94536-63-7; *cis*-[Cr(cyclam)$(NO_3)_2$]NO_3, 94484-07-8; *cis*-[Cr(cyclam)Cl_2]Cl, 27435-95-6; *trans*-[Cr(cyclam)$(NH_3)_2$]$(ClO_4)_3$, 94484-09-0; *trans*-[Cr(cyclam)$(NH_3)_2$]$(PF_6)(NO_3)_2$, 94484-10-3; deutd *trans*-[Cr(cyclam)$(NH_3)_2$]$(ClO_4)_3$, 94484-12-5; *cis*-[Cr(cyclam)$(NH_3)_2$]$(BF_4)_2(NO_3)$, 94595-32-1; *cis*-[Cr(cyclam)$(NH_3)_2$]$(PF_6)_2(NO_3)$, 94595-33-2; deutd *cis*-[Cr(cyclam)$(NH_3)_2$]$(PF_6)_2NO_3$, 94536-65-9; *trans*-[Cr(cyclam)$(H_2O)(NH_3)$][Co(CN)$_6$], 94484-14-7; *cis*-[Cr(cyclam)$(H_2O)(NH_3)$][Co(CN)$_6$], 94536-67-1; *cis*-[Cr(cyclam)en]$(NO_3)_3$, 94484-15-8; *trans*-Cr(cyclam)$(NH_3)_2^{3+}$, 94484-08-9; deutd *trans*-Cr(cyclam)$(NH_3)_2^{3+}$, 94484-11-4; *cis*-Cr(cyclam)$(NH_3)_2^{3+}$, 94536-68-2; deutd *cis*-Cr(cyclam)$(NH_3)_2^{3+}$, 94536-64-8; K_3[Co(CN)$_6$], 13963-58-1; D_2, 7782-39-0.

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Specific Sequestering Agents for the Actinides. 11. Complexation of Plutonium and Americium by Catecholate Ligands[1]

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The results of the first in vitro experiments regarding the complexation of plutonium and americium by catechol and tetracatechoylamide ligands are presented. Electrochemical techniques have allowed the elucidation of the protonation behavior of Pu(IV)– and Pu(III)–catecholate complexes. Above pH 12, the Pu(IV) complex is a tetrakis(catecholate) complex and the Pu(III) complex is a tetrakis- or tris(catecholate) complex, depending upon ligand concentration. At neutral pH, the Pu(IV) complex of the octadentate ligand 3,4,3-LICAMS appears to be a tris(catecholate) complex, indicating that the full denticity of the ligand is not utilized in vivo. Spectroscopic evidence is presented for the complexation of Am(III) by tetracatechoylamide ligands. The inability to observe the Am(IV)/Am(III)–catecholate reduction couple indicates that the free-ion Am(IV)/Am(III) reduction potential is greater than +2.6 V vs. NHE.

Introduction

Although the wider use of nuclear fuel sources has increased the risk of exposure to actinide contamination (in particular exposure to plutonium and uranium), development of new complexing agents for decorporation of actinides has lain nearly dormant and those compounds presently used were not designed with this intent. As part of an ongoing research project to develop chelating agents to sequester actinide ions, a series of tetracatechoylamide ligands have been synthesized.[2-4] It was surmised that the catecholate dianion would be a good choice to bind and decorporate Pu(IV), the oxidation state most prevalent in vivo, because of this ion's similarity to Fe(III). Previous work has shown that catechoylamide ligands form extremely stable complexes with Fe(III) and other highly charged, hard cations.[5-11] Several comprehensive reviews have been published regarding the rationale of ligand design for these catecholate ligands.[12-14]

Test results of several catechoylamide ligands used to decorporate Pu(IV) from dogs and mice indicate that these ligands are exceptional in their ability to remove Pu(IV) from the body.[4,15] In fact, one derivative, 3,4,3-LICAMC (Figure 1), has been shown to be the most effective chelating agent for Pu(IV) tested to date that has no toxic side effects.[13,14,16]

Aside from the fact that tetrakis(catecholates) are known to complex effectively Pu(IV) in vivo, there has been no direct evidence about the nature of the complexes formed. Previous work demonstrated that catechols preferentially stabilize the higher oxidation states of metal ions such as Fe(III),[8] Ti(IV),[11] and Ce(IV)[7] to the extent that standard potentials of the uncomplexed ions shift negative in excess of 2.0 V upon complexation of catechol in basic solution. Since the Pu(IV)/Pu(III) reduction potential is +0.98 V vs. NHE,[17,18] complexation by catechol should shift it to about −1.0 V vs. NHE, well within the operating range of a hanging-mercury-drop electrode in basic solution.[19] When the ligand concentration and pH of Pu–catecholate solutions are varied, electrochemistry can be used not only to elucidate the relative stability of Pu(IV) vs. Pu(III) complexes but also to study the protonation behavior and stoichiometry of complexes.[20] These studies can be carried out in dilute solution (less than 0.2 mM in Pu) utilizing differential-pulse voltammetry,[21] allowing experiments to be performed with relatively small amounts of ligand and radionuclide. Presented here is the electrochemistry of the Pu(IV)/Pu(III)–catecholate reduction couple studied as a function of pH and ligand concentration for catechol, 3,4,3-LICAMS, 3,4-LICAMS, and 3,4,3-LICAMC (Figure 1).

The study of americium–catecholate complexation was prompted by results of in vivo experiments in mice and dogs regarding americium removal by the tetracatechoylamides, 3,4,3-LICAMS and 3,4,3-LICAMC (Figure 1).[16] Originally it was thought that complexation of Am(III) in vivo by catecholate ligands would not be of sufficient stability to remove Am(III) from

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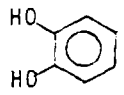
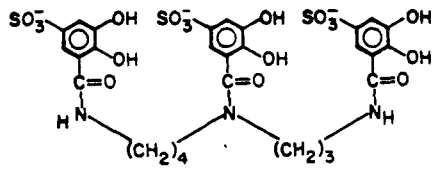
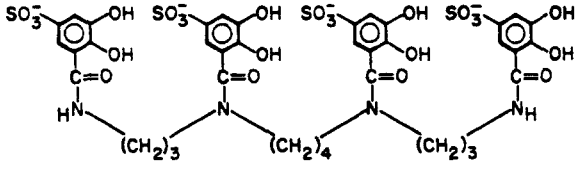


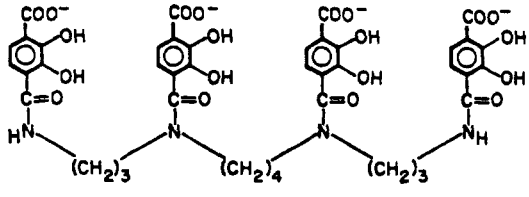
catechol



3,4 -LICAMS



3,4,3-LICAMS



3,4,3-LICAMC

Figure 1. Structural formulas for catecholate ligands: catechol, 3,4,3-LICAMS, 3,4-LICAMS, 3,4,3-LICAMC.

test animals. However, dogs injected with Am(III) followed 30 min later by injection of 3,4,3-LICAMS or 3,4,3-LICAMC excreted 34% and 29%, respectively, of the Am after 7 days; controls excreted 11%. The trisodium salt of calcium diethylenetriaminepentaacetate ($Na_3CaDTPA$), the current therapeutic chelating agent for Am, is much more efficient at sequestering Am under similar conditions (83% excreted).[16] However, the plasma clearance curves of Am for dogs tested were particularly puzzling following the injection of catecholate ligand: i.e., the amount of americium in the plasma increased and then was retained in a manner not present in the controls. This implied the formation of a very stable, nonfilterable Am–protein complex, the formation of which was promoted by the presence of the ligand. Presumably the protein associated with this complex is transferrin, the iron-transport protein known to bind Pu(IV) and Am(III) in vivo. Since transferrin binding to Am(III) is weak,[22,23] it was hypothesized that perhaps the catecholate ligand was facilitating oxidation of Am(III) to Am(IV) in the presence of oxygen and thus promoting the formation of a stable transferrin complex; although stabilization of Am(IV) is difficult [Am(IV)/Am(III) $\approx$ +2.2–2.9 V vs. NHE].[24-28] The electrochemical experiments of Am(III) with the tetrakis(catecholates), 3,4,3-LICAMS and 3,4,3-LICAMC, on reticulated vitreous carbon[29] were performed to test this hypothesis. In addition, visible spectra of the Am–3,4,3-LICAMS and Am–3,4,3-LICAMC complexes were used to elucidate the oxidation state of the metal ion.[30]

Experimental Section

Reagents. The $^{242}PuO_2$ was obtained from Oak Ridge National Laboratory, dissolved in HCl with a minimal amount of NaF, and cleaned by an anion-exchange process with HNO_3 as detailed elsewhere.[31] The resulting solution was checked for purity by spark emission spectroscopy to ensure a minimum of contaminant metal ions.[32] The HCl stock solution (10 mM) of Pu(IV) was standardized with xylenol orange indicator by direct titration with disodium ethylenediaminetetraacetic acid (Na_2H_2EDTA).[33]

The americium, primarily ^{243}Am, was obtained through the Department of Energy's National Heavy Element Production Program at Oak Ridge. Initial purification was made via cation-exchange chromatography using ammonium α-hydroxyisobutyrate (0.4 M, pH 4.05, room temperature) as eluant[34] on a Dowex 50-X12 cation-exchange resin (50-μm diameter). Before use, a final purification was performed via cation-exchange resin (50-μm diameter).[35] The americium fraction was made 0.1 M in HCl and loaded onto the column and washed with 3 column volumes of 0.1 M HCl and then 3 column volumes of 3 M HCl to remove contaminants. The Am was eluted with 6 M HCl. Spark emission spectroscopy[32] and α-particle energy analysis verified sample purity. The concentration of Am(III) was determined by α-particle radiometry.

Catechol (Crown Zellerbach) was recrystallized twice from benzene. The synthesis and characterization of 3,4,3-LICAMS,[3] 3,4-LICAMS,[6] and 3,4,3-LICAMC[4] are reported elsewhere. Molecular weight determinations of 3,4-LICAMS and 3,4,3-LICAMS were done by potentiometric titration.

The 0.10 M KOH (carbonate-free) solutions were prepared from twice-distilled water and a Baker Chemical Co. Dilut-It ampule. It was stored under argon to minimize CO_2 dissolution.

Electrochemical and Spectral Measurements. All experiments were carried out at room temperature and 1.0 M ionic strength (0.1 M KOH/0.9 M KCl). The electrochemical cell consisted of a saturated calomel electrode as reference electrode, a Pt wire as auxiliary electrode, and a Metrohm hanging-mercury-drop electrode as the working electrode (for the Pu experiments) or reticulated vitreous carbon mounted in glass tubing with 5-min epoxy and a Pt lead (for the Am experiments). High base concentrations were necessary to ensure full deprotonation of the catechol ligands and optimum complexation of metal. All measurements were done with at least 10-fold excess ligand. Metal concentrations were typically 0.1–0.5 mM. These conditions provide reversible electrode kinetics at the slow scan rates used with differential pulse.

The potentiostat used was a PAR 173 for all Pu experiments. An IBM EC225 potentiostat was used for the Am experiments. The potentiostat is interfaced to a Digital Equipment Corp. (DEC) MINC 11-2/8 microcomputer. All data are obtained digitally and stored on 8-in. floppy disks.[36] The digital accumulation of data allows highly accurate determination of current and potential values. The determination of values for E was from the relation[19] $E = E_{1/2} - \Delta E/2$. A homemade staircase desk supplied pulses for the pulsed voltammetry and

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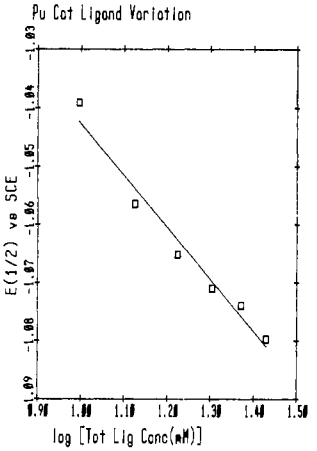

Figure 2. Plot of the dependence of $E_{1/2}$ on total ligand concentration for Pu–catechol (L_T = 9.0–32.0 mM).

Table I. Formal Potential Shifts of Catecholate-Bound Pu and Ce

ligand	shift, V: Ce(IV)/Ce(III)[a]	shift, V: Pu(IV)/Pu(III)[b]
catechol	−2.00	−1.82
3,4-LICAMS		−1.87
3,4,3-LICAMS	−2.11	−1.91
3,4,3-LICAMC	−2.16	−2.03

[a] The formal potential of Ce(IV) + e^- = Ce(III) has been determined in 1 M $HClO_4$ to be +1.7 V vs. NHE: Hugus, Z. UCRL-1379, 1951. [b] The formal potential of Pu(IV) + e^- = Pu(III) has been determined in 1 M $HClO_4$ to be +0.98 V vs. NHE. See ref 17 and 18.

signaled initial and final voltages for the potentiostat. The parameters used for this experiment were those done on a time scale resulting in reversible electrode kinetics. Unless otherwise stated, the parameters used were 0.5 s between pulses, 34.0-ms pulse width, 75.0-mV pulse height, 3.0-mV potential step. Occasionally slower scan rates were used (1.5 mV/s) to increase sensitivity.

Spectral measurements of the Am solutions were done on a Cary 17 spectrophotometer at slow scan rates (0.1 nm/s) and narrow slit widths.

Data Analysis. Noise in the voltammograms was eliminated by Fourier filtering.[37] A DEC LSI-11 was used for this purpose. Subroutines used for filtering are described elsewhere.[38,39] Background voltammograms of the ligand solution before addition of the metal were substracted from the metal complex voltammograms, usually with little consequence.

Results and Discussion

Electrochemistry. Pu(IV)/Pu(III)–Catechol. The low acidity of catechol and the relatively weak complexation of lower oxidation states require that the electrochemical experiments be conducted under very basic conditions. The measurements of formal potential as a function of ligand concentration were always maintained at pH values >12.3. Above this pH catechol is fully deprotonated; the formal potential is independent of pH and demonstrates only a ligand dependence. A very large negative shift in formal potential is observed for Pu–catechol, which increases with total catechol concentration (Figure 2). The Ce(IV)/Ce(III)–catechol couple (Table I) demonstrates a similar negative shift in formal potential with increasing total ligand concentration.[40] Both systems show quasi-reversible electrode kinetics. The theoretical[19] criteria used in establishing quasi-reversibility were as follows: (1) The ratio of cathodic to anodic peak currents equals 1. (2) The separation of anodic and cathodic peaks by the pulse height was 75 mV in these experiments. (3) Peak widths at half-height were 90.4 mV for a one-electron process.

Table II. Summary of Am(III) Spectra

	band I,[a] nm	band II,[b] nm
free Am(III)	503 (450)	812 (77)
Am(III)–3,4,3-LICAMS	507 (822)	815 (80)
	516 (97)	
	523 (24)	
Am(III)–3,4,3-LICAMC	508 (482)	830 (126)
	520 (59)	
	526 (28)	

[a] Sharp band and satellites. Extinction coefficients in units of M^{-1} cm^{-1} are in parentheses. [b] Broad band. Extinction coefficients in units of M^{-1} cm^{-1} are in parentheses.

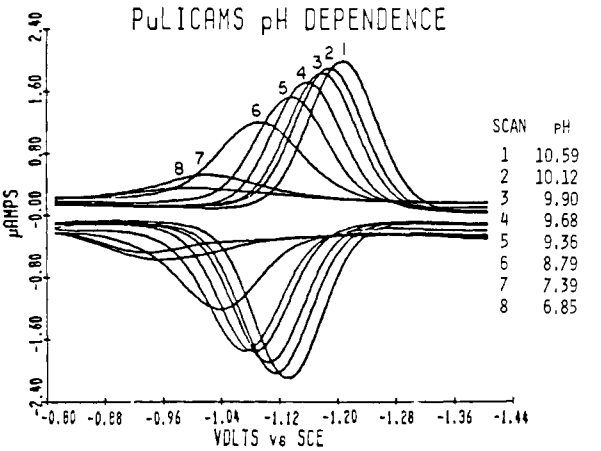

Figure 3. Differential-pulse voltammograms of Pu–3,4,3-LICAMS as a function of pH.

The observed parameters for the plutonium–catechol system were peak widths at half-height of 100–115 mV and $i_c/i_a \approx 0.95$. The indicated reversible, one-electron process was also supported by the anodic linear sweep voltammogram,[19] for which $E_p - E_{p/2}$ = 53–55 mV. The cathodic CV scan showed some evidence of electrode absorption (the ratio i_c/i_a was 0.85–0.90, and the peak separation was about 40 mV), which was assigned as due to a trace of the quinone oxidation product of the catechol ligand. This was confirmed by deliberately air oxidizing a sample solution. This problem was minimized in the DPP scans, which in any case is much more sensitive at the low concentrations used for these radioactive solutions. The cerium–catechol system (the origin of the data in Table II) was at least as well-behaved.

The DPP voltammograms (Figure 3) for the Pu–3,4,3-LICAMS solutions were highly reversible: i_c/i_a = 0.95–0.99 with anodic to cathodic peak separations of 75 mV. The peak widths at half-height were 100 mV. Below pH 8.8, as precipitate begins to form, irreversibility increases. Similarly, the DPP voltammograms of Pu–3,4,3-LICAMC solutions were quasi-reversible, with i_c/i_a = 0.9, peak separations of 60–75 mV, and peak widths at half-height of 110 mV.

The X-ray structures of $[M^{IV}(cat)_4]^{4-}$ complexes (M = Ce, Hf, Th, U), isolated under similar conditions of excess ligand and high base concentrations, have been determined.[7] Thus, the stoichiometries of the cerium(IV), and presumably Pu(IV), complexes are known. The variation of formal potential of an electroactive metal complex with increasing ligand concentration gives information on the stoichiometry of the Pu(III) complexes that are formed.[20] For plutonium, using the two half-reactions (L^{2-} = catechol(2−))

$$Pu(IV) + e^- = Pu(III) \qquad E^\circ = +0.98 \text{ V vs. NHE}$$

$$Pu^{IV}L_4^{4-} + e^- = Pu^{III}L_q^{(3-2q)} + (4-q)L^{2-} \qquad E_f$$

and the two dissociation constants

$$K_{IV} = \frac{[Pu(IV)][L^{2-}]^4}{[Pu^{IV}L_4^{4-}]} \qquad K_{III} = \frac{[Pu(III)][L^{2-}]^q}{[Pu^{III}L_q^{(3-2q)}]}$$

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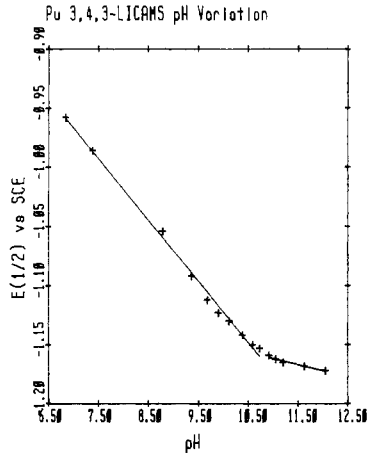

Figure 4. Plot of the variation of $E_{1/2}$ with pH for Pu–3,4,3-LICAMS.

a Nernstian expression can be written that includes a dependence on total ligand concentration (L_T) assuming reversible electrode kinetics at 25 °C:

$$E_f - E^\circ = \frac{0.059}{n}\left[\log \frac{K_{IV}}{K_{III}} - (4-q)\log L_T\right] \quad (1)$$

Differentiation of this equation gives

$$d(E_f)/d(\log L_T) = (-0.059/n)(4-q)$$

Thus a plot of potential vs. the log of the total ligand concentration gives a line with a slope containing the value of $4 - q$ where q is the stoichiometric coefficient for Pu(III)–catechol complexes. If the stoichiometry of the Pu(III)–catechol complex is $[Pu(cat)_4]^{5-}$, there would be no variation of E_f with total ligand concentration and the total potential shift would be proportional to $\log (K_{IV}/K_{III})$. The plot for plutonium–catechol is illustrated in Figure 2. The slope of the line indicates $q = 2.5$; the slope for Ce(IV)/Ce(III)–catechol is identical. This implies a net stoichiometry for the Pu(III)–catechol complex of 2.5 catechols/Pu. Presumably this is a 2:5 dimer that is in rapid equilibrium (on the time scale of our electrochemical studies) with the reduced monomeric Pu(III) species; X-ray crystal structures of dimeric $[Gd^{III}(cat)_3]_2^{6-}$ and $[Gd^{III}(cat)_4]^{5-}$ have been determined recently.[41]

Although the electrochemistry of these systems shows quasi-reversible behavior, the theory developed for reversible systems[20] appears to apply.

Pu(IV)/Pu(III)–3,4,3-LICAMS and Pu(IV)/Pu(III)–3,4-LICAMS. Upon addition of Pu(IV) to a solution of 3,4,3-LICAMS at high pH (>12), a fairly intense amber color is observed due to a broad charge-transfer band at 435 nm ($\epsilon = 750\ M^{-1}\ cm^{-1}$). This same color is observed for Pu(IV)–catechol at high pH. Lowering the pH of the Pu(IV)–3,4,3-LICAMS (pH 10.9) shifts λ_{max} to 441 nm ($\epsilon = 460\ M^{-1}\ cm^{-1}$), similar to the shifts and intensity loss seen for Fe(III)–3,4-LICAMS upon protonation.[6] Thus, at high pH (>12) the 3,4,3-LICAMS complex of Pu(IV) seems to be a tetracatecholate complex.

The negative shift in formal potential for the Pu(IV)–3,4,3-LICAMS complex as compared to free Pu(IV)/Pu(III) is in Table I. The shifts observed in the Ce(IV)/Ce(III) system are included for comparison.[40,7]

The formal potential of the Pu(IV)/Pu(III)–3,4,3-LICAMS couple does not appear to shift with increasing ligand concentration. A Pu(IV) ion complexed by 3,4,3-LICAMS is bound by four catecholate arms of the same ligand. Upon reduction of the metal center to Pu(III), any concomitant reduction in the number of catecholate groups bound (as indicated by the Pu– and Ce–catechol studies) simply requires the removal of one or two catecholate arms of the ligand, with no concentration dependence. Thus, a shift in formal potential, dependent on total ligand concentration, is not expected for any encapsulating macrochelate.

If the Pu(III)–3,4,3-LICAMS complex is similar to the Pu(III)–catechol complex, at high pH there are one, or possibly two, pendant arms of the macrochelate that are not bound to the metal, yet are deprotonated. Figure 3 shows the differential-pulse voltammograms of Pu(IV)–3,4,3-LICAMS as a function of pH. A positive shift in formal potential and a loss of current is seen between pH 10.8 and pH 6.5, whereas no shift in formal potential and a small loss of current are observed between pH 12.1 and pH 11.0. Precipitation is evident at pH 9.4 and increases as the pH is lowered. Dependence of formal potential on pH can be interpreted in two ways.[20]

Case 1: Acidity of the oxidized complex causes the potential shift

$$O + qH^+ = OH_q \qquad OH_q + ne^- = RH_q$$

where

$$K = [OH_q]/[O][H^+]^q$$

$$\text{oxidized electroactive species} = [OH_q] + [O]$$

$$\text{reduced electroactive species} = [RH_q]$$

Then, the expression for the Nernst equation is

$$E_{1/2} = E^\circ + \frac{0.059}{n}\log\left(\frac{[H^+]^q K}{[H^+]^q K + 1}\right) \quad (2)$$

where E° = the formal potential describing this process. Therefore, if $[H^+]^q K \gg 1$, then H_qO predominates and $E_{1/2}$ is independent of pH; if $[H^+]^q K \ll 1$, then O predominates and in this region $E_{1/2}$ is dependent on pH and differentiation of (2) yields

$$\frac{dE_{1/2}}{dpH} = (-0.059/n)q \quad (3)$$

Case 2: Acidity of the reduced complex causes the potential shift

$$O + qH^+ + ne^- = RH_q \qquad RH_q = qH^+ + R$$

where

$$K = [R][H^+]^q/[RH_q]$$

$$\text{oxidized electroactive species} = [O]$$

$$\text{reduced electroactive species} = [RH_q] + [R]$$

Then, the expression for the Nernst equation is

$$E_{1/2} = E^\circ - \frac{0.059}{n}\log\left(\frac{[H^+]^q}{[H^+]^q + K}\right) \quad (4)$$

where E° = the formal potential of the electron-transfer process. Therefore, under acidic conditions, $[H^+]^q \gg K$, the reduced form will exist predominantly as RH_q, and the variation in $E_{1/2}$ will be described by eq 3; if $[H^+]^q \ll K$, then $E_{1/2}$ will be independent of pH.

A plot of $E_{1/2}$ vs. pH for Pu–3,4,3-LICAMS is shown in Figure 4. It shows a region at high pH with very little change in $E_{1/2}$ and a region between pH 10.8 and 6.5 with a slope of –0.053. From eq 3, this corresponds to a one-proton equilibrium best described by case 2, involving the acidity of the reduced species. The intersection of the two lines is at pH = pK_a = 10.9. If Pu(III)–3,4,3-LICAMS has one or two pendant catechol arms free, this pK_a corresponds very well with the protonation of a phenolic oxygen meta to the carbonyl. In the free ligand, with no metal bound, this pK_a is estimated to be about 11.5.[42]

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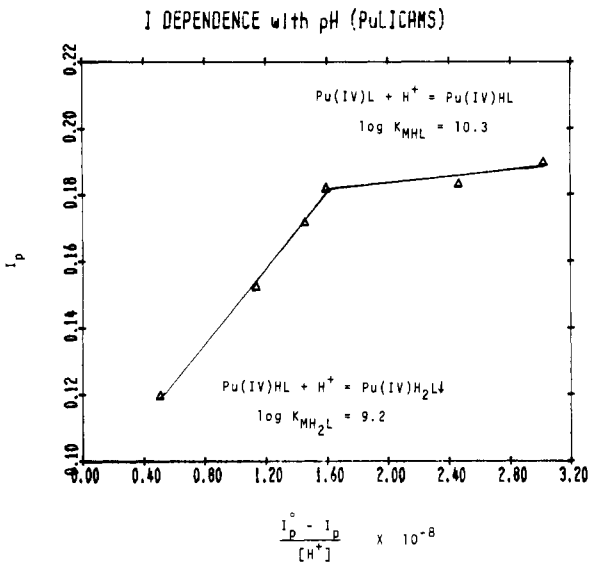

Figure 5. Plot of the variation of peak current (mV) with pH for Pu(IV)–3,4,3-LICAMS.

An additional experiment performed to test this hypothesis of protonation of the free catechol arm of Pu(III)–3,4,3-LICAMS involves monitoring the shift in $E_{1/2}$ with pH for Pu–3,4-LICAMS (this ligand is a tris(catecholate), Figure 1). Under conditions of 10-fold excess ligand at pH 12, the Pu(IV) may be surrounded by three catecholate arms of one ligand molecule and perhaps a fourth arm from another ligand molecule. However, upon reduction it is likely that the Pu(III) complex is bound by only three catecholate arms of one 3,4-LICAMS molecule. Under these conditions *no* shift in $E_{1/2}$ with pH is observed; however, a decrease in current is observed and precipitation is evident at pH 9.

The decrease in peak current with decreasing pH observed in Figure 3 [and also for Pu–3,4-LICAMS] can be attributed to a protonation phenomenon, but the protonation here involves the Pu(IV)–ligand complex. The bulk solution contains the Pu(IV) complex, and the peak current is directly proportional to the concentration. For differential pulse at a stationary electrode, the peak current can be expressed as[43]

$$\Delta i_p = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}} \frac{1-\beta}{1+\beta}$$

where n = number of electrons, F = Faraday constant, A = electrode area, D = diffusion coefficient of bulk electroactive species, C = concentration of bulk electroactive species, t = pulse width, $\beta = \exp[nF(\Delta E)/RT]$, and ΔE = pulse height. Thus, one can consider that for two electroactive species in solution with differing diffusion coefficients, the peak current is

$$\Delta i_p = kD_1^{1/2}c_1 + kD_2^{1/2}c_2$$

where k is a constant containing the aforementioned parameters. Consider that c_1 and c_2 be related by the protonation equilibrium

$$K_H = c_1[H^+]^n/c_2$$

and that $c_T = c_1 + c_2$. For this relationship the expression

$$\Delta i_p = kD_2^{1/2}c_T + (\Delta i_p^0 - \Delta i_p)K_H/[H^+]^n \qquad (5)$$

can be developed where Δi_p^0 = the peak current at high pH with only species c_1 present and Δi_p = the peak current at any pH other than Δi_p^0 where c_1 and c_2 are in equilibrium.

This is analogous to an expression developed by Schwarzenbach for vis–UV spectra, only in this case diffusion coefficients rather than extinction coefficients are used.[44]

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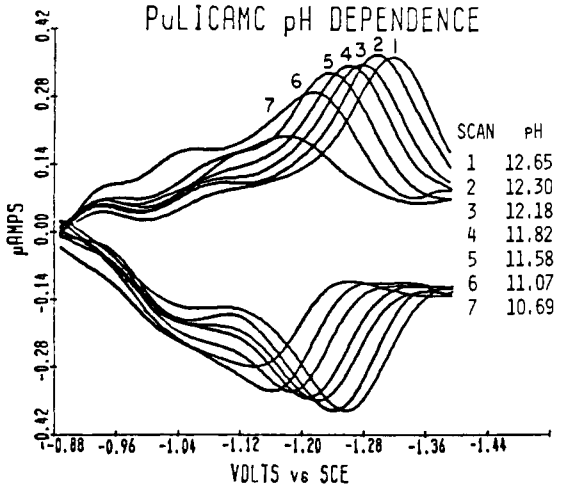

Figure 6. Differential-pulse voltammograms of Pu–3,4,3-LICAMC as a function of pH.

A plot of Δi_p vs. $(\Delta i_p^0 - \Delta i_p)/[H^+]^n$ with proper choice of n gives a straight line with slope K_H. Figure 5 illustrates such a plot for Pu(IV)–3,4,3-LICAMS. The estimated standard deviation for the current in this plot is ≈ 2 μV, or 1% of the mean current value in the high pM region (see supplementary material). Two straight-line segments are observed. The line segment with shallow slope corresponds to the protonation

$$\text{Pu(IV)–3,4,3-LICAMS}^{8-} + H^+ = \text{Pu(IV)–3,4,3-HLICAMS}^{7-}$$

The shift in λ_{max} in the visible spectra obtained over this pH range also indicates that protonation is occurring. The plot shown in Figure 5 implies that the monoprotonated Pu(IV) complex has a diffusion coefficient 30–40% smaller than that of the deprotonated Pu(IV) complex. This seems unlikely, since to a first approximation the diffusion coefficient is proportional to the volume of the complex. Therefore, large changes in the diffusion coefficient would not be expected upon a single protonation. When the pH is lowered further, a *white, flaky* precipitate is formed [$Pu(OH)_4$ is green and gelatinous] and a linear decrease in current is also observed (and included in Figure 5 for interest). This line segment cannot be interpreted by the same method used for the line segment of shallow slope since two species are not in equilibrium in solution as is required to use this method. Instead, an alternate graphical method can be used. The formation constant for such a precipitate would be

$$K = 1/[\text{Pu(IV)–HLICAMS}][H^+]^n$$

Therefore, a plot of ln Δi_p vs. ln $[H^+]$ should give a line of slope n. Such a plot for Pu(IV)–3,4,3-HLICAMS is linear (correlation −0.9999), but the slope is nonintegral (slope −0.20). Since this gives the change in the *average* number of bound protons on going from the oxidized to the reduced species, it may indicate a mixture of protonated species exists in this pH range. It does appear that this precipitate is at least a deprotonated Pu(IV) complex. Complexes of Pu(IV) are prone to hydrolysis and polymerization. In addition, the bridging capabilities of catechol are well illustrated in the $[Gd^{III}(cat)_3]_2^{6-}$ structure, which contains two bridging catechol dianions.[41]

The question that arises is why a variation in $E_{1/2}$ with pH is not seen for Pu(IV) complexes, as theorized in case 1. If the kinetics for protonation of the free catechol or of Pu(III)–3,4,3-LICAMS is faster than that of protonation of Pu(IV)–3,4,3-LICAMS, then for the time scale of the experiment (3-mV/s scans) the polymerization of the protonated Pu(IV)–3,4,3-LICAMS complex (a relatively slow process) may not influence the potential.

Pu(IV)/Pu(III)–3,4,3-LICAMC. The electrochemistry of Pu(IV)/Pu(III)–3,4,3-LICAMC can be analyzed in the same manner as the complexes with 3,4,3-LICAMS. There is one

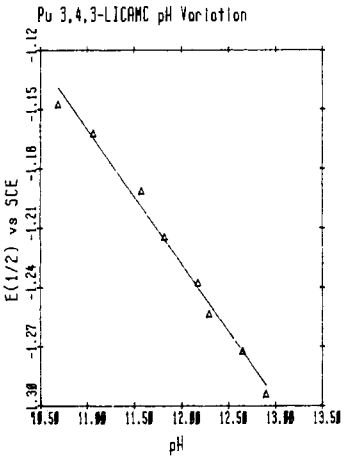

Figure 7. Plot of the variation of $E_{1/2}$ with pH for Pu-3,4,3-LICAMC.

notable difference—the phenolic oxygens of 3,4,3-LICAMC are considerably less acidic than those of the sulfonated ligand.[45] The corresponding protonation constants of the *complexes* are also considerably higher.

Figure 6 illustrates the differential-pulse voltammograms of Pu-3,4,3-LICAMC as a function of pH. There is a positive shift in $E_{1/2}$ with a decrease in pH, similar to that observed for Pu-3,4,3-LICAMS. There is also a decrease in current with a decrease in pH. The features of the individual voltammograms do differ. Table I shows that the negative shift in formal potential for the complex as compared to the free ion is greater for LICAMC complexes than for LICAMS or catechol complexes. In addition, the Pu-3,4,3-LICAMC voltammogram shows an additional peak at -1.07 V vs. SCE that has no pH dependence. This peak is not seen in the electrochemistry of the free ligand and is assumed to be a Pu complex. The carboxylate group para to the carbonyl provides an additional binding mode for the Pu(IV) ion, which does not exist in the sulfonated derivative, and this may be the explanation for an additional peak. These scans also show a 5-fold decrease in current as compared to the Pu-3,4,3-LICAMS pulse voltammograms.

A plot of $E_{1/2}$ vs. pH is shown in Figure 7 (slope -0.068). The same reasoning used for potential dependence with pH for Pu-3,4,3-LICAMS can be applied; i.e., the acidity of the reduced species is responsible (case 2). This implies the pK_a for protonated Pu(III)-3,4,3-LICAMC is above 13.0. The highest pK_a of 2,3-dihydroxybenzoic acid, the monomer analogue, is 13.1.[42]

Likewise, analysis of the decrease in current with decrease in pH (eq 5) gives two straight line segments for $n = 1$, similar to that observed for Pu(IV)-3,4,3-LICAMS (Figure 5); however, the protonation of Pu(IV)-3,4,3-LICAMC occurs at pH values higher than that of Pu(IV)-3,4,3-LICAMS [log K_{MHL} = 11.9 for Pu(IV)-3,4,3-LICAMC] with the appearance of a precipitate at pH 10.7.

Americium–Catecholate Complexation. The negative shift in the metal ion formal potential observed for Pu(IV)/Pu(III)-catecholate and Ce(IV)/Ce(III)-catecholate are greatest for the tetrakis(catecholates), 3,4,3-LICAMS and 3,4,3-LICAMC (Table I); these ligands were thus the first investigated. Addition of Am(III) (~0.1 mM) to a solution of 3,4,3-LICAMS or 3,4,3-LICAMC (~1 mM) at pH 13 resulted in no precipitate formation. Since Am(III) will form a hydroxide precipitate at this pH without catecholate ligands,[30] and the 3,4,3-LICAMS solution with added Am(III) was a lime green color, it was assumed that complexation by catechol was occurring.

Differential-pulse voltammetry of Am-3,4,3-LICAMS and Am-3,4,3-LICAMC from -0.4 to +0.7 V vs. SCE at slow scan rates (1.5 mV/s) showed only electrochemistry associated with the ligand. Providing the negative shifts in the IV/III potential

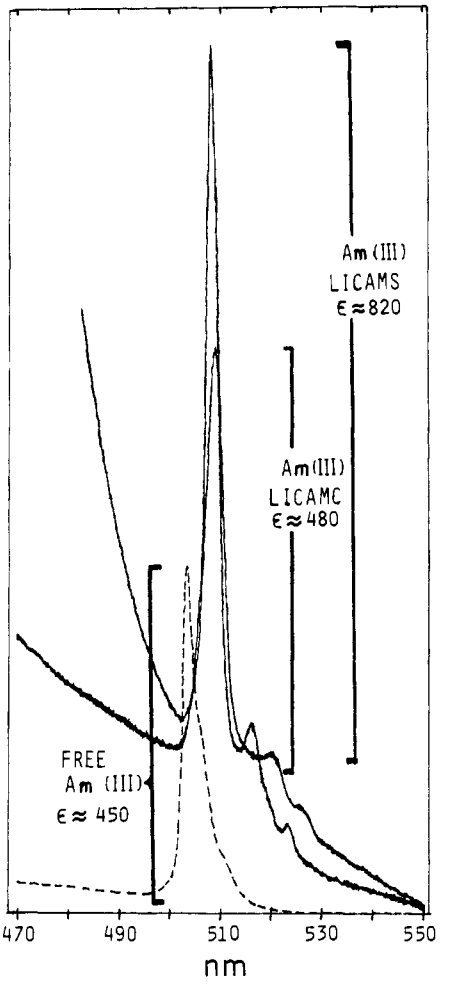

Figure 8. Visible spectra: free Am(III) (0.20 mM, pH 2); Am-3,4,3-LICAMS (0.12 mM, pH 13); Am-3,4,3-LICAMC (0.12 mM, pH 13).

seen for plutonium and cerium are similar for americium, the free metal ion potential for Am(IV)/Am(III) must be at least +2.6 V vs. NHE. If this is true, the Am(IV)/Am(III)-catecholate potential is more positive than the reduction potential for the free ligand, so it is not observable.

When the pH is lowered, a precipitate is formed in both the Am-3,4,3-LICAMS (pH 10.0) and the Am-3,4,3-LICAMC (pH 10.4) cases. This may be due to some oligomerization process that occurs. Results of gel chromatography experiments indicate that 3,4,3-LICAMS forms a complex with Am at pH 7.4 of higher molecular weight than the Pu(IV) complex.[16]

One method by which to determine whether or not an Am(III)-catecholate complex is formed is by visible spectroscopy. Free Am(III) has a large, sharp absorbance at 503 nm in acidic media due to a transition assigned as $^7F_0 \rightarrow {}^5L_6$ as well as a broad band at 812 nm due to a $^7F_0 \rightarrow {}^7F_6$ transition.[46] Upon complexation of Am(III) by various ligands these bands are known to shift and change in intensity. Figure 8 illustrates the spectral changes observed in the 503-nm band upon complexation by 3,4,3-LICAMS and 3,4,3-LICAMC. The spectrum of free Am(III) is of a diluted sample of stock Am(III), included for comparison (in HCl, pH 2). The sloping base line in the Am-tetrakis(catecholate) spectra is due to partial oxidation of the ligand. Although the ligand solutions were prepared under argon and rigorously degassed, the transfer procedure into the cuvette causes a limited exposure to air and consequent partial oxidation of the free ligand. Nonetheless, the shift in the 503-nm band observed is conclusive evidence of complexation of Am(III) by 3,4,3-LI-

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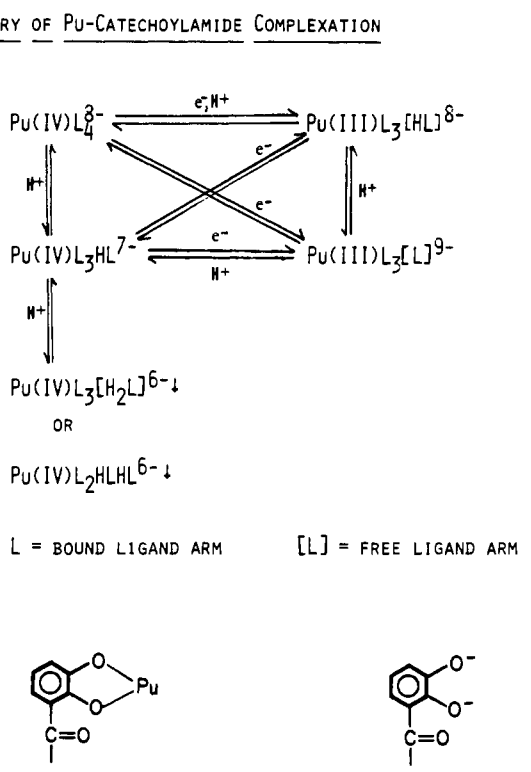

Figure 9. Summary of the Pu–polycatecholate equilibria as determined by electrochemistry.

CAMS and 3,4,3-LICAMC. Table II contains a summary of the spectral characteristics.

It is noteworthy that the spectra of Am(III) with 3,4,3-LICAMS and with 3,4,3-LICAMC are significantly different. This is indicative of a different type of bonding of the two tetrakis(catecholates) with Am(III). Although it is impossible to determine the identity of the coordinating groups, the 3,4,3-LICAMC ligand does posses carboxylate groups capable of coordinating Am(III). Polycarboxylate amines are known to bind Am(III) with high affinity.[47]

The results of these experiments indicate that americium is not present as Am(IV) in vivo. Indeed, it proves that 3,4,3-LICAMS and 3,4,3-LICAMC form complexes with Am(III) of undetermined stability. Titrations of Eu(III), the lanthanide homologue of Am(III), with 3,4,3-LICAMS indicate that a complex is formed in which 1.5 catechol arms bind Eu(III) at pH 5.5. At higher pH values, some hydroxide also appears to be involved in coordination and the titrations proceed slowly.[48] It seems very likely that the Am(III)–3,4,3-LICAMS complex is similar.

Summary

A summary of the protonation behavior of complexes of Pu(IV)–Pu(III) with 3,4,3-LICAMS and 3,4,3-LICAMC as determined by electrochemical methods is diagrammed in Figure 9.

The implications of this study are that the complex of Pu(IV)–3,4,3-LICAMS, which exists at pH 7.4 (plasma pH), is probably a tris(catecholate) complex. In vivo work on Pu(IV) removal from mice using the same concentrations of 3,4,3-LICAMS and 3,4-LICAMS indicates that 3,4-LICAMS is more effective at removal of radionuclide *per functional catechol group.* Indeed, results obtained here indicate that use of functional groups more acidic than catechol may be warranted. Development of macrochelates of the more acidic *N*-hydroxypyridinone ligand is currently under way.

Any concern over precipitation of Pu(IV) complexes of 3,4,3-LICAMS of 3,4,3-LICAMC in vivo is invalid since concentrations encountered in vivo are 100- to 1000-fold less than those encountered here.

Spectroscopic results indicate that the tetrakis(catecholates), 3,4,3-LICAMS and 3,4,3-LICAMC, complex Am(III). The Am(IV)/Am(III)–catecholate couple (where catecholate = 3,4,3-LICAMS or 3,4,3-LICAMC) is not observed, probably due to the large currents associated with ligand oxidation. These experiments indicate that the formal reduction potential of free, aqueous Am(IV)/Am(III) is probably ≥2.6 V vs. NHE.

Acknowledgment. The authors express special thanks to Dr. Robert Silva of the Lawrence Berkeley Laboratory for preparing the americium stock solution and to Professor R. Connick for helpful discussions. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract N. DE-AC03-76SF00098.

Registry No. $Pu^{IV}L_4^{4-}$, 94090-53-6; 3,4-LICAMS, 71659-79-5; 3,4,3-LICAMS, 82044-95-9; 3,4,3-LICAMC, 75956-67-1; catechol, 120-80-9; Pu, 7440-07-5.

Supplementary Material Available: A tabulation of the current vs. pH data plotted in Figure 5 (1 page). Ordering information is given on any current masthead page.

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