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Thermodynamic Study of the Complexation of Protactinium(V) with Diethylenetriaminepentaacetic Acid

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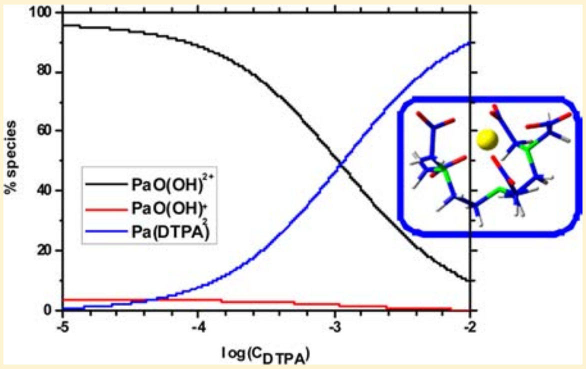
S *Supporting Information*

ABSTRACT: The complex formation of protactinium(V) with DTPA was studied at different temperatures (25−50 °C) and ionic strengths (0.1−1 M) with the element at tracer scale. Irrespective of the temperature and ionic strength studied, only one neutral complex with (1:1) stoichiometry was identified from solvent extraction and capillary electrophoresis coupled to ICP-MS (CE-ICP-MS) experiments. Density Functional Theory (DFT) calculations revealed that two complexes can be considered: Pa(DTPA) and $PaO(H_2DTPA)$. The associated formation constants were determined from solvent extraction data at different ionic strengths and temperatures and then extrapolated to zero ionic strength by SIT methodology. These constants are valid, regardless of complex form, Pa(DTPA) or $PaO(H_2DTPA)$. The standard thermodynamic data determined with these extrapolated constants revealed a very stable complex formed energetically by an endothermic contribution which is counter balanced by a strong entropic contribution. Both, the positive enthalpy and entropy energy terms suggest the formation of an inner sphere complex.



■ INTRODUCTION

Protactinium, located in the periodic table between thorium and uranium, is the first actinide element with 5*f* electrons and vacant 5*f* orbitals involved in the bonding. Its most stable oxidation state +5 corresponds to the formal electronic configuration 5*f* ⁰. Unlike all other light actinides at oxidation states +5 that form a linear trans-dioxo moiety, protactinium species are characterized most commonly by one single Pa−O oxo bond.[1−3] The occurrence of this short mono-oxo bond in Pa species depends on the medium. The mono-oxo bond has been observed in highly concentrated sulfuric and oxalic acid as $PaO(SO_4)_3^{3-}$ and $PaO(C_2O_4)_3^{3-}$, but it is absent in hydrofluoric acid, where the species PaF_7^{2-} has been identified.[4,5] In the system Pa(V)−HF, the breaking of the single oxo bond occurs after the coordination of Pa by 4 or 5 fluoride ions. The cleavage of Pa═O is likely to be favored by the decrease in the partial charge on central atom due to the back-donation of fluoride. But the formal reaction ″$PaO^{3+} \rightarrow Pa^{5+}$″ that occurs during the complexation of Pa(V) by fluoride has never been characterized.

Protactinium displays a strong tendency toward hydrolysis and sorption on any solid support, especially vessel walls. Moreover, concentrated solutions of Pa are not stable, except in the presence of fluoride ions or in concentrated sulfuric acid. Polymerization of Pa(V) is currently observed in concentrated HCl with erratic induction time as well as in 4 M H_2SO_4.[1−3,6] Thus, thermodynamic data relevant to protactinium chemistry are rather scarce in the literature and mainly collected with the element at tracer scale ($C_{Pa} < 10^{-10}$ M) using partition or transport methods. Hydrolysis of Pa(V) has been studied in that way, and a set of thermodynamic data relative to the equilibrium between the first ($PaO(OH)^{2+}$) and the second ($PaO(OH)_2^{+}$) hydrolyzed species is available in the literature.[2,7] However, the previous step that corresponds to the formation of $PaO(OH)^{2+}$ by hydrolysis of PaO^{3+} remains unknown.

With the aim to get a better knowledge about the interaction of actinides, especially protactinium, with organic ligands, this paper focuses on the complexation of Pa(V) with DTPA (diethylenetriaminepentaacetic acid). This polyaminopolycarboxylic acid via 5 oxygen and 3 nitrogen atoms is expected to

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form a very stable octadentate complex with Pa, as reported for actinides(III) and (IV).[8−11]

Due to its high affinity toward actinides, DTPA is namely the reference ligand for decorporation, allowing the efficient removal of Pu(IV) and Am(III) from the body.[12,13] Moreover, this ligand is used in the separation of An(III) from lanthanides (Ln) in the TALSPEAK process (Trivalent Actinide Lanthanide Separation by Phosphorus Extractants and Aqueous Komplexes).[14]

Literature devoted to the behavior of protactinium(V) toward polyaminopolycarboxylic acids is rather scarce. Only the system Pa−EDTA has been investigated using ion exchange chromatography at pH 2.4−2.7 and solvent extraction at pH 0.5−1.2.[15,16] Variations of the distribution K_d of Pa(V) as a function of C_{EDTA} were obtained on anion as well as on cation exchangers. The observed K_d values were interpreted by the author as formation of the complexes (1:1) and (1:2) with H_3EDTA^- and (1:1) with H_2EDTA^{2-}.[15] The dependence of the complex order on the ligand as well as a defect in the material balance do not allow one to consider this work as reliable. The variations of the partition coefficient D as function of the ligand, protons, and extractant concentrations in a later study by Shiokawa et al. revealed an anionic (1:1) complex with an associated apparent formation constant of log $\beta = 22.1 \pm 0.1$.[16] Shiokawa et al. proposed the species $Pa(OH)_2EDTA^-$, that corresponds to $PaO(EDTA)^-$ with the Rydberg's formalism.[17] However, the initial form of Pa(V) has been written under the form PaO^{3+} (equivalent to $Pa(OH)_2^{3+}$) which does not exist under the acidic conditions of Shiokawa's work.

The present article reports the formation constants of the complex Pa(V)−DTPA that are deduced from experiments involving Pa at tracer scale investigated by solvent extraction and capillary electrophoresis. The analysis of the formation constants as a function of ionic strength and temperature allows one to complete the thermodynamic data with enthalpy and entropy terms as well as an extrapolation of the complexation constant to infinite dilution. DFT calculations have been performed on the most probable complexes in order to identify the most stable complex structure. This work reports the first data obtained on the interaction of Pa(V) with DTPA.

■ RESULTS AND DISCUSSION

In order to avoid the polymerization of protactinium, that is known to occur at concentrations of element higher than 10^{-5} M, the whole experimental study was performed at tracer scale ($C_{Pa} < 10^{-8}$ M) whatever the isotope, ^{233}Pa or ^{231}Pa.

Identification of Complexes. *Solvent Extraction.* At tracer scale, solvent extraction leads only to differences in the properties of the species present in aqueous and organic phases: the derivation of the mathematical expression of the distribution coefficient D with respect to the equilibrium concentration of extractant or ligand is equal to the differences between the mean number of extractant or ligand molecules per metal atom in the complexes present in each phase. The charge of the complexes in aqueous phase is deduced from the derivation of D with respect to proton concentration.[18] Moreover, working at constant ionic strength and temperature ensures that activity coefficients are constant throughout solvent extraction experiments.

The Pa species involved in the system TTA/toluene/H_2O/$NaClO_4$/$HClO_4$/H_5DTPA have been characterized in the same way. In Figure 1, the variations of the distribution coefficient D of Pa(V) are plotted as a function of the total DTPA concentration (C_{DTPA}). A D value named D_0 is obtained in a media without a complexing agent and represented arbitrarily at $C_{DTPA} = 10^{-8}$ M. D_0 values are followed by a plateau. The absence of a maximum in the extraction curve indicates that there is no DTPA in the extracted complex.[19] The subsequent decrease in D values for $C_{DTPA} > 10^{-3}$ M can be correlated with the formation of Pa(V)−DTPA complexes in aqueous phase.

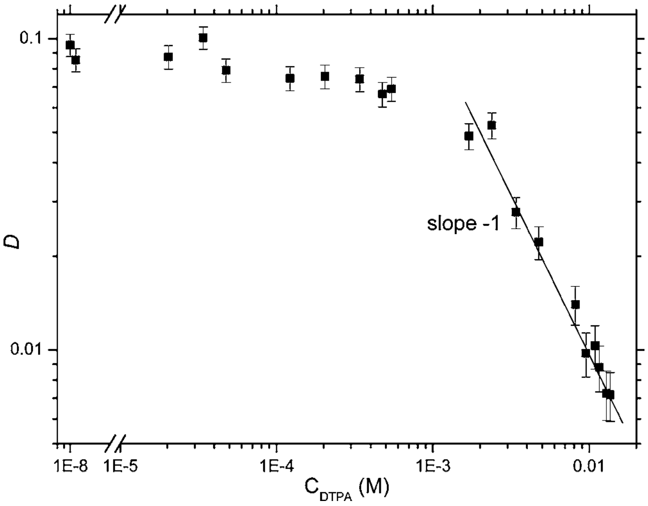

Figure 1. Distribution coefficients of Pa(V) as a function of total DTPA concentration at $\mu = 3$ M. ($C_{TTA} = 0.05$ M, $C_{Pa} \sim 10^{-10}$ M, $\theta = 50$ °C, and $[H^+] = 0.25$ M).

At constant ionic strength and temperature, the slopes of the logarithmic variations of D with ligand concentration represent the mean number of ligands per Pa atom of the predominant species in aqueous phase. The slope of the curve at $C_{DTPA} > 10^{-3}$ M equals −1 which is consistent with the formation of a (1:1) Pa(V)−DTPA complex.

A mean value of $n_{TTA} = 4.3 \pm 0.3$ molecules of TTA per Pa atom in the extracted species was determined for DTPA concentration lower than 2.10^{-2} M when varying the chelatant concentration from 0.045 to 0.085 M (Figures S1 and S2). A previous systematic study on the extraction of Pa(V) by TTA from $NaClO_4$/$HClO_4$ mixed solutions has been performed in the absence of any ligand in aqueous phase at 25 °C. The concentration ranges were as follows: 0.1−3 M for ionic strength, 5.10^{-4}−0.1 M for TTA concentration, and between 3.10^{-4} M and 0.05 to 0.4 M for proton concentration. This study revealed an increase of the number of TTA molecules per Pa atom (n_{TTA}) as acidity increases, reaching 4 for $[H^+] \geq 0.2$ M in keeping with literature data.[2,20,21] Moreover, the n_{TTA} value in systems involving Pa(V) extraction with TTA depends on the acidity and not on the complexing agent.[2] For instance, the study of Pa(V) with oxalic acid performed with $[H^+] = 0.5$ M led to $n_{TTA} = 4$, whereas with sulfate and $[H^+] = 0.1$ M, the n_{TTA} value was found equal to 3. The n_{TTA} value obtained in the Pa(V)−DTPA system agrees with previous work.

Under the experimental conditions of Figure 1 ($[H^+] = 0.25$ M) the first hydrolyzed species of Pa(V), $PaO(OH)^{2+}$, predominates in solution.[2,20,21] Since no ligands are present in the extracted neutral chelate complex, the protactinium species in the organic phase must be $PaO(OH)(TTA)_2(HTTA)_2$. Neutralization of Pa(V) cation occurs via TTA bidentate molecules, and the coordination is completed with two undissociated HTTA, leading to the formation of self-adducts.[22,23] At the lowest acidity investigated in this work

($[H^+] = 0.01$ M), Pa(V) is present as $PaO(OH)^{2+}$ (~20%) and $PaO(OH)_2^+$ (80%).[21] Both hydrolyzed species are extracted by TTA: 3 and 4 chelate molecules are involved in the extraction of $PaO(OH)_2^+$ and $PaO(OH)^{2+}$, respectively.[2] The hydrolysis constant that relates both species has been previously determined by one of us for different values of temperature and ionic strength.[21] In the following, this value is used to fit the experimental variations of the distribution ratio.

CE-ICP-MS. The investigated sample presents a ligand-protactinium ratio of around 10^5 (with $C_{^{231}\text{Pa}} \sim 10^{-8}$ M) corresponding to conditions where the limiting complex is expected. Figure 2 represents the electropherogram registered in anionic mode. The dotted line observed at 674.8 s represents the time when neutral species appears. The observation of the Pa(V)−DTPA complex at the same time implies that it is a neutral complex. Therefore, the complex could be Pa(DTPA), PaOH(HDTPA), or $PaO(H_2DTPA)$.

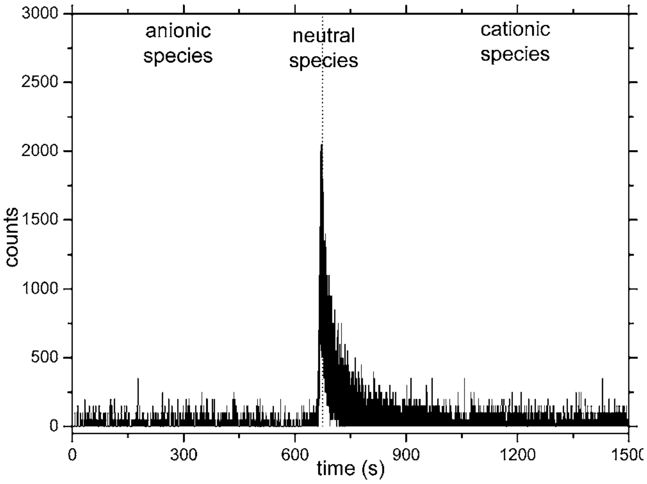

Figure 2. Electropherogram of Pa(V) ~ 10^{-8} M at $\mu = 1$ M, $\theta = 25$ °C, $[H^+] = 0.25$ M, and $C_{DTPA} = 10^{-2}$ M. The vertical dotted line corresponds to the position related to the bulk electrolyte velocity.

The loss of the mono-oxo bond, as proposed in the Pa(DTPA) complex has been observed in fluoro-complexes of protactinium (PaF_6^-, PaF_7^{2-}, and PaF_8^{3-}), otherwise characterized by a great stability especially with respect to hydrolysis.[1−3,24,25] Moreover compounds without a mono-oxo bond at solid state have also been isolated, for instance $KPaF_6$, K_2PaF_7, and Na_3PaF_8.[25,26] In case of chloro and bromo complexes at solid state, oxy halogeno and pure halogeno species have been synthesized and characterized, whereas in concentrated HCl, there is a disagreement over the form of complexes ($PaCl_8^{3-}$, $PaOCl_6^{3-}$).[2]

Complexes with protonated species of DTPA, such as proposed in the $PaO(H_2DTPA)$ complex, have been observed with trivalent lanthanides and actinides.[11,27−29] With actinides-(IV) only the nonprotonated complex has been observed regardless of the acidity of the solution.[30−32]

Actinides in oxidation state +5 and +6 - except Pa - display the linear transdioxo moiety O=M=O, which constrains the coordination to the equatorial plane.[33] Thus, the number of donor atoms of a polydentate ligand that interact with an actinyl form is limited.[33−36] No structural data on the system U(VI)−DTPA are available in the literature. However, the thermodynamic study of Gandolfo et al. indicates the existence of mono- and diprotonated complexes UO_2HDTPA^{2-} and $UO_2H_2DTPA^-$.[36] Protonation on a binding oxygen atom is also observed in various inorganic U(VI) species like arsenate complexes.[37] Although a direct comparison between Pa(V) and U(VI) is questionable (the mono-oxo bond in Pa species does not provide the same steric effect as the actinyl moiety in U(VI)), the existence of a neutral diprotonated complex $PaO(H_2DTPA)$ has to be considered. In addition, this assumption is supported by recent calculations on th Am(III)−DTPA system that involved di-, tri-, and tetra-protonated complexes.[38] Finally, the formation of the other protonated species like Pa(OH)(HDTPA) is doubtful since it would correspond to a replacement of the strong Pa oxo bond by the polydentate DTPA ligand, instead of the weaker hydroxo bond. Moreover, complexes of Pa(V) with a hydroxyl group that are described in the literature contain also the mono-oxo bond, for instance $PaO(OH)^{2+}$ and $PaO(OH)Cl^+$.[1−3] The Pa−

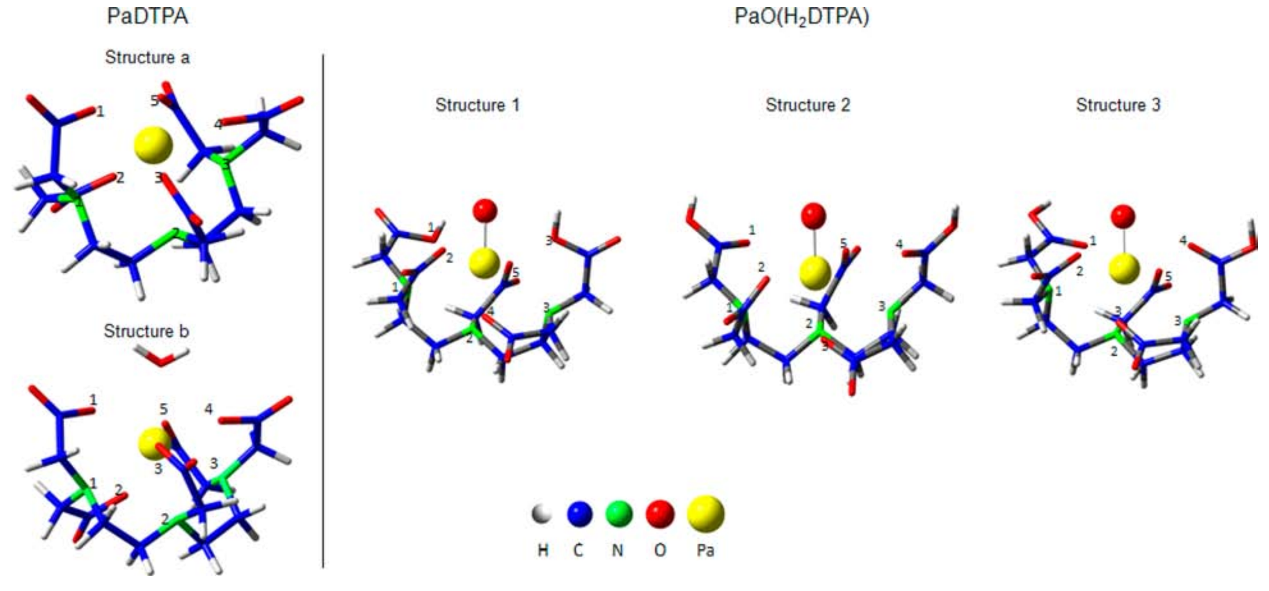

Figure 3. Optimized structures of the Pa(DTPA), $Pa(DTPA)H_2O$, and $PaO(H_2DTPA)$ complexes obtained by DFT calculations.

Table 1. Geometrical Parameters Associated with Figure 3 Obtained by DFT Calculations[a]

distance	Pa(DTPA)	Pa(DTPA)H_2O	PaO(H_2DTPA) structure 1	PaO(H_2DTPA) structure 2	PaO(H_2DTPA) structure 3
Pa−O_1	2.25	2.22	2.85	3.77	2.80
Pa−O_2	2.23	2.25	2.37	2.37	2.39
Pa−O_3	2.25	2.25	2.30	2.32	2.32
Pa−O_4	2.24	2.24	2.68	3.76	2.61
Pa−O_5	2.25	2.25	2.34	2.35	2.34
Pa−O(H_2O)		2.44			
Pa−O_{oxo}	-	-	1.88	1.88	1.89
Pa−N_1	2.76	2.76	2.84	2.85	2.82
Pa−N_2	2.65	2.65	2.80	2.77	2.79
Pa−N_3	2.69	2.70	2.91	2.90	2.92

[a] All distances are in Ångströms.

O moiety remains stable in the presence of ligands with moderate strength like sulfate and oxalate, whereas the hydroxyl disappears.[1−6]

A structural study would be required for a precise identification of species. Unfortunately, X-ray Absorption Spectroscopy (XAS) data registered at ESRF could not be used, because of too low Pa concentration or the presence of residual fluoride ions. The strong tendency of Pa(V) to polymerize and precipitate, especially in the absence of fluoride ions, makes namely concentrated samples difficult to prepare. Therefore, spectroscopic techniques like infra-red and Raman spectroscopy cannot be used, and interferences with DTPA absorption are expected in UV−vis absorption spectrophotometry. Thus, in the following, DFT calculations have been performed on the two most possible neutral complexes: Pa(DTPA) and PaO(H_2DTPA).

DFT Calculations. In a first step, the structure optimization of Pa(DTPA) was performed with and without a supplementary water molecule in the first coordination sphere of protactinium (see Figure 3, structures a and b). In a second step, as previous studies demonstrated that protonated carboxylic functions of DTPA could be involved in the complexation of the metal, geometry optimizations of PaO(H_2DTPA) were performed by considering successively the interaction of Pa with OH (protonated carboxylic functions, structure 1), with oxygen atoms (non protonated carboxylic functions, structure 3), and the structure 2 where there is no interaction with the two protonated carboxylic functions.[11,38,39] Optimized structures of Pa(DTPA), Pa(DTPA)H_2O, and PaO(H_2DTPA) are presented in Figure 3, and associated geometrical parameters are summarized in Table 1.

The structure of Pa(DTPA)H_2O was optimized in order to determine the influence of the water molecule on the coordination geometry of Pa. The distances, indicated in Table 1, revealed that the presence of a water molecule in the inner sphere of Pa(DTPA) does not alter the coordination geometry around the cation. Therefore, the protactinium complex Pa(DTPA) appears stable whatever the coordination number (8 or 9).

For the PaO(H_2DTPA) complexes, each optimized structure is stable whatever the proton position on carboxylic functions as observed in the literature.[11,38] One could notice that the bonds distances Pa−O and Pa−N are longer in PaO(H_2DTPA) relative to Pa(DTPA) with or without H_2O molecule. The stronger interaction observed in Pa(DTPA) can be related to the charge of the metal: Pa(DTPA) and PaO(H_2DTPA) involve the ions "Pa^{5+}" and "PaO^{3+}", respectively. Moreover, the presence of the Pa−O mono-oxo bond may induce steric effects that are also responsible for the distance lengthening.

From the optimized structures of all the complexes we can deduce the relative stability between Pa(DTPA)H_2O and PaO(H_2DTPA) by using the overall energy of each complex since they are composed of exactly the same atoms. The relative stability of each complex is calculated according to eq 1 by using the most stable Pa(DTPA)H_2O complex as reference. In this equation, E[complex] refers to the overall energy of the complex PaO(H_2DTPA) for the three structures. The energy difference ΔE is found equal to 82.0, 67.5, and 35.2 kJ·mol^{-1} for structures 1, 2, and 3, respectively.

$$\Delta E = \mathrm{E[complex]} - \mathrm{E[Pa(DTPA)H_2O]} \tag{1}$$

The overall energy of the structures 1 and 2 is higher than the one of structure 3. This tends to indicate that the structure in which Pa interacts with nonprotonated oxygen atoms is more stable. This result is similar to the one observed with An(III) in the literature where theoretical calculations indicate that protonation occurs more likely on noncoordinating carboxylate oxygen.[11,38]

Whatever the optimized structure of PaO(H_2DTPA), its overall energy is always higher than that of Pa(DTPA)H_2O. This could be related to a higher stability of Pa(DTPA)H_2O. However, the energy is not high enough to discriminate definitely between the two structures considering the limitations of such calculations for ions in aqueous solution with large solvation effects. However, even if DFT calculations should be used with caution, they have shown unambiguously that both complexes are stable. In other words, not only the nonprotonated form DTPA^{5-} but also the diprotonated one H_2DTPA^{3-} can be coordinated to a metal ion through the 8 donor atoms. This agrees with the recent DFT calculations of Bridges et al.[38]

Thermodynamical Study. Solvent extraction and capillary experiments have led to the conclusion that Pa(V) forms a neutral (1:1) complex with DTPA. Moreover, overall energy differences between Pa(DTPA)H_2O and PaO(H_2DTPA) are not significant. Therefore, in the thermodynamic study, the complex, arbitrarily written as Pa−DTPA, can correspond to Pa(DTPA) or PaO(H_2DTPA) which are equivalent according to Rydberg's formalism.[17,18]

Determination of Formation Constants. The determination of stability constant of Pa−DTPA has been conducted in two steps:

i. Conditional constant β_{cond} is related to eq 2. In this equation, DTPA stands for the chelating agent regardless of its chemical form. Charges are therefore omitted. The β_{cond} values

Table 2. Equilibrium Constants Relative to Successive Dissociation of $H_{8-i}DTPA$ with $1 \le i \le 7$

I (M)	T (°C)	pK_{a_1}	pK_{a_2}	pK_{a_3}[a]	pK_{a_4}[b]	pK_{a_5}[c]	pK_{a_6}[d]	pK_{a_7}[e]
3	25		2.15[f]	2.19	2.78	4.17	8.37	9.58
1	25	0.80[g]	1.20[g]	2.13	2.73	4.10	8.36	9.52
	37	0.80[g]	1.20[g]	2.12	2.73	4.17	8.53	9.70
	50	0.80[g]	1.20[g]	2.11	2.74	4.25	8.71	9.88
0.5	25	1.16[h]	1.41[h]	2.16	2.80	4.20	8.51	9.71
	37	1.16[h]	1.41[h]	2.15	2.83	4.25	8.68	9.90
	50	1.16[h]	1.41[h]	2.14	2.86	4.31	8.85	10.10
0.25	25	1.34[h]	1.52[h]	2.20	2.89	4.34	8.71	9.95
	37	1.34[h]	1.52[h]	2.19	2.91	4.38	8.86	10.12
	50	1.34[h]	1.52[h]	2.18	2.93	4.43	9.01	10.28
0.1	25	1.45[i]	1.58[i]	2.27	3.02	4.54	8.98	10.29
	37	1.45[i]	1.58[i]	2.26	3.04	4.58	9.12	10.44
	50	1.45[i]	1.58[i]	2.25	3.05	4.62	9.26	10.59

[a]Values of uncertainties at 2σ: = 0.01. [b]Values of uncertainties at 2σ: = 0.05. [c]Values of uncertainties at 2σ: = 0.05. [d]Values of uncertainties at 2σ: = 0.03. [e]Values of uncertainties at 2σ: = 0.02. [f]Values of uncertainties at 2σ: = 0.04. [g]Values of uncertainties at 2σ: = 0.2. [h]Values of uncertainties at 2σ: = 0.25. [i]Values of uncertainties at 2σ: = 0.15.

are deduced from the variations of (D/D_0-1) as a function of the total DTPA concentration for each ionic strength and temperature investigated. In the case of experiments performed with $[H^+] = 0.01$ M, hydrolysis of Pa(V), characterized by the equilibrium constant K_2^{Hyd}, has been taken into account, and the slope of the linear variations $(D_0/D-1)$ has been determined according to eq 3.

$$Pa^V + DTPA \overset{\beta_{cond}}{\rightleftharpoons} Pa{-}DTPA \tag{2}$$

$$\frac{D_0}{D} - 1 = \frac{[H^+]}{[H^+] + K_2^{Hyd}} \cdot \beta_{cond} \cdot C_{DTPA} \tag{3}$$

ii. Apparent formation constant β_{app} related to equilibrium 4 involves free $DTPA^{5-}$ concentration and is deduced from β_{cond} according to eq 5

$$PaO(OH)^{2+} + DTPA^{5-} + 3H^+ \overset{\beta_{app}}{\rightleftharpoons} Pa{-}DTPA + 2H_2O \tag{4}$$

$$\beta_{app} = \alpha \times \beta_{cond} \times [H^+]^{-3} \tag{5}$$

where α stands for the inverse of the molar fraction of $DTPA^{5-}$ according to eq 6.

$$\begin{aligned} \alpha &= \frac{C_{DTPA}}{[DTPA^{5-}]} \\ &= 1 + 10^{pK_{a_7}}[H^+] + 10^{pK_{a_6}+pK_{a_7}}[H^+]^2 + ... \\ &\quad + 10^{pK_{a_1}+...+pK_{a_7}}[H^+]^7 \end{aligned} \tag{6}$$

In eq 4, Pa(V) is written under its predominant form $PaO(OH)^{2+}$, whereas the two hydrolyzed species, $PaO(OH)^{2+}$ and $PaO(OH)_2{}^+$, are taken into account in the fitting of extraction curves (eq 3). Moreover, the replacement of Pa(DTPA) by the species $PaO(H_2DTPA)$ would only lead to a difference in the number of water molecules ($PaO(OH)^{2+}$ + $DTPA^{5-}$ + $3H^+$ ↔ $Pa(H_2DTPA)$ + H_2O). All equations are therefore valid for both complexes if $PaO(OH)^{2+}$ is considered as initial species.

Calculation of α requires values of acid dissociation constants K_{a_i} of DTPA (eq 7) at the ionic strength and temperature investigated.

$$H_{8-i}DTPA^{(3-i)+} \overset{K_{a_i}}{\rightleftharpoons} H_{7-i}DTPA^{(2-i)+} + H^+ \tag{7}$$

The values used in this work are reported in Table 2, whereas method and models used for their calculations are described in the Experimental Section.

Figure 4 illustrates the variations of D of Pa(V) as a function of C_{DTPA} for different temperatures. A decrease in D values with increasing temperature is observed with a difference of about 2 orders of magnitude between the upper and the lower temperature. This effect is similar to the one observed on Pa(V) complexation in sulfate media.[6]

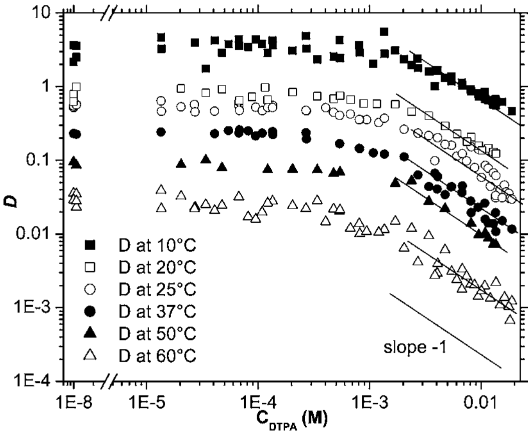

Figure 4. Distribution coefficients of Pa(V) as a function of total DTPA concentration at $\mu = 3$ M, $C_{TTA} = 0.05$ M, and $[H^+] = 0.25$ M for different values of temperature.

The variations of $(D_0/D)-1$ and the corresponding adjustment are illustrated in Figure 5 for $\theta = 25$ °C and $\mu = 0.1$ M. The procedure was repeated for different ionic strengths and temperatures, leading to a set of apparent formation constants β_{app} that are listed in Table 3.

It appears that the stability constants related to the formation of the Pa−DTPA complex increase with the temperature. On the other hand, these stability constants seem to increase from $\mu = 1$ M to $\mu = 0.1$ M.

Standard Thermodynamic Data. The stability constants of the formation of Pa−DTPA at $\mu = 0$ were determined using eq 8 leading to

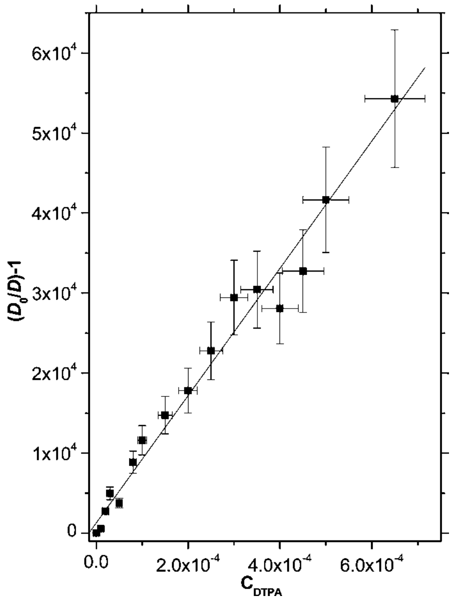

Figure 5. Fit example: $((D_0/D)-1)$ as a function of total DTPA concentration at μ = 0.1 M, θ = 25 °C, $[H^+]$ = 0.01 M, and C_{TTA} = 0.05 M.

$$\log \beta_{app} = \log \beta^0_{app} - 32\cdot D_{DH}(I_m) - \Delta\varepsilon\cdot I_m \qquad (8)$$

where $\Delta\varepsilon = -\varepsilon(PaO(OH)^{2+},ClO_4^-) - \varepsilon(Na^+,DTPA^{5-}) - 3\cdot\varepsilon(H^+,ClO_4^-)$. $\varepsilon(H^+, ClO_4^-)$ = 0.14 ± 0.02 at 25 °C and is supposed to be constant on the range of temperature studied.[40] $\varepsilon(PaO(OH)^{2+}, ClO_4^-)$ was determined in a previous study.[23,41] These adjustments lead to the stability constants listed in Table 4 for μ = 0.

Standard thermodynamic data were determined with the stability constants obtained at μ = 0. The linear variations of log β^0 as a function of $1/T$ (Figure S3) allow the determination of the following parameters: $\Delta G^0_{298.15K} = -179 \pm 10$ kJ·mol^{-1}, $\Delta H^0 = 86 \pm 5$ kJ·mol^{-1}, and $\Delta S^0 = 886 \pm 15$ J·mol^{-1}·K^{-1}.

These values indicate that the complex Pa–DTPA is very stable, and its formation reaction is endothermic. The unfavorable enthalpic contribution is counterbalanced by a strong entropic one. Since complexation involves dehydration and cation-ligand interactions, the positive enthalpy variation means, in the case of $PaO(H_2DTPA)$ that the cleavage of the bounds reagents-water (endothermic) prevails over the formation of metal–ligands bonds (exothermic).[42–44] If the complex is Pa(DTPA), the breaking of the mono-oxo bond takes even more energy that is not fully compensated by the formation of the new Pa–ligand bonds.

If the complexation of Pa(V) with DTPA occurs without the breaking of Pa═O, the positive entropic contribution shows that the disruption of the water structure around cation and ligand is not counterbalanced by the new structure of water molecules around the chelate. These values of entropy and enthalpy, both positive, suggest that dehydration governs the complexation.[42–44] However, the entropic variation relative to the formation of Pa–DTPA is three times higher than the ones relative to the formation of $PaO(SO_4)_3^{3-}$ and $PaO(C_2O_4)^{3-}$. This high value of ΔS can be assumed to reflect a higher disruption caused by the breaking of Pa═O and a different ordering around "Pa^{5+}". Unfortunately, there are no thermodynamic data on the complexation of Pa(V) with fluoride ions that could allow a comparison with a system involving the breakage of the mono-oxo bond.

Table 4. Stability Constants of Pa–DTPA for μ = 0 and Corresponding $\Delta\varepsilon$ Parameters at Different Temperatures

	25 °C	37 °C	50 °C
log β^0	31.2 ± 0.2	31.9 ± 0.2	32.4 ± 0.2
$\Delta\varepsilon$	−0.65 ± 0.04	−1.06 ± 0.25	−1.37 ± 0.23

■ DISCUSSION

Thermodynamic Data. Since DFT calculations alone cannot be used to demonstrate unambiguously the structure of the Pa–DTPA complex, discussion is focused on the two possible complexes: Pa(DTPA) (with or without additional water molecule in the Pa coordination sphere) and $PaO(H_2DTPA)$. Both complexes can be formed according to eq 4. For tentative comparison purposes, the formation constants of An–DTPA complexes (involving the form $DTPA^{5-}$) are given in Table 5. According to the literature, regardless of the oxidation state, the complexation of actinides by DTPA leads to the formation of (1:1) complexes.[8–11,27,29–32,34–36,45–54] There is no evidence of complexes formed with more than one DTPA molecule, although ternary complexes have been observed with other polyaminopolycarboxylic acids, especially EDTA.[10]

As reported in Table 5, An(IV) and An(III) form very strong complexes with DTPA: log β values are between 27 and 30 for An(IV)–DTPA complexes and between 21 and 25 for An(III)–DTPA ones. Moreover, values of stability constants increase along the actinide series, i.e. with decreasing of the metal ionic radius. This is in keeping with the predominantly electrostatic interactions between hard acceptor (An) and hard donor (O). The stability constants of Np(V) and U(VI) are smaller than the ones of An(IV) and An(III) by more than 10 orders of magnitude. For a given ligand without steric constraint, the stability of the complexes follows usually the order $An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+}$. This sequence reflects the variation of the effective charge on the acceptor actinide atom.[33] The strength of complexation by DTPA follows the order $An^{4+} > An^{3+} \gg AnO_2^{2+} > AnO_2^{+}$. This can be related to steric constraints due to both metal (actinyl moiety) and ligand (spatial arrangement of donor atoms and size of chelate rings).

With regards to protactinium, it is not possible to make a direct comparison with values in Table 5 since the initial form of Pa(V) is $PaO(OH)^{2+}$, whereas other actinides are considered as aquo ions. Moreover, our experimental and theoretical

Table 3. Apparent Formation Constants of the Pa–DTPA Complex at Different Temperatures and Ionic Strengths (in Molar Scale); $[H^+]$ = 0.01 M, C_{TTA} = 0.05 M

μ	1 M	0.5 M	0.25 M	0.1 M
25 °C	25.34 ± 0.12	25.96 ± 0.10	26.74 ± 0.11	27.79 ± 0.10
37 °C	25.69 ± 0.12	26.72 ± 0.11	27.45 ± 0.12	28.45 ± 0.10
50 °C	26.38 ± 0.13	27.22 ± 0.11	27.90 ± 0.14	28.84 ± 0.12

Table 5. Stability Constants of An(DTPA) Complexes Available in the Literature, An(HDTPA) Complexes Are Not Included

M^{n+}	I (mol·L^{-1})	T (°C)	log β_{app}	ref
Th^{4+}	0.5	20	26.64 ± 0.03	8
	0.1 KNO_3	25	28.80 ± 0.10	45
	1 NaCl/HCl	25	29.6 ± 1.0	52
U^{4+}	1 HNO_3		29.90	46
	1 NaCl/HCl	25	31.8 ± 0.1	52
Np^{4+}	1 $HClO_4/NH_4Cl$		29.79 ± 0.07	30
	1 $NaClO_4$	25	30.33 ± 0.12	47
	0.5 $NaClO_4$	20	29.29 ± 0.02	47
	1 HNO_3		30.50	46
	1 NaCl/HCl	25	32.3 ± 0.1	52
Pu^{4+}	1 $HClO_4/NH_4Cl$		29.38 ± 0.1	32
	0.5	20	29.49 ± 0.10	9
	1 HNO_3		31.4	46
	1 NaCl/HCl	25	33.67 ± 0.02	52
Pa(V)	0.1 Na/$HClO_4$	25	27.79 ± 0.12	p.w.
	1 Na/$HClO_4$	25	25.34 ± 0.12	p.w.
Pu^{3+}	1 NH_4Cl		21.20	31
	1 KCl	25	21.47 ± 0.01	48
	1 KCl	25	20.58 ± 0.04	52
Am^{3+}	0.1 NH_4ClO_4	25	22.92	53
	0.1	25	22.74	27
	0.1 NH_4ClO_4	25	24.03	54
	0.1 NH_4ClO_4	25	24.23 ± 0.51	29
	1 NH_4Cl		21.3	31
	0.5	20	22.09 ± 0.05	49
	0.1 NaCl	25	23.45 ± 0.18	50
	0.1 Na/HCl	25	23.1 ± 0.7	11
Cm^{3+}	0.1 NH_4ClO_4	25	22.99	53
	0.1 KNO_3	25	22.83	27
	0.1 NH_4ClO_4	25	24.32 ± 0.41	29
	1 NH_4Cl		21.4	31
	0.5	20	22.85 ± 0.08	51
	0.1 NaCl	25	23.53 ± 0.18	50
	0.1 Na/HCl	25	23.1 ± 0.5	11
Bk^{3+}	0.1 NH_4ClO_4	25	22.79	53
Cf^{3+}	0.1 NH_4ClO_4	25	22.57	53
	0.1 NH_4ClO_4	25	25.19 ± 0.26	29
	0.1 NaCl	25	23.95 ± 0.14	50
	0.1 Na/HCl	25	23.7 ± 0.4	11
UO_2^{2+}	3 $NaClO_4$	25	13.63 ± 0.02	36
	0.7 NaCl	25	11.80 ± 0.01	35
NpO_2^{+}	0.05 NH_4Cl		10.83 ± 0.03	30

studies do not allow for discrimination between $PaO(H_2DTPA)$ and Pa(DTPA).

If the complex is $PaO(H_2DTPA)$, its formation may be divided in two steps, according to

$$PaO(OH)^{2+} \xrightarrow{\text{Step 1a}(1/K_1^{Hyd})} PaO^{3+} \xrightarrow{\text{Step 2a}(\beta^*)} PaO(H_2DTPA) \qquad (9)$$

Step 1a corresponds to a dehydration process (inverse hydrolysis reaction) and step 2a to the complexation with DTPA such as reactions in Table 5 for the other actinides. The experimentally determined value β_{app} corresponds to the product of β^* and $1/K_1^{Hyd}$.

If the complex is Pa(DTPA), then an additional step has to be considered: the breaking of Pa═O (Step 2b in eq 10).

$$PaO(OH)^{2+} \xrightarrow{\text{Step 1b}(1/K_1^{Hyd})} PaO^{3+} \xrightarrow{\text{Step 2b}(1/K_0^{Hyd})} Pa^{5+} \xrightarrow{\text{Step 3b}(\beta^*)} PaDTPA \qquad (10)$$

According to eqs 9 and 10, the initial form $PaO(OH)^{2+}$ results from the hydrolysis of PaO^{3+} which is assumed to exist in concentrated perchloric acid. In the first theoretical approach on Pa(V) species in noncomplexing medium indeed, Toraishi et al. have shown that mono-oxo cation is more stable than the dioxo one and that $PaO(H_2O)_6^{3+}$ may coexist with $PaO(OH)(H_2O)_5^{2+}$ in strong acidic solution.[55] Unfortunately, the hydrolysis constant of PaO^{3+} is not known as well as that of Pa^{5+}, and they could not be estimated by means of DFT calculations. Nevertheless, some qualitative information may be deduced from eqs 9, 10, and Table 5.

The formation constant of $PaO(H_2DTPA)$ from the initial species PaO^{3+} (β^*) is expected to be higher than 25−28, since log $\beta^*(PaOH_2DTPA)$ = log β_{app} + log K_1^{Hyd} (eq 9). This value is therefore higher than those corresponding to actinide ions bearing the same global cationic charge +3. With regards to the complex Pa(DTPA), its formation constant starting from the hypothetical Pa^{5+} appears to be much higher than those corresponding to An^{4+} (log $\beta^*(PaDTPA)$ = log β_{app} + log K_1^{Hyd} + log K_0^{Hyd}). Under the assumption that the complex may be Pa(DTPA), the strength of complexation would follow the order $An^{5+} > An^{4+} > An^{3+}$ in agreement with the strength of electrostatic interaction.

The stability constant of Pa−DTPA in Table5 can be compared to the formation constant of other Pa complexes starting from $PaO(OH)^{2+}$. For instance, the complexation of Pa(V) by sulfate and oxalate ions has been proved to occur without the cleavage of the single oxo bond but with the departure of the hydroxyl. The three successive formation constants are 7.4−7−5 and 1.7−2.9−2.6 for oxalate and sulfate systems, respectively. The cumulative formation constants of $PaO(C_2O_4)_3^{3-}$ and $PaO(SO_4)_3^{3-}$ equal 19.1 and 7.2, respectively, values much lower than that of Pa−DTPA. The stability of Pa species could be enhanced by the breaking of the oxo bond that allows a better availability of coordination sites. In the system Pa(V)−HF, the breaking of the single oxo bond occurs after the coordination of Pa by 4 or 5 fluoride ions. The complexation of Pa(V) by DTPA could occur in the same way: due to the flexibility of DTPA, the formation of $Pa-O_{DTPA}$ and $Pa-N_{DTPA}$ bonds could involve the coordinating atoms of DTPA successively, leading to a progressive weakening of the single oxo bond up to its cleavage, but this needs to be confirmed by attempting new XAS measurements. The thermodynamic study performed at tracer scale should also be extended to higher Pa concentration, the formation of polymer being perhaps favored by the presence of the mono-oxo bond if present in the complex.

Structural Data. To the best of our knowledge, there is no experimental structure data of actinides−DTPA complexes available in the literature. Only structure data on Am and Cm−DTPA complexes determined by DFT calculations are available.[11,38] However, crystal structure data on lanthanides−DTPA (for Eu, Gd, Dy, Ho, Er, and Yb) as well as structure data in solution (for Gd) or deduced from theoretical calculations (for Nd and Eu) are available.[38,39,56−60] Although protonated complexes $Ln^{III}HDTPA^-$ and $An^{III}HDTPA^-$ have been observed, present discussion is limited to nonprotonated ones.

In Ln^{III}DTPA complexes, DTPA coordinates to the lanthanide ion with 5 carboxylate oxygen and 3 amine nitrogen atoms, the inner sphere being completed by another oxygen atom coming from a water molecule. Based on the literature available for Gd and Yb, there is no significant influence of the oxygen completing the inner sphere on the mean values of the distance Ln−O_{DTPA}.[56,60] Along the lanthanide series, from Nd to Yb, the average distance Ln−O_{DTPA} decreases from 2.44 to 2.34 Å, and the distance Ln−N decreases from 2.81 to 2.61 Å. Variation of the bond distances Ln−O_{DTPA} as a function of the inverse of ionic radius is illustrated in Figure 6 considering a coordination number equal to 9. The distances available for Am and Cm have been included as well as calculated Pa−O_{DTPA} distances in the two possible complexes Pa(DTPA)H_2O and PaO(H_2DTPA) (Table 1). Effective ionic radii have been taken from refs 61 and 62 except for PaO(H_2DTPA). In that case, the ionic radius was calculated by using the mean value of Pa−O_{ligand} distances observed in $PaO(C_2O_4)_3^{3-}$ and $PaO(SO_4)_3^{3-}$ and the ionic radius of O^{2-} available in the literature.[4,5,61]

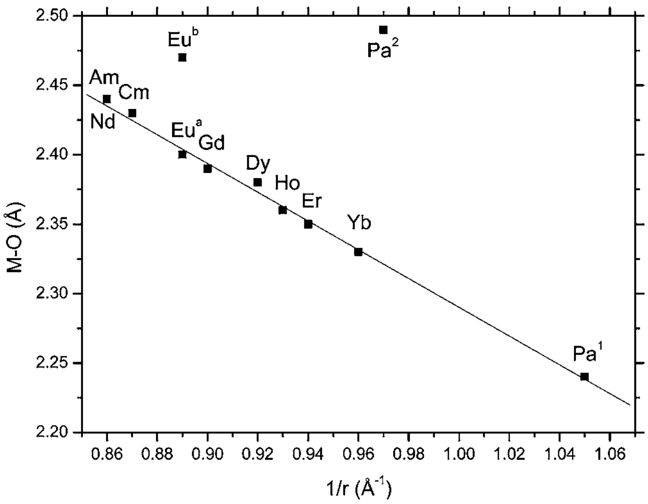

Figure 6. Values of the M−O_{DTPA} distances in Pa(DTPA)H_2O, structure 3 of PaO(H_2DTPA), Ln(DTPA)H_2O^{2-}, Am(DTPA)H_2O^{2-}, and Cm(DTPA)H_2O^{2-} as a function of 1/*r* where *r* is the ionic radius of Pa^V, Ln^{III}, Am^{III}, and Cm^{III} for a coordination number of nine. a and b refer to refs 58 and 39, respectively, while 1 and 2 refer to Pa(DTPA)H_2O and PaO(H_2DTPA), respectively.

One could notice that the mean value of Eu−O_{DTPA} obtained by DFT calculations by Tian et al. differs significantly from the ones observed in solid state.[39,60] However, according to the work of Bénazeth et al. it seems that the distances in Gd(DTPA)H_2O^{2-} observed in solution are quite similar to the ones observed in solid state.[56] Moreover, the work of Bridges et al. shows a really good agreement between Nd^{III}−O_{DTPA} distances obtained experimentally and by DFT calculations.[38] The discrepancy about the value determined by Tian et al. could be explained by the fact that DFT calculations have been performed in the gas phase by using a different functional.

It appears that the mean Pa−O_{DTPA} distance in Pa(DTPA)H_2O is in good agreement with Ln−O_{DTPA} ones. Therefore, it can be assumed that the M−O bond is purely ionic due to the regular decrease observed as a function of 1/*r*. On the other hand, the mean Pa−O_{DTPA} distance from structure 3 of PaO(H_2DTPA) does not fit with the variation of the Ln−O_{DTPA} ones. This observation could indicate that the most probable structure of the Pa(V)−DTPA complex should be Pa(DTPA)H_2O.

■ CONCLUSION

In order to bypass the strong tendency of Pa(V) toward polymerization, the thermodynamic study of the complexation of Pa(V) by DTPA was performed at tracer scale by using solvent extraction. Solvent extraction experiments on the Pa−DTPA system revealed the formation of a complex with (1:1) stoichiometry. This species is neutral as indicated by capillary electrophoresis. Data analysis was performed based on the formation of the neutral Pa(V)−(DTPA) complex from $PaO(OH)^{2+}$. In order to determine standard thermodynamic data, the experimental stability constants were converted to an ionic strength of $\mu = 0$ by using the SIT methodology. The formation of Pa−DTPA was found to be endothermic but counterbalanced by a strong entropic contribution.

DFT calculations have been performed in order to determine the most probable formula of the Pa(V)−DTPA complex, which could be either Pa(DTPA) or PaO(H_2DTPA) including possibly one water molecule in the coordination sphere. The DFT calculations revealed that both structures are stable, the energy difference being not significant to allow one to discriminate definitely between the two structures, but whatever the complex form, all the donor atoms of DTPA (5 carboxylic oxygen and 3 nitrogen atoms) are involved in the coordination of Pa.

■ EXPERIMENTAL SECTION

Samples Preparation. *Isotope 231.* The 231 isotope of protactinium comes from a stock available at the Nuclear Physic Institute of Orsay. Due to the accumulation of the decay products ^{227}Ac, ^{227}Th, and ^{223}Ra, protactinium was purified from its daughters by ion-exchange chromatography. The efficiency of purification was followed by γ-spectroscopy, as already described in previous papers.[4,6]

The purified Pa solution was stored in 1 mL HF 1 M/HCl 8 M. For CE-ICP-MS measurements, aliquots of this solution were evaporated to dryness in Teflon crucibles, and the residue was taken up in concentrated HCl. This procedure was conducted at least eight times in order to ensure the elimination of fluoride ions that behave as strong ligand toward Pa(V). For capillary electrophoresis, a residue corresponding to 200 Bq was taken up with 500 μL of 8 M $HClO_4$. An aliquot of that freshly prepared solution was then injected in an aqueous $NaClO_4$/$HClO_4$/H_5DTPA solution leading to final concentrations of 0.75 M $NaClO_4$, 0.25 M $HClO_4$, 10^{-2} M H_5DTPA, and 2.65×10^{-7} M Pa(V). That solution was then sent to the CEA of Bruyères-le-châtel and analyzed two weeks after sample preparation by CE-ICP-MS.

Isotope 233. The isotope ^{233}Pa was produced by neutron irradiation of thorium at the Osiris reactor of CEA Saclay. The whole procedure is described in a previous article.[6]

CE-ICP-MS Experiments. The capillary electrophoresis system (Beckman Coulter P/ACE MDQ), the coupled mass spectrometer (VG Elemental), and the micronebulizer (Mira Mist CE) are described elsewhere.[63]

Background electrolytes (BGE) were prepared from weighted amounts of H_5DTPA (Aldrich, > 99%) dissolved in deionized water (Millipore, Alpha-Q, 18.2 MΩcm) to get a final concentration of 10^{-2} M H_5DTPA. Samples were prepared by mixing Pa(V) stock solution, the BGE, and 0.2 μL of DMF (BDH, AnalaR ≥ 99.5%). The concentration of Pa(V) in the sample was about 10^{-8} M.

Before each separation, the capillary was washed with BGE during 5 min at 20 psi. Separations were completed within 15 min. Sample injections are carried out hydrodynamically at 1 psi during 5 s. To avoid clogging, the separations were performed at −3 kV and at constant pressure of 0.8 psi. The voltage value is chosen with respect to the Ohm law.

Solvent Extraction Experiments. The initial aqueous phase consists of a mixture of three solutions: $NaClO_4$, $HClO_4$, and the ligand DTPA introduced in its acid form H_5DTPA. Each aqueous phase is prepared starting from concentrated solutions of the individual components. Sodium perchlorate salt (Fluka, 99%) as well as perchloric acid (Aldrich, 70%) and diethylenetriaminepentaacetic acid (Sigma-Aldrich, >99%) were dissolved/diluted in deionized water (18.2 MΩcm). Their concentrations were determined by gravimetry ($NaClO_4$) and by pH titration using NaOH solution ($HClO_4$ and H_5DTPA). The organic phase was prepared according to ref 5 just prior to use by dissolving the appropriate amount of chelatant 2-thenoyltrifluoroacetone (TTA, Aldrich, 99%) in its hydrate form into toluene (FISHER, 99.99%). Toluene used as diluent was pre-equilibrated with the corresponding aqueous phase for three days.

The distribution coefficient D of Pa(V) in the system TTA/toluene/H_2O/$NaClO_4$/$HClO_4$/H_5DTPA was calculated according to eq 11, where A_{org} and A_{aq} refer to the gamma activity of ^{233}Pa in the organic and aqueous phases, respectively. The corresponding aqueous and organic phases were measured directly one after another. Since the time elapsed between the measurement of two phases did not exceed a few hours, the decay of ^{233}Pa was not taken into account.

$$D = \frac{A_{\text{org}}}{A_{\text{aq}}} \qquad (11)$$

Experimental uncertainties have been calculated by taking into account the systematic uncertainties that may occur when preparing the solution as well as random uncertainties associated with gamma activity measurements. It should be noted that any uncertainty associated with the volume lead to uncertainties in free H^+ concentration and may have a strong influence on D, because of acid−base properties of the extractant and the ligand.

Kinetics of TTA partition between both phases have been proved to be slow due to the keto−enol equilibria in aqueous and organic phases.[21,64] At 25 °C, the equilibrium is achieved in 26 h (at least 90% of the distribution equilibrium value) in the absence as well as in the presence of ligand like sulfate, oxalate, and DTPA in aqueous phase.[6,41] Kinetics of Pa(V) partition illustrated in Figure S4 confirms that the rate limiting step is the partition of TTA. Moreover, in order to check the equilibrium reversibility of Pa(V) distribution, a study was performed by analyzing direct extraction (Pa(V) initially in aqueous phase) and back extraction (Pa(V) initially in organic phase) for different values of DTPA concentration. Coherent values of D obtained in direct and back extractions (Figure S5) indicate that a contacting time of 26 h at 25 °C is sufficient to achieve the partition equilibrium of extractant and aqueous Pa(V).

DFT Calculations. As no structural data on the Pa(V)−DTPA complexes are available, structure parameters of the well-known structure of Gd^{III}(DTPA) were used as starting model.[56] Structures were optimized using the density functional theory (DFT) approach as implemented in the Gaussian03 package.[65] Calculations were performed using the hybrid B3LYP functional.[66] Energy-adjusted relativistic effective core potentials (RECPs) developed by Kuchle et al. were used (60 core electrons for Pa) with its associated basis set to describe protactinium valence electron density (14s13p10d8f) contracted in [10s9p5d4f].[67,68] A 6-31+G* basis set was used for others. To take into account part of the solvent effect, the solvation was introduced using a dielectric continuum model of permittivity $\varepsilon_0 = 80$. The conductor-like polarizable continuum model (CPCM) implemented in Gaussian was used.[69]

Acid−Base Equilibria of DTPA. The determination of stability constants of the complexes Pa/DTPA requires the values of the acid dissociation constants K_{a_i} of the ligand DTPA (eq 7) at the ionic strength and temperature of the investigated system. With 3 amine groups and 5 carboxylic groups the ligand DTPA can be involved in 8 equilibria characterized by the constant K_{a_i} (eq 12).

$$K_{a_i} = \frac{[H_{7-i}DTPA^{(2-i)+}][H^+]}{[H_{8-i}DTPA^{(3-i)+}]} \qquad (12)$$

In the present work, only equilibria from $i = 1$ to 7 have been taken into account. Dissociation constants K_{a_3} to K_{a_7} are given in the literature at infinite dilution and were adjusted to our ionic strength using SIT methodology (eq 13)[40,70]

$$pK_{a_i} = pK^0_{a_i} - \Delta z_i^2 \times D_{\text{DH}}(I_{\text{m}}, \theta) + \Delta\varepsilon_i \times I_{\text{m}} \qquad (13)$$

where Δz_i^2 stands for the stoichiometric difference between the squared charges of the products and reactants, $\Delta\varepsilon_i$ stands for the SIT term, and D_{DH} stands for the Debye−Hückel coefficient. The temperature dependence of D_{DH} has been taken into account using OECD tabulated values.[70] Values of K_{a_1} and K_{a_2} are only available at specific ionic strength and were used at the ionic strength they were defined.[36,71−79]

Values of K_{a_1} and K_{a_2} are not defined at $\mu = 0.25$ M and $\mu = 0.5$ M. Therefore, values at these ionic strength were calculated by interpolation between $\mu = 0.1$ and 1 m assuming a linear variation of log $K_{a_i} + \Delta z_i^2$ as a function of the ionic strength in molal unit (SIT methodology).

Due to the lack of data concerning K_{a_1} and also the lack of thermodynamic data available at 3 M, acidity constants of DTPA at that ionic strength were not used to determine the stability constants of the formation of the Pa(DTPA) complex.

Enthalpy variations relative to the dissociation constants K_{a_3} to K_{a_7} of DTPA are available in the literature for ionic strength of 0.1 M, 0.5 M, and 1 M.[76−79]

Due to the lack of thermodynamic values for K_{a_1} and K_{a_2} and assuming that the associated enthalpy variations are close to the ones of K_{a_3}, K_{a_1} and K_{a_2} were regarded to be independent of temperature variations. Enthalpy values at $\mu = 0.25$ M are not available in the literature. Thus, acidity constants at that ionic strength were calculated at each temperature different from 25 °C by interpolation using the SIT methodology where log $K_{a_i} + \Delta z_i^2$ as a function of ionic strength is assumed to behave linearly. Accordingly, the SIT parameters $\Delta\varepsilon$ were assumed to be independent of temperature, and the values available at 25 °C were used.[40] The acidity constants at temperatures different from 25 °C were calculated using the Van't Hoff equation (eq 14), where T is the temperature in Kelvin.[80]

$$\log K(T) = \log K_{298.15} + \frac{\Delta H_{298.15}}{R{\cdot}\ln(10)} \cdot \left(\frac{1}{298.15} + \frac{1}{T}\right) \qquad (14)$$

■ ASSOCIATED CONTENT

Supporting Information

Variation of D values as a function of DTPA concentration for different concentrations of TTA, as a function of TTA concentration for different concentrations of DTPA, as function of time, as a function of DTPA concentration in direct and back extraction. Variation of log β^0 as a function of $1/T$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Brown, D.; Maddock, A. G. Analytical Chemistry. In *Progress in Nuclear Energy*; Pergamon Press: Oxford & New York, 1967; p 8-1.

(2) Muxart, R.; Guillaumont, R. Protactinium. In *Compléments au Nouveau Traité de Chimie Minérale*; Masson; Paris, 1974.

(3) Myasoedov, B.; Kirby, H. W.; Tananaev, I. G. Protactinium. In *The Chemistry of the Actinide and Transactinide Elements*; Springer: Netherlands, 2006.

(4) Le Naour, C.; Trubert, D.; Di Giandomenico, M. V.; Fillaux, C.; Den Auwer, C.; Moisy, P.; Hennig, C. *Inorg. Chem.* **2005**, *44*, 9542.

(5) Mendes, M.; Hamadi, S.; Le Naour, C.; Roques, J.; Jeanson, A.; Den Auwer, C.; Moisy, P.; Topin, S.; Aupiais, J.; Hennig, C.; Di Giandomenico, M. V. *Inorg. Chem.* **2010**, *49*, 9962.

(6) Di Giandomenico, M. V. Ph.D. Thesis, Université Paris Sud, Orsay, France, 2007

(7) Trubert, D.; Le Naour, C.; Jaussaud, C.; Mrad, O. *J. Solution Chem.* **2003**, *32*, 505.

(8) Piskunov, E. M.; Rykov, A. G. *Radiokhimiya* **1972**, *14*, 260.

(9) Piskunov, E. M.; Rykov, A. G. *Radiokhimiya* **1972**, *14*, 332.

(10) Choppin, G. R.; Thakur, P.; Mathur, J. N. *Coord. Chem. Rev.* **2006**, *250*, 936.

(11) Leguay, S.; Vercouter, T.; Topin, S.; Aupiais, J.; Guillaumont, D.; Miguirditchian, M.; Moisy, P.; Le Naour, C. *Inorg. Chem.* **2012**, *51*, 12638.

(12) Ansoborlo, E.; Amekraz, B.; Moulin, C.; Moulin, V.; Taran, F.; Bailly, T.; Burgada, R.; Hengé-Napoli, M. H.; Jeanson, A.; Den Auwer, C.; Moisy, P. *C. R. Chim.* **2007**, *10*, 1010.

(13) Taylor, D. M.; Stradling, G. N.; Hengé-Napoli, M. H. *Radiat. Prot. Dosim.* **2000**, *87*, 11.

(14) Nilsson, M.; Nash, K. L. *Solvent Extr. Ion Exch.* **2007**, *25*, 665.

(15) Galateanu, I. *Can. J. Chem.* **1966**, *44*, 647.

(16) Shiokawa, T.; Kikuchi, M.; Omori, T. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 105.

(17) Rydberg, J. *Ark. Kemi* **1954**, *13*, 101.

(18) Adloff, J. P.; Guillaumont, R. *Fundamentals of Radiochemistry*; CRC Press: FL, 1993.

(19) Guillaumont, R.; Muxart, R.; Bouissières, G. Solvent extraction of hydroxo- and acido-complexes in the presence of a chelating agent. The phosphato- and trichloroaceto-complexes of pentavalent protactinium. In *Solvent Extraction Chemistry*; Dyrssen, D., Liljenzin, J. O., Rydberg, J., Eds.; Wiley: New York, 1967.

(20) Guillaumont, R. Ph.D. Thesis, Paris, France, 1966.

(21) Jaussaud, C. Ph.D. Thesis, Université Paris Sud, Orsay, France, 2003.

(22) Rydberg, J.; Sekine, T. *Principles and Practices of Solvent Extraction*; Rydberg, J., Musikas, C., Choppin, G. R., Eds.; Marcel Dekker: New York, 1992.

(23) Di Giandomenico, M. V.; Trubert, D.; Le Naour, C. *Radiochim. Acta* **2007**, *95*, 617.

(24) Bukhsh, M. N.; Flegenheimer, J.; Hall, F. M.; Maddock, A. G.; Ferreira de Miranda, C. *J. Inorg. Nucl. Chem.* **1966**, *28*, 421.

(25) Asprey, L. B.; Kruse, F. H.; Rosenzweig, A.; Penneman, R. A. *Inorg. Chem.* **1966**, *5*, 659.

(26) Brown, D.; Easey, J. F. *J. Chem. Soc. A* **1966**, 254.

(27) Lebedev, I. A.; Filimonov, V. T.; Shalinets, A. B.; Yakovlev, G. N. *Sov. Radiochem.* **1968**, *10*, 93.

(28) Moeller, T.; Thompson, L. C. *J. Inorg. Nucl. Chem.* **1962**, *24*, 499.

(29) Brandau, E. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 1177.

(30) Moskvin, A. I. *Radiokhimiya* **1971**, *13*, 570.

(31) Moskvin, A. I. *Radiokhimiya* **1971**, *13*, 575.

(32) Moskvin, A. I. *Radiokhimiya* **1971**, *13*, 641.

(33) Katz, J. J.; Seaborg, G. T.; Morss, L. R. *The Chemistry of Actinide Elements*, 2^{nd} ed.; Chapman and Hall: London, 1986.

(34) Overvoll, P. A.; Lund, W. *Anal. Chim. Acta* **1982**, *143*, 153.

(35) De Stefano, C.; Gianguzza, A.; Milea, D.; Pettignano, A.; Sammartano, S. *J. Alloys Compd.* **2006**, *424*, 93.

(36) Gandolfo, F.; Amorello, D.; Romano, V.; Zingales, R. *J. Chem. Eng. Data* **2011**, *56*, 2110.

(37) Gezahegne, W. A.; Hennig, C.; Tsushima, S.; Planer-Friedrich, B.; Scheinost, A. C.; Merkel, B. *Environ. Sci. Technol.* **2012**, *46*, 2228.

(38) Bridges, N. J.; Roy, L. E.; Klug, C. L. *Computation and Spectroscopic Investigation of the DTPA Complexes*; Savannah River National Laboratory Report, SRNL-TR-2012-00185; 2012.

(39) Tian, G.; Martin, L. R.; Zhang, Z.; Rao, L. *Inorg. Chem.* **2011**, *50*, 3087.

(40) Allard, B.; Banwart, S. A.; Bruno, J.; Ephraim, J. H.; Grauer, R.; Grenthe, I.; Hadermann, J.; Hummel, W.; Jakob, A.; Karapiperis, T.; Plyasunov, A. V.; Puigdomenech, I.; Rard, J. A.; Saxena, S.; Spahiu, K. *Modelling in Aquatic Chemistry*; OCDE: Paris, 1997.

(41) Mendes, M. Ph.D. Thesis, Université Paris Sud, Orsay, France, 2010.

(42) Choppin, G. R.; Strazik, W. F. *Inorg. Chem.* **1965**, *4*, 1250.

(43) Choppin, G. R.; Graffeo, A. J. *Inorg. Chem.* **1965**, *4*, 1254.

(44) Anderegg, G. *Adv. Mol. Relax. Interact. Processes* **1980**, *18*, 79.

(45) Kinard, W. F.; Grant, P. M.; Baisden, P. A. *Polyhedron* **1989**, *8*, 2385.

(46) Bonin, L. Ph.D. Thesis, Université Paris Sud, Orsay, France, 2008.

(47) Yoshida, Z.; Johnson, S. G.; Kimura, T.; Krsul, J. R. Neptunium. In *The Chemistry of the Actinide and Transactinide Elements*; Springer: Netherlands, 2006.

(48) Merciny, E.; Gatez, J. M.; Duyckaerts, G. *Anal. Chim. Acta* **1978**, *100*, 329.

(49) Piskunov, E. M.; Rykov, A. G. *Radiokhimiya* **1972**, *14*, 638.

(50) Topin, S. Ph.D. Thesis, Université Paris Sud, Orsay, France, 2009.

(51) Piskunov, E. M.; Rykov, A. G. *Radiokhimiya* **1972**, *14*, 641.

(52) Brown, M. A.; Paulenova, A.; Gelis, A. V. *Inorg. Chem.* **2012**, *51*, 7741.

(53) Baybarz, R. D. *J. Inorg. Nucl. Chem.* **1965**, *27*, 1831.

(54) Delle Site, A.; Baybarz, R. D. *J. Inorg. Nucl. Chem.* **1969**, *31*, 2201.

(55) Toraishi, T.; Tsuneda, T.; Tanaka, S. *J. Phys. Chem. A* **2006**, *110*, 13303.

(56) Bénazeth, S.; Purans, J.; Calbot, M. C.; Nguyen-van-Duong, M. K.; Nicolas, L.; Keller, F.; Gaudemer, A. *Inorg. Chem.* **1998**, *37*, 3667.

(57) Inomata, Y.; Sunakawa, T.; Howell, F. S. *J. Mol. Struct.* **2003**, *648*, 81.

(58) Liu, B.; Wang, Y. F.; Wang, J.; Gao, J.; Xu, R.; Kong, Y. M.; Zhang, L. Q.; Zhang, X. D. *J. Struct. Chem.* **2009**, *50*, 880.

(59) Inoue, M. B.; Inoue, M.; Fernando, Q. *Inorg. Chim. Acta* **1995**, *232*, 203.

(60) Hardcastle, K. I.; Botta, M.; Fasano, M.; Digilio, G. *Eur. J. Inorg. Chem.* **2000**, 971.

(61) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

(62) David, F. H.; Fourest, B. *New J. Chem.* **1997**, *21*, 167.

(63) Topin, S.; Aupiais, J.; Baglan, N.; Vercouter, T.; Vitorge, P.; Moisy, P. *Anal. Chem.* **2009**, *81*, 5354.

(64) Sekine, T.; Hokura, A.; Tanaka, I. *Anal. Sci.* **1996**, *12*, 747.

(65) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.;

Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.02*; Gaussian, Inc.: Wallingford, CT, 2004.

(66) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(67) Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1994**, *100*, 7535.

(68) Cao, X.; Dolg, M.; Stoll, H. *J. Chem. Phys.* **2003**, *118*, 487.

(69) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.

(70) Thakur, P.; Mathur, J. N.; Moore, R. C.; Choppin, G. R. *Inorg. Chim. Acta* **2007**, *360*, 3671.

(71) Lemire, R. J.; Fuger, J.; Nitsche, H.; Potter, P.; Rand, M. H.; Rydberg, J.; Spahiu, K.; Sullivan, J. C.; Ullman, W. J.; Vitorge, P.; Wanner, H. *Chemical Thermodynamics of Neptunium and Plutonium*; Elsevier, OCDE: Paris, 2001.

(72) Anderegg, G.; Arnaud-Neu, F.; Delgado, R.; Felcman, J.; Popov, K. *Pure Appl. Chem.* **2005**, *77*, 1445.

(73) Letkeman, P.; Martell, A. E. *Inorg. Chem.* **1979**, *18*, 1284.

(74) Mentasti, E.; Pelizzetti, E.; Saini, G. *J. Chem. Soc.* **1974**, 1944.

(75) Kragten, J.; Decnop-Weever, L. G. *Talanta* **1983**, *30*, 623.

(76) Mioduski, T. *Talanta* **1980**, *27*, 299.

(77) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum Press: New York, 1974; Vol. *1*.

(78) Gritmon, T.; Goedken, M.; Choppin, G. R. *J. Inorg. Nucl. Chem.* **1977**, *39*, 2021.

(79) Tian, G.; Rao, L. *Sep. Sci. Technol.* **2010**, *45*, 1718.

(80) Puigdomènech, I.; Rard, J. A.; Plyasunov, A. V.; Grenthe, I. *TDB-4. Temperature corrections to thermodynamic data and enthalpy calculations*; OCDE, Issy-les-Moulineaux: France, 1999.