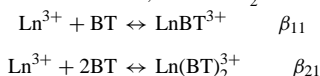


Aqueous Geochemistry of Rare Earth Elements and Yttrium. XII: Potentiometric Stability Constant Determination of *Bis*-Tris Complexes with La, Nd, Eu, Gd, Yb, Dy, Er, Lu, and Y

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Conditional stability constants of 2-[*bis*(2-hydroxyethyl)amino]-2(hydroxymethyl)-1,3-propanediol (BT) complexes of trivalent rare earth element (Ln) ions (La, Nd, Eu, Gd, Yb, Dy, Er, Lu) and Y were determined potentiometrically in aqueous NaCl solutions at 30°C and 0.1 M ionic strength. Least-squares fitting shows that, at <0.04 molal BT, the complex LnBT^{3+} is dominant, with LnBT_2^{3+} forming a secondary complex, where:



Conditional stability constants appear to be directly related to the ionic radius of the trivalent ion in question. The optimal ionic radius, 104–105 pm, yields values of $\log \beta_{21}^* = 10.93 \pm 0.63$ (Gd) and $\log \beta_{11}^* = 6.83 \pm 0.14$ (Yb). Complexation drops off steeply on either side of the ideal ionic radius. In relating the stability constants to ionic radius, it is assumed that BT complexes with Gd, Dy, Er, and Lu have coordination number eight, whereas those with La, Nd, and Eu have coordination number nine. The smoothest trend of stability constants with ionic radius is obtained if Yb–BT complexes are assumed to have coordination number nine. These results may reflect the ability of BT to form an ionic radius-specific chelate structure.

KEY WORDS: Bis-tris; BT; potentiometry; lanthanides; REE; stability constants.

1. INTRODUCTION

The burial and storage of radioactive waste, particularly actinide waste, has become the subject of much research around the world. More research is needed to

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improve our understanding of the fate and transport of contaminants in the earth's subsurface and to aid in decisions regarding both short- and long-term management of waste sites.⁽¹⁾ The ability to accurately predict and influence the behavior of contaminants is central to this understanding. One of the fundamental problems faced is the separation of actinides from other elements and, hence, the isolation and reduction of specific forms of actinide waste.

The actinides are radioactive with their stability decreasing with increasing atomic number, which has serious consequences. It is necessary to employ elaborate radiation-shielding techniques when working with these substances. Hence, research is often performed on the nonradioactive lanthanides, which are analogs to the actinides due to filling of the $4f$ and $5f$ orbitals, respectively.

The lanthanide series (Ln) ranges from Ce to Lu, although, due to their similar nature, La and Y are often included. The lanthanides are chemically similar metal ions because of the shielding of the progressively filled inner $4f$ orbitals by the filled outer $5s$ and $5p$ orbitals. They differ only by the progressive decrease of their ionic radii along the series. Therefore, the coordination properties are mainly governed by electrostatic and steric factors.

Bis-Tris {BT; 2-[*bis*(2-hydroxyethyl)amino]-2(hydroxymethyl)-1,3-propanediol or 2,2-*bis*(hydroxymethyl)-2,2',2''-nitrioltriethanol; Fig. 1a} was originally designed as a pH buffer by Lewis⁽²⁾ ($pK_a = 6.483$ at 25°C). The large size, low charge density, thermal stability, and low toxicity of BT make it an extremely useful buffer in studies of mineral solubilities, metal complexation, marine chemistry, and biochemistry.

Previous work has shown that BT will complex the alkali or alkaline earth ions, including Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , Ba^{2+} , and various other metal ions. The species CaBT^{2+} is the most stable of these complexes in aqueous solution with $\log \beta_1 = 2.25$.^(3,4) It was concluded that the stability of these complexes is neither related simply to the order of the ionic radii nor that of the hydrated radii of the cations. Although Ca^{2+} forms the strongest complex with BT, it is neither the largest nor the smallest of the alkaline earth cations. The complexation of BT with other metal ions has also been studied, *e.g.*, Cu(II), aluminate anions, Eu(III), and La(III), as shown in Fig. 1b.⁽⁵⁻⁹⁾ In all cases, metal-BT complexes were formed, although the relative strength of the conditional stability constants varied greatly. Our interest in the complexation of the rare earth elements (REE) by BT was stimulated when it was found that the presence of relatively small amounts of BT increased the solubility of $\text{Nd}(\text{OH})_3(\text{s})$ by many orders of magnitude (see below). Previous studies^(9,10) have also found that complexation by BT inhibits hydrolytic precipitation of the REE. We initially postulated that, if the optimum size for complexation by BT is that of the Ca^{2+} ion, then we might expect the REE, and, therefore, by analogy, the actinides, to also exhibit an optimum size for complexation somewhere in the middle of their respective series. If this were the case, then BT might represent an

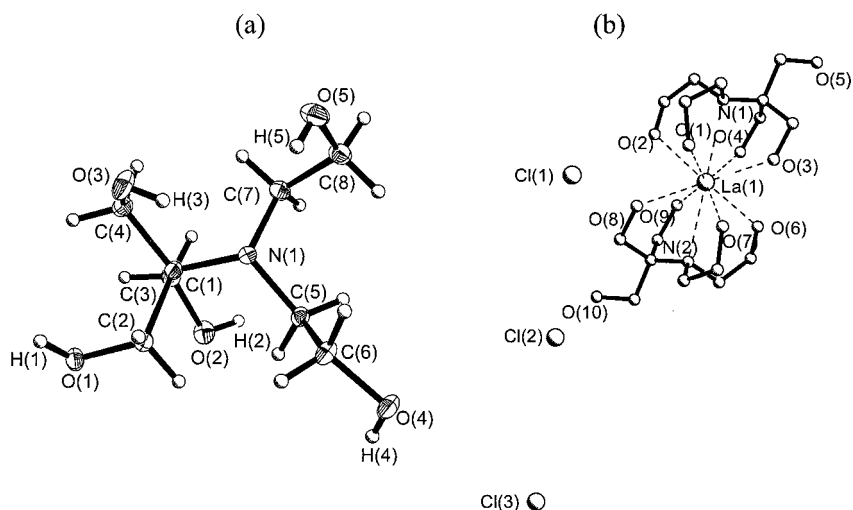


Fig. 1. Schematic diagrams of the crystal structure of (a) *bis-tris* (Ref. 43) and (b) LaBT_2Cl_3 (Ref. 9).

important ligand for the separation of actinides from one another and from other elements.

There has been some interest in the complexation of REE by BT from the biochemical viewpoint. It appears that uncomplexed aqueous Ln^{3+} ions serve as catalysts for the hydrolysis of phosphate esters, including RNA and DNA, whereas most aqueous Ln -complexes do not exhibit catalytic activity.^(9,10) However, it is difficult to maintain sufficient Ln(III) in solution for catalytic activity at near neutral to alkaline pH in the absence of complexing ligands. It has been discovered that Ln-BT complexes maintain catalytic activity while increasing the solubility of the REE in aqueous solution,^(9,10) making the stability constants of aqueous REE-BT complexes of biochemical interest. However, to our knowledge, no systematic studies of the stability constants of these complexes as a function of REE, ionic strength or temperature have been conducted.

The ability of BT to complex the REE is also potentially important because the REE (including the lanthanides) are useful as geological tracers. They are generally considered to be immobile and comparatively immune to weathering, diagenesis, metamorphism, and hydrothermal alteration. The geologically incompatible high field strength elements (Sc, Y, Th, Zr, Hf, Ti, Nb, Ta, and P) tend to be immobile,⁽¹¹⁻¹³⁾ whereas the low-field strength elements (Cs, Sr, Rb, K, and Ba) can be mobilized during geological processes, particularly at high temperatures.⁽¹⁴⁾ However, many exceptions to this generalization exist.⁽¹⁵⁻²⁰⁾ Mobility and fractionation of the REE in aqueous fluids can greatly complicate the use of these elements as tracers. Assessment of the degree of mass transfer of the REE by aqueous fluids

in a given environment requires accurate stability constants. This type of data is often unavailable or of uncertain quality. Although BT is not known to occur naturally in the geological environment, it may be present in contaminated sites and it may also represent a useful analog for more complicated natural organic matter.

This study uses potentiometry to determine the conditional stability constants of Ln–BT complexes as a function of atomic number at a single temperature and ionic strength. In a future contribution, we will report stability constants of Nd–BT complexes as a function of ionic strength and temperature. Potentiometry is one of the most convenient and successful techniques used to measure equilibrium constants of metal complexes. Hence, these results will make a significant contribution to the understanding of REE, specifically lanthanide, behavior in aqueous solution. In addition, using the lanthanides as analogs for the actinides, it is possible that the selectivity, in terms of ionic radius, of the BT ligand (or similar chelating ligands) can be applied as a tool for the separation of the lanthanides and actinides in waste remediation.

2. METHODS

2.1. Materials

All solutions were prepared by weight, employing reagent-grade chemicals and 18M Ω -cm deionized water that had been purged with ultrapure argon for 30 min or more. Stock solutions of NaCl and HCl were prepared from reagent-grade chemicals, purged with argon to remove traces of CO₂, and stored under positive argon pressure in polypropylene vessels. In some instances, reagent-grade stock solutions of the desired strength of NaCl, HCl, and NaOH were purchased from Fisher. BT (Aldrich, >99.9% pure) was dissolved in purified water to make a stock solution with a concentration of approximately 0.3 M and purged with argon. Lanthanide–chloride salts (Aldrich) were, in most cases, better than >99.99% pure. The stated purity of the Ln salts was verified by ICP–MS analyses. The Ln salt was dissolved in purified water to make a reference solution with a concentration approximately 0.1 M and purged with argon.

The concentrations of all the stock solutions, except for Ln solutions, were determined using simple acid/base titrations. A minimum of four titrations were done for each solution until the relative standard deviation was less than 1.0%. The concentrations of Ln solutions were determined by passing the Ln solutions through a cation-exchange column. This allows the exchange of the Ln cation with hydrogen ions, which can then be titrated with standard base to ascertain the exact concentration. For a more detailed description of the method see Kolthoff *et al.*⁽²¹⁾ and Ding and Wood.⁽²²⁾ Again, at least four titrations were completed in order to determine the concentration to within 1.0% error.

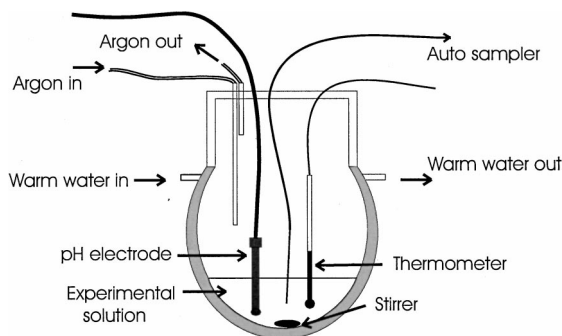


Fig. 2. Reaction vessel.

2.2. Equipment and Potentiometric Measurements

The stability constants of La, Nd, Eu, Dy, Gd, Er, Yb, Lu, and Y complexes with BT were measured potentiometrically at an ionic strength of 0.1 *M*, a temperature of 30°C, and with sodium chloride as the supporting electrolyte. BT concentrations never exceeded 0.035 *M*. As the ionic strength was held constant, activity coefficients can be taken as constant during the experiments.

A jacketed glass reaction vessel (Fig. 2) allowed the temperature to be kept constant by a circulating constant-temperature bath (HAAKE D8). It was possible to maintain temperature in the reaction cell to within $\pm 0.05^\circ\text{C}$. Five sealed openings in the cap of the reaction vessel allowed for a combination glass pH electrode, thermometer, argon-gas inlet, argon-gas outlet, and titrant inlet (PEEK tubing) to be introduced into the cell. PEEK tubing was used, as the small diameter of the tubing reduced the precipitation of Ln hydroxide in the reaction vessel due to local supersaturation before mixing occurs. Argon was continuously passed through the cell at approximately 1 atm to exclude CO_2 . Ultrapure argon was first passed through ASCARITE II to remove CO_2 and then through an aqueous solution at the same temperature and ionic strength as the reaction cell to presaturate the argon and minimize evaporation.

Before each experimental run, the system was calibrated by performing a simple acid-base titration. Weighed amounts of NaCl (4.28 *M*) and NaOH (0.1 *M*) were added to H_2O in the reference cell and stir bar. After the system had equilibrated (*ca.* 1 hour), the first pH measurement was taken. Then, 1 *M* HCl was added in 0.25-mL aliquots using a syringe pump. After each addition, the system was again allowed to equilibrate (*ca.* 5 min) and the pH measured.

When the solution had reached $\text{pH} \approx 2$ the calibration titration was stopped and the excess acid was calculated. At this point, both BT (*ca.* 0.3 *M*) and the Ln (*ca.* 0.1 *M*) were added through one of the openings in the cap. The addition of the BT generally resulted in the pH increasing to approximately 2.5. HCl was

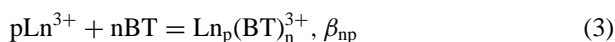
replaced by NaOH in the syringe pump and reverse titrations were begun. Aliquots of 0.3 mL of 0.1 M NaOH were added and the system was allowed to equilibrate (until there was no appreciable drift in mV, i.e., <0.1 mV/min, generally <2 min) before the pH was measured. Eventually a pH was reached where precipitation of $\text{Ln}(\text{OH})_3$ was observed. Titration was stopped after precipitation occurred and the last few data points prior to precipitation were discarded to eliminate any effects of hydrolysis.

2.3. Experimental Method and Theory

In this study, conditional stability constants are defined in the following manner.



or most generally

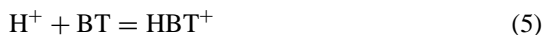


$$\beta_{np} = \frac{a_{\text{Ln}_p(\text{BT})_n^{3+}}}{a_{\text{Ln}^{3+}}^p a_{\text{BT}}^n} \quad (4)$$

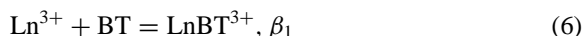
Where Ln^{3+} is any trivalent REE ion, BT is the *bis*-tris ion, a_i is the activity of species i , and n is the ligand number, assumed to range from 1 to 4. The overall coordination number for Ln ions in aqueous solutions is 8 for the heavy REE and 9 for the light REE.^(23–27) For all Ln, an oxidation state of 3 was assumed. Higher oxidation states and coordination numbers were modeled for the Ln, but did not improve the fit to the potentiometric data.⁽²²⁾

Our method is relatively simple. It is based on the fact that there are two principal equilibria assuming only the 1:1 complex is formed.

The protonation reaction is



and the complexation reaction is



When the complexation reaction proceeds to the right, the protonation reaction will proceed to the left, decreasing the pH (or vice versa). Complex formation can be monitored by measuring the H^+ concentration of the solution containing Ln and BT when neutralized by stepwise addition of a strong base.^(28,29) The protonation constant of BT in aqueous solution was determined ($\text{p}K_a = 6.483$ at 25°C). Hence, the nature and concentration of all the species present in the solution containing BT

(a base) and Ln, can be determined from the pH by subtracting out the effect of BT in H₂O. The effectiveness of the potentiometric method relies on the competition between hydrogen and Ln metal with respect to the association with BT anions. The stability constants are computed from the hydrogenion concentration of the complex solutions.

Experiments were carried out at constant ionic strength maintained by the addition of NaCl. As a result, the activity coefficients are maintained approximately constant and Eq. (4) can be rewritten:

$$\beta_{np}^* = \frac{m_{Ln_p(BT)_n^{3+}}}{m_{Ln^{3+}}^p m_{BT}^n} \quad (7)$$

The β_{np}^* are conditional stability constants, which are constant only at the ionic strength at which they were determined. Determination of conditional stability constants at a series of ionic strengths permits the determination of the stability constant at infinite dilution by extrapolation to zero ionic strength. Here, the conditional stability constants have been determined at only a single ionic strength (0.1 M). In a future contribution, we will present data over a range of ionic strengths for the Nd–BT system. In this paper, pH_m is defined as the negative logarithm of the stoichiometric hydrogen ion molality, *i.e.* pH_m = –log m_{H^+} . The convention employed is that H⁺ is not complexed by the chloride ion and ionpairing is treated implicitly by the activity coefficient model used.⁽²⁹⁾ A NaCl medium was used in all experiments as recommended by Millero^(30,31) in order to maintain constant ionic strength. Furthermore, Ln–chloride complexes are known to be relatively weak at the temperatures employed in this investigation.^(27,31)

2.4. Calculation of the Stability Constants

Many computer programs are available for calculating stability constants of complexes in solution from experimental data. One of the more recent programs is BEST,⁽²⁹⁾ which was written specifically for processing potentiometric data. For a detailed description of the program and its code see Martell and Motekaitis.⁽²⁹⁾ Basically, this program obtains the best-fit stability constants for a system by using the least-squares method. It minimizes the difference between the calculated and observed pH values for all the titration points. The core algorithm consists of computation by successive approximations of the pH_m values at each equilibrium point from an initial set of stability constants based on the equilibrium model. Each approximation results in adjustment of the equilibrium constants that are being refined in order to improve the fit between calculated and observed pH_m values.

All the concentrations and conditional stability constants reported are given in molality units (mol·kg⁻¹). Conversions between volume and weight and

molarity and molality were accomplished using the density of aqueous sodium chloride solutions [calculated using the expression of Fabuss *et al.*⁽³²⁾]. This method assumes that, as NaCl is the dominant component in solution, the density of the solution will be equal to the density of a NaCl solution of the same concentration. Additional data required by BEST are the dissociation products of water.⁽³³⁾

In order to determine the number and identity of species present in the titration experiments a number of models containing various combinations of the species LnBT^{3+} , $\text{Ln}(\text{BT})_2^{3+}$, $\text{Ln}(\text{BT})_3^{3+}$, $\text{Ln}_2\text{BT}^{6+}$, and LnBTOH^{2+} were fit to the titration data. The best fit was determined to be that which minimized the overall standard error of the fit using the least number of species. In addition, for a species to be included in the model, it must account for a significant percentage of the total Ln present over some portion of the titration and the standard error of the conditional stability constant for the species had to be relatively small.

3. RESULTS

3.1. Conditional Protonation Constants of BT

The conditional protonation constants of BT in NaCl media were measured in order to check our methodology and data reduction procedures. The results are given in Table I and are compared to the results of Paabo and Bates,⁽³⁴⁾ McGlothlin and Jordan,⁽³⁵⁾ Kitamura and Itoh,⁽³⁶⁾ and Wesolowski and Palmer.⁽³⁷⁾ The various sets of measured stability constants are in excellent agreement at the temperatures and ionic strength used. These results suggest that our experimental apparatus and procedures are capable of yielding high-quality conditional stability constants.

Table I. Summary of Protonation Constant Determinations Available in the Literature for BT at 25°C

Log <i>K</i>	Ionic strength ^d	Method	°C	Reference
6.48 ± 0.11	0.1001	Potentiometric	30	This study
6.481 ± 0.003	0.1	Emf ^b	25	(37)
6.4835 ± 0.0006	0	Emf ^c	25	(34)
6.41	0	Cal. ^d	25	(35)
6.50	0	Dil. ^e	25	(36)

^aUnits: ionic strength, molal.

^bResults given in Wesolowski and Palmer (Ref. 37) incorporate the results from Paabo and Bates (Ref. 34).

^cPt/H₂ vs. Ag/AgCl electrodes with no liquid junction.

^dAdiabatic titration calorimetry.

^eVolume change on neutralisation of BT solution with HCl in a dilatometer.

3.2. Conditional Stability Constants of Ln–BT Complexes

The conditional stability constants and ionic radii for the Ln series (La, Nd, Eu, Gd, Yb, Dy, Er, Lu) and Y are shown in Table II and Fig. 3. Regression analysis shows that under all experimental conditions and for all Ln studied, the LnBT^{3+} complex was required to fit the titration data. The $\text{Ln}(\text{BT})_2^{3+}$ complex was required to fit the data for most of the other Ln–BT systems, the exceptions being Er and Lu, which have the smallest ionic radii of the ions studied. The $\text{Ln}_2\text{BT}^{6+}$ complex was needed to fit the data for both Er and Lu, but was generally too low in concentration to measure accurately for the other Ln studied. This was evident after fitting a three-species model [LnBT^{3+} , $\text{Ln}(\text{BT})_2^{3+}$, $\text{Ln}_2\text{BT}^{6+}$] to the data and calculating the distribution of species based on the stability constants obtained. It was found that the maximum amount of total Ln for the third complex was generally very low (<1 ppm) and the standard error for the estimated stability constant was almost as large as the calculated value itself. Similarly, when calculating the stability constant for the $\text{Ln}(\text{BT})_2^{3+}$ complex with either Er or Lu, the standard error was sometimes larger than the calculated value for the stability constant. Thus, the estimated conditional stability constants for all three BT complexes are shown with associated errors (Fig. 3). However, only the effective complexes are listed in Table II.

The solubility of $\text{Nd}(\text{OH})_3(\text{s})$ in BT solution was calculated in order to check the potentiometrically determined stability constants for Nd–BT complexes (Fig. 4). The modeling used both Nd–BT stability constants measured potentiometrically in this study and the solubility product of $\text{Nd}(\text{OH})_3(\text{s})$ determined experimentally by Wood *et al.*⁽³⁸⁾ These data were used to calculate the solubility

Table II. Results of this Study Showing the Stability Constants for Ln–BT Complexes^a

Element	Ionic radius ^b (pm)	Log β_{11}^*	Log β_{21}^*	Log β_{12}^*
La	122	3.76 ± 0.05	8.20 ± 0.65	N/O ^c
Nd	116	4.54 ± 0.24	8.40 ± 0.75	N/O
Er	112	5.13 ± 0.10	8.75 ± 0.55	N/O
Gd	105	6.23 ± 0.42	10.93 ± 0.63	N/O
Yb	104	6.83 ± 0.14	10.75 ± 0.21	N/O
Dy	103	5.48 ± 0.34	8.76 ± 1.28	N/O
Er	100	2.66 ± 0.38	N/O	2.00 ± 0.64
Lu	98	2.34 ± 0.37	N/O	2.00 ± 0.27
Y	102	5.76 ± 0.32	9.01 ± 0.89	6.01 ± 1.05

^aHere β_{11}^* , β_{12}^* , and β_{21}^* represent LnBT^{3+} , $\text{Ln}_2\text{BT}^{6+}$, and $\text{Ln}(\text{BT})_2^{3+}$ respectively. Note the relationship between the stability constant β_1^* and ionic radius.

^bFrom Ref. 42

^cN/O, not observed.

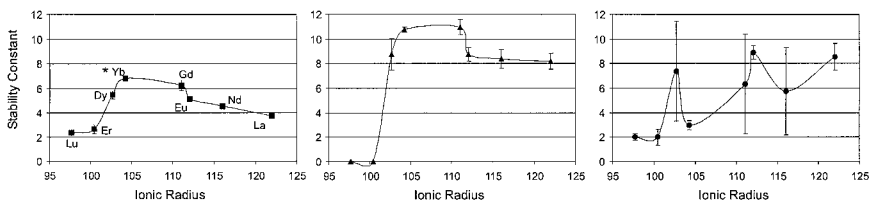


Fig. 3. Stability constant versus ionic radius for Ln–BT complexes. Squares, β_{11} ; triangles, β_{21} ; circles, β_{12} ; and *, eight fold coordinated Yb. Values for β_{12} are shown here but not listed in Table II due to their high error.

of $\text{Nd}(\text{OH})_3(\text{s})$ in BT solutions as a function of pH_m and these values were compared to directly measured solubilities obtained by Wood *et al.* (unpublished data). Figure 4a demonstrates that there is excellent agreement between the calculated and the directly measured solubilities of $\text{Nd}(\text{OH})_3(\text{s})$ in BT solutions over the pH_m range from 8 to *ca.* 9.5. A slight mismatch between calculated and measured solubilities occurs at $\text{pH}_m < 8$, which can be attributed to the fact that the determination of the concentration of free BT depends on an iterative solution. At $\text{pH}_m < 8$, the concentration of Nd is so high that almost all BT present is bound in complexes with Nd. Thus, the free BT concentration is a small difference between two larger numbers (*i.e.*, total BT and Nd-bound BT) and there is a comparatively large uncertainty in the calculated concentration of free BT.

Figure 4a shows that there is also a mismatch between calculated and measured solubilities at $\text{pH}_m > 9.5$. This discrepancy suggests that additional dissolved Nd species not accounted for in the model may be present. It seems likely one of these species might involve complexation by both BT and hydroxide. In fact, we found that the discrepancy in the high pH_m data could be resolved by the inclusion of the species $\text{Nd}(\text{BT})_2(\text{OH})_2^+$ with a conditional stability constant of $\log \beta^* = 4.56$. Figure 4b demonstrates that the model now provides an excellent fit to the experimental data at all pH_m values greater than 8. The excellent

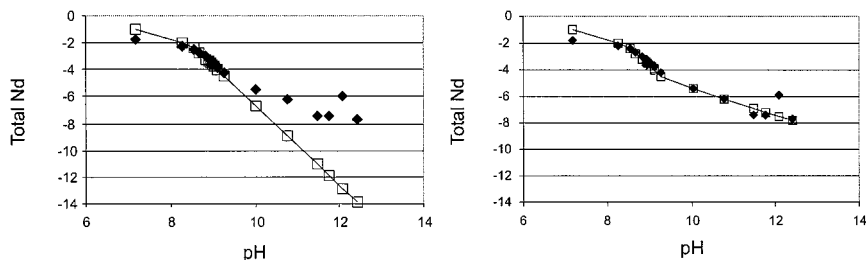


Fig. 4. Calculated and observed solubility data for total Nd versus pH for (a) Nd–BT complexes and (b) Nd–BT and Nd–OH–BT complexes. Solid line (squares), calculated solubilities; Diamonds, experimental data of Woods, where $\text{BT}_{(\text{total})} = 0.02 \text{ m}$ and ionic strength = 0.1076.

agreement between the calculated and measured solubilities of $\text{Nd}(\text{OH})_3(\text{s})$ in BT solutions from pH_m 8 to 9.5 is strong evidence of the validity of our potentiometrically derived conditional stability constants for the Nd–BT complexes and the absence of significant hydrolysis effects up to $\text{pH}_m \approx 9$. These results also show that complexes of lanthanides with BT are surprisingly strong and are capable of greatly increasing the solubility of lanthanide-bearing solid phases. It might be expected that the trivalent actinides would also form complexes of similar strength.

4. DISCUSSION

The only previous measurement of stability constants for Ln–BT complexes of which we are aware is that of Oh *et al.*⁽⁹⁾ They report a stability constant for LaBT^{3+} of $\log \beta_{11} = 4.7$. This is almost an order of magnitude higher than the value we determined ($\log \beta_{11} = 3.76$). However, Oh *et al.*⁽⁹⁾ do not specify the ionic strength to which this constant applies, nor do they provide the raw potentiometric data or the details of their regression fit. Moreover, they do not appear to have included $\text{La}(\text{BT})_2^{3+}$, $\text{Ln}_2\text{BT}^{6+}$, or other potentially important species in their model. This omission would result in an overestimation of β_{11} .

The ionic radius of the Ln^{3+} decreases across the series (from La to Lu) as a result of the filling of the 4*f* shell (the lanthanide contraction). The results shown in Figs. 3 and 5 suggest that the stability constants of Ln–BT complexes are directly related to the ionic radius of the Ln in question, but that the stability is not a monotonically increasing function of decreasing ionic radius as is the case with most other Ln complexes. The optimal ionic radius is between 105 and 104 pm, which correspond to Gd and Yb, respectively. Complexation with BT drops off steeply on either side of the ideal ionic radius. Figure 5 shows the data for Lu, Y, and Er. The Y^{3+} ion has an ionic radius of 102 pm, which is closest to Dy (ionic radius 103 pm). As expected, Y and Dy behave remarkably similarly with BT. The stability of Er (ionic radius 100 pm) and Lu (ionic radius 98 pm) complexes with BT drops significantly, in support of the hypothesis that BT is size-selective and preferentially complexes ions with a radius of approximately 104–105 pm.

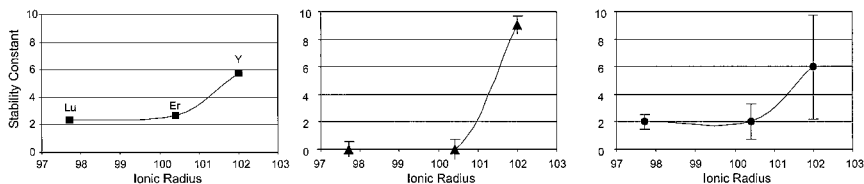


Fig. 5. Stability constant versus ionic radius for Lu–BT, Er–BT, and Y–BT complexes. Square, β_{11} ; triangles, β_{21} , and circles, β_{12} .

4.1. The Behavior of Yb

In all instances, the Ln have been assumed to possess a +3 charge, which is the most stable under the given conditions. The ionic radii selected for comparison of the stabilities of the Ln–BT complexes refer to coordination number nine for the light REE (La, Nd, Eu) and eight for the heavy REE (Gd, Dy, Er, Lu, and Y.^(23–27,39)) The Yb–BT system seems to be anomalous because it fits most smoothly in the trend of stability constants *vs.* ionic radius assuming coordination number nine. However, as this study has not attempted the identification of coordination numbers, why Yb³⁺, and not the other heavy REE, should exhibit ninefold coordination is unclear.

Other possible explanations for the anomalous behavior of Yb are that (a) Yb is present primarily in the +2 oxidation state, and/or (b) there is something special about the 4*f* electron shell configuration of Yb³⁺ which imparts an unusual stability to its complex with BT. Although, these factors may play a part in the behavior of Yb in solution with BT, they are unlikely to be major considerations. First, ytterbium can exist in the +2 oxidation state, but is not stable in water. In fact, Yb²⁺ is oxidized in the presence of water.⁽⁴⁰⁾ Moreover, divalent Eu is known to be more stable than divalent Yb, so it is unclear why Eu would not also be present in the divalent state. However, Eu²⁺ has an ionic radius far too large to fit the BT structure, which would probably prevent the formation of stable complexes with BT. Second, variations in the filling of the 4*f* electron shell are seen in the metals of both Eu and Yb, which are composed predominantly of larger Ln²⁺ ions with 4*f*^{*n*+1} configuration and only two electrons in the conduction band. Although this configuration is significant in the metal phase of the element, it is unlikely to have any influence on the behavior of the ion in aqueous solution.

Coordination numbers for the Ln series are generally high and stereochemistries are determined largely by the requirements of the ligands and lack the directional constraints of covalency (*i.e.*, Ln–ligand bonding is mostly ionic). Hence, the coordination numbers are frequently ill defined and the complexes distinctively labile.⁽⁴⁰⁾ Because of the chelating nature of the BT ligand, the most likely explanation for the behavior of the Yb–BT complex is that Yb exhibits coordination number nine in this complex.

Specific examples in which Yb is known to show unusual behavior include the lanthanide diketonate complexes and complexes of EDTA.⁽⁴¹⁾ The coordination number for Ln in the complex Ln(acac)₃(H₂O)₂ (Ln = La, Pr, Nd, Eu, Ho, Y) is 8, whereas, the complex Yb(acac)₃(H₂O) has seven-fold coordination. In this example, Yb alone exhibits a unique coordination number relative to the remaining Ln elements studied. Complexes of Ln³⁺ with EDTA are easily prepared, generally forming Na [Ln(EDTA)(H₂O)_{*x*}nH₂O]. In these Ln compounds, La–Dy form nine-coordinate ions whereas Er and Yb form eight-coordinate ions. In this case, both Yb

and Er are unusual. In both examples, the different coordination numbers reflect the size dependency of the chelating ligand. Thus, it is plausible that Yb–BT complexes can have a coordination number of nine, as indicated by the modeling in this study.

4.2. Coordination of the Central Metal Ions by Hydroxyl Groups

BT forms complexes in aqueous solution with the amino nitrogen involved as a binding site.⁽³⁾ However, it is sterically possible for all five of the BT hydroxyl groups (Figs. 1a and 1b) to reach the vicinity of the central nitrogen and, therefore, to participate in complex formation. Scheller *et al.*⁽³⁾ show that the coordination of hydroxyl groups by metals in the BT structure leads to a systematic decrease of basicity, which is fairly independent of the type of amine and, hence, the pK . In addition they show that the complexes of BT do not follow the Irving–Williams series, where $Ba < Sr < Ca < Mg < Mn < Fe < Co < Ni < Cu < Zn$. Ca–BT is significantly more stable than the complexes of Sr, Ba, Mg, and Mn. This is explained by a chelatelike orientation of the hydroxyl groups and the nitrogen. Into this cavity, Ca, Gd, and Yb (ionic radius 100, 105, and 104, respectively) fit well. This is a similar phenomenon seen in crown ethers and other macrocyclic ligands.

There is no question that Ln–BT complexes exist in aqueous solution in the form of several isomers, which are in equilibrium with each other and differ by the number of coordinated hydroxyl groups.^(8,9) It appears as if the minimum number of participating hydroxyl groups is 2, leaving BT as a tridentate ligand. Moreover, the degree of hydroxyl group participation is somewhat different for each ion, where the alkaline earth Ca and the lanthanide Yb have a high percentage of highly coordinated isomers. Hence, the apparent relationship between ionic size and conditional stability constant for Ln–BT complexes is probably a result of the chelating nature of aqueous BT.

It is interesting to note that many of the bidentate metals exhibit a similar ionic size dependence when complexing with BT. Ca–BT is the most stable of the alkaline earth–BT complexes with $\beta_{11} = 2.25^{(3,4)}$ (Table III). The Ca^{2+}

Table III. Stability Constants for Various Metal–BT Complexes Showing the Strength Dependence of the Complex with Ionic Radius

Element	Ionic radius (pm)	Log β_{11}	Reference
Cd^{2+}	95	2.47	3
Ca^{2+}	100	2.25	3,4
Na^+	102	0.82	4
Pb^{2+}	119	4.32	3
Sr^{2+}	126	1.44	3,4
Ba^{2+}	142	0.85	3,4

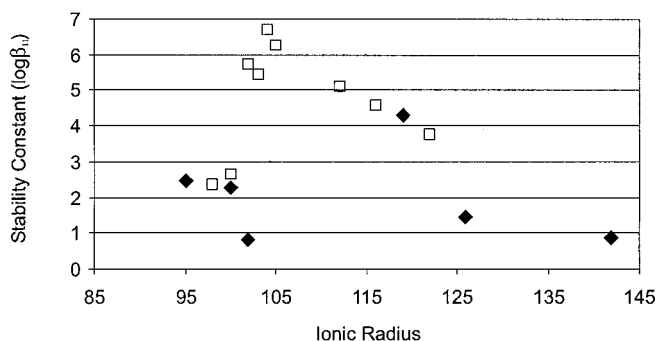


Fig. 6. Stability constants for various metal–BT complexes showing the strength dependence of the complex with ionic radius. Triangles, Refs. 3,4; squares, data from this study. See Table III and text for greater detail.

ion has a radius of 100 pm, which is the same as Er and close to Lu (ionic radius 98). The conditional stability constants for Er and Lu are $\beta_{11}^* = 2.66$, $\beta_{12}^* = 2.00$, and $\beta_{11}^* = 2.34$, $\beta_{12}^* = 2.00$, respectively. It should be noted that Er, Lu, and Ca form BT complexes of very similar strengths, irrespective of ionic charge (Fig. 6). Figure 6 shows that many of the metal–BT complexes follow roughly the same pattern of ionic radius-dependant stability, regardless of ligand number—hence supporting the hypothesis that BT forms a chelate structure, which preferentially complexes ions with a specific ionic radius of approximately 104–105 pm.

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