction in its +4 oxidation state, it would appear that Y^{3+} could then be removed rather easily from

the other (trivalent) lanthanons since the closest Ln^{3+} neighbor would then be Pr^{3+} , and the Pr-Y separation factor would be ca. 2.1.

As for the estimation of the minimum Am-Ln separation factor (Am^{3+} from Sm^{3+} or Eu^{3+}), if one presumes from an interpolation (see Figure 2) that the Am^{3+} - Nd^{3+} $\Delta \log K_{ML}$ is 0.61 (about the same as in the case of TEDTA) and subtracts 0.49 ($\log K_{SmL} - \log K_{NdL}$), the Am-Sm separation factor can be inferred to be $\text{antilog}(0.12) = 1.3$. When Ho^{3+} - Y^{3+} separation factors are plotted in a similar manner (Figure 3) against the logarithm of the Ho-L affinity, the Ho-Y separation factor for DETAP is seen to be abnormally high—well off the trend established by the other data. Because $\log K_{YL}$ in the case of DETAP is abnormally low relative to $\log K_{HoL}$, one wonders if $\log K_{AmL}$ might not be abnormally high relative to $\log K_{NdL}$. If so, $\log \alpha_{Nd}^{Am}$ could be considerably larger than the interpolated value of 0.61 (Figure 2), and the Am-Sm separation factor (minimum Am-Ln separation factor) would then be substantially higher than the 1.3 that has been estimated in a conservative way above. This possibility needs to be checked out via the elution chromatographic technique.⁷⁻⁹

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Fluorosulfate Derivatives of Manganese and Rhenium

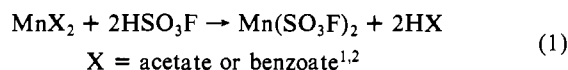
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The oxidation of manganese by bis(fluorosulfonyl) peroxide ($S_2O_6F_2$) in HSO_3F allows the preparation of $Mn(SO_3F)_3$ and the ternary fluorosulfates $M'_2[Mn(SO_3F)_5]$ ($M' = K$ or Cs), with manganese oxidized to the +3 oxidation state. The oxidation of $Mn_2(CO)_{10}$ by $S_2O_6F_2$, or the further oxidation of $Mn(SO_3F)_2$ by $S_2O_6F_2$, in either the absence or the presence of HSO_3F provides alternate routes to $Mn(SO_3F)_3$. Solutions of $M'_2[Mn(SO_3F)_5]$ in HSO_3F are unstable and produce polymeric $Mn(SO_3F)_2$. Rhenium is oxidized to the +7 oxidation state, and a yellow oil of the composition $ReO_2(SO_3F)_3$ is identified as one of the reaction products. The reaction of Re_2O_7 with $S_2O_6F_2$ provides an alternate route to $ReO_2(SO_3F)_3$. The metal carbonyl fluorosulfates $Re(CO)_5SO_3F$ and $Mn(CO)_5SO_3F$ are obtained from the reaction of $Re(CO)_5Cl$ and $Mn(CO)_5Br$, respectively, with $AgSO_3F$ in CH_2Cl_2 . Controlled pyrolysis of $Mn(CO)_5SO_3F$ at $\sim 70^\circ C$ allows isolation of $Mn(CO)_4SO_3F$.

Introduction

A number of fluorosulfate derivatives of both manganese and rhenium have been reported previously. Manganese(II) fluorosulfate is conveniently prepared by a displacement reaction of the type



Interestingly, solvolysis of manganese(III) acetate in HSO_3F also produces $Mn(SO_3F)_2$ in what appears to be a redox reaction.¹ Limited structural information on $Mn(SO_3F)_2$ is available. A magnetic moment, μ_{eff} , of $5.8 \mu_B$ at 293 K suggests³ a high-spin configuration for Mn^{2+} , and the vibrational spectra² suggest a three-dimensional polymer with O-tridentate fluorosulfate groups and a regular octahedral environment for the central atom, a rather common structural type for $M(SO_3F)_2$.^{2,4} Bis(fluorosulfonyl)

peroxide ($S_2O_6F_2$) has been found⁵ to produce quantitatively an oxo fluorosulfate of the composition $MnO(SO_3F)$ when reacted with $MnCO_3$. On the other hand, the reaction of dimanganese decacarbonyl ($Mn_2(CO)_{10}$) with a large excess of $S_2O_6F_2$ is said⁶ to afford quantitatively manganese tetrakis(fluorosulfate) ($Mn(SO_3F)_4$). Since both reactions are said to proceed smoothly at room temperature with comparable reaction times, it is not immediately obvious why there should be a difference in the oxidizing ability of $S_2O_6F_2$, reflected in the different oxidation states of manganese in the resulting products.

The oxidation of rhenium metal by $S_2O_6F_2$ ⁷ does lead to oxo fluorosulfates of rhenium. Depending on the reaction conditions, $ReO_2(SO_3F)$, described as a yellow liquid, or $ReO_2(SO_3F)_3$, a white solid, forms with Re in the +7 oxidation state.

Our interest in these systems is focused primarily on $Mn(SO_3F)_4$ ⁶ for two reasons: (a) binary Mn(IV) oxyacid salts and halides appear to be quite rare,⁸ and very little is known about

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