Specific Sequestering Agents for the Actinides. 29. Stability of the Thorium(IV) Complexes of Desferrioxamine B (DFO) and Three Octadentate Catecholate or Hydroxypyridinonate DFO Derivatives: DFOMTA, DFOCAMC, and DFO-1,2-HOPO. Comparative Stability of the Plutonium(IV) DFOMTA Complex[1]

Donald W. Whisenhunt, Jr.,[†,‡] **Mary P. Neu,**[‡] **Zhiguo Hou,**[†] **Jide Xu,**[†] **Darleane C. Hoffman,**[†,‡] **and Kenneth N. Raymond***[†]

Department of Chemistry and Chemical Sciences Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720, and G. T. Seaborg Institute for Transactinium Science, Lawrence Livermore National Laboratory, MS L-231 Livermore, CA 94550

The metal complex stability constants of Th(IV) with desferrioxamine B (DFO) and three octadentate derivatives [*N*-(2,3-dihydroxy-4-carboxybenzoyl)desferrioxamine B (DFOCAMC), *N*-(1,2-dihydro-1-hydroxy-2-oxopyridin-6-yl)carbonyl)desferrioxamine B (DFO-1,2-HOPO) and *N*-(2,3-dihydroxy-4-(methylamido)benzoyl)desferrioxamine B (DFOMTA)] have been determined. The formation constant of the Pu(IV)/DFOMTA complex has also been determined, and the formation constants have been estimated for the other Pu(IV) complexes of octadentate DFO derivatives. The DFO derivatives form 1:1 complexes with Th(IV) in aqueous solution. The solution chemistry of the Th(IV) complexes has been studied by spectrophotometric, potentiometric and proton NMR titrations. The Th(IV) formation constants are as follows (log K_f values and esd's): DFO, 26.6(1); DFOMTA, 38.55(5); DFOCAMC, 37.2(3); DFO-1,2-HOPO, 33.7(4). The Pu(IV)/DFOMTA formation constant, determined by competitive spectrophotometric titration is (log K_f value) 41.7(2). The estimation of the other Pu(IV) formation constants are as follows (log K_f values): DFOCAMC, 40.4; DFO-1,2-HOPO, 36.9. The selectivity of DFO and the three derivatives for actinide(IV) ions is discussed.

Introduction

Specific chelation of actinide(IV) ions is of relevance to actinide decontamination, waste treatment, and waste containment. For example, chelating agents may be developed which reduce the actinide burden of an individual exposed to these radionuclides. Actinides may be specifically removed from waste streams, allowing for a significant reduction in the volume of high-level waste that requires storage in a geologic repository. Actinide-containing soils may be decontaminated using methods which rely on chelating agents. Natural complexing agents which are present in soils could drastically affect the migration of actinide ions in the case of accidental release.

New approaches to plutonium separation are particularly important because of the properties of plutonium nuclides (i.e., mammalian toxicity[2,3] and long half-lives[4]), and because plutonium is the most prevalent transuranic environmental contaminant.[5−7] Plutonium(IV) is the dominant oxidation state in production and reprocessing wastes,[8] and is, therefore, the ion of greatest concern. Because both Fe^{3+} and Pu^{4+} are "hard" Lewis acids, plutonium complexing agents have been designed based on naturally-occurring, highly selective, ferric ion chelators.[9−11] A series of ligands based on the siderophore desferrioxamine B (DFO), shown in Figure 1, are potentially selective actinide(IV) sequestering agents. DFO, a microbially produced trihydroxamate ligand, is commercially produced and is currently the only drug approved for the treatment of iron overload. DFO binds Fe^{3+} over a large pH range (1−12),[12,13] and should complex Pu^{4+} strongly. DFO has been shown to solubilize plutonium from a hydrous plutonium(IV) oxide,[14] and both DFO and derivatives of DFO have been found to enhance the excretion of plutonium from laboratory animals.[15,16]

DFO is interesting not only for chemical separations applications but also from an environmental migration standpoint since it or similar siderophores occur naturally in soils. The ability of a complexing agent to transport actinide(IV) ions depends on many factors, including the rate of dissolution from solid

(1) For the previous article in this series see: *J. Med. Chem.* **1995,** *38,* 2606−2614.
(2) Bulman, R. A. *Coord. Chem. Rev.* **1980,** *31,* 221−250.
(3) Raymond, K. N.; Smith, W. L. In *Structure and Bonding*; Springer-Verlag: Berlin, Heidelberg, Germany, 1981; Vol. 43, pp 159−186.
(4) Katz, J. J.; Seaborg, G. T.; Morss, L. R. *The Chemistry of the Actinide Elements,* 2nd ed.; Chapman and Hall: London, 1986; Vols 1 and 2.
(5) Bunzl, K.; Kracke, W.; Schimmack, W. *Analyst* **1992,** *117,* 469−474.
(6) Iranzo, E.; Rivas, P.; Mingarro, E.; Marin, C.; Espinosa, M. A.; Iranzo, C. E. *Radiochim. Acta* **1991,** *52/53,* 249−256.
(7) Rawson, S. A.; Walton, J. C.; Baca, R. G. *Radiochim. Acta* **1991,** *52/53,* 477−486.
(8) Navratil, O.; Hala, J.; Kopunec, R.; Macasek, F.; Mikulaj, V.; Leseticky, L. *Nuclear Chemistry*; Ellis Horwood Ltd.: Chichester, England, 1992.
(9) Raymond, K. N. Specific Sequestering Agents for Iron and Actinides. In *Environmental Inorganic Chemistry*; Irgolic, K. J., Martell, A. E., Eds.; Proceedings, U.S.-Italy International Workshop on Environmental Inorganic Chemistry, San Miniato, Italy, June 5−10, 1983, VCH Publishers, Inc.: Deerfield Beach, FL, 1985; pp 331−347.
(10) Uhlir, L. C.; Durbin, P. W.; Jeung, N.; Raymond, K. N. *J. Med. Chem.* **1993,** *36,* 504−509.
(11) Raymond, K. N.; Kappel, M. J.; Pecoraro, V. L.; Harris, W. R.; Carrano, C. J.; Weitl, F. L. *Actinides in Perspective*; Pergamon Press: Oxford, England, and New York, 1982; pp 491−507.
(12) Martell, A. E.; Smith, R. M. *Crit. Stability Constants*; 1974, 1975, 1976, 1977, 1982, 1989 ed.; Plenum: New York, 1974; Vols. 1−6.
(13) Schwarzenbach, G.; Schwarzenbach, K. *Helv. Chim. Acta.* **1963,** *154,* 1390−1400.
(14) Brainard, J. R.; Strietelmeirer, B. A.; Smith, P. H.; Langston-Unkefer, P. J.; Barr, M. E.; Ryan, R. R. *Radiochim. Acta* **1992,** 357−363.
(15) Raymond, K. N.; Carrano, C. J. *Acc. Chem. Res.* **1979,** *12,* 183−190.
(16) White, D. L.; Durbin, P. W.; Jeung, N.; Raymond, K. N. *J. Med. Chem.* **1988,** *31,* 11−18.
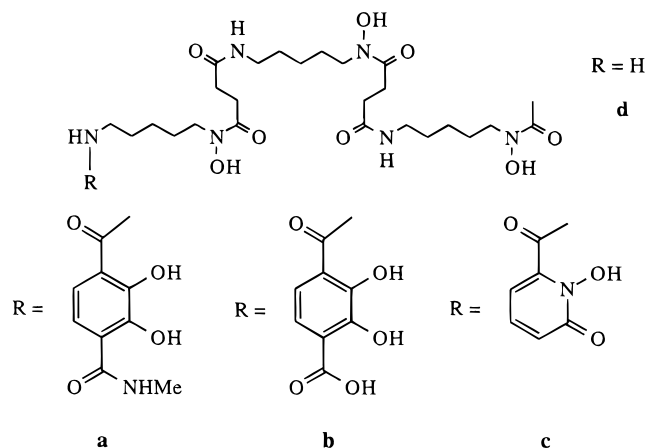
Figure 1. Molecules studied in this work: (a) H₅DFOMTA, *N*-(2,3-dihydroxy-4-(methylamido)benzoyl)desferrioxamine B; (b) H₆-DFOCAMC, *N*-(2,3-dihydroxy-4-carboxybenzoyl)desferrioxamine B; (c) H₄DFO-1,2-HOPO, *N*-(1,2-dihydro-1-hydroxy-2-oxopyridin-6-yl)-carbonyl)desferrioxamine B; (d) H₃DFO, desferrioxamine B.

hydrolysis products and other natural substrates, the adsorption of the metal−ligand complex onto substrates, and the stability of the metal−ligand complex as compared to other complexes that could form (i.e., protonated forms of the metal−ligand complex or other ligand complexes). The effects of EDTA,[17] DTPA, citrate, humic acid, fulvic acid, NTA, and siderophores (including DFO) on the migration of Pu^{4+} and Th^{4+} have been studied.[18−24] Both EDTA and DTPA have been shown to increase the uptake of plutonium and americium into certain plants,[25−29] with major implications for the introduction of actinides into the food chain. To model accurately the migration of actinide(IV) ions in soil and ground water, accurate formation constants with the metal ions of interest must be determined.

An important difference between the complexation chemistry of Pu^{4+} and Fe^{3+} is the preferred coordination number—Fe^{3+} typically has a coordination number of six, while the larger Pu^{4+} ion is likely to have a coordination number of eight with strong oxygen donors. The free amine of DFO allows for the derivatization of this siderophore to produce new ligands with higher denticity which should bind plutonium even more strongly than DFO and provide some selectivity for Pu^{4+} on the basis of coordination number. DFOMTA and DFOCAMC (Figure 1) contain two types of catechol functionality—methyl terephthalamide (MTA), and carboxylcatecholamide (CAMC) respectively—while DFO-1,2-HOPO contains a 1,2-hydroxy-pyridinonate (1,2-HOPO) group. These groups have different charges and basicities and therefore are each expected to have a different solution behavior in the presence of metal ions.

The octadentate derivatives of DFO are an important class of actinide sequestering agents. To gain an understanding of

Table 1. Protonation Constants of H₄DFO⁺ and the Three DFO Derivatives

	H₄DFO⁺ *a*	H₆DFOCAMC*b*	H₅DFOMTA*b*	H₄DFOHOPO*b*
$\log K_1^H$	10.89	13.0	11.1	9.71
$\log K_2^H$	9.70	9.83	9.71	9.18
$\log K_3^H$	9.03	9.31	9.24	8.50
$\log K_4^H$	8.30	8.78	8.58	4.92
$\log K_5^H$		7.83	6.22	
$\log K_6^H$		3.24		

a From ref 12. *b* From ref 30.

the behavior of these molecules in soil, and to fully realize their potential as extracting agents, the thermodynamic stability constants of the metal complexes must be determined. Recently, we reported the protonation and Fe^{3+} complex formation constants of these DFO derivatives.[30] In this paper we report (1) the stability of the Th^{4+} complexes of DFO and its derivatives, (2) the stability constant of the DFOMTA complex of Pu^{4+}, and (3) estimates of the Pu^{4+} stability constants with DFOCAMC and DFO-1,2-HOPO.

Results and Discussion

Ligand Protonation Constants. Protonation constants for DFO and its derivatives[30] are listed in Table 1. The constants correspond to proton associations:

$$H_{n-1}L + H^+ \rightleftharpoons H_nL$$

$$K_n^H = \frac{[H_nL]}{[H_{n-1}L][H^+]}$$

For DFO, $n = 4$, there are three protonations, K_2^H to K_4^H, assigned to the three hydroxamate groups, and K_1^H assigned to protonation of the free amine. For DFO-1,2-HOPO, $n = 4$, where K_4^H refers to the protonation constant for the 1,2-HOPO group, and K_1^H to K_3^H correspond to protonations of the hydroxamate groups. For DFOMTA, $n = 5$, with K_1^H corresponding to a catecholate oxygen, K_2^H to K_4^H correspond to the three hydroxamate groups and K_5^H corresponds to the second protonation of the catechol group. For DFOCAMC, $n = 6$ and the same convention applies as for DFOMTA, except K_6^H corresponds to the carboxylic acid group on the catecholate ring.

Solution Chemistry of the Th^{4+}/H₄DFO⁺ Complex. The overall stability constant for the complex of Th^{4+} with H₄DFO⁺ is defined as follows:
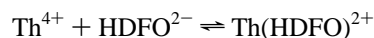
$$Th^{4+} + HDFO^{2-} \rightleftharpoons Th(HDFO)^{2+}$$

$$K_f = \frac{[Th(HDFO)^{2+}]}{[Th^{4+}][HDFO^{2-}]} \quad (1)$$

The formation constant is defined using $HDFO^{2-}$ because the proton associated with the complex is on the free amine of the ligand which is not (apparently) displaced by Th^{4+}.

Potentiometric titrations were carried out to quantify the interaction between Th^{4+} and H₄DFO⁺ in aqueous solution. The solution behavior of the complex [Th(HDFO)²⁺] was modeled

(17) Abbreviations used: EDTA, *N,N,N′,N′*-ethylenediaminetetraacetic acid; DTPA, *N,N,N′,N′,N″*-diethylenetriaminepentaacetic acid; NTA, nitrilotriacetic acid.
(18) Vejmelka, P.; Rudolph, G.; Köster, R. *Radiochim. Acta* **1991**, *52/53*, 65−67.
(19) Keiling, C.; Marx, G. *Radiochim. Acta* **1991**, *52/53*, 287−290.
(20) Lieser, K. H.; Hill, R.; Mühlenweg, U.; Singh, R. N.; Shu-De, T.; Steinkopff, T. *J. Radioanal. Nucl. Chem., Articles* **1991**, *147*, 117−131.
(21) Dozol, M.; Hagemann, R. *Pure Appl. Chem.* **1993**, *65*, 1081−1102.
(22) Choppin, G. R. *Radiochim. Acta* **1988**, *44/45*, 23−28.
(23) Choppin, G. R. *Journal of Radioanal. Nucl. Chem., Articles* **1991**, *147*, 109−116.
(24) Swanson, J. L. *Organic Complexant-Enhanced Mobility of Toxic Elements in Low-Level Wastes*; Pacific Northwest Laboratory: Richland, WA, 1986.
(25) Bulman, R. A. *Struct. Bonding* **1978**, *34*, 39−71.
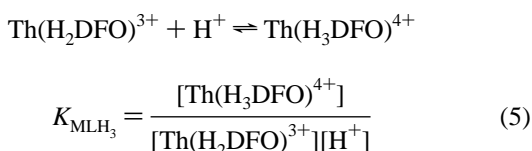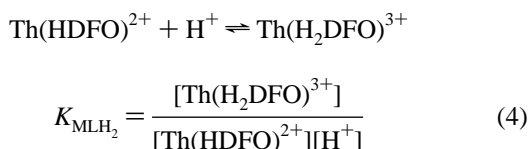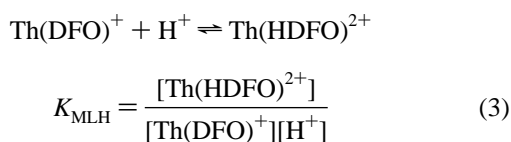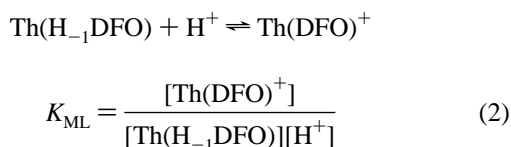(26) Price, K. R. *J. Environ. Qual.* **1973**, *2*, 63.
(27) Hakonson, T. E. *Health Phys.* **1975**, *29*, 583.
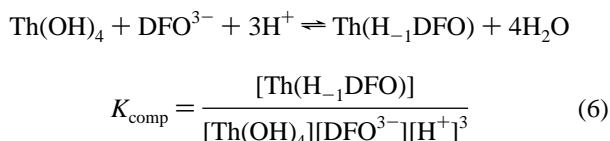(28) Francis, C. W. *J. Environ. Qual.* **1973**, *2*, 67.
(29) Vyas, B. N.; Mistry, K. B., *Plant Soil* **1983**, *73*, 345−353.

(30) Hou, Z.; Whisenhunt, D. W. J.; Jide, X.; Raymond, K. N. *J. Am. Chem. Soc.* **1994**, *116*, 840−846.
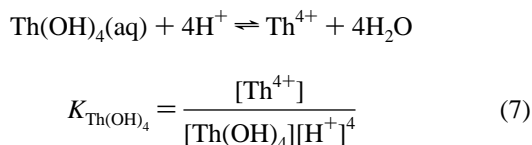
including the four stepwise protonations as follows.

$$\text{Th}(\text{H}_{-1}\text{DFO}) + \text{H}^+ \rightleftharpoons \text{Th}(\text{DFO})^+$$

$$K_{\text{ML}} = \frac{[\text{Th}(\text{DFO})^+]}{[\text{Th}(\text{H}_{-1}\text{DFO})][\text{H}^+]} \quad (2)$$

$$\text{Th}(\text{DFO})^+ + \text{H}^+ \rightleftharpoons \text{Th}(\text{HDFO})^{2+}$$

$$K_{\text{MLH}} = \frac{[\text{Th}(\text{HDFO})^{2+}]}{[\text{Th}(\text{DFO})^+][\text{H}^+]} \quad (3)$$

$$\text{Th}(\text{HDFO})^{2+} + \text{H}^+ \rightleftharpoons \text{Th}(\text{H}_2\text{DFO})^{3+}$$

$$K_{\text{MLH}_2} = \frac{[\text{Th}(\text{H}_2\text{DFO})^{3+}]}{[\text{Th}(\text{HDFO})^{2+}][\text{H}^+]} \quad (4)$$

$$\text{Th}(\text{H}_2\text{DFO})^{3+} + \text{H}^+ \rightleftharpoons \text{Th}(\text{H}_3\text{DFO})^{4+}$$

$$K_{\text{MLH}_3} = \frac{[\text{Th}(\text{H}_3\text{DFO})^{4+}]}{[\text{Th}(\text{H}_2\text{DFO})^{3+}][\text{H}^+]} \quad (5)$$

Reaction 3 is assigned to the protonation of the free amine, while reaction 2 is assigned to the protonation of a metal hydroxide species. At high pH (ca. 10.5) the data are best modeled by the reaction (written as a protonation for consistancy):

$$\text{Th}(\text{OH})_4 + \text{DFO}^{3-} + 3\text{H}^+ \rightleftharpoons \text{Th}(\text{H}_{-1}\text{DFO}) + 4\text{H}_2\text{O}$$

$$K_{\text{comp}} = \frac{[\text{Th}(\text{H}_{-1}\text{DFO})]}{[\text{Th}(\text{OH})_4][\text{DFO}^{3-}][\text{H}^+]^3} \quad (6)$$

K_{comp} represents the competition between the ligand and hydroxide for the metal ion. Using the known stability constant of the aqueous $\text{Th}(\text{OH})_4$ species ($K_{\text{Th}(\text{OH})_4}$, eq 7),[31] the overall formation constant was calculated using eq 8.

$$\text{Th}(\text{OH})_4(\text{aq}) + 4\text{H}^+ \rightleftharpoons \text{Th}^{4+} + 4\text{H}_2\text{O}$$

$$K_{\text{Th}(\text{OH})_4} = \frac{[\text{Th}^{4+}]}{[\text{Th}(\text{OH})_4][\text{H}^+]^4} \quad (7)$$

$$K_{\text{f}} = \frac{(K_{\text{ML}})(K_{\text{MLH}})(K_{\text{comp}})}{(K_{\text{Th}(\text{OH})_4})(K_1^{\text{H}})} \quad (8)$$

The constants K_{ML} and K_{MLH} must be included in the model since at high pH the competition is between $\text{Th}(\text{H}_{-1}\text{DFO})$ and $\text{Th}(\text{OH})_4$. The constant K_1^{H} must also be included in the model because the species released is the free ligand DFO^{3-}, while the species in eq 1 is HDFO^{2-}.

The potentiometric titration curve shown in Figure S1 (supporting information) was fit using the model above and iterating on K_{MLH_2}, K_{MLH_3}, K_{MLH}, K_{ML}, and K_{comp} to calculate K_{f}. The conditions and results are presented in Table 2.

The $\text{Th}(\text{OH})_4$ species is metastable above 0.5 μM under the conditions of these experiments (log $K = -6.3$ for the reaction of $\text{ThO}_2(\text{s}) + 2\text{H}_2\text{O} \leftrightarrow \text{Th}(\text{OH})_4(\text{aq})^{31}$), but precipitation is very slow. No precipitation was visible over a 2-h period in solutions that were 0.6 mM in $\text{Th}(\text{OH})_4$, nor did the titration curve display

(31) Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; John Wiley & Sons: New York, 1976.

Table 2. Experimental Conditions and Results from Potentiometric Titrations of $\text{Th}(\text{HDFO})^{2+}$ and Th(DFO-1,2-HOPO) Complexes

	$\text{Th}(\text{HDFO})^{2+}$	Th(DFO-1,2-HOPO)
temp, °C	25.0 ± 0.1	25.0 ± 0.1
added electrolyte	0.1 M KCl	0.1 M KCl
no. of points, range	80–97	47–50
no. of experiments	3	3
C_{Th}, mM	1.25	0.925
C_{L}, mM	1.35	1.04
pH, range	2.1–10.7	2.6–11.5
log K_{f}	26.6(1)	33.7(4)
log K_{MLH}	7.8(1)[a,b]	4.2(1)
log K_{MLH_2}	2.7(1)	2.26(5)
log K_{MLH_3}	1.8(1)[c]	
log K_{ML}	10.2(2)	
log β_{110}	18.9	33.7
log β_{111}	26.6	37.9
log β_{112}	29.3	40.2
log β_{113}	31.1	
log β_{11-1}	8.6	

[a] The value in parentheses is the standard deviation based on the variance in at least three independent measurements. [b] See the text for how the formation constants are defined for the DFO system. [c] This protonation constant was not confirmed by spectrophotometric or ^{1}H NMR titrations.

any pH fluctuations which often accompany precipitation. Supersaturation of hydrous $\text{Th}(\text{OH})_4$ is known.[31]

Two factors involved in the potentiometric titrations encouraged the determination of the complex formation constant and lower protonation constants using another method. First, two protonations were observed for the complex $[\text{Th}(\text{HDFO})^{2+}]$. This seemed unusual since only one protonation constant has been reported for similar complexes, $\text{Ga}(\text{HDFO})^+$ and Fe-$(\text{HDFO})^+$ at 1.1[32] and 0.95[12] respectively. The protonations of the $\text{Th}(\text{HDFO})^{2+}$ complex, log $K_{\text{MLH}_2} = 2.7$ and log $K_{\text{MLH}_3} = 1.8$, are inconsistent. Second, the stability constant was determined by competition with hydroxide at high pH. Slight changes in pH are difficult to extrapolate in the high pH region of the titration curve corresponding to the formation of Th-$(\text{OH})_4$ and the low pH region corresponding to the formation of $\text{Th}(\text{H}_2\text{DFO})^{3+}$ and $\text{Th}(\text{H}_3\text{DFO})^{4+}$. For these reasons spectrophotometric titrations of the complex were carried out from pH 2.6 to 0.8. The data were analyzed using both a least-squares refinement program and the method of Schwarzenbach[33] (Figure S2). The plot of A_{obs} va $[A_0 - A_{\text{obs}}]/[\text{H}]^n$ was linear only for $n = 1$, indicating a one-proton step with an associated protonation constant, log $K_{\text{MLH}_2} = 1.9$, while the refinement program yielded a constant of 2.0. The addition of K_{MLH_3} to the model did not improve the fit; the value determined for log K_{f} was found to be 26.5, in excellent agreement with the value determined from the potentiometric titrations (see Table 3 for conditions and results).

To confirm K_{MLH_2} and determine if MLH_3 is a significant species, a pH titration was performed on the metal/ligand complex and was followed by ^{1}H NMR between pD 5.5 and 1.1 (Figure S3). By observation of the change in the chemical shift of the ligand's terminal methyl protons, the protonation of the complex was observed. At low pD only one break region was observed, around pD 2.5, with a change in chemical shift

(32) Borgias, B. A.; Barclay, S. J.; Raymond, K. N. *J. Coord. Chem.* **1986**, *15*, 109–123.

(33) For a simple protonation equilibrium, such as $\text{A} + n\text{H}^+ = \text{H}_n\text{A}$ in which two species have different extinction coefficients at a certain wavelength, an equation can be derived as $A_{\text{obs}} = (A_0 - A_{\text{obs}})/K_{\text{H}_n\text{A}}$-$[\text{H}^+]^n + C$, where A_{obs} is the absorbance at the same wavelength for each pH value, A_0 is the initial absorbance, and C is a constant. The protonation constant, $K_{\text{H}_n\text{A}}$, can be calculated from the slope of a linear correlation A_{obs} vs $(A_0 - A_{\text{obs}})/[\text{H}^+]^n$. For a more detailed description see: Anderegg, G.; L'Eplatternier, F.; Schwarzenbach, G. *Helv. Chim. Acta* **1963**, *46*, 1409.

Table 3. Experimental Conditions and Results for the Spectrophotometric Titrations of the Th^{4+} Complexes of H_4DFO^+ and the Three DFO Derivatives

	$Th(HDFO)^{2+}$	$Th(DFOMTA)^-$	$Th(DFOCAMC)^{2-}$	$Th(DFOHOPO)$	$Pu(DFOMTA)^-$
temp, °C	25.0 ± 0.1	25.0 ± 0.1	25.0 ± 0.1	25.0 ± 0.1	23 ± 2
added electrolyte	0.1 M KCl[b]	0.1 M KCl	0.1 M KCl	0.1 M KCl	none, $I = 0.22 \pm 0.02$ M
no. of points, range	9–35	32–61	33–58	17–39	10–17
no. of experiments	6	6	5	15	5
spectral conditions	1.0 cm cell	1.0 cm cell	1.0 cm cell	10.0 cm cell	1.0 cm cell
C_M, mM	0.049	0.038	0.042	.0089	0.203
C_L, mM	0.053	0.039	0.042	.0090	0.203
C_{EDTA}, mM		4.95	4.15		23.7
pH, range	2.9–0.81	7.0–2.5	10.0–2.5	11.5–8.0	7.6–2.8
$\log K_{M(EDTA)}$		23.2[a]	23.2		25.6[d]
$\log K_{M(HEDTA)}$		1.98	1.98		2.6
$\log K_f$	26.5(1)	38.55(5)	37.2(3)	33.0(1.0)	41.7(2)
$\log K_{MLH}$		5.69(3)	8.9(2)		5.9(1)
$\log K_{MLH2}$	2.0(1)[c]				
$\log \beta_{110}$		38.55	37.2	33	41.7
$\log \beta_{111}$	26.5	44.24	46.1		47.6
$\log \beta_{112}$	28.5				

[a] From ref 12. [b] During this titration pH values below 1.0 had a higher ionic strength than 0.1 M as discussed in the text. [c] No evidence was found for a MLH_3 species as was reported for the potentiometric titrations. This value was determined by the refinement program; the value determined by the Schwarzenbach plot was 1.9. [d] From ref 44.

of 0.02 ppm. The change in chemical shift was compared to the titration of the free ligand (not shown). On the basis of the chemical shift of the fully protonated free ligand, each protonation should change the methyl chemical shift an average of 0.017 ppm. This indicates that only one proton is bound by the complex between pD 2.6 and 1.7. The relationship between pD and pH is pD = pH + 0.4,[34] leading to a measured protonation constant $\log K_{MLH_2} = 2.1$. This value is in excellent agreement with the other determinations of this constant.

Solution Chemistry of the $Th^{4+}/H_5DFOMTA$ and $Th^{4+}/H_6DFOCAMC$ Complexes. The procedure for the spectrophotometric competition titrations of $Th(DFOMTA)^-$ and $Th(DFOCAMC)^{2-}$, using EDTA as a competing ligand, were very similar and will be discussed together. The overall formation constant for these complexes is defined as follows:
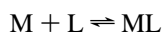
$$M + L \rightleftharpoons ML$$

$$K_f = \frac{[ML]}{[M][L]}$$

Due to the high stability of the complex, no free metal was present even at low pH (<2), so K_{ML} could not be measured directly. Instead, K_{comp} was measured.
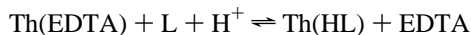
$$Th(EDTA) + L + H^+ \rightleftharpoons Th(HL) + EDTA$$

$$K_{comp} = \frac{[Th(HL)][EDTA]}{[Th(EDTA)][L][H^+]} = \frac{(K_{ML})(K_{MLH})}{K_{Th(EDTA)}} \quad (9)$$

where $K_{Th(EDTA)}$ is the known formation constant of the $Th^{4+}/EDTA$ complex, L is either fully deprotonated DFOMTA or DFOCAMC, and K_{MLH} corresponds to:
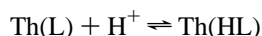
$$Th(L) + H^+ \rightleftharpoons Th(HL)$$

$$K_{MLH} = \frac{[Th(HL)]}{[Th(L)][H^+]}$$

K_{MLH} and K_{comp} were determined by spectrophotometric titration, allowing K_f to be calculated.

Representative spectra collected during the titration of the Th/DFOMTA/EDTA complexes are shown in Figure 2. The
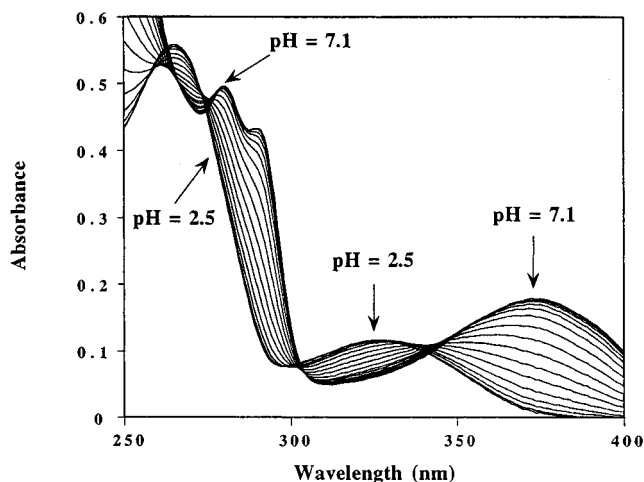
(34) Bates, R. G. *Determination of pH*, *Theory and Practice*; John Wiley & Sons: New York, 1964.

Figure 2. Competition spectrophotometric titration of $Th(DFOMTA)^-$ in the presence of excess EDTA in 0.100 M KCl at 25.0 ± 0.1 °C from pH 7.1 to 2.5. $[Th]_{tot} = 0.043$ mM, $[DFOMTA]_{tot} = 0.043$ mM, and $[EDTA]_{tot} = 5.54$ mM.

ligand has two absorption bands associated with the catecholate ring. The extinction coefficients and absorption maxima of the mono- and diprotonated species for the DFOMTA and DFO-CAMC are listed in Table 4. At pH ~7 the $Th(DFOMTA)^-$ complex is fully formed (λ_{max} 373 nm (4600 cm^{-1} M^{-1}) and 280 nm (13 600 cm^{-1} M^{-1})) (Figure 5). As the pH was lowered there was a shift of the absorption maxima to lower wavelength as one of the catechol groups was protonated, corresponding to the species $Th(HDFOMTA)$. At still lower pH, EDTA displaces DFOMTA, as evidenced by the spectra of the fully protonated ligand $H_5DFOMTA$ (λ_{max} 336 nm (2700 cm^{-1} M^{-1}) and 264 nm (14 900 cm^{-1} M^{-1})). The closely related DFOCAMC behaved similarly except there was an additional protonation (of the carboxylate group), yielding the species $H_6DFOCAMC$. The absorption maxima and extinction coefficients for the complexes are summarized in Table 4. The formation constants determined from the spectrophotometric titrations are summarized in Table 3. Attempts to determine the lower protonation constants of the complexes (i.e., K_{MLH_2}), in the absence of EDTA, were unsuccessful due to the precipitation of an unidentified species at pH 5–6.

Solution Chemistry of the $Th^{4+}/H_4DFO-1,2-HOPO$ Complex. Potentiometric titrations of the $Th(DFO-1,2-HOPO)$ complex were modeled using two protonations of the complex

Table 4. Spectral Features of H_4DFO^+ and the Three DFO Derivatives and Their Th^{4+} and Pu^{4+} Complexes[a]

	H_4DFO^+	$H_5DFOMTA$	$H_6DFOCAMC$	$H_4DFOHOPO$
L	233 (17.7)			345 (4.6)
LH	233 (17.7)[b]	358 (4.0)	360 (3.7)	
LH_4[e]	205 (17.6)			306 (6.3)
LH_5		336 (2.7)	337 (2.8)	
		264 (14.9)	259 (13.1)	
LH_6			337 (2.8)	
			260 (14.8)	
		Th(IV) Complexes		
ML		373 (4.6)	359 (4.1)	324 (3.7)[d]
		280 (13.6)	274 (7.9)	
MLH	230 (15.0)	363 (4.5)	357 (3.0)	
		276 (14.6)	269 (8.0)	
MLH_2	222 (11.6)[c]			
		Pu(IV) Complexes		
ML		366 (6.0)		314 (5.4)
MLH		342 (4.6)		

[a] Wavelength at the absorbance maximum, nm (molar extinction coefficient, 10^3 M^{-1} cm^{-1}). [b] Protonation of the amine does not change the spectrum. [c] Shoulder. [d] The protonation constants of this complex were not determined. [e] The protonations of the hydroxamate groups (LH_2 and LH_3 for all ligands) does not significantly affect the spectrum of the aromatic groups.
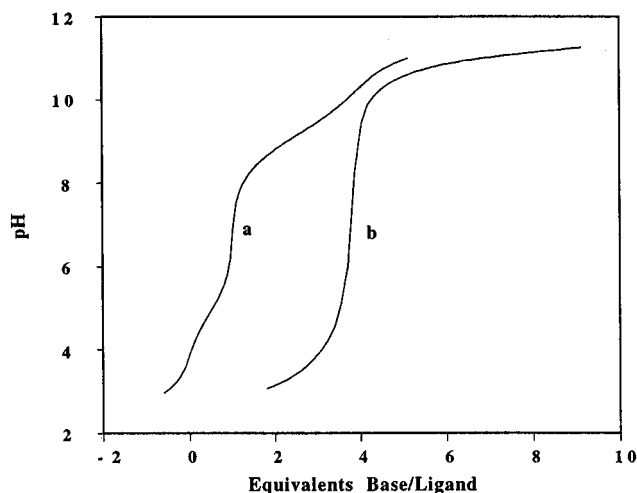

Figure 3. Potentiometric titration curves of (a) DFO-1,2-HOPO and (b) Th^{4+}/DFO-1,2-HOPO. $[Th]_{tot} \sim 1.0$ mM and [DFO-1,2-HOPO]$_{tot}$ ~ 1.0 mM, in 0.100 M KCl, at 25.0 ± 0.1 °C.

at low pH and the dissociation of the complex into $Th(OH)_4$ and free ligand at high pH. The titration curve of the free ligand and of the complex are shown in Figure 3. Model refinement yielded log $K_{MLH} = 4.1$ and log $K_{MLH_2} = 2.2$ and a formation constant log $K_f = 33.7$ (see Table 2).

Because of electrode limitations the accuracy of determining a stability constant at high pH by potentiometric methods is low. To confirm the value obtained for the formation constant, a spectrophotometric competition titration was attempted using EDTA as the competing ligand. Unfortunately, at low pH the formation of the Th(EDTA) complex did not fit the data. Instead, using a mixed ligand species of the type Th(HDFO-1,2-HOPO)(H_xEDTA), where x varies with pH, yielded the best fit of the data.

Since it was not possible to determine the stability constant of the complex by competition methods a direct spectrophotometric titration at high pH was carried out. The conditions and results for these titrations are listed in Table 3. The uncertainty in the formation constant was large, but the constant is in good agreement with the formation constant determined by pH titration. The spectrophotometric titration of the complex below pH 7.0 yielded spectra that were difficult to model. The

protonation constants of the complex varied from titration to titration, while the potentiometric titrations were consistent. In order to understand the solution chemistry of the complex better, a ^{1}H NMR potentiometric titration was carried out with both the free ligand and the metal/ligand complex. The three aryl protons of the 1,2-HOPO group and the three equivalent protons of the terminal methyl group of DFO were appropriate signals to observe the protonation of the ligand and the complex.

The chemical shift changes in the aryl region of the ^{1}H NMR of both the free ligand and the complex, as a function of pD, are shown in Figure 4 (parts A and B). The assignment of the protons is shown in Scheme 1: H_a is a doublet of doublets but appears as a triplet; H_c is the most shifted by the deprotonation of the 1,2-HOPO group due to the change in conformation of the amide carbonyl; the remaining doublet is assigned as H_b. The protonation constant (pD) of 5.4 (pH 5.0) determined by the ^{1}H NMR titration is in excellent agreement with log K_n^4 (Table 1) determined for DFO-1,2-HOPO previously.[30]

For the metal/ligand complex, the 1,2-HOPO group appears to be bound to the metal ion at low pD, since H_c was shifted downfield to $\sim$7.15 ppm. As the pD is increased, a second set of 1,2-HOPO signals appear (designated as $H_a{}'$, $H_b{}'$ and $H_c{}'$). Only the signal corresponding to $H_c{}'$ (Figure 4B) is shifted sufficiently from the first set of signals to be resolved. The signals of H_a ($H_a{}'$) and H_b ($H_b{}'$) merely broaden and become multiplets.

The change in chemical shifts as a function of pD gives some indication of the solution behavior of this complex. The intensity of H_c decreases as the intensity of $H_c{}'$ increases with increasing pD. All signals coalesced and had relatively constant chemical shifts by pD 6 and higher. The protonation constant (pD) of 4.1 (pH 3.7) determined by this method is in good agreement with the log K_{MLH} of 4.2 determined by potentiometric titration of the metal/ligand complex (Table 2). From the small change in the chemical shift of the 1,2-HOPO protons it is apparent that the protonation of the complex is not of the 1,2-HOPO group, but instead is of a hydroxamate group.

The chemical shifts of methyl protons for the free ligand and for the complex are shown in Figure 4 (parts C and D). The free ligand showed the expected protonation behavior with an average protonation constant of 9.0. The metal complex is also partially protonated at low pD. The signal plotted in Figure 4 (parts C and D) is the largest peak in the spectrum. There were at least three different isomers present at low pD. By pD 5, however, the peak is a sharp singlet with invariant chemical shift until pD $\geq$10, where presumably $Th(OH)_4$ and free ligand are beginning to form. The shift of the methyl protons of the complex indicate that there are two protonations with an average protonation constant of 3.0, which is in good agreement with the potentiometric titrations (Table 2).

More than one set of signals in the ^{1}H NMR for the Th-(DFO-1,2-HOPO) complex can be interpreted as follows: At low pH two of the hydroxamates are protonated and this species isomerizes slowly on the NMR time scale, giving rise to multiple methyl signals, while at the same time this process causes only slight broadening of the 1,2-HOPO protons resonances. As the pH is increased one of the hydroxamates is deprotonated at pH $\sim$2.0. At higher pH ($\sim$4.0) the second hydroxamate proton is removed. Because of the relatively large shift of the H_c resonance it is assigned to the hydroxamate proton closest to the 1,2-HOPO group. The two sets of 1,2-HOPO signals around pH 4 are most likely due to a slow exchange between two conformers. This equilibrium is represented in Scheme 2 between conformers **A** and **C**. Conformer **C**, with the hindered conformation, exchanges slowly on the NMR time scale conformer **A**. These conformers have the same proton stoichi-
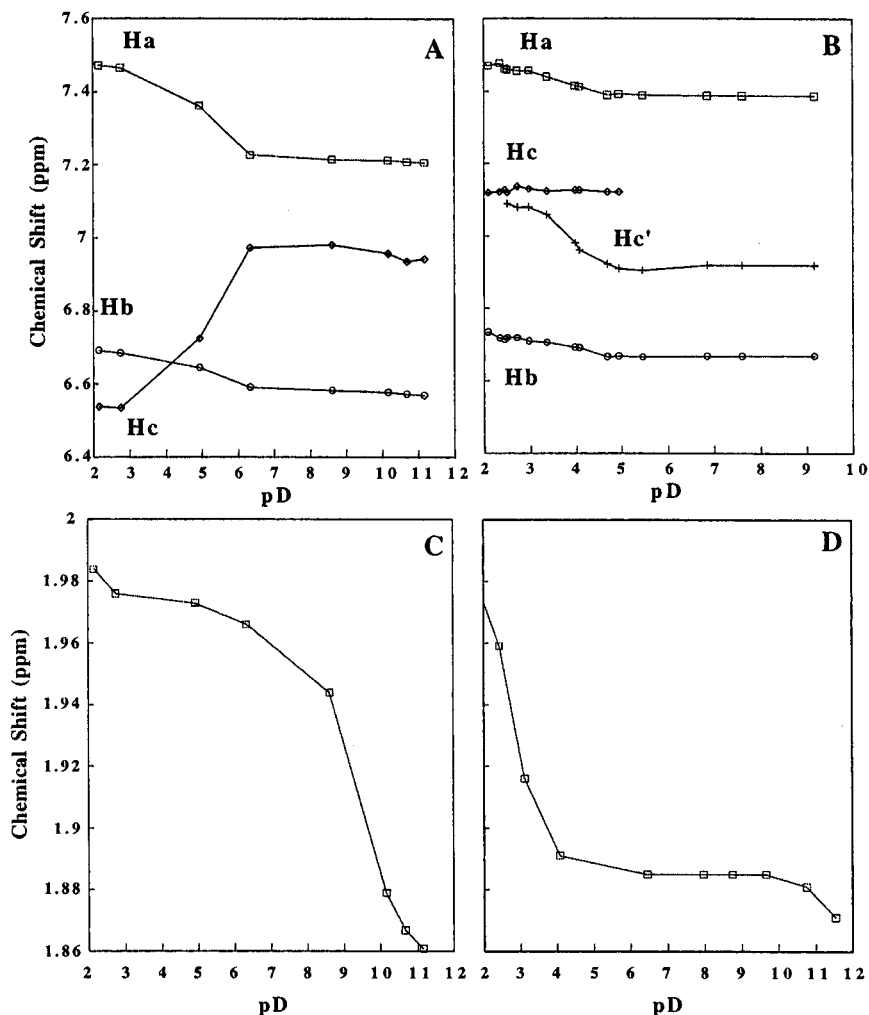
Figure 4. ¹H NMR titration of DFO-1,2-HOPO aryl protons (A), Th(DFO-1,2-HOPO)aryl protons (B), DFO-1,2-HOPO methyl protons (C), and Th(DFO-1,2-HOPO) methyl protons (D) in D_2O at ∼0.03 M. H_a, H_b, H_c, and H_c' are defined in the text.
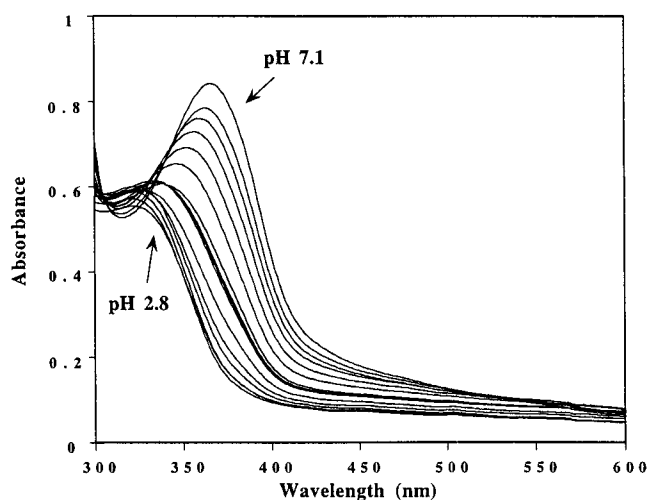

Figure 5. Spectrophotometric competition titration of Pu(DFOMTA)⁻ in the presence of excess EDTA. The ionic strength was 0.22 ± 0.02 M and the temperature was 23 ± 2 °C. $[Pu]_{tot} = 0.20$ mM, $[DFOMTA]_{tot} = 0.20$ mM, and $[EDTA]_{tot} = 23.7$ mM over the pH range 7.1−2.8.

ometry but different protonation constants. The formation of conformer **A** is favored as the pH is raised, due to the formation of **B** (the fully formed complex). The ¹H NMR signal due to isomer **C** (H_c in Figure 4B) is observed to decrease in intensity but does not shift as a function of pD since it is only in slow equilibrium with **A**. The average signal (H_c' in Figure 4B) due to **A** and **B** is observed to shift due to the increasing abundance

Scheme 1. Predicted Conformational Change of DFO-1,2-HOPO upon Deprotonation of the 1,2-HOPO Group
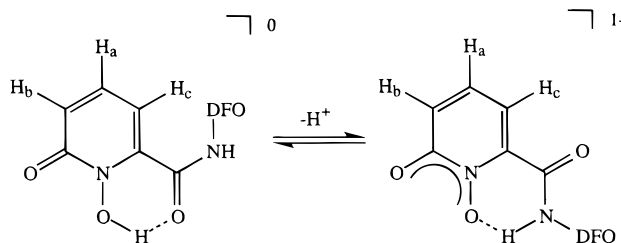
in **B** relative to **A**. This average signal also increases in overall intensity due to the increasing abundance of **A** and **B** relative to **C**.

The appearance of slowly exchanging conformers explains why the spectrophotometric titration was difficult to model. The data analysis program assumes only one spectrum exists for each protonation state; different conformers with the same number of protons and slightly different spectra cannot be modeled. This equilibrium would not affect the potentiometric titrations since only the proton stoichiometry is considered. Another possible explanation would be the formation of a dimer in slow equilibrium with a monomer, although hydroxo- and oxo-bridged dimer/monomer equilibria where the number of protons is constant seem unlikely.

Solution Chemistry of the Pu⁴⁺/H₅DFOMTA Complex. The same general procedure and definitions as detailed for Th(DFOMTA)⁻ and Th(DFOCAMC)²⁻ were used in the determination of the stability constant of Pu(DFOMTA)⁻.

Scheme 2. Proposed Solution Chemistry of the Th^{4+}/DFO-1,2-HOPO Complex
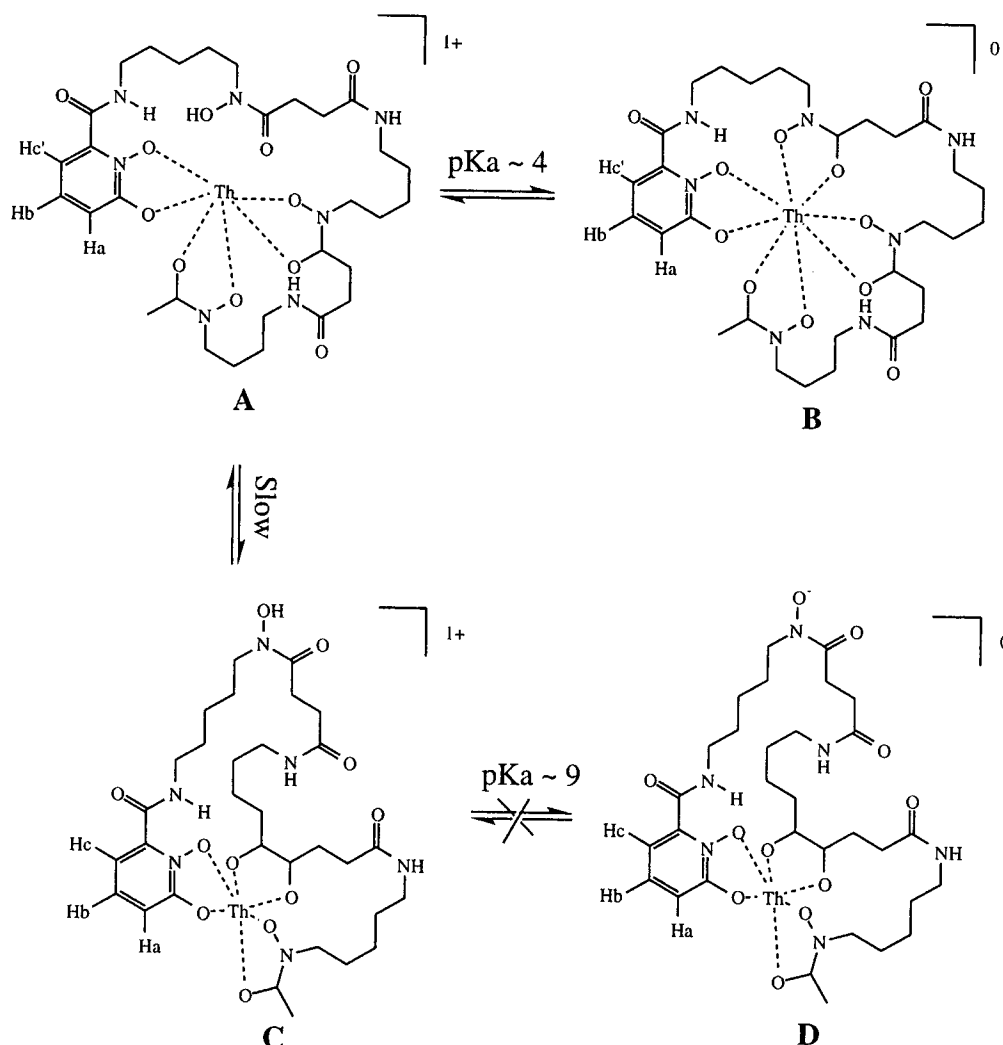
Spectra obtained during the spectrophotometric competition titration of the Pu^{4+}/DFOMTA complex in the presence of EDTA are shown in Figure 5. The conditions and results of the experiments are tabulated in Table 3. The protonation constant determined for this complex (5.69) is almost the same as the Th^{4+} complex (5.90). This is surprising since Pu^{4+}, as the stronger Lewis acid, should form a stronger complex with the terephthalamide group and make the complex harder to protonate.

Estimation of the Stability Constants for the Pu^{4+} Complexes of H$_4$DFO-1,2-HOPO and H$_6$DFOCAMC. The spectrophotometric competition titration of the Pu(DFO-1,2-HOPO) complex using EDTA as competitor produced only mixed-ligand species as observed for the Th^{4+}/DFO-1,2-HOPO competition titration. It is possible to estimate the Pu(DFO-1,2-HOPO) and Pu(DFOCAMC)$^{2-}$ stability constants by assuming a linear free energy relationship between the Th^{4+} complexes and the Pu^{4+} complexes.[35-37] From the relative stability between the Th(DFOMTA)$^-$ and Pu(DFOMTA)$^-$ complexes ($10^{3.2}$) it is possible to estimate the Pu^{4+} constants with DFO-1,2-HOPO and DFOCAMC by simply adding 3.2 to the log K's of the Th^{4+} complexes. Table 5 is a summary of all measured and estimated formation constants.

Table 5. Summary of Stability Constants for H$_4$DFO$^+$ and the DFO Derivatives with Fe^{3+}, Th^{4+}, and Pu^{4+}

|		DFO	DFOMTA	DFOCAMC	DFOHOPO
Fe(III)	log K_f	30.6^a	34.8^f	34.9^f	30.7^f
	log K_{MLH}		9.21	9.71	7.3
	log K_{MLH_2}	0.95	4.0	7.7	
Th(IV)	log K_f	26.6(1)^b	38.55(5)	37.2(3)	33.7(4)^d
	log K_{MLH}	7.8(1)^d	5.69(3)	8.9(2)	4.2(1)
	log K_{MLH_2}	2.0(1)^c			2.26(5)
	log K_{MLH_1}	10.2(1)^d			
Pu(IV)	log K_f	30.8^e	41.7(2)	40.4^g	36.9^g
	log K_{MLH}		5.9(1)		

^{a} From ref 12. ^{b} Average of potentiometric and spectrophotometric titrations. ^{c} Determined by spectrophotometric titrations and confirmed by ^{1}H NMR. ^{d} Determined by potentiometric titration. ^{e} From ref 49. ^{f} From ref 30. ^{g} Estimated stability constant.

Selectivity of DFO Derivatives. The DFO derivatives studied display high thermodynamic stability with Th^{4+} and Pu^{4+} and are currently being modified to be used as liquid/liquid (by addition of lipophilic side chain) or solid/liquid (by attachment to a insoluble polymer) extraction agents. These materials are able to bind Pu^{4+} in the presence of a large excess of most other metal cations. Sodium ion and nitrate ion are two ions that are important for nuclear waste remediation, since they occur in high concentrations in a number of waste streams.[38] The DFO derivatives studied here can completely saturate the coordination sphere of Pu^{4+} and Th^{4+} in the presence of at least a 10^{10} excess of Na$^+$ and NO$_3^-$. Complexing agents such as EDTA, NTA, and citric acid are also

(35) Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875−1914.
(36) Smith, R. M.; Martell, A. E.; Motekaitis, R. J. *Inorg. Chim. Acta* **1985**, *99*, 207−216.
(37) Smith, R. M.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chim. Acta* **1985**, *103*, 73−82.

important from a waste remediation perspective. These derivatives can bind Pu^{4+} and Th^{4+} in a solution that is up to 1000 times more concentrated in EDTA at pH 5.0.

The most important competitive ion is Fe^{3+}, for which the relative selectivity of DFO derivatives for Pu^{4+} is determined by the following equilibrium:
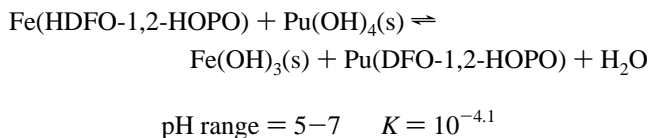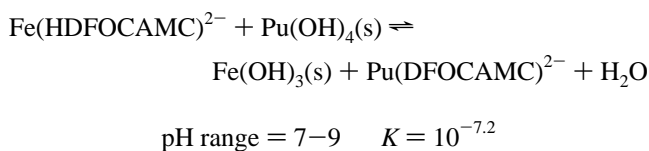
$$Fe(HDFOMTA)^- + Pu(OH)_4(s) \rightleftharpoons$$
$$Fe(OH)_3(s) + Pu(DFOMTA)^- + H_2O$$
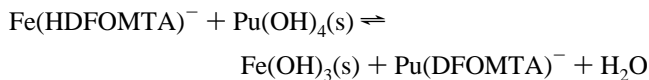
This is a proton-independent reaction that predominates when the species $Fe(HDFOMTA)^-$ and $Pu(DFOMTA)^-$ are dominant, pH 7−8. The equilibrium constant is given by

$$K = \frac{(K_{Pu(OH)_4})(K_w)(K_{PuL})}{(K_{Fe(OH)_3})(K_{FeL})(K_{FeHL})}$$

where $K_{Fe(OH)_3}$ (10^{-38}) and $K_{Pu(OH)_4}$ (10^{-55}) are the solubility products of solid $Fe(OH)_3$ and $Pu(OH)_4$, respectively;[31] K_w is the autodissociation constant of water, K_{PuL} and K_{FeL} are the formation constants for the Pu^{4+} and Fe^{3+}/DFOMTA complexes, respectively, and K_{FeHL} is the protonation constant of the $Fe(DFOMTA)^{2-}$ complex. The calculated equilibrium constant, obtained using the values in Table 3, is $10^{-5.6}$, showing that in these conditions DFOMTA is selective for Fe^{3+} over Pu^{4+}, driven by the insolubility of $Pu(OH)_4$ below pH 5. The overall reaction is

$$Fe(H_2DFOMTA) + Pu(OH)_4(s) \rightleftharpoons$$
$$Fe(OH)_3(s) + Pu(HDFOMTA) + H_2O,$$
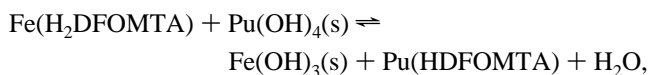
for which the equilibrium constant is $10^{-3.4}$, still favoring complexation of Fe^{3+} over Pu^{4+}. The same results are obtained for DFOCAMC and DFO-1,2-HOPO using the equilibria below in the specified pH ranges:

$$Fe(HDFOCAMC)^{2-} + Pu(OH)_4(s) \rightleftharpoons$$
$$Fe(OH)_3(s) + Pu(DFOCAMC)^{2-} + H_2O$$

$$\text{pH range} = 7-9 \quad K = 10^{-7.2}$$

$$Fe(HDFO\text{-}1,2\text{-}HOPO) + Pu(OH)_4(s) \rightleftharpoons$$
$$Fe(OH)_3(s) + Pu(DFO\text{-}1,2\text{-}HOPO) + H_2O$$

$$\text{pH range} = 5-7 \quad K = 10^{-4.1}$$

However the presence of other chelating ligands reverses these trends. For example

$$FeHL^- + Pu(EDTA) \rightleftharpoons Fe(EDTA)^- + PuHL$$
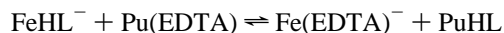
where L is DFOMTA. Again this a proton neutral reaction is the dominant equilibrium between pH 3 and 4.5. The $Fe(EDTA)^-$ formation constant is log $K_{Fe(EDTA)} = 25.0$.[12] The formation constant for the reaction is (see Tables 3 and 5):
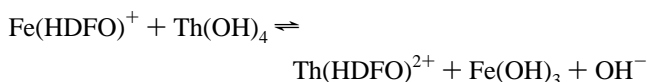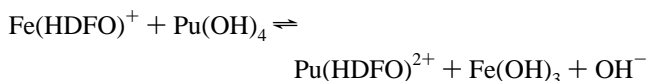
$$K = \frac{(K_{Fe(EDTA)}^-)(K_{PuHL})(K_{PuL^-})}{(K_{Pu(EDTA)})(K_{FeL_2-})(K_{FeHL^-})} = 10^{3.0}$$

In the presence of EDTA the $Pu(HDFOMTA)$ complex is

(38) Allen, G. K. *Estimated Inventory of Chemicals Added to Underground Waste Tanks, 1944 Through 1975*; Waste Solidification Engineering and Design Research and Engineering Division Development Engineering Department: 1976.

favored, a very encouraging result since EDTA is a component in many iron-containing waste streams.

Migration of Th^{4+} and Pu^{4+} as the DFO Complex. The siderophore DFO has been investigated as a possible solubilizing and transporting agent for actinide(IV) ions in soil and ground water.[14] DFO does form stable and soluble complexes with both Th^{4+} and Pu^{4+}. However, the affinity of DFO for ferric ion would significantly influence the role of DFO in actinide migration in natural systems. As described above, the equilibrium constants for the following exchange reactions are

$$Fe(HDFO)^+ + Pu(OH)_4 \rightleftharpoons$$
$$Pu(HDFO)^{2+} + Fe(OH)_3 + OH^-$$

$$Fe(HDFO)^+ + Th(OH)_4 \rightleftharpoons$$
$$Th(HDFO)^{2+} + Fe(OH)_3 + OH^-$$

These are pH-dependent reactions, and so the equilibrium constant has been calculated between the boundary pH values of natural systems, pH 5 and 9, where

$$K = \frac{(K_{Fe(OH)_3})(K_{M(HDFO)^+})[OH^-]}{(K_{Fe(HDFO)^+})(K_{M(OH)_4})}$$

and M is Th^{4+} or Pu^{4+}. For M = Th^{4+}, the equilibrium constant is 10^{-16} at pH 5 and 10^{-12} at pH 9. This calculation shows that the formation of the $Fe(HDFO)^+$ complex is strongly favored under these conditions. The same situation is true for M = Pu^{4+}, where the equilibrium constant is 10^{-26} at pH 5 and 10^{-21} at pH 9. These reactions are largely driven by the extreme stability of the actinide hydroxide species. However, as discussed above, the presence of complexing agents with a high affinity for ferric ion can reverse the reaction.

Conclusions

The stability constants of Th^{4+} with DFO and three DFO derivatives, DFOMTA, DFOCAMC, and DFO-1,2-HOPO, have been determined along with the stability constant of the Pu^{4+}/DFOMTA complex. The stability constants of Pu^{4+} with the other two DFO derivatives have been estimated. The constants have been determined by either potentiometric, spectrophotometric, competition spectrophotometric, ^1H NMR titrations or a combination of these techniques. The determination of these basic thermodynamic constants has led to the conclusion that DFO has the potential to play a significant role in the migration of Pu^{4+} in the presence of strong ferric complexing agents. These studies also suggest that the DFO derivatives would make excellent liquid/liquid or solid/liquid extractants since they form extremely stable Th^{4+} and Pu^{4+} complexes in the presence of most competing ions.

We note that the addition of the fourth bidentate chelating group did not result in these ligands alone being selective for metals that prefer a coordination number of eight. This raises the question of whether it is possible to design an octadentate ligand that would show selectivity for Pu^{4+} over Fe^{3+} in the absence of a second chelating group.

Experimental Section

General Data. All solutions were prepared using deionized, distilled water, which was further purified using a Millipore cartridge system (resistivity 18 MΩ-cm). The water was saturated with argon by boiling it for at least 20 min and letting it cool while argon was bubbled through it. Once prepared the water was stored under an argon atmosphere to prevent dissolution of CO_2. Titrant solutions were prepared from

carbonate-free Baker Dilut-IT concentrates. The base (0.1 M KOH) was standardized against potassium hydrogen phthalate; the acid (0.1 M HCl) was standardized against the KOH solution. Phenolphthalein was used as an indicator in both cases. The ionic strength of all solutions (unless otherwise stated) was adjusted to 0.100 M by the use of 0.100 M KCl. KCl (Fisher 99.99%) was used without further purification. The pH electrode (Orion Semimicro Ross combination glass pH electrode) was calibrated in concentration units (throughout this paper pH refers to $-\log[H^+]$ except for plutonium titrations) by titrating 2.00 mL of standardized HCl in 50 mL 0.100 M KCl solution with 4.200 mL of standardized KOH. The calibration titration data were analyzed using a nonlinear least-squares refinement program.[39] For the titrations involving plutonium the electrode was calibrated using standard buffers, pH 4.01, 7.00, and 10,00, which were purchased or prepared from concentrates (Fisher, NIST certified). Concentrated perchloric acid (Mallinckrodt, Vycor, double distilled) was used in plutonium stock solution preparations, and 1.00 M and 0.10 M $HClO_4$ stock solutions were prepared by dilution. Hydroiodic acid used in an anion exchange plutonium purification procedure was either (Aldrich, 99.99%) or freshly distilled from reagent grade solution (Baker Analytical), to which hydrazine (Aldrich) was added as a preservative. Nitric acid was reagent grade (Baker Analytical). Dowex AG 1-X8, 100−200 mesh, anion exchange resin (Biorad) was pretreated by preparing a suspension and removing very fine particulates, followed by conversion to the chloride form using concentrated HCl (Fisher). For the proton NMR titration, pD was adjusted with fresh D_2O solutions of 10% NaOD or 20% DCl.

Materials. Desferrioxamine B was supplied as a generous gift from Nicomed/Salutar as Desferal, the mesylate salt of the ligand, and was used as received. $ThCl_4 \cdot 3H_2O$ (99.9%) was from ROC/RIC and was dissolved in H_2O to make solutions ∼0.05 M in Th^{4+}. The solutions were standardized with standard Na_2EDTA (0.0997 M Aldrich) using pyrocatechol violet as indicator.[40] DFOMTA, DFOCAMC, and DFO-1,2-HOPO were synthesized as described previously.[16,30,41] The plutonium used throughout was ^{242}Pu, originally obtained as $^{242}PuO_2$ from the U.S. Department of Energy's Heavy Element Production Program at Oak Ridge National Laboratory. The α and γ spectroscopic analyses indicated the plutonium was 99.85% ^{242}Pu by mass; the remainder was $^{238-240}Pu$, and ^{241}Am. Aliquots of the solutions were purified using anion exchange chromatography to separate $PuCl_6^{2-}$ from fission products and other contaminants.[42] Conversion to the perchlorate form was accomplished by fuming with concentrated HNO_3 followed by fuming with $HClO_4$ three times. The final solutions were approximately 0.1 M in $HClO_4$. The plutonium concentration was determined using liquid scintillation counting and α spectroscopic analysis. Plutonium(IV) was prepared electrochemically using a three-electrode quartz electrolysis cell with a platinum grid working electrode, platinum auxiliary electrode, and Ag/AgCl reference electrode (207.5 mV vs NHE, hydrogen electrode). The potential was supplied by a Princeton Applied Research Model 264A polarographic analyzer/stripping voltammeter. The oxidation state purity was verified spectrophotometrically by comparison with previously reported spectra.[43] Pu^{4+}/EDTA titration solutions were prepared in an argon atmosphere, as needed, by electrochemically reducing an aliquot of the PuO_2^{2+} stock solution (−0.110 V vs Ag/AgCl) to Pu^{3+}, adding Na_2EDTA as a solution or solid and either aerobically or electrochemically (+0.160 V vs Ag/AgCl) oxidizing the solution to Pu^{4+}/EDTA. The Pu^{3+}/EDTA oxidation was followed spectroscopically and judged to be complete by comparison with the reported Pu^{3+}/EDTA and Pu^{4+}/EDTA UV/visible spectra.[44]

Physical Measurements. UV/visible absorbance measurements were made using an HP8450A spectrophotometer for the Th^{4+} titrations and a Cary (Model 2300) or a Guided Wave, fiber optic (Model 200) spectrophotometer for the Pu^{4+} titrations. ^1H NMR measurements were performed using a commercial Bruker AM-500 MHz spectrometer (1.7-T magnet) controlled by a Bruker Aspect 3000 Data system or a 300 MHz custom built spectrometer.

Potentiometric Titrations (Thorium). The apparatus and method used for potentiometric titrations have been described in detail elsewhere.[45−47] The solutions were maintained at a constant ionic strength (0.100 M KCl) and at a constant temperature 25.0 ± 0.1 °C (constant temperature bath). The thermodynamic reversibility of each potentiometric titration was checked by carrying out titrations starting at low pH and going to high pH and vice versa. The models used to fit the titration data were refined by the nonlinear least-squares program BETA90.[45−47] All results presented here are the average of at least three separate titrations. The exact conditions for each of the potentiometric titrations are presented in Table 2.

Spectrophotmetric Titrations (Thorium). The apparatus and method for spectrophotometric titrations have been described in detail elsewhere.[48] Where necessary EDTA (Aldrich standard solution 0.0997 M) was added as a competitive ligand. The solutions were maintained at a constant ionic strength (0.100 M KCl) and at a constant temperature 25.0 ± 0.1 °C (constant temperature bath). For the titration of Th^{4+}/DFO at the lowest pH values, the ionic strength of the acid itself was greater than 0.1 M (i.e. at pH 0.8, $I = 0.16$ M). Since this was not the only method used to determine the stability constant and the agreement with the potentiometric titrations was good, this amount of ionic strength change was considered negligible. The thermodynamic reversibility of each spectrophotometric titration was checked by carrying out titrations strating at low pH and going to high pH and vice versa. The models used were refined by starting at low pH and going to high pH and vice versa. The models used were refined by the factor analysis program FINDCOMP and the nonlinear least-squares refinement program REFSPEC.[48] All results presented here are the average of at least three separate titrations. Table 3 presents the exact conditions used for each of the spectrophotometric titrations.

Spectrophotometric Titration (Plutonium). Titrations involving plutonium recorded manually the volume of titrant added, pH, and a spectrum for each point. The titrations were carried out in a specially designed UV/visible cuvette equipped with a stirring bar and Teflon screw top to prevent contamination. The ionic strength ($I = 0.22 \pm 0.02$ M) and temperature (23 ± 2 °C) were constant only within the limits noted. Typical volumes were 3−5 mL. The exact conditions used for these titrations are presented in Table 3.

Supporting Information Available: Figures S1−S3 showing potentiometrics titration curves, spectrophotometric titration curves, and a plate of chemical shift vs pD (3 pages). Ordering information is given on any current masthead page.

IC951064R

(39) Martell, A. E.; Motekaitis, R. J. *Computantional Methods for the Determination of Formation Constants*; Plenum Press: New York, 1985; Chapter 3.

(40) Welcher, F. L. *The Analytical Uses of Ethylenediamine Tetraacetic Acid*; D. Van Nostrand Company, Inc.: Princeton, NJ, 1985.

(41) Rodgers, S. J.; Raymond, K. N. *J. Med. Chem.* **1983**, *26*, 439−442.

(42) Hoffman, D. C. *Collected Radiochemical and Geochemical Prodedure*, 5th ed.; Hoffman, D. C., Ed.: Los Alamos, NM, 1989; Vol. Report No. LA-1721, p 194.

(43) Cohen, D. *J. Inorg. Nucl. Chem.* **1961**, *18*, 211−218.

(44) Cauchetier, P.; Guichard, C. *Radiochim. Acta* **1973**, *19*, 137−146.

(45) Harris, W. R.; Raymond, K. N.; Weitl, F. L. *J. Am. Chem. Soc.* **1981**, *103*, 2667−2675.

(46) Kappel, M.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 3437−3442.

(47) Franczyk, T. S. Ph.D. Dissertation, University of California, Berkeley, 1991.

(48) Turowski, P. N.; Rodgers, S. J.; Scarrow, R. C.; Raymond, K. N. *Inorg. Chem.* **1988**, *27*, 474−481.

(49) Jarvis, N. V.; Hancock, R. D. *Inorg. Chim. Acta* **1991**, *182*, 229−232.