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Coordination Chemistry of Lanthanide Catecholates*

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Abstract

The solution complexation chemistry of Eu(III) and Lu(III) with several monocatecholates [1,2-dihydroxy(3,5-disulfo)benzene (tiron); 4-nitrocatechol (n-cat); catechol; 5-sulfo-2,3-dihydroxy-*N*,*N*-dimethylbenzamide (DMBS)], and a tetracatecholate (3,4,3-LICAMS) has been investigated using potentiometric and spectrophotometric methods. These two trivalent lanthanides form complexes of the same composition with those of Lu(III) more stable. At pH 8 only 1:1 complexes of Eu(III) and Lu(III) with tiron are formed, regardless of the amount of excess ligand present. Complexes of Eu(III) with catechol of 1:1, 1:2 and 1:3 are formed at pH 8.0, 10.0 and 12.0, respectively. The octadentate ligand 3,4,3-LICAMS and the simple catechols 4-nitrocatechol and DMBS form complexes with 1.5 catechol groups per Eu(III) or Lu(III). The formation constants of these complexes have been determined. Discussion of these differences in catecholate coordination chemistry with lanthanides, as well as comparison of these results with those obtained for trivalent and tetravalent transition metals and actinides, are presented.

Introduction

Although metal complexes of simple catecholates (1,2-dihydroxybenzene) have been extensively studied for transition metals, [2–5] relatively little has been done to evaluate the complexes of lanthanide catecholates. This might seem surprising, considering the affinity of lanthanide(III) ions for oxygen anions, as in the complexes of lanthanide(III) in aqueous solution with such oxygen donor ligands as the 4-diketonates and salicylaldehyde [6]. However, as will be shown, the strong affinity of catecholate ligands for metals with high charge/radius ratios makes them relatively poor ligands for the large lanthanide(III) ions.

A program to develop chelating agents which are to be used in the specific complexation of actinide(IV) ions, including decontamination applications, is underway in this laboratory. The first such macrochelates synthesized have used the catecholate dianion as the chelating entity, attached to an amine backbone through an amide linkage. Many of these chelates have been tested *in vivo* and have demonstrated a remarkable ability to complex Pu(IV) [7–10]. Several comprehensive reviews have been published on this subject [11–14].

The trivalent lanthanides are excellent models for trivalent actinides. Although uranium and transuranium actinides demonstrate a variety of oxidation states (and in this way do not resemble the trivalent lanthanides, which are usually trivalent) it is significant to note the size similarity between trivalent lanthanides in the same column as their trivalent actinide counterparts [15]. Since charge to ionic radius ratio appears to play a key role in determining the stability and coordinating capabilities of synthetic catecholate chelating agents [16], studies of the lanthanide(III) catecholates may be extended to determining the stability of the corresponding actinide(III) catecholates, particularly since we have recently studied the redox potentials of several lanthanide(IV)/(III) and actinide(IV)/(III) tetracatechol complexes.

This paper includes a study by potentiometric and spectrophotometric techniques of several complexes of Eu(III) and Lu(III) with a number of catecholates: catechol, 1,2-dihydroxy(3,5-disulfo)benzene [tiron], 4-nitrocatechol [n-cat], and 5-sulfo-2,3-dihydroxy-*N*,*N*-dimethylbenzamide [DMBS]; as well as one tetracatecholate, 1,5,10,14-tetrakis-(2,3-dihydroxy-5-sulfobenzoyl)-1,5,10,14-tetraazatetradecane [3,4,3-LICAMS]. The selection of these particular lanthanides was deliberate. Lutetium, the smallest of the lanthanides, should form the strongest complexes with catecholates. Europium is similar in size to Am(III), and *in vivo* testing has shown a relative inability of the synthetic chelating agents to remove Am(III)

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from mice. Structural formulas for the ligands are shown in Fig. 1.

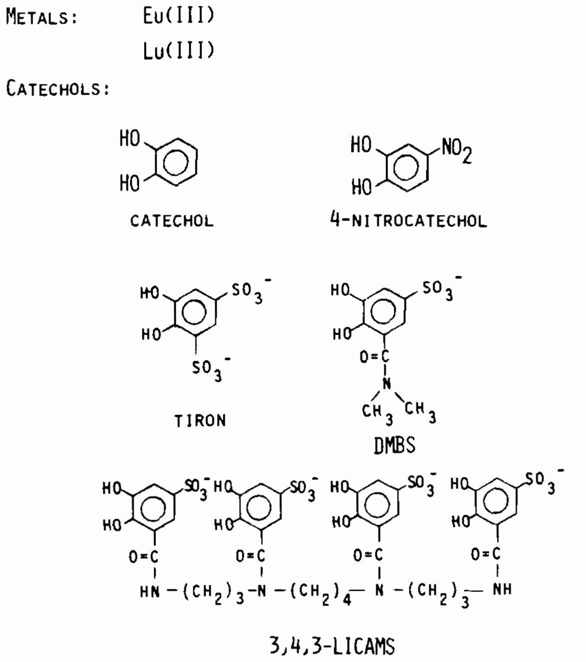

Fig. 1. Structural formulas of the catecholate ligands studied.

Experimental

Potentiometric Titrations

All potentiometric titrations were performed at 25.0 ± 0.1 °C in 0.1 M KNO_3. The stock $LnCl_3$ solutions were standardized by back titration with standardized Zn(II) following an addition of excess EDTA [17]. Catechol (Crown Zellerbach) and nitrocatechol (Aldrich, 97%) were recrystallized from benzene and toluene, respectively. Tiron (disodium salt) was obtained from Eastman and required no further purification. The syntheses of DMBS and 3,4,3-LICAMS are reported elsewhere [18, 19]. All ligands were titrated alone to determine the molecular weight and protonation constants (Table I) [20, 21]. Titrations were performed under argon on 0.2 mM to 0.05 mM solutions with standardized carbonate-free 0.1 M KOH (prepared from Baker (Dilut-It analytical concentrate). The pH electrodes were standardized in acetic acid buffer and dilute nitric acid to read hydrogen ion concentration, not activity. The details of the automatic titration apparatus and procedures followed have been described previously [22].

TABLE I. Ligand Protonation Constants[a]

Ligand	log K_2	log K_1
Catechol	9.13	13.0[b]
Tiron	7.55	13.5[b]
n-cat	6.72	10.85[b]
DMBS	7.30	12.3[c]
3,4,3-LICAMS	7.30[d]	12.5[c,d]

[a] $K_n = [H_nL]/[H^+][H_{n-1}L]$, $\mu = 0.1$ M (KNO_3), 25 ± 0.1 °C. [b] From ref. 20. [c] From ref. 21. [d] These are average values for the four nearly equivalent phenolate groups of the catechol groups of this ligand.

Spectrophotometric Titrations

Spectral titrations of Eu-tiron were performed under argon in a 10 cm cell at 25.0 ± 0.2 °C on an HP8450a UV/Vis spectrophotometer. Concentrations of solution were typically 10^{-5} M and the pH was adjusted by adding small aliquots of HNO_3. The reference cell contained 0.10 M KNO_3. Measurements of pH were made on a Beckman 102 pH meter equipped with a Sigma Tris electrode calibrated with standard buffer solutions at pH 4.01 and 7.00.

The formation constants were determined using eqns. (1) and (2)

$$A_{\mathrm{obs}} = \epsilon_{\mathrm{MHL}} C_{\mathrm{M}} l + \frac{1}{K_{\mathrm{MHL}}} \left(\frac{A_{\mathrm{o}} - A_{\mathrm{obs}}}{[\mathrm{H}]} \right) \tag{1}$$

$$K_{\mathrm{ML}} = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} \tag{2}$$

where A_{obs} = absorbance of solution, ϵ_{MHL} = extinction coefficient of complex MHL, C_{M} = total initial concentration of metal, l = cell path length, K_{MHL} = formation constant of MHL complex, A_{o} = the initial absorbance of pure ML, K_{ML} = formation constant of complex ML, [M] = concentration of free metal, [L] = concentration of free ligand, [ML] = concentration of complex ML, [H] = concentration of H^+.

Job's Method of Continuous Variation [23]

The molar ratios of catecholate to Ln(III) were varied over a wide range while maintaining [Ln(III)] + [catecholate] constant. Solutions were buffered with HEPES (Biorad) at pH 8.3 to 8.8 to ensure full complexation of the Ln(III) by the catecholate (the optimum pH was determined from the potentiometric studies). The differences in optical densities of the catecholate-Ln(III) complex and of an equivalent amount of ligand were determined on a Cary 17 or HP8450a spectrophotometer at 430 nm for Eu/Lu–n-cat and Eu/Lu–tiron, and 320–329 nm for Eu/Lu–DMBS, Eu/Lu–tiron and Eu/Lu–3,4,3-LICAMS. These differences were in accordance with eqn. (3):

$$\Delta = A - l[\epsilon_1 M(1 - X) + \epsilon_2 MX] \tag{3}$$

where ϵ_1 = extinction coefficient of ligand, ϵ_2 = extinction coefficient of Ln(III), X = mole fraction of Ln(III) in solution, M = total initial concentrations of Ln(III) and ligand, l = cell path length, A = absorbance of solution.

Typically ten to fifteen different mole fractions (10^{-4}–10^{-5} M) were prepared to determine the maximum in the Δ *versus* X plot, which gives the reaction stoichiometry.

Isolation of Eu(cat)OH·4H$_2$O

When a 1:1 catechol Eu(III) solution was prepared and adjusted to pH 7.4, a precipitate formed, which was filtered, washed with water and dried under vacuum at ambient temperature overnight. The sample was then dried at 110 °C to constant weight and analyzed for Eu. This was accomplished by oxidizing all organic material in the sample by adding 5 ml conc. HNO_3 and boiling; to the cooled sample was added 1 ml conc. $HClO_4$ and the solution was boiled again. Evaporation under vacuum gave a residue that was dissolved in 5 ml H_2O to yield a colorless solution. Excess EDTA was added and back titrated with standardized Zn(II) to give %Eu. Carbon and hydrogen analyses of the anhydrous precipitate were performed by Analytical Services at the University of California, Berkeley. *Anal.* Calc. for $C_6H_5O_3Eu$: C, 26.01; H, 1.82; Eu, 54.85. Found: C, 26.25; H, 1.75; Eu, 55.03%.

The extent of hydration was determined by placing the fresh precipitate in a bottle over 50% H_2O/50% ethylene glycol until constant weight was maintained. The precipitate was then dried in an oven at 105 °C to constant weight. This weight loss corresponded to 4.06 waters of hydration per mole.

Results and Discussion

The stoichiometries of the metal–ligand complexes formed with Eu(III) were identical to those formed with Lu(III) for tiron, n-cat, DMBS and 3,4,3-LICAMS. The only difference between the two metals and their coordination by catecholate ligands is that the relative stability of the Lu(III) complexes is always greater, a result of its smaller size.

Catechol and Tiron Complexes

In all titrations of catechol and Eu(III) with ligand to metal ratios greater than one, the process of equilibration was extremely slow after the addition of 2 equiv OH$^-$/mol Eu(III). In 1:1 and 2:1 titrations of catechol:Eu(III) (Fig. 2) a white precipitate formed at neutral pH. The precipitate was characterized as Eu(cat)OH·4H$_2$O (see above).

The equilibrium constants derived from the titration data of the Eu(III):catecholate system are presented in Table II. From these data, the protonation constants of the ligand, and the water dissociation constant, and the equilibrium constant for the disproportionation reaction shown below can be calculated.

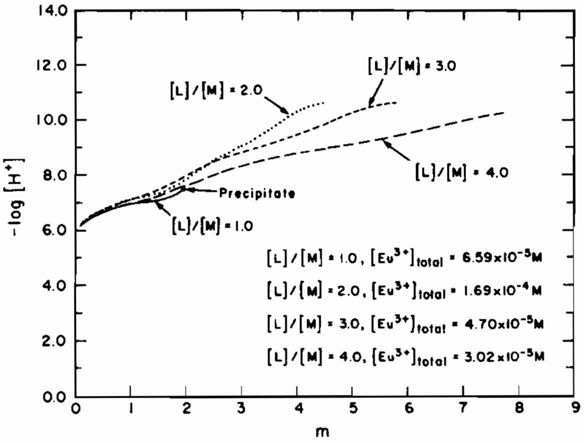

Fig. 2. Potentiometric equilibrium curves for the catechol/Eu(III) system, μ = 0.10 M (KNO_3), T = 25 °C.

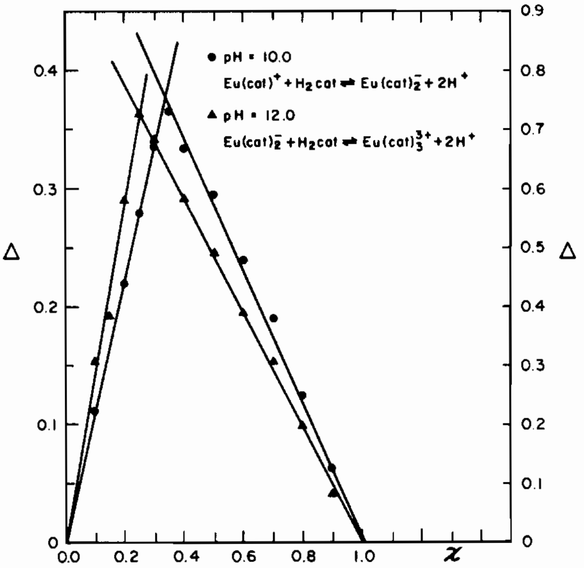

Fig. 3. Continuous variation plot of the optical density difference *vs.* mole fraction of Eu(III) at [Eu^{3+}] + [cat] = 1.6 × 10^{-4} M, pH 10 and pH 12.

$$Eu(cat)_2^- + H_2O + H^+ = Eu(cat)(OH)_{(solid)} + H_2cat \quad (4)$$

$$\log K = 1.4 - \log K_{sp}$$

Since the log(solubility product) for [Eu(cat)(OH$^-$)$_{(solid)}$ $\rightleftharpoons$ Eu(cat)$^+$ + OH$^-$] is certainly much less than zero, the disproportionation is expected to occur until the pH is high enough so that the catechol ligand is largely deprotonated. The stoichiometry is confirmed by Job's plot (Fig. 3). However, it should be expected that more acidic catecholates, particularly with additional negative charge, should be capable of binding lanthanides to a greater extent, since the insoluble neutral mixed hydroxide will not form.

TABLE II. Equilibrium Constants for Lanthanide Catechol Complexes[a]

Ligand[b]	Metal ion	Constant type[c]	log (Constant)
cat	Eu(III)	ML	10.1(2)[d]
cat	Eu(III)	ML_2	6.7(3)[d]
cat	Eu(III)	MLH	7.3(3)[d]
cat	Eu(III)	ML_3	3 to 4[h]
cat	Eu(III)	ML_4	−4 to −3[h]
cat	Eu(III)	β_4	16.8[h]
cat	Eu(IV)	β_4	51
tiron	Eu(III)	ML	13.2(2)[e]
tiron	Eu(III)	MLH	5.7(4)[e]
tiron	Lu(III)	ML	14.0(4)[e]
tiron	Lu(III)	MLH	5.8(9)[e]
DMBS	Eu(III)	ML	12.0(5)[f]
DMBS	Eu(III)	M_2L_3	25.0(1)[f]
DMBS	Lu(III)	ML	13.3(2)[f]
DMBS	Lu(III)	M_2L_3	27.6(2)[f]
n-cat	Eu(III)	ML	8.9(1)[g]
n-cat	Eu(III)	M_2L_3	18.4(1)[g]
n-cat	Lu(III)	ML	9.2(4)[g]
n-cat	Lu(III)	M_2L_3	19.0(1)[g]

[a] Estimated standard deviations are from averages (when more than one estimate) and least-squares refinement, and (in parentheses) are the errors in the least significant digits. All values at 25 °C and 0.1 molar ionic strength. [b] Ligand abbreviations (as deprotonated anions of the indicated ligands) are the same as those used in the text: cat = catechol; tiron = 2,4-disulfocatechol; n-cat = 4-nitrocatechol; DMBS = 5-sulfo-2,3-dihydroxy-*N,N*-dimethylbenzamide; 3,4,3-LICAMS = 1,5,10,14-tetrakis-(2,3-dihydroxy-5-sulfobenzoyl-1,5,10,14-tetraazatetradecane. [c] Stability constants are defined by: $ML_{n-1} + L = ML_n$, $K_{ML_n} = [ML_n]/[ML_{n-1}][L]$, $ML + H = MLH$, $K_{MLH} = [MLH]/[ML][H]$, $M + nL = ML_n$, $\beta_n = [ML_n]/[M][L]^n$. In each case L represents the fully deprotonated ligand, M represents the aqueous metal ion, and H is H^+. [d] Averages of values determined at total metal ion concentrations of 7.02×10^{-5} and 3.7×10^{-5} M. [e] Potentiometric equilibrium values determined for several different metal ion concentrations. Values presented are averages of potentiometric and spectrophotometric values, which agreed within stated standard deviations. For Eu(III), the equilibrium was sampled at total metal ion concentrations of 9.97×10^{-5}, 6.70×10^{-5} and 4.63×10^{-5} M. The resultant equilibrium constants agreed with stated error limits. [f] As in other determinations, averages are presented. Total metal ion concentrations were 3.42×10^{-5}, 2.55×10^{-5}, 1.72×10^{-5} and 1.29×10^{-5} M. [g] As in other determinations, averages are presented. Total metal ion concentrations were 4.85×10^{-5}, 3.67×10^{-5}, 2.45×10^{-5} and 1.82×10^{-4} M. [h] Stability constants were refined assuming average values for the ligand protonation constants. [i] These values are estimated from the Ce(IV)/Ce(III) redox potential data (see text). The values for the hypothetical Lu(IV) and Eu(IV) ions should be applicable to the corresponding actinide (IV) ions.

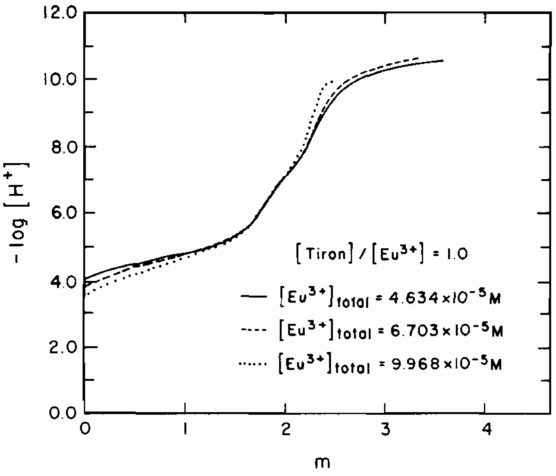

Fig. 4. Potentiometric equilibrium curves for the tiron/Eu(III) at 1:1 ratio.

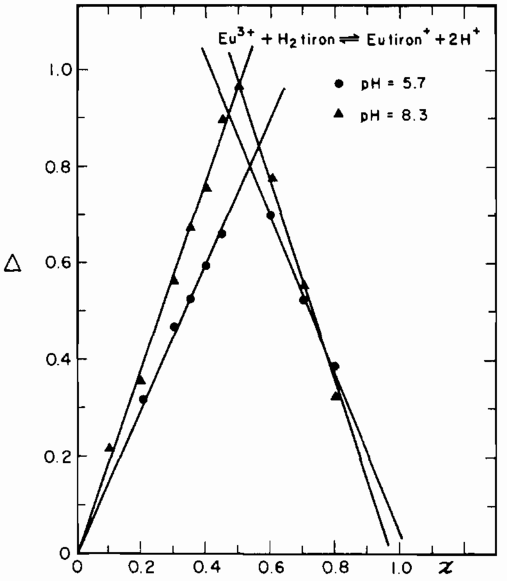

Fig. 5. Continuous variation plot of the optical density difference *vs.* mole fraction of Eu(III) at $[Eu^{3+}] + [tiron] = 8 \times 10^{-5}$ M, pH 5.7; and $[Eu^{3+}] + [tiron] = 1.6 \times 10^{-4}$ M, pH 8.3.

Tiron is a more acidic catecholate, with pK_a values of 7.55 and 13.5 for the phenolic oxygens (see Table I), and this ligand has a four minus charge when fully deprotonated. Thus, charge repulsion may affect tiron–lanthanide complexation. By potentiometric (Fig. 4) and spectrophotometric titration, as well as by Job's method of continuous variation (Fig. 5), the tiron complexes of Lu(III) and Eu(III) are one to one at pH 8, regardless of excess ligand present. There is no observable inflection of 2 equiv of base per mole of metal (neglecting the sulfonate deprotonation) for the europium–tiron titrations with ligand/metal ratios greater than one, because the pH at which deprotonation of one of the phenolic oxygens of the excess tiron overlaps with the deprotonation accompanying complex formation.

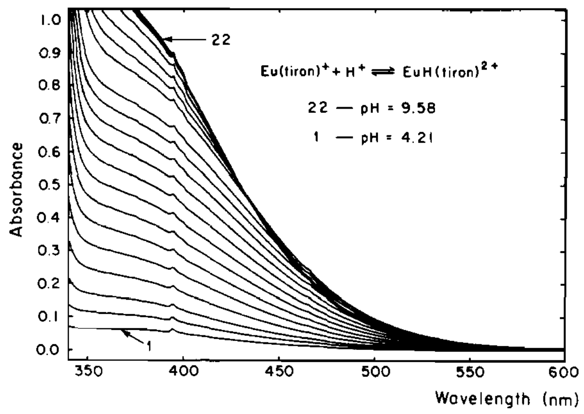

Fig. 6. Visible spectra of a 1.25:1 solution of tiron and Eu(III), recorded as a function of pH; $[Eu^{3+}]_{total} = 8 \times 10^{-4}$ M, $\mu = 0.1$ M (KNO_3), $T = 25$ °C.

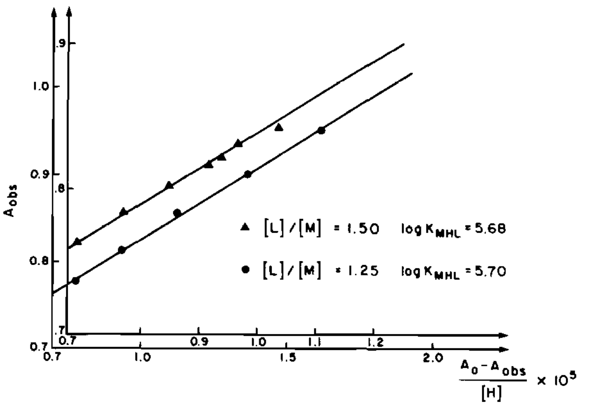

Fig. 7. *A* plot of $(A_o - A_{obs})/[H^+]$ *versus* A_{obs} for the Eu(III)/tiron system, where A_{obs} is the absorbance average between 370 to 390 at a given pH.

The Lu(III)–tiron potentiometric titration curves are similar to those obtained for Eu(III) tiron, except that the buffer region of metal complexation is lowered in pH by about 0.2 pH units, indicating the formation of a stronger complex.

Using a non-linear least squares program to refine formation constants for the potentiometric data[§], log K_{ML} for Eu(III)–tiron was found to be 13.2 and log $K_{MHL} = 5.7$ (Table II). The same formation constants were obtained in analyzing spectral data (Figs. 6 and 7), with an isosbestic point present at 435 nm for the equilibrium $ML + H^+ = MHL$. The formation constants K_{ML} and K_{MHL}, for other lanthanide–tiron complexes have been determined [24]. The value obtained for log K_{MHL} compares favorably to those obtained for other lanthanide–tiron complexes, but the value of log K_{ML} is considerably lower than what one would predict from the reported values for log K_{ML} of Sm(III)–tiron (13.9) and log K_{ML} of Gd(III)–tiron (14.1). The difference here may partly be attributed to use of KNO_3 as the supporting electrolyte for these studies *versus* the use of perchlorate in the study by Shtenke *et al.* [24].

The 1:1 formulation for the lanthanide(III)–tiron complexes disagrees somewhat with results obtained by analyzing perturbations of lanthanide f–f transitions to assess the extent of tiron coordination [25]. These perturbations are also sensitive to hydroxide coordination and this effect was not considered by Tserkasevich *et al.*. These authors report complexes from alcohol of $Na_3Nd(tiron)_{1.5}$, $Na_5Nd(tiron)_2$, and $Na_9Nd(tiron)_3$ based on analyses of Nd^{3+} and Na^+.

DMBS and 4-Nitrocatechol Complexes

Both DMBS and 4-nitrocatechol have electron withdrawing groups which make them more acidic than catechol itself (Table I). In addition, when fully deprotonated, they do not possess as high a negative charge as does tiron. This should make these two ligands likely candidates for forming catecholate–lanthanide complexes of higher stoichiometry. However, no complexes of n-cat–Ln(III) and DMBS–Ln(III) (*Ln* = Eu, Lu) with ligand/metal ratios greater than 1.5 were characterized, regardless of excess ligand present; in each case the Lu complexes are slightly more stable. This stoichiometry was consistent with results obtained from potentiometric titration (Fig. 8) and Job's method (Fig. 9). The final stability constants are presented in Table II. It is interesting to note that one to one titrations of n-cat: Eu gave a precipitate after the addition of two equivalents of base/mole Eu(III). This precipitate presumably has the same formulation as the Eu–catechol precipitate, $Eu(n\text{-}cat)OH \cdot xH_2O$. Higher ratios of ligand to metal did not give a precipitate. The Eu n-cat titrations at higher ligand to metal ratios equilibrated very slowly above pH 10.4.

[§] Given an initial set of guesses for the log β's, values for pH, pL, and pM were calculated for each data point by varying these parameters to minimize the differences between calculated and analytical concentrations of total hydrogen, total ligand, and total metal. The weighted residual for each data point is $r_i = (1/\sigma_i)(pH_{obs} - pH_{calc})_i$. The derivatives $D_{ij} = (\partial r_i / \partial \log \beta_j)$ were computed numerically and the shifts in β values, computed to minimize the sum of the squares of the residuals, were applied from the vector-matrix equation:

$$(\Delta \log \beta) = (D^T D)^{-1} D^T r$$

The weighting factor, $1/\sigma_i$, was based on the estimated uncertainty in the pH reading at each point in the titration curve. This uncertainty has two components: the precision of the pH meter itself and the precision of titrant delivery (volume V_T). Thus the weight was calculated as

$$\sigma_i^2 = \sigma_{meter}^2 + \left(\frac{\partial pH}{\partial V_T}\right)^2 \sigma_{V_T}^2$$

where $\sigma_{meter} = 0.003$ pH unit, $\sigma_{V_T} = 0.002$ ml and $\partial pH / \partial V_T$ is the slope of the titration curve at each point in the titration. This weighting scheme emphasizes the more accurate data from buffer regions and minimizes the relatively inaccurate pH readings from the steep inflections.

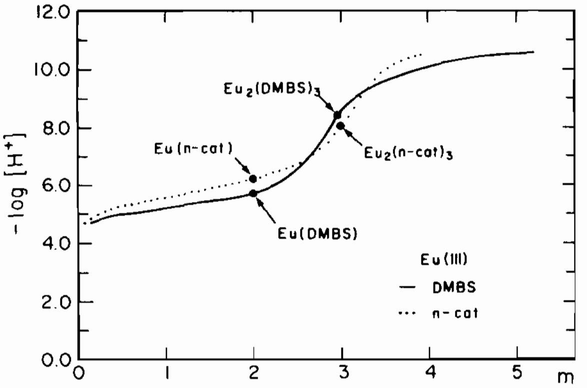

Fig. 8. Potentiometric equilibrium curves for a 1.5:1 solution of n-cat or DMBS with Eu(III); $\mu = 0.10$ M (KNO_3), $T = 25$ °C.

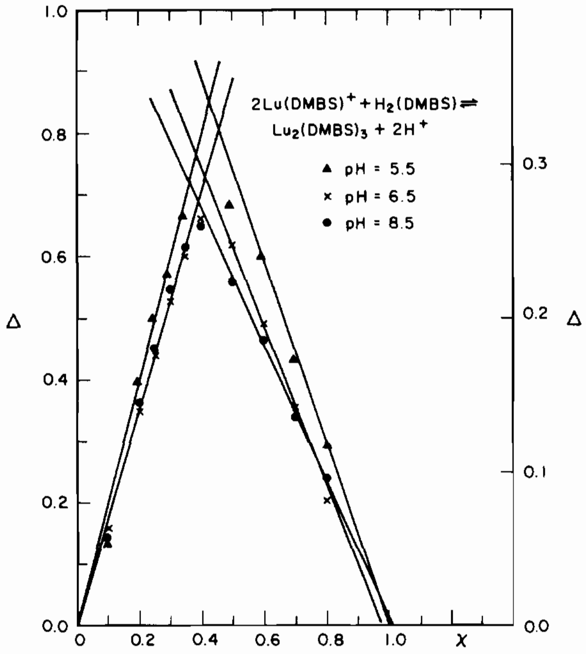

Fig. 9. Continuous variation plot of optical density difference *vs.* mole fractions of Lu(III) at $[Lu^{3+}] + [DMBS] = 2.80 \times 10^{-4}$ M, pH 5.5, 6.5 and 8.5.

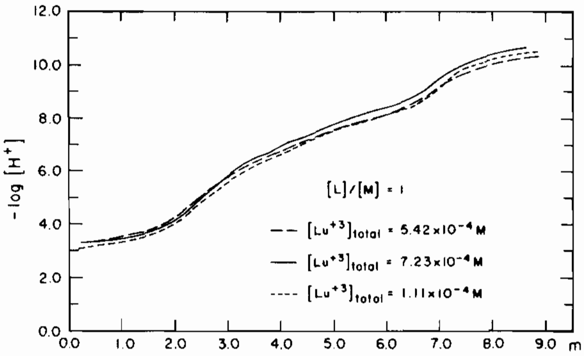

Fig. 10. Potentiometric equilibrium curves of 1:1 solution of Lu(III) and 3,4,3-LICAMS, $\mu = 0.10$ M (KNO_3), $T = 25$ °C.

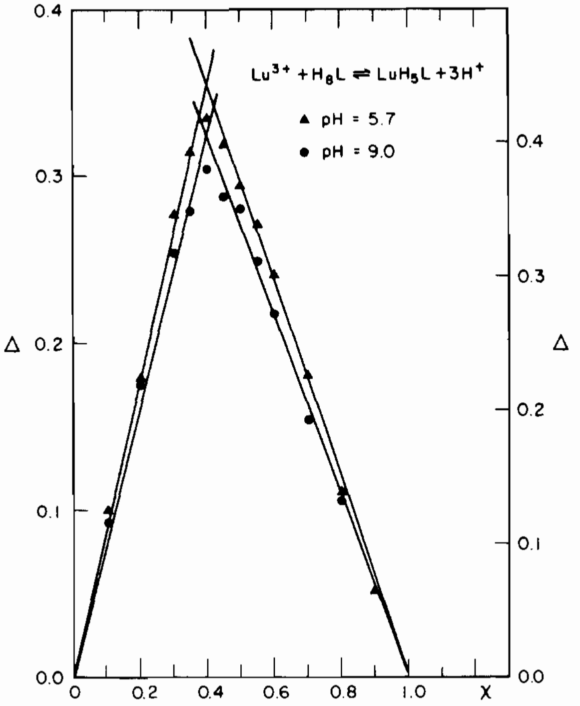

Fig. 11. Continuous variation plot of optical density difference *vs.* mole fraction of Lu(III) at $[Lu^{3+}] + [L] = 1.6 \times 10^{-4}$ M, pH 5.7 and pH 9.0.

3,4,3-LICAMS

It might be thought that the macrochelate 3,4,3-LICAMS would coordinate Ln(III) ions more strongly than monomeric catechol ligands because of a more favorable entropy of complex formation (*i.e.*, there is only a single particle involved in formation of the tetracatechol complex *versus* four for a complex of a simple catecholate). This is not the case, since both potentiometric titrations (Fig. 10) and spectrophotometric data (Job's method, Fig. 11) indicate that only 1.5 catecholate arms bind each Eu(III) or Lu(III) below pH 9. There is evidence that the complexes are also partially hydrolyzed, since the titrations proceed slowly and the final inflection in the titration curve is at 7 equivalents of OH^-/mol metal at pH 9 (there is another inflection at 2.7–3.0 equivalents at pH 5–6) and is independent of total complex concentration. This would not be expected if the complex were simply 1.5 catecholate arms to every Ln(III) plus deprotonation of the phenolic oxygen ortho to the carbonyl on the remaining catecholate arms, since an inflection would then occur at 5.5 equivalents. Thus, the Ln(III) ion appears to be bound by at least one hydroxide with the added possibility of being hydroxide bridged to another Ln ion. This would explain the stoichiometry and slow kinetics.

In conclusion, the lanthanide(III) (or by extension actinide(III)) complexes are not nearly as stable as the corresponding metal ion(IV) complexes. For the higher 3:1 and 4:1 complexes the metal ion/catecholate stepwise formation constants are small, and so cannot be accurately measured by the techniques used in this study. They can be better determined from the ligand concentration dependence of the redox potentials for the couple $Ce(cat)_4^{4-/5-}$. The tetracatecholate cerium(IV) complex is known in solution [26, 27] and from crystal structures of salts of $[Ce(cat)_4]^{4-}$ [28] and $Ce(tiron)_4^{12-}$ [29]. Since the Ce(IV) complex is so much more stable than that of Ce(III), the ligand concentration dependence of the potential of the Ce(IV)/Ce(III) couple at pH 13 (where the catecholate ligands are fully deprotonated) is due entirely to the reactions $Ce^{III}(cat)_{n-1} + cat^{2-} = Ce^{III}(cat)_n$ for $n = 4$ (and perhaps 3). This allows an estimate of β_4, the cumulative stability constant, for the Ce(III) complex. By extension (in part from the Eu(III) comparison), estimates of K_3, K_4 and the resultant cumulative stability constants, β_4^{III}, can be made for the Eu(III) complexes. These are presented in Table II. Since the 2.0 volt potential change in lanthanide or actinide IV/III couples in strong base and excess catechol correspond to differences of $\log \beta_4^{IV} - \log \beta_4^{III} = 34$, estimates (good to ±1) of the cumulative stability constants for the metal(IV) species can be made and are included in Table II.

The estimate of the stability constants for 3,4,3-LICAMS involve less extrapolation. The redox potential for the Ce(IV)/(III) couple shows no ligand dependence in only a slight excess (over 1:1) of ligand at high pH [28]. The redox potential is independent of pH above 13. Below this pH the protonation of the Ce(III) complex involves stepwise removal of the catechol groups of the ligand. From the protonation constants of the ligand and the protonation constants of the complex, determined from the dependence of the potential on pH, the overall stability constant of the complex can be determined. This is very similar to β_4^{III} for the DMBS ligand, a monocatecholate. In summary, while the tetracatechol complexes have relatively weak stability constants [($\log \beta$) on the order of 20 for the lanthanide(III) ions], they form extremely strong complexes with lanthanide- and actinide(IV) ions, with $\log \beta$ values above 50.

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