for face-to-face carbonyl scrambling. In this rearrangement carbonyl B undergoes an edge–face movement on the top face while carbonyl A undergoes the inverse face–edge movement below, and bridging carbonyl C flips from an upper edge position to a lower one. Intermediate Y then equilibrates with the lower energy forms (**2c, 2d**) involving a terminal carbonyl. There does not appear to be any reported precedent for the bridge-flipping motion proposed, but the overall transformation X → Y is attractive in that the synchronous movement of the three carbonyls is sterically and electronically balanced.[12,13]

Registry No. **1**, 12148-54-8; **2**, 12305-50-9; ^{13}C, 14762-74-4.

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Synthesis and Lanthanide Complex Formation Constants of *N′*-Benzylethylenediamine-*N*,*N*,*N′*-triacetic Acid

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One of the major practical uses of polyaminopolycarboxylic acids is in the ion-exchange separation of yttrium and the individual lanthanides. Although several such complexants have been found useful in this regard, each has one or more shortcomings which make the search for new complexing agents one of continued interest. The low water solubility of ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetic acid (EDTA) and its lanthanide complexes necessitates the use of a retaining ion other than hydrogen.[1] *N′*-Hydroxyethylethylenediamine-*N*,*N*,*N′*-triacetic acid (HEDTA) exhibits poor selectivity in the mid-lanthanon range (Sm–Ho), a fact which may be overcome only by working at elevated temperatures.[2] The use of certain other chelating agents is discouraged by the low lability of their metal complexes, a condition which leads to undesirably high plate heights in the ion-exchange process.[3-6]

Recently, *N′*-methylethylenediamine-*N*,*N*,*N′*-triacetic acid (MEDTA) has been synthesized and studied.[7,8] Like the unsymmetrical HEDTA species, it exhibits much better solubility characteristics than EDTA. Though producing no improvement with regard to plate heights (compared to HEDTA), it does show selectivity for the middle lanthanons at room temperature.

An article on the synthesis and cursory study of other unsymmetrical *N′*-benzyl- and *N′*-alkylethylenediamine-*N*,*N*,*N′*-triacetates (alkyl: *n*-butyl, *n*-octyl, *n*-dodecyl, cyclohexyl) reported some interesting results.[9] The *N′*-benzyl derivative (BEDTA) exhibited much higher stability constants for complexes formed with both Ca^{2+} and Cu^{2+} than did the alkyl-substituted acids. Steric arguments were invoked to explain the stability behavior with Cu^{2+}, but the explanation with Ca^{2+} was not so simple. The authors suggested that greater electron release by the benzyl moiety might explain the higher stability of its complexes (though this is in contradiction to the accepted order of aryl vs. alkyl inductive effects). Also of interest were the much lower constants obtained for the cyclohexyl-substituted analogue, since the cyclohexyl group would be expected to exhibit a steric effect similar to that of the benzyl group. Purity may have been a substantial factor, since all of the acids studied were only moderately pure. Nevertheless, the unique behavior of BEDTA suggests a favorable interaction attributable to the benzyl substituent and merits further study.

The purpose of the present work was to synthesize BEDTA in better purity and to study its complexing behavior with the tervalent lanthanide sequence (wherein cationic radius is the principal variable). Evaluation of its utility in possible rare-earth separation schemes was also of interest.

Experimental Section

Synthesis of *N′*-Benzylethylenediamine-*N*,*N*,*N′*-triacetic Acid. The previously reported[9] BEDTA synthesis involved carboxymethylation of *N*-benzylethylenediamine with formaldehyde and sodium cyanide. Product recovery was accomplished tediously and inefficiently by successive recrystallizations from an alcohol–water mixture containing a large amount of sodium sulfate, as well as substantial amounts of reaction by-products such as nitrilotriacetic acid (NTA). Since NH_3 forms in the carboxymethylation step, subsequent reaction to form NTA (or incompletely carboxymethylated intermediates) could be expected. The reported melting point was 130–131 °C. The potentiometrically determined molecular weight was 336 (theoretical 324).

The present procedure was a modification of the above, utilizing an ion-exchange purification scheme which previously proved useful in the preparation of MEDTA.[7] A solution of 2 mol of *N*-benzylethylenediamine dissolved in 500 mL of water and 500 mL of *tert*-butyl alcohol was heated to the boiling point. To this were added simultaneously (and slowly) 1 L of an aqueous solution containing 397 g of NaCN and 23.2 g of NaOH and a 1-L solution of 687 mL of 37% formaldehyde in water. During addition, the mixture was heated under reflux and swept with air. After 34 h the solution had turned deep red and the evolution of NH_3 had ceased. The *tert*-butyl alcohol was then eliminated and the pH adjusted to about 1 with H_2SO_4. (*Caution* noticeable HCN was evolved.) The acid solution was then refluxed for 7 h to complete the hydrolysis of the nitrile groups.

The cooled solution was next loaded onto the first of two 2-in. diameter × 4-ft length cation-exchange columns containing H^+-form Dowex 50W-X8. The loaded system was first rinsed with water to eliminate NTA and H_2SO_4 and then eluted with 0.1 N NaOH. During elution a light-colored band formed and progressed down the column system followed by a darker band and the increasing band of sorbed Na^+. The acid eluate was collected in fourteen 800-mL fractions. All fractions were evaporated to powders which were analyzed titrimetrically. Material from samples 7–11 (found to contain crude BEDTA) were combined. To achieve a high degree of purification, the combined material was reprocessed on the cation-exchange system. The new fractions were evaporated slowly, and the BEDTA which formed was removed periodically. The more soluble impurities remained in solution. After recrystallization from water, the yield was 70 g (11%) of a white powder that melted at 176–178 °C (much higher than previously reported). Anal. Calcd for $C_{15}H_{20}N_2O_6$: C, 55.55; H, 6.18; N, 8.64. Found: C, 55.95; H, 6.25; N, 8.65. Mol wt: calcd, 324.3; found, 325.5.

Measurements. All measurements were made in a sealed vessel thermostated at 25 ± 0.05 °C under a nitrogen atomosphere. The hydrogen ion concentration was measured using a Corning Model 101 digital electrometer, adjusted with standard HNO_3 or KOH. The ionic strength was adjusted with KNO_3.

The successive protonation constants, $K_n = [H_nL]/[H_{n-1}L][H]$, were determined from pH_c measurements on a series of independently

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Table I. Consecutive Formation Constants of H_n(BEDTA)[a]

$K_1 = 1.21 \times 10^{10}$ $\alpha_1 = K_1 = 1.21 \times 10^{10}$
$K_2 = 1.72 \times 10^{5}$ $\alpha_2 = K_1K_2 = 2.07 \times 10^{15}$
$K_3 = 3.48 \times 10^{2}$ $\alpha_3 = K_1K_2K_3 = 7.20 \times 10^{17}$
$K_4 = 4.7 \times 10^{1}$ $\alpha_4 = K_1K_2K_3K_4 = 3.4 = 10^{19}$
K_5 not determined α_5 not determined

[a] Species at 25 °C and $I = 0.100$ M (KNO_3).

Table II. Formation Constants of the 1:1 Chelate Species Formed by Rare-Earth Cations and the BEDTA Anion at 25 °C and $I = 0.100$ M (KNO_3)

Cation	$\log K_{\mathrm{LnCh}}$	Cation	$\log K_{\mathrm{LnCh}}$
La^{3+}	10.81 ± 0.01	Tb^{3+}	12.79 ± 0.01
Ce^{3+}	11.28 ± 0.03	Dy^{3+}	13.02 ± 0.01
Pr^{3+}	11.69 ± 0.02	Ho^{3+}	13.26 ± 0.01
Nd^{3+}	11.82 ± 0.02	Er^{3+}	13.47 ± 0.02
Sm^{3+}	12.19 ± 0.02	Tm^{3+}	13.65 ± 0.01
Eu^{3+}	12.35 ± 0.02	Yb^{3+}	13.85 ± 0.03
Gd^{3+}	12.40 ± 0.01	Lu^{3+}	13.93 ± 0.01
Y^{3+}	12.69 ± 0.01		

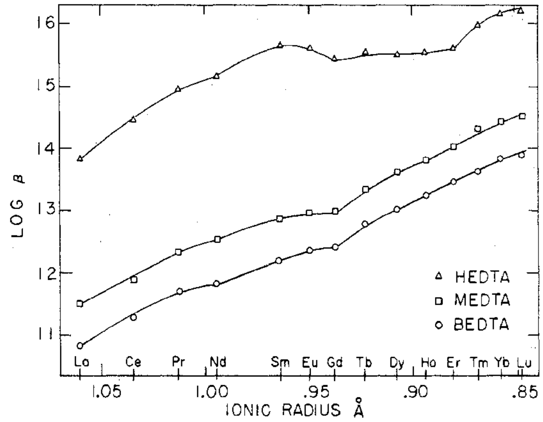

Figure 1. Comparison of the formation constants of some rare-earth complexes.

prepared solutions, at 25 °C and 0.100 M ionic strength. The value for K_1 was determined on a series of solutions in which the BEDTA was between two-thirds and completely neutralized by potassium hydroxide. The other protonation constants were determined in the 2.9–5.5 pH range, obtained by addition of HNO_3 or KOH to individual solutions. The latter constants we determined simultaneously using a weighted, multiple linear regression. The individual weighting factors, $w_i = 1/s_i^2$, were determined from the standard deviations of the residuals.[10] To accomplish this, an iterative procedure was used. A standard deviation defined in terms of the pH_c, the total anion, and the total ionizable hydrogen was found to give the lowest mean-square s^2, an estimation of σ^2 in the regression fit.[11]

The stability constants of the normal chelate complexes of the individual lanthanons were also determined potentiometrically. Again a series of independently prepared solutions was used. The calculations were performed in the usual manner.

Results and Discussion

The BEDTA synthesis is complicated by the variety of impurities and by-products mentioned earlier. Utilization of ion-exchange chromatography is the key to obtaining the desired pure product. Apparently, like HEDTA and MEDTA,[1,7] BEDTA forms a cationic species (either H_4A^+ or H_5A^{2+}) which has considerable affinity for cation-exchange resins. NTA, a primary impurity in the reaction mixture, shows no such affinity and is easily separated. The other main impurities, which arise from incomplete carboxymethylation of ammonia and *N'*-benzylethylenediamine, also show affinity for the H^+-form resin. These can be separated by displacement chromatography, taking advantage of the differing H^+ affinities.

A few comments are in order regarding future syntheses. Sweeping the reaction mixture with air is definitely recommended. Otherwise, the amount of NTA produced may be excessive. The hydrolysis step is not as rapid as one would hope and should be monitored for completion. The major impurity remaining after separation is thought to be incompletely hydrolyzed material. Finally, to achieve maximum product separation and yield, the ion-exchange conditions should be carefully controlled.

The successive protonation constants of the BEDTA trianion are shown in Table I. These are lower than those of their MEDTA analogues.

The determined lanthanide–BEDTA stability constants are shown in Table II and graphed in Figure 1 (along with those of HEDTA and MEDTA). The behavior of BEDTA is similar to that of MEDTA and suggests uniform coordination behavior across the lanthanide series, presumably via pentadentate coordination.

Of interest is the fact that all of the BEDTA stability constants lie below those of MEDTA, a fact which could be rationalized by invoking either steric or inductive arguments. This lower stability of chelates of the benzyl-substituted acid is in constrast to those reported in the case of Ca^{2+} and Cu^{2+} previously. While that comparison did involve alkyl groups larger than methyl, it now seems possible that the "unique" behavior previously reported for BEDTA may have been due to impurities in the various acids studied.

From a rare-earth separation standpoint, BEDTA may hold some limited promise. The cation separation factors[1,8] for adjacent lanthanons were computed from the data in Table II and are reported in Table III, along with those of some other complexing agents. In the middle of the series, specifically with the important Gd–Eu and Eu–Sm pairs, BEDTA shows the highest room-temperature separation factors. If these were to increase with temperature, analogous to the HEDTA and EDTA factors, BEDTA would be a superior reagent for use in the isolation of pure europium.

Perhaps of greater interest is the behavior of Y(BEDTA). In contrast to the behavior of YCh in other systems, its stability falls between those of Gd(BEDTA) and Tb(BEDTA). The resultant Dy–Y separation factor is about 2.1, significantly

Table III. Cation-Exchange Separation Factors at 25 °C

Pair A–B	α_B^A(EDTA)	α_B^A(HEDTA)	α_B^A(MEDTA)	α_B^A(BEDTA)
Lu–Yb	1.9	1.3	1.2	1.2
Yb–Tm	1.8	1.6	1.3	1.6
Tm–Er	3.1	2.0	1.5	1.5
Er–Ho	1.8	1.2	1.7	1.6
Ho–Dy	2.6	Ca. 1.0	1.6	1.7
Dy–Tb	2.3	Ca. 1.0	1.8	1.7
Tb–Gd	4.2	Ca. 1.0	2.3	2.5
Gd–Eu	1.05	0.7	1.05	1.12
Eu–Sm	1.5	Ca. 1.0	1.3	1.4
Sm–Nd	3.2	2.6	2.2	2.3
Nd–Pr	1.8	1.8	1.5	1.3
Pr–Ce	2.5	2.8	2.9	2.6
Ce–La	3.7	5.0	2.3	2.9

higher than the factor obtained with EDTA. This behavior could be utilized in preparing pure yttrium from naturally occurring mixtures, where the main impurity is generaly dysprosium. A two-step ion-exchange process using first BEDTA to eliminate the Dy and then hot EDTA to eliminate the Tb would offer a definite advantage over separations using only EDTA. An improvement in both separation time and purity could be expected. Ion-exchange schemes using cold HEDTA to separate yttrium from the heavier lanthanides have not proven successful.

Finally, the water solubility of BEDTA is around 7 g/L, lower than that of either MEDTA or HEDTA but markedly higher than the solubility of EDTA. Therefore H^+ can be used as the retaining ion in systems employing BEDTA as the eluent. In addition to the lower costs and easy recycle associated with the H^+ retaining ion, the resultant faster kinetics at the front of the band would be advantageous.

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Registry No. BEDTA, 65311-06-0; *N*-benzylethylenediamine, 4152-09-4; formaldehyde, 50-00-0; NaCN, 143-33-9; La(BEDTA), 65338-61-6; Ce(BEDTA), 65338-60-5; Pr(BEDTA), 65338-59-2; Nd(BEDTA), 65338-58-1; Sm(BEDTA), 65338-57-0; Eu(BEDTA), 65338-56-9; Gd(BEDTA), 65338-70-7; Y(BEDTA), 65366-45-2; Tb(BEDTA), 65338-69-4; Dy(BEDTA), 65338-68-3; Ho(BEDTA), 65338-67-2; Er(BEDTA), 65338-66-1; Tm(BEDTA), 65452-42-8; Yb(BEDTA), 65338-65-0; Lu(BEDTA), 65338-64-9.

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Nitrogen Nuclear Magnetic Resonance Spectroscopy. 10. *N*-Sulfinylamines and *N*-Sulfenamides

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We report ^{14}N shifts, measured by wide-line methods, which help to establish characteristic regions for sulfur–nitrogen groupings. In the sulfenamides $R_2N{-}SAr$ the lines are at high field in what may be termed the S–N single-bond region, since the resonances of (cyclic) *N*-methylsulfurimides[1] are nearby, as are those of the singly bonded nitrogen in $R_2\mathit{N}SNSO$ (Table I).

Sulfinylamines $XN{=}S{=}O$ were formerly thought to be analogues of thiocyanates $XN{=}C{=}S$; however, imido nitrogen in linear systems with cumulated double bonds (such as thiocyanate XNCS,[2a] cyanate XNCO,[2b] carbodiimide $RN{=}C{=}NR$,[2c] and azide $X\mathit{N}NN$[2d]) resonates at fairly high field. The –NSO region is some 200–300 ppm downfield of this, at medium field, as for $XN{=}Y$ and conjugated groupings, examples of which are sulfimide $-N{=}S{=}N-$ as in S_4N_2[1] and other cyclothiazenes[3,4] and azines such as pyridine or pyrimidine.[5] In accordance with this the XNSO grouping is cis-bent in the molecules that have been measured (MeNSO,[6] H_3SiNSO,[7] $S(NSO)_2$,[8] ClNSO,[9] and HNSO[10]) with bond angles of about 120° at nitrogen and sulfur.

Table I. Nitrogen Chemical Shifts in *N*-Sulfinylamines, *N*-Sulfenamides, and Related Compounds

Compd[a]	δ(NH_4^+)/ ppm[b]	*w*/ Hz[c]	*tw*/ Hz[d]	S:N	Ref (NMR)	λ_{max}/ nm[e]	log ε[f]	Ref (UV)
1,4-$S_6(NMe)_2$ (CS_2)	−2 (5)				1			
S_7NMe (CS_2)	−2 (5)				1			
Me_2NSPh	4 (10)	700		3.5:1				
Et_2NSPh	9	720		1.3:1				
$Me_2\mathit{N}SNSO$	18 (5)		450					
n-$Pr_2\mathit{N}SNSO$	30 (10)	900		1.3:1				
FSO_2NSO	274	225		75:1				
$S(NSO)_2$ (100 °C)	282					377	4.0	*g*
PhNSO	294					315	4.0	*h*
PhSNSO	296 (4)	600		40:1				
n-$Pr_2NS\mathit{N}SO$	303	730						
Me_3SiNSO	309		47			283[i]	1.5[i]	7[i]
$Me_2NS\mathit{N}SO$	322 (2)		210					
Me_3CNSO	332 (2)		76	10:1		305	1.6	16
CF_3SNO (−80 °C)	695			10:1	12	570	0.8	12
EtSNO	765			7:1	12	550	1.3	12

[a] Measured as neat liquids at room temperature unless a solvent or temperature is given. [b] Relative to NH_4^+(aq), positive downfield. The precision depends on the line width (figures in parentheses are the estimated probable errors in the last digit, usually better than ±5 ppm). [c] Peak-to-peak width (±5–10%) of the derivative line, with modulation at 20–40 Hz. The lines are modulation broadened, particularly at low S:N ratios. [d] Line width at half-height, measured by the side-band method, with modulation at 500 Hz. [e] Wavelength of longest wavelength band. [f] The units of ε are L mol^{-1} cm^{-1}. [g] M. Becke-Goehring and J. Heinke, *Z. Anorg. Allg. Chem.*, 272, 297 (1953). [h] G. Kresze and H. Smalla, *Ber. Dtsch. Chem. Ges.*, 92, 1042 (1959). [i] These values are for H_3SiNSO.

An inverse dependence of the paramagnetic term on the energy of the $n_N \rightarrow \pi^*$ circulation in $XN{=}Y$ compounds has been observed.[11,12] We find that the XNSO region follows in the sequence[11] in which the nitrogen line goes downfield (and the $n_N \rightarrow \pi^*$ band to longer wavelengths) as the electronegativity of the atom Y doubly bonded to nitrogen decreases; that is, δ and λ increase in order $XN{=}S{=}O \sim XN{=}CR_2 < XN{=}NX < XNO$. Thus the *N*-sulfinylamines resonate in the same region as the azomethines $RN{=}CR_2$. The –NSO group is colorless; for the isomeric thionitrosyl compounds $XSN{=}O$, which are red, the nitrogen resonance appears 400 ppm to lower field, and the blue *C*-nitroso compounds resonate at lower field still (Table I).[11,12]

Within the XNSO series, however, δ does not correlate with the longest wavelength band (Table I) because this represents excitation from sulfur not nitrogen. These compounds are imido derivatives of SO_2, for which the $n_S \rightarrow \pi^*$ singlet absorption is at 290 nm;[13] cf. 210 nm for R_2SO.[14] The $n_N \rightarrow \pi^*$ absorption is expected to be at shorter wavelengths and has not as yet been characterized.

Among the XNSO compounds the resonance at highest field is that of FSO_2NSO, in which the electronegative X group stabilizes the σ relative to the π^* MO's. If allowance is made for the diamagnetic effect of heavy-atom ligands (Si, S) on

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