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Thermodynamic Study of the Complexation of Trivalent Actinide and Lanthanide Cations by ADPTZ, a Tridentate N-Donor Ligand

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To better understand the bonding in complexes of f-elements by polydentate N-donor ligands, the complexation of americium(III) and lanthanide(III) cations by 2-amino-4,6-di-(pyridin-2-yl)-1,3,5-triazine (ADPTZ) was studied using a thermodynamic approach. The stability constants of the 1:1 complexes in a methanol/water mixture (75/25 vol %) were determined by UV–visible spectrophotometry for every lanthanide(III) ion (except promethium), and yttrium(III) and americium(III) cations. The thermodynamic parameters ($\Delta H°$, $\Delta S°$) of complexation were determined from the temperature dependence of the stability constants and by microcalorimetry. The trends of the variations of $\Delta G°$, $\Delta H°$, and $\Delta S°$ across the lanthanide series are compared with published results for other tridentate ligands and confirm strongly ionic bonding in the lanthanide–ADPTZ complexes. Comparison of the thermodynamic properties between the Am– and Ln–ADPTZ complexes highlights an increase in stability of the complexes by a factor of 20 in favor of the americium cation. This difference arises from a more exothermic reaction enthalpy in the case of Am, which is correlated with a greater degree of covalency in the americium–nitrogen bonds. Quantum chemistry calculations performed on a series of trivalent actinide and lanthanide–ADPTZ complexes support the experimental results, showing a slightly greater covalence in the actinide–ligand bonds that originates from a charge transfer from the ligand σ orbitals to the 5f and 6d orbitals of the actinide ion.

1. Introduction

The partitioning of long-lived α-emitting actinide elements (An) from other components of nuclear waste is one of the scenarios being seriously considered for the future management of nuclear wastes. In this scheme, the minor actinides (Np, Am, Cm) would be isolated from the spent nuclear fuel while the major actinides (U, Pu) would be recycled.[1,2] The minor actinides could then be transmuted into short-lived, easier-to-manage radionuclides by neutron irradiation. However, fission product lanthanides (Ln) with large neutron capture cross sections are abundant in spent nuclear fuels, and transmutation of the minor actinides will only be possible after separation of the minor actinides from the lanthanides. This separation is often difficult because of the high Ln/An molar ratio in wastes and the great chemical similarity of these two series of f-elements, which occurs because the lanthanides and transplutonium actinides both exist predominantly in their trivalent oxidation state in solution, the size of the An(III) and Ln(III) cations are very similar,[3] and both An(III) and Ln(III) cations are hard acids in the Pearson classification of “hard and soft acids and bases” (HSAB),[4] indicating that their chemistries are essentially determined by electrostatic and steric factors. Consequently, they tend to form very ionic compounds preferentially with oxygen-

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(1) Proceedings of the 5th OECD/NEA Information Exchange Meeting, Mol, Belgium, Nov 25−27, 1998.

(2) Madic, C.; Hudson, M. J.; Liljenzin, J. O.; Glatz, J. P.; Nannicini, R.; Facchini, A.; Kolarik, Z.; Odoj, R. New Partitioning Techniques for Minor Actinides. Final Report, EUR 19149, Nuclear Science and Technology, 2000.

(3) Rizkalla, E. N.; Choppin, G. R. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Eyring, L, Jr., Choppin, G. R., Lander, G. H., Eds.; Elsevier Science: New York, 1994; Vol. 18, p 529.

(4) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

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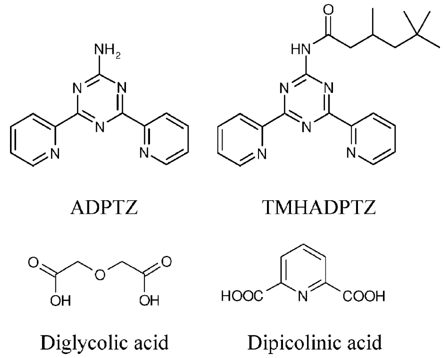
bearing molecules, and because the size and charge of the Ln(III) and An(III) ions are so similar, the bond strengths and thermodynamic parameters for formation of the complexes with oxygen-bearing ligands are very similar.

Nevertheless, it is possible to discriminate between the two series of ions because of a small difference in their affinities for softer donor ligands. Nitrogen or sulfur donor ligands are not considered as classical soft donor ligands on the Pearson HSAB scale, but they are softer than oxygen-donor ligands and show a modest preference for An(III) over Ln(III). This property can be exploited to design An/Ln group separation processes. For the sake of simplicity of expression, we will use the term “soft” to imply “softer than oxygen” in this paper. Polydentate nitrogen ligands can efficiently separate An(III) from Ln(III) by biphasic liquid−liquid extraction, even from nitric acid solutions.[5] Among this class of molecules, planar tridentate nitrogen ligands, such as 2,2′:6′,2″-terpyridine,[6] and its derivatives,[7] 2,4,6-tris(4-tert-butyl-2-pyridyl)-1,3,5-triazine[8] and 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine (BTP),[9,10] have been the most effective selective extractants for An(III) in preference to Ln(III).

Previous work on nitrogen-donor ligands hints that their selectivity for An(III) cations arises from a slightly greater degree of covalency in the bonds between the An ions and the N-donor atoms of the ligands.[11,12] Structural studies by X-ray diffraction of crystalline lanthanide(III) and uranium(III) complexes with polydentate N-donor ligands attributed the contraction in U−N distances as compared to the Ln−N distances to covalency.[13,14] DFT calculations suggest that the enhanced covalence in the bonds of the actinide complex is due to electron transfer from the 5f orbitals of U^{3+} to the lowest unoccupied π^* orbitals of the ligand.[14] Within a thermodynamic framework, such greater covalence should be reflected by a more exothermic bond formation.[15] Comparing the complexation of actinide(III) and lanthanide(III) ions having similar radii and hydration numbers by N-donor complexants, and assuming that the An(III)−N bonds are slightly more covalent than the Ln(III)−N bonds, the complexation enthalpy of the An complexes should be more exothermic or less endothermic, which is in either case more favorable. Studies of the thermodynamics of solvent extraction reactions with soft donors, Cyanex 301[16] or BTP,[17] have demonstrated a better extraction of Am(III) than of Eu(III) and enthalpic stabilization of the An complexes. However, to our knowledge, no experimental thermodynamic measurements directly support the hypothesized increased covalence in An−soft donor bonds in monophasic systems. The small difference in the enthalpy values measured for the complexation of Eu(III) and Cm(III) by EDTA was close to the experimental uncertainties,[18] and although the stability constants for the complexation of TPEN (*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine), a hexadentate nitrogen-donor ligand, are 100 times larger for the Am(III) complex as compared to the Sm(III) complex,[19] the enthalpy value for Am complexation was only estimated by assuming that the entropies of the samarium and americium complexes were similar.

Chart 1. Structures of ADPTZ, TMHADPTZ, Diglycolic Acid, and Dipicolinic Acid



Considering the small amount of thermodynamic data available in the literature to judge the relative enthalpies for the complexation of trivalent actinide and lanthanide cations with a soft donor ligand, the aim of the present study is thus to acquire a complete set of enthalpies and entropies for the complexation of these cations by 2-amino-4,6-di-(pyridin-2-yl)-1,3,5-triazine (ADPTZ), a nitrogen-donor ligand. This molecule is a good model because it presents the same coordination environment as the 4,6-di-(pyridin-2-yl)-2-(3,5,5-trimethylhexanoylamino)-1,3,5-triazine (TMHADPTZ), a selective extractant for actinide(III) cations.[20] Both ligands are depicted in Chart 1. To probe the metal−ligand interaction in these systems, the thermodynamic parameters (ΔG°, ΔH°, ΔS°) for the formation of ADPTZ complexes were measured for americium(III), yttrium(III), and all lanthanide cations (except promethium), in a homogeneous 75/25 vol % methanol/water solution. In such solutions, the cations are still primarily solvated by water molecules,[21] but ADPTZ is a strong enough complexant to displace some solvent molecules from the inner coordination sphere of the metal

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(5) Nash, K. L. *Solvent Extr. Ion Exch.* **1993**, *11*, 729.
(6) Hagström, I.; Spjuth, L.; Enarsson, A.; Liljenzin, J. O.; Skalberg, M.; Hudson, M. J.; Iveson, P. B.; Madic, C.; Cordier, P. Y.; Hill, C.; François, N. *Solvent Extr. Ion Exch.* **1999**, *17*, 221.
(7) Drew, M. G. B.; Iveson, P. B.; Hudson, M. J.; Liljenzin, J. O.; Spjuth, L.; Cordier, P.-Y.; Enarsson, A.; Hill, C.; Madic, C. *J. Chem. Soc., Dalton Trans.* **2000**, 821.
(8) Boubals, N.; Drew, M. G. B.; Hill, C.; Hudson, M. J.; Iveson, P. B.; Madic, C.; Russel, M. L.; Youngs, T. G. A. *J. Chem. Soc., Dalton Trans*. **2002**, 55.
(9) Kolarik, Z.; Müllich, U.; Gassner, F. *Solvent Extr. Ion Exch*. **1999**, *17*, 23.
(10) Kolarik, Z.; Müllich, U.; Gassner, F. *Solvent Extr. Ion Exch*. **1999**, *17*, 1155.
(11) Nash, K. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Eyring, L., Jr., Choppin, G. R., Lander, G. H., Eds.; Elsevier Science: New York, 1994; Vol. 18, p 197.
(12) Choppin, G. R. *J. Alloys Compd.* **2002**, *344*, 55.
(13) Berthet, J.-C.; Miquel, Y.; Iveson, P. B.; Nierlich, M.; Thuéry, P.; Madic, C.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans*. **2002**, 3265.
(14) Mazzanti, M.; Wietzke, R.; Pécaut, J.; Latour, J.-M.; Maldivi, P.; Remy, M. *Inorg. Chem*. **2002**, *41*, 2389.
(15) Ahrland, S. *Helv. Chim. Acta* **1967**, *50*, 306.
(16) Zhu, Y.; Chen, J.; Jiao, R. *Solvent. Extr. Ion Exch.* **1996**, *14*, 61.
(17) Charbonnel, M.-C.; Flandin, J.-L.; Giroux, S.; Presson, M.-T.; Madic, C.; Morel, J.-P. International Solvent Extraction Conference, Cape Town, South Africa, 2002; p 1154.
(18) Choppin, G. R.; Rizkalla, E. N.; Sullivan, J. C. *Inorg. Chem.* **1987**, *26*, 2318.
(19) Jensen, M. P.; Morss, L. P.; Beitz, J. V.; Ensor, D. D. *J. Alloys Compd.* **2000**, *303*−*304*, 137.
(20) Madic, C.; Lecomte, M.; Baron, P.; Boullis, B. *C. R. Phys. 3* **2002**, 797.
(21) Tanaka, F.; Kawasaki, Y.; Yamashita, S. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1083.

cations and soft enough to be selective for the actinides over the corresponding lanthanides.

Because these reactions involve metal, ligands, and solvent, the measured thermodynamic parameters contain potentially useful information about the interactions of all of these species. For reactions in aqueous solution with f-element cations, complexation enthalpies contain information about the breaking and formation of chemical bonds involving the metal ions, the ligand, and the solvent, with a large component reflecting most strongly the number, nature, and strength of metal−ligand bonds. Complexation entropies, on the other hand, measure the order in the system and primarily reflect the change in solvation between the uncomplexed and complexed states of the metal ion and ligands, as well as the binding sites of the ligands.[22] Therefore, a comparison of the thermodynamic parameters of the Ln− and Am−ADPTZ complexes can be used to assess possible differences in An(III) and Ln(III) bonding to aromatic nitrogen donors. Our results confirm, for the first time by a thermodynamic approach, an enhanced covalence in actinide−soft ligand bonds in homogeneous solutions. Such concrete demonstrations of this long-hypothesized effect will build a better understanding of this system and improve our ability to model the chemical bonding of f-element with soft donor ligands, especially later in the actinide series. To this end, we have also performed quantum chemistry calculations on some representative systems to probe the electronic nature of the metal−ligand bonds and examine the probable structures of the complexes formed.

2. Experimental Section

2.1. Solution Preparation. The ligand ADPTZ was prepared according to literature methods[23] and isolated with a purity greater than 99.5%. Stock solutions (7.5×10^{-4} M) of ADPTZ were prepared by dissolution of 47.3 mg in 250 mL of HPLC grade methanol (MeOH). Lanthanide chloride stock solutions were prepared by dissolution of 99.9% $LnCl_3 \cdot 6H_2O$ (Aldrich) in pure water. The Ln^{3+} concentration in each stock solution was measured using a Jobin-Yvon ICP-AES spectrometer against standard solutions of the lanthanide cations.

The americium used for the microcalorimetric experiments was purified from a ^{243}Am perchlorate solution (99.85 mol % Am-243, 0.14 mol % Am-241, 0.0066 mol % Cm-244) after two cycles of evaporation in concentrated perchloric acid. The americium was precipitated as Am(III) hydroxide, washed with water, and redissolved in dilute HCl. The Am concentration in the stock solution (0.0018 M) was measured by UV−visible spectrophotometry at 503.5 nm and liquid scintillation counting with α/β discrimination. A second americium stock solution for UV−visible spectrophotometry was prepared by dissolution of AmO_2 (99.96% mol % Am-241) in HCl followed by Am(III) purification using Dowex-50 cation-exchange resin. Am^{3+} in 0.1 M HCl was sorbed on the resin, washed several times with 0.1 M HCl, and eluted with 5 M HCl. Americium hydroxide was then precipitated, washed, and redissolved in dilute HCl. The Am^{3+} concentration in this stock solution (0.019 M) was measured by UV−visible spectrophotometry, and α- and γ-spectrometry.

For the lanthanide experiments, the samples were prepared by addition of weighed amounts of the ADPTZ and lanthanide stock solutions and of sufficient water and methanol to maintain a constant 71/29 mass % MeOH/H_2O ratio. The densities of the stock solutions and the samples were measured with an Anton Paar densimeter to transpose to the volumic proportions (corresponding to 75/25 vol %). For the americium experiments, it was not possible to weigh the americium aliquot, but accurate calibrated pipets were used and the volumes were corrected based on the lanthanide experiments to take into account the volumic contraction between water and methanol. The pH of the mixed solution was measured between 5 and 5.5 even for the most concentrated samples ($[Ln^{3+}] = 10^{-2}$ M), buffered by the ADPTZ solution. The pK_a's of ADPTZ, determined by UV-spectrophotometry in 75/25 vol % methanol/water, are lower than 3.5 ($pK_{a1} = 1.7$ and $pK_{a2} = 3.5$),[24] which ensure nearly complete deprotonation of the ADPTZ ligand in the samples. Background electrolytes were not added to the solutions to control the ionic strength of the solutions because trial runs indicated that interactions between ADPTZ and common alkali metal cations would skew the measured thermodynamic parameters. However, given the low concentration of the neutral ligand (3.75×10^{-5} or 5×10^{-4} M) and of the metal ions ($10^{-5}-10^{-2}$ M), the ratio of the solute activity coefficients was considered constant.

2.2. Spectrophotometric Studies. Spectrophotometric titrations of the lanthanides were carried out with a Cary 5 spectrophotometer between 200 and 400 nm by following the ligand $\pi-\pi^*$ absorption bands with increasing concentrations of the metal ion. Generally, seven samples with a constant concentration of ADPTZ were used with [Ln(III)]/[ADPTZ] ratios between 0 and 300 ($0 < [Ln] < 0.01$ M). Spectra were measured at different temperatures (every 5 °C from 5 to 55 °C) to determine the enthalpy and entropy of complexation using the van't Hoff relation:

$$\ln \beta = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R} \tag{1}$$

where β is the stability constant for complex formation. Spectra were measured from 25 to 5 °C, and then from 25 to 55 °C. A final, third spectrum at 25 °C was systematically measured after the "hot ramp" and compared to the other two 25 °C spectra measured at the beginning and end of the "cold ramp" to confirm that the sample was not degraded by the temperature gradient. The density of every solution was measured for each temperature to account for changes in volume. Spectrophotometric titrations of the actinide containing samples were carried out using a Shimadzu 3101 spectrophotometer coupled to a thermostated cell compartment in a glovebox following the same protocol as the lanthanide experiments. A second set of titrations with Am(III) was conducted by following the changes in the $^7F_0 \rightarrow {}^5L_6$ absorption (503 nm) of 0.0003 M Am as a function of the ADPTZ concentration using a computer-controlled Cary-14 spectrophotometer.

2.3. Microcalorimetric Studies. Microcalorimetry also was used to determine the enthalpy of ADPTZ complexation with lanthanum, europium, holmium, and americium. Calorimetric experiments with lanthanide cations were performed using a Thermal Activity Monitor microcalorimeter (Thermometric). Titrations were carried out at 25.000 ± 0.0005 °C beginning with 2.8 mL of 5×10^{-4} M ADPTZ in 75/25 vol % MeOH/H_2O in the glass reaction cell. The heats of formation of the 1:1 $LnADPTZ^{3+}$ complexes of La(III), Eu(III), and Ho(III) were measured by adding 15 μL aliquots of 0.02 M Ln^{3+} in 75/25 vol % MeOH/H_2O to the reaction cell. The

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[22] Jensen, M. P.; Nash, K. L. *Radiochim. Acta* **2001**, *89*, 557.

[23] Case, F. H.; Croft, E. *J. Am. Chem. Soc.* **1959**, *81*, 905.

[24] François, N. Towards an interpretation of the mechanism of the actinides(III)/lanthanides(III) separation by synergistic solvent extraction with nitrogen-containing polydendate ligands. Thesis, Université Henri Poincaré, Nancy I, 2000.

necessary corrections for the heats of dilution of the metal ions were determined in separate blank runs. The stability constants of the Ln(III)−ADPTZ complexes were obtained either from the spectrophotometry or by simultaneously fitting the stability constant and the enthalpy of complexation to the calorimetric data.

Microcalorimetric measurements on americium were performed using a CSC 4200 Isothermal Titration calorimeter. Four titrations were carried out at 25.000 ± 0.0005 °C beginning with 0.8 mL of 5×10^{-4} M Am^{3+} in 75/25 vol % $MeOH/H_2O$ in a Hastelloy cell. The heat of formation of the 1:1 $AmADPTZ^{3+}$ complex was measured by adding 15 μL aliquots of 5×10^{-4} M ADPTZ solution in 75/25 vol % $MeOH/H_2O$ into the reaction cell. The necessary corrections for the heats of dilution of the ligand were determined in separate runs before and after the titration by adding 15 μL aliquots of 5×10^{-4} M ADPTZ solution to 75/25 vol % $MeOH/H_2O$. The solution composition at each point of the microcalorimetric titrations of Am was calculated from the stability constant measured by spectrophotometry.

2.4. Quantum Chemical Calculations. The geometries and electronic structures of the complexes were calculated using density functional theory (DFT) with the Amsterdam Density Functional (ADF) program package.[25−27] Relativistic effects were considered by the zeroth-order regular approximation (ZORA).[28−30] Spin−orbit effects were not taken into account. Uncontracted triple-ζ Slater valence orbitals with one set of polarization functions were used for all atoms. The frozen-core approximation was used where the core density was obtained from four-component Dirac−Slater calculations on all of the atoms and kept frozen during molecular calculations. The $1s^2$ core electrons were frozen for carbon, nitrogen, and oxygen. The valence space of the heavy elements included the 5s, 5p, 5d, 4f, and 6s shells of the lanthanides and the 6s, 6p, 6d, 5f, and 7s shells of the actinides. The numerical integration parameter was set to 6.0. The density functional consists of a local density part using the parametrization of Vosko, Wilk, and Nusair and exchange-correlation gradient corrected parts of Becke[31] and Perdew(BP86).[32]

3. Results

The Lanthanide(III)/ADPTZ System. (a) UV−Visible Spectrophotometry. The thermodynamic parameters (β_1, $\Delta G°$, $\Delta H°$, and $\Delta S°$) for the complexation by ADPTZ of all lanthanide cations (except promethium) and yttrium(III) were determined by UV−visible spectrophotometry in 75/25 vol % methanol/water solution. A sample spectrophotometric titration of ADPTZ by La^{3+} is shown in Figure 1. Stability constants, β_1, were calculated from each set of UV absorption spectra over a wavelength range of 200−400 nm using Modeling Factor Analysis[33] for the equilibrium (2), which is appropriate because the spectrophotometric data support the formation of only the 1:1 Ln(III)/ADPTZ complex for all of the cations studied.

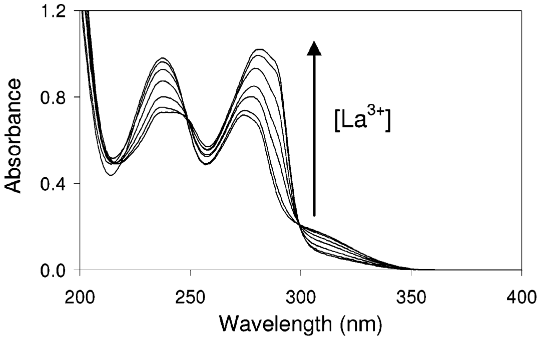

Figure 1. Spectrophotometric titration of a 3.8×10^{-5} M ADPTZ solution with increasing concentrations of La^{3+} in 75/25 vol % $MeOH/H_2O$ at 25 °C, path length: 1 cm, $0 < [La^{3+}]/[ADPTZ] < 300$.

$$Ln^{3+} + ADPTZ \xrightleftharpoons{\beta_1} LnADPTZ^{3+} \tag{2}$$

In Table 1 are reported the values determined for log β_1 at every temperature between 5 and 55 °C for all lanthanide cations and yttrium. The slope and the *Y*-intercept of the linear plot of log β_1 versus $1/T$ (eq 1) were used to calculate the values for the enthalpy ($\Delta H°$) and the entropy ($\Delta S°$) of complexation, respectively.

The results obtained are summarized in Table 2. All reported errors are the uncertainties at the 95% ($\pm 2\sigma$) confidence level. The determination of the standard deviation σ includes the experimental uncertainties in the dilutions and in the standardization of the lanthanide stock solutions by ICP-AES as well as the calculated uncertainties in the fitted parameters.

(b) Microcalorimetry. Microcalorimetric experiments were carried out with three lanthanide cations to confirm the values for enthalpy determined by the van't Hoff method. Data were treated by the following method. After each addition *i* of titrant, an observed heat Q^i is released. The observed heat released after each addition corresponds to the sum of the heat of formation of the $LnADPTZ^{3+}$ complex $Q_{complex}{}^i$ and the heat of dilution $Q_{dil}{}^i$. For *k* additions, the cumulative reaction heat $Q_{total}{}^k$ is defined as:

$$Q_{total}{}^k = \sum_{i=1}^{k} Q^i \tag{3}$$

The cumulative reaction heats measured for the lanthanum, europium, and holmium experiments are plotted in Figure 2 versus concentration of lanthanide cation. A positive sign is associated with an exothermic heat. The complexation enthalpy for the formation of the 1:1 $LnADPTZ^{3+}$ complex, $\Delta H°$, is directly correlated to the dilution corrected heat by the following relation:

$$Q_{complex}{}^i = Q^i - Q_{dil}{}^i = -\Delta H°.\Delta n_{LnADPTZ}{}^i \tag{4}$$

where $\Delta n_{LnAdptz}{}^i$ is the number of moles of complex formed after the *i*th addition, which can be calculated at each point of the titration from the stability constant measured by

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(25) ADF2002.03, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

(26) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391.

(27) te Velde, G.; Bickelhaupt, F. M.; Bacrends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

(28) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597.

(29) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1994**, *101*, 9783.

(30) van Lenthe, E.; Ehlers, A.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943.

(31) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(32) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(33) Malinowski, E. R. *Factor Analysis in Chemistry*, 2nd ed.; Wiley-Interscience: New York, 1991.

Table 1. Stability Constants (log β_1) for 1:1 Lanthanide and Yttrium(III) Complexes with ADPTZ in 75/25 vol % Methanol/Water at Different Temperatures between 5 and 55 °C

	log β_1										
T (°C)	5	10	15	20	25	30	35	40	45	50	55
La^{3+}	4.00	3.97	3.92	3.89	3.85	3.81	3.77	3.74	3.71	3.68	3.64
Ce^{3+}	4.48	4.42	4.37	4.33	4.28	4.24	4.19	4.15	4.11	4.07	4.05
Pr^{3+}	4.63	4.58	4.52	4.48	4.43	4.39	4.34	4.30	4.25	4.21	4.17
Nd^{3+}	4.85	4.78	4.72	4.66	4.62	4.56	4.51	4.46	4.41	4.36	4.32
Sm^{3+}	4.87	4.82	4.74	4.69	4.62	4.59	4.52	4.47	4.41	4.37	4.32
Eu^{3+}	4.75	4.67	4.61	4.57	4.51	4.44	4.39	4.34	4.29	4.25	4.20
Gd^{3+}	4.52	4.45	4.39	4.34	4.29	4.25	4.21	4.16	4.11	4.07	4.03
Tb^{3+}	4.33	4.27	4.23	4.19	4.15	4.12	4.07	4.04	4.01	3.97	3.94
Dy^{3+}	4.22	4.18	4.14	4.10	4.07	4.04	4.01	3.98	3.95	3.92	3.90
Ho^{3+}	4.16	4.12	4.10	4.07	4.05	4.03	4.00	3.98	3.96	3.94	3.91
Er^{3+}	4.21	4.18	4.15	4.13	4.10	4.08	4.06	4.04	4.01	3.99	3.97
Tm^{3+}	4.34	4.31	4.28	4.26	4.23	4.21	4.19	4.16	4.14	4.12	4.09
Yb^{3+}	4.42	4.39	4.35	4.33	4.30	4.27	4.25	4.22	4.19	4.17	4.10
Lu^{3+}	4.53	4.50	4.46	4.43	4.40	4.37	4.35	4.32	4.29	4.26	4.23
Y^{3+}		3.68	3.64	3.63	3.61	3.59	3.57	3.56	3.54	3.53	

Table 2. Thermodynamic Parameters for 1:1 Lanthanide, Yttrium(III), and Americium(III) Complexes with ADPTZ at 25 °C in 75/25 vol % Methanol/Water

Ln^{3+}	log β_1	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})
La^{3+}	3.85 ± 0.02	−22.0 ± 0.1	−13.5 ± 0.3	28 ± 1
	3.7[a]	−21.1[a]	−14 ± 3[a]	24[b]
Ce^{3+}	4.28 ± 0.04	−24.4 ± 0.2	−16.4 ± 0.6	27 ± 2
Pr^{3+}	4.43 ± 0.01	−25.3 ± 0.1	−17.5 ± 0.7	26 ± 2
Nd^{3+}	4.62 ± 0.04	−26.4 ± 0.3	−19.6 ± 0.7	23 ± 2
Sm^{3+}	4.62 ± 0.03	−26.4 ± 0.2	−21.0 ± 0.4	18 ± 1
Eu^{3+}	4.51 ± 0.10	−25.7 ± 0.6	−20.4 ± 0.7	18 ± 2
	4.5[a]	−25.7[a]	−22 ± 2[a]	12[b]
Gd^{3+}	4.29 ± 0.05	−24.5 ± 0.3	−18.0 ± 0.8	22 ± 3
Tb^{3+}	4.15 ± 0.06	−23.7 ± 0.4	−14.4 ± 0.6	31 ± 2
Dy^{3+}	4.07 ± 0.02	−23.2 ± 0.2	−12.0 ± 0.4	38 ± 1
Ho^{3+}	4.05 ± 0.03	−23.1 ± 0.2	−8.8 ± 0.6	48 ± 2
	4.1[a]	−23.4[a]	−11 ± 3[a]	42[b]
Er^{3+}	4.10 ± 0.05	−23.4 ± 0.3	−8.8 ± 0.7	49 ± 2
Tm^{3+}	4.23 ± 0.03	−24.1 ± 0.2	−8.9 ± 0.5	51 ± 2
Yb^{3+}	4.30 ± 0.03	−24.5 ± 0.2	−10.3 ± 0.8	48 ± 3
Lu^{3+}	4.40 ± 0.03	−25.1 ± 0.2	−11.1 ± 0.4	47 ± 1
Y^{3+}	3.61 ± 0.1	−20.6 ± 0.6	−6.7 ± 0.5	47 ± 2
Am^{3+}	5.8 ± 0.1	−32.9 ± 0.6	−28.9 ± 3[a]	14 ± 10[b]

[a] Determined by microcalorimetry. [b] Calculated from the Gibbs relation.

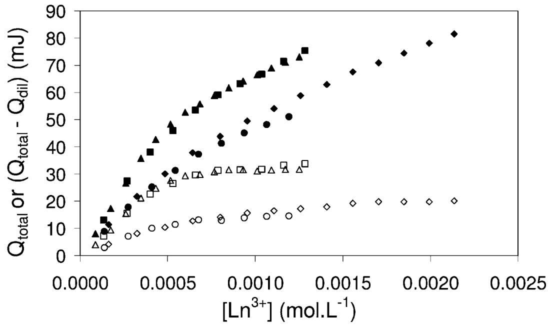

Figure 2. Microcalorimetric titrations of a 3.8 × 10^{-5} M ADPTZ solution by addition of Ln^{3+} in 75/25 vol % MeOH/H_2O at 25 °C. Total heat measured Q_{total} (closed symbols) and corrected heat measured ($Q_{total} - Q_{dil}$) (open symbols) (◆,◇), La^{3+}; (▲,△), (■,□), Eu^{3+}; (●,○), Ho^{3+}.

spectrophotometry. $\Delta H°$ can be determined by the following equation, where k is the number of injections:

$$\Delta H° = -\frac{\sum_{i}^{k} \frac{Q_{\mathrm{complex}}{}^{i}}{\Delta n_{\mathrm{LnADPTZ}}{}^{i}}}{k} \tag{5}$$

Before final analysis of the data, the Dixon statistic test[34] was applied to test the validity of data points near the end of the calorimetric titration. The uncertainty on the enthalpy value corresponds to the standard deviation of the chosen data.

When the experimental conditions and the stability constants are appropriate, it is also possible to fit both the enthalpy and the stability constant directly from the microcalorimetric data. In our case, the concentrations of the species and the stability constant of the complexes formed were large enough to allow the simultaneous determination of both values for each of the experiments on the three lanthanide cations studied calorimetrically. The microcalorimetric results are summarized and compared to the van't Hoff results in Table 2. No consistent uncertainties for the stability constant could have been determined by the program with the simultaneous fit method. The calorimetrically determined enthalpy values and the stability constants confirm the results obtained by the van't Hoff method for

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(34) *Statistique appliquée à l'exploitation des mesures*; CEA: Masson, 1978.

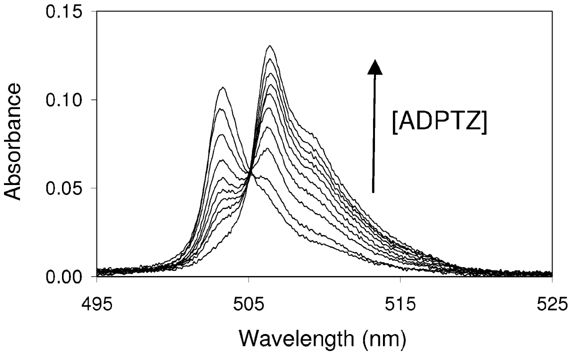


Figure 3. Spectrophotometric titration of a 3 × 10^{-4} M Am^{3+} solution with increasing concentrations of ADPTZ in 75/25 vol % MeOH/H_2O at 25 °C, path length: 1 cm, $0 < [ADPTZ]/[Am^{3+}] < 1.3$.

each of the three cations studied (La^{3+}, Eu^{3+}, and Ho^{3+}). This agreement between both methods clearly shows the absence of secondary phenomena that might perturb the determination of the thermodynamic parameters. A larger uncertainty is associated with the enthalpy values determined by microcalorimetry than with those determined by the van't Hoff method. This is unusual, but arises from the low solubility of the ligand in the medium and the comparatively large contribution of the heat of dilution. Together, they limit the precision of the microcalorimetric measurements in these systems.

The Americium(III)/ADPTZ System. Microcalorimetric experiments were carried out to determine the enthalpy of formation of the Am−ADPTZ complex. The different experimental conditions applied to the system due to the radioactivity of americium prevent the simultaneous determination of both the enthalpy and the stability constant by microcalorimetry. Therefore, the stability constant for Am−ADPTZ was determined by spectrophotometric titration in separate experiments. Two different sets of spectrophotometric experiments have been conducted at 25 °C. First, the absorption of Am(III) was followed at 503 nm by keeping constant the Am^{3+} concentration and by adding increasing concentrations of ADPTZ in solution (Figure 3). The stability constant was calculated by nonlinear regression using the program SQUAD.[35] The absorption of ADPTZ also was followed in the UV domain similar to the lanthanide experiments, and the stability constant was estimated by Modeling Factor Analysis. Both sets of experiments agreed, giving $\log \beta = 5.8 \pm 0.1$.

This value was used to analyze the microcalorimetric data by the same method applied for the lanthanide complexation. A sample microcalorimetric thermogram, given in Figure 4, shows the variations of the power (P) released after each addition of ADPTZ in the Am^{3+} solution versus the experiment time. Equation 5 was used to determine the value for $\Delta H°$ by taking the average of four experiments carried out under the same conditions. The complexation entropy was estimated from the Gibbs equation: $\Delta G° = -RT \ln \beta = \Delta H° - T\Delta S°$.

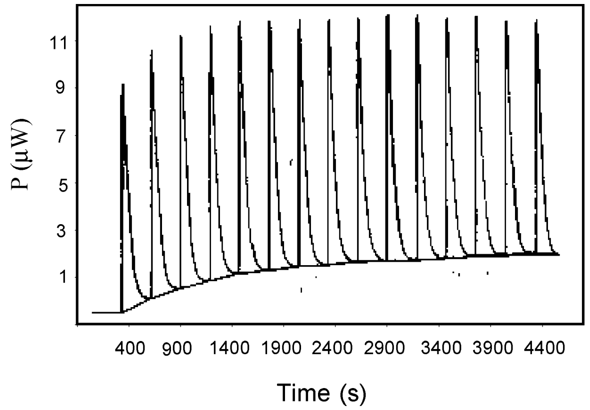
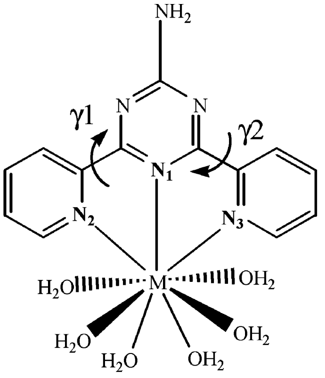


Figure 4. Microcalorimetric titration of 0.8 mL of 5 ×10^{-4} M Am^{3+} (in the cup) by addition of 15 × 15 μL of 5 × 10^{-4} M ADPTZ in 75/25 vol % MeOH/H_2O at 25 °C. $\Delta t = 300$ s between two injections.

Chart 2. Schematic Structure of $[M(ADPTZ)(H_2O)_6]^{3+}$ Complexes



$M = La^{3+}, Nd^{3+}, Gd^{3+}, Pu^{3+}, Am^{3+}, Cm^{3+}$

Table 3. Calculated Metal−Nitrogen (R(M−N)) and Metal−Oxygen (R(M−O)) Bond Distances (Å), and Dihedral Angles (γ^1,γ^2) (deg) in $[M(ADPTZ)(H_2O)_6]^{3+}$ Complexes

An^{3+}	$R(M-N_1)$	$R(M-N_2)$	$R(M-N_3)$	$\langle R(M-O)\rangle^a$	$\gamma1$	$\gamma2$
La^{3+}	2.558	2.650	2.647	2.655	1.5	2.3
Nd^{3+}	2.485	2.596	2.594	2.602	1.2	1.9
Gd^{3+}	2.439	2.559	2.563	2.535	1.2	2.0
Pu^{3+}	2.474	2.578	2.578	2.617	1.1	1.7
Am^{3+}	2.486	2.591	2.589	2.612	1.6	1.9
Cm^{3+}	2.467	2.581	2.580	2.591	1.5	1.9

[a] Average value.

DFT Calculations. Calculations were performed on $[M(ADPTZ)(H_2O)_6]^{3+}$ clusters, depicted in Chart 2, where M is a trivalent cation of the first half of the lanthanide (M = lanthanum, neodymium, gadolinium) or actinide (M = plutonium, americium, curium) series. The geometries of the clusters were fully optimized without any symmetry constraint. All clusters except La(III) systems are open shell with a $4f^n$ ground-state configuration for lanthanide(III) and a $5f^n$ configuration for actinide(III); $n = 3$ for Nd, $n = 5$ for Pu, $n = 6$ for Am, and $n = 7$ for Cm and Gd. The results reported in the next sections were obtained from ground-state configurations with the highest spin multiplicity. Selected bond distances and angles are presented in Table 3. The molecular orbitals were localized by the Boys−Foster method.[36] All of the molecular orbitals deriving from the

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(35) Legett, D. In *Computational Methods for the Determination of Formation Constants*; Legett, D. J., Ed.; Plenum Press: New York, 1985; p 159.

Table 4. Major Orbital Character (%) for Metal−Ligand Bonding Molecular Orbitals in $[M(ADPTZ)(H_2O)_6]^{3+}$ Complexes (α Spin-Orbitals)

	σ_1				σ_2				σ_3			
	M (%)			ADPTZ (%)	M (%)			ADPTZ (%)	M (%)			ADPTZ (%)
	d	f	s		d	f	s		d	f	s	
La^{3+}	6	<1	<1	92	6	<1	<1	91	6	<1	<1	91
Nd^{3+}	6	<1	<1	90	5	<1	<1	91	5	1	<1	92
Gd^{3+}	7	<1	<1	90	5	<1	<1	92	6	<1	<1	93
Pu^{3+}	6	3	<1	89	6	2	<1	92	6	2	<1	92
Am^{3+}	7	<1	<1	89	6	1	<1	91	5	1	1	93
Cm^{3+}	7	<1	<1	91	6	1	<1	91	6	1	<1	93

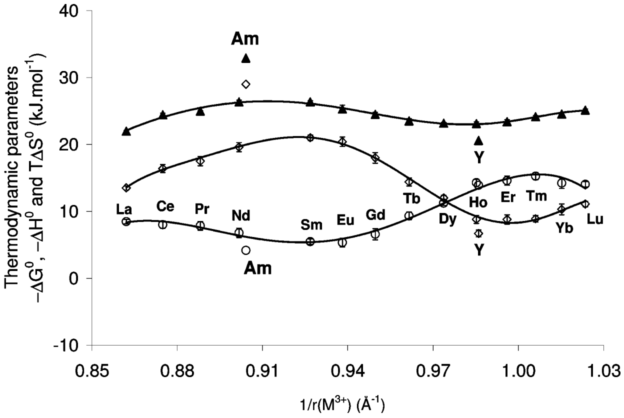

Figure 5. Thermodynamic properties of 1:1 lanthanide, yttrium, and americium complexes with ADPTZ in 75/25 vol % MeOH/H_2O at 25 °C. (▲), $-\Delta G°$ (kJ mol^{-1}); (◇), $-\Delta H°$ (kJ mol^{-1}); (○), $T\Delta S°$ (kJ mol^{-1}). Ionic radius corresponds to a coordination number of 8.

ligand and the metal atomic orbitals and having a metal or ligand contribution at least greater or equal to 1% are listed in Table 4.

4. Discussion

The Lanthanide(III)/ADPTZ System. The stability constants for the 1:1 LnADPTZ complexes vary nonmonotonically across the series (Figure 5). The stability increases from La to Sm, decreases between Eu and Dy, then slowly increases from Ho to Lu. S-shaped curves are also observed for the enthalpies and entropies of complexation, with extrema around Eu and Ho. The complexation enthalpies are negative as expected for a strong metal−ligand interaction, whereas the entropy values are positive which is consistent with inner sphere coordination with displacement of solvent molecules from the hydration sphere of the metal ion. An increase in $\Delta S°$ from Eu to Ho is often observed in Ln complexes and is explained by the well-known change in hydration number of the Ln^{3+} ions from 9 to 8 over this range of elements. However, this increase in $\Delta S°$ is counterbalanced by a less favorable complexation enthalpy in that area, making changes in the free energy of complexation small. These trends combined with the magnitude of the enthalpic and entropic contributions that are similar to the stability constants for all lanthanides lead to a change in the nature of the main driving force of the reaction throughout the lanthanide series. The reaction is driven mainly (>65%) by enthalpy from La to Dy, while the majority of the complex stability (>65%) is derived from the entropy from Dy through Lu.

Comparison of these trends with studies of other ligands can help illuminate the thermodynamic behavior of this system. Figure 6 shows the variations of $\Delta H°$ and $\Delta S°$ across the 4f series for the 1:1 complexes of three tridentate ligands, ADPTZ, dipicolinic acid, and diglycolic acid (Chart 1),[37] which present different charge densities (the formal charge and the donor atoms are different when we compare ADPTZ to these acids) but similar coordination geometries. Despite the differences in the type of donor atoms and the magnitude of the stability constants, each of the three ligands displays very similar trends in $\Delta H°$ and $\Delta S°$. All are tridentate with analogous coordination site geometries induced by the formation of two five-membered chelate rings upon complexation. In the case of ADPTZ, this coordination mode has been confirmed in the solid state for several lanthanide cations from X-ray diffraction data.[38] NMR spectra also show that La^{3+} is coordinated by the three ADPTZ nitrogens in methanol−water solutions.[39] Thermodynamic data for dipiconilate and diglycolate complexes were measured in pure water, while ADPTZ complexation was studied in 75/25 vol % methanol/water. More negative $\Delta H°$ values are obtained for the complexation by the two N-donor ligands (dipicolinic acid and ADPTZ) as compared to the O-donor ligand (diglycolic acid), a commonly observed effect. One can argue that the more exothermic heats suggest that either stronger bonds are formed between the nitrogen and the lanthanide cation as compared to Ln−O bonds or the dehydration enthalpy is more favorable in the case of the nitrogen-donor ligand. Concerning the discussion of the entropic variation, larger $\Delta S°$ values are observed in the case of dipicolinic and diglycolic acid, which could arise either from the greater ligand desolvation entropies associated with carboxylic acid ligands[19] or from the differences in the solution composition (water versus methanol/water).

The similarity between the variations of $\Delta H°$ and $\Delta S°$ for different ligands across the lanthanide series indicates that this pattern is caused mainly by some properties of the metal ion. The magnitude of the enthalpies and entropies of complexation of hard Lewis acids such as the Ln^{3+} cations are usually dominated by the thermodynamics of solvation/desolvation reactions. Yet two competing factors, the regular

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(36) Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296.

(37) Grenthe, I. *Acta Chem. Scand.* **1963**, *17*, 2487.

(38) Drew, M. G. B.; Hudson, M. J.; Iveson, P. B.; Madic, C.; Russell, M. L. *J. Chem. Soc., Dalton Trans.* **2000**, 2711.

(39) Miguirditchian, M. Thermodynamic study on the complexation of actinide(III) and lanthanide(III) ions by polydentate N-donor ligands in homogeneous conditions. Thesis, Université Paris XI, Orsay, 2003.

decrease of the ionic radius and the change of hydration number of the lanthanide cations from 9 to 8 in the middle of the series, also contribute to the variations of the thermodynamic parameters from one lanthanide to another along the series. Because the complexation geometries of tridentate ADPTZ, dipicolinate, and diglycolate ligands are similar, the complexation-induced changes in the hydration shell of a given metal ion and therefore the patterns of the enthalpies and entropies should also be similar. Moreover, because the lanthanide−dipicolinate and diglycolate interactions are essentially governed by electrostatic and geometric factors,[40] the similar trends observed for ADPTZ complexes indicate that the interaction of 4f cations with a N-donor ligand is also essentially ionic. No distinct covalent effect is apparent in the lanthanide data, but it might be hidden by the importance of steric and solvation factors in these systems.

The case of yttrium(III) complexation also confirms the great influence of steric and hydration factors on the thermodynamics of complexation. Similar values for entropy were measured between Y^{3+} and Ho^{3+}, cations having the same ionic size and hydration number.[41] However, the enthalpy for the complexation of yttrium is less exothermic than any of the values observed for the lanthanide cations. Overall, this leads to a lower stability of the $Y(ADPTZ)^{3+}$ complex formed as compared to lanthanide complexes.

The Americium(III)/ADPTZ System. The americium−ADPTZ complex is about 20 times (or ca. 7 kJ/mol) more stable than the corresponding lanthanide complexes (Table 2 and Figure 5), which confirms the greater selectivity of N-donor ligands for actinide cations in homogeneous conditions. The thermodynamic data suggest that the observed selectivity arises from a difference in the enthalpies of complexation: the enthalpic term is more exothermic for the formation of the americium complex ($\Delta\Delta H_{Am/Ln}^\circ \geq 8.9$ kJ·mol^{-1}). This is consistent with greater covalence in the Am−N bonds. The complexation entropy is positive and slightly lower than the values measured for the lanthanide complexes. Comparison between the americium and neodymium complexes, cations having similar size and hydration properties, shows a $T\Delta\Delta S_{Nd/Am}^\circ$ approximately of 2.9 kJ·mol^{-1} in favor of the Nd complex. The roughly comparable entropy values for Am and Nd complexes confirm that the complexation entropies in this system depend essentially on solvation and geometric factors, whereas the complexation enthalpy provides more information on the metal−ligand bond formation.

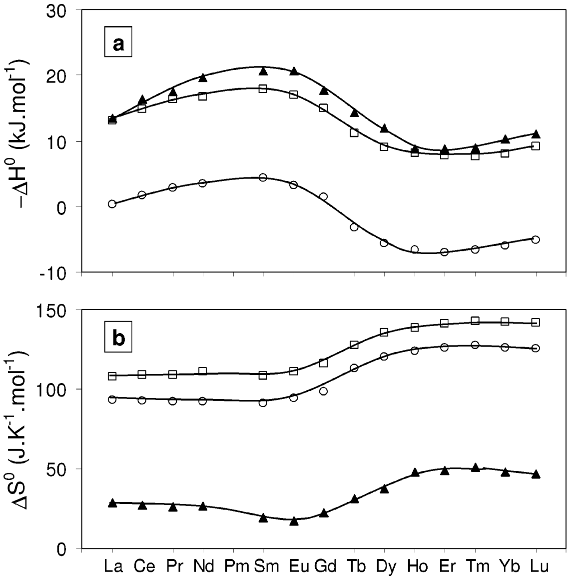

Figure 6. Trends for the complexation enthalpy and entropy of the 1:1 lanthanide complexes with ADPTZ and other tridentate ligands. (▲), ADPTZ (this work); (○), diglycolic acid;[37] (□), dipicolinic acid.[37] (a) $-\Delta H°$; (b) $\Delta S°$.

DFT Calculations. As might be expected from the regular change in the radii of the trivalent lanthanide and actinide cations and the smooth variation in the thermodynamic properties of their complexes (Figures 5 and 6), the structural parameters calculated for $[M(ADPTZ)(H_2O)_6]^{3+}$ complexes change smoothly as a function of the trivalent cation across both the lanthanide and the actinide cations studied. According to the calculations, each of the three aromatic rings in the ADPTZ complexes is nearly coplanar with dihedral angles between 1° and 2°. The average lanthanide−nitrogen distances follow the evolution of the ionic radius with La−N(ADPTZ) > Nd−N(ADPTZ) > Gd−N(ADPTZ). However, a different trend is obtained for An−N distances. The calculated Pu−N(ADPTZ) distances are 0.01 Å shorter than Am−N(ADPTZ), whereas the ionic radius of Pu^{3+} is ~0.02 Å larger than Am^{3+}.[42] Furthermore, if we compare the mean values of the three M−N(ADPTZ) distances with the mean values of the six M−O(H_2O) distances, we find that Ln−N(ADPTZ) distances are 0.01−0.04 Å shorter than the Ln−O(H_2O) distances, whereas the An−N(ADPTZ) distances are 0.05−0.07 Å shorter than the An−O(H_2O) distances. This calculated contraction in the An−N bond lengths supports the idea of An−N bonds that are slightly stronger than the corresponding Ln−N bonds.

The calculated orbital occupancies also confirm that the bonding between the trivalent metal cations and the ligand is mainly ionic for both the lanthanides and the actinides and furthermore that the covalent effects are very small from an electronic perspective. For all of the metal ions considered, three molecular orbitals are found to be shared by the metal and ADPTZ, each of which has less than 10% metal character. The bonding molecular orbitals correspond to ligand to metal donation involving the ligand σ orbital and the empty metal orbitals (Figure 7). Among metal orbitals, the vacant 5d or 6d orbitals are the main contributors to the bond (Table 4). In the lanthanide complexes, the 5d orbitals are the only metal centered orbitals involved in the bonding. However, the behavior is slightly different for the actinide complexes: the 5f as well as the 6d orbitals are active in bond formation. The largest contribution of f orbitals is observed for Pu^{3+}. The singly occupied 4f or 5f orbitals are pure with 99−100% 4f or 5f contribution and do not participate in the bonding.

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

(41) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(42) David, F. J. *Less Common Met* **1986**, *121*, 29.

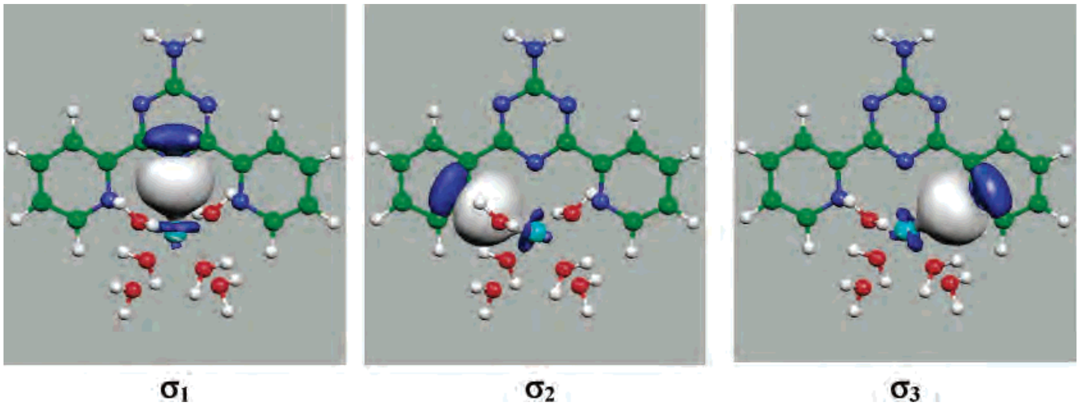

Figure 7. Metal−ligand bonding orbitals in[M(ADPTZ)(H$_2$O)$_6$]$^{3+}$ complexes.

Overall, as expected from the small energy differences measured for Δ*H*° between lanthanide(III) and actinide(III) cations, the calculated structural and electronic differences between the two series of complexes are small. Unlike the computations on the uranium(III) complexes with other nitrogen-donor ligands,[14,43] no π back-donation from the filled 5f orbitals of Pu, Am, and Cm to the ADPTZ π* orbitals was indicated in the calculations.

5. Conclusion

This first systematic thermodynamic study of the complexation of trivalent lanthanide and actinide ions with a tridentate N-donor ligand has provided a complete set of data on the complexation of f-element with a soft-donor ligand in the framework of actinide/lanthanide separation processes. The lanthanide data confirm the strongly ionic character of the metal−ligand bonding even with a N-donor ligand, and the similar thermodynamic trends observed for the ADPTZ, dipicolinate, and diglycolate complexes across the lanthanide series confirmed that steric and solvation factors predominate the energetics of bonding for all three ligands. In addition, there is little thermodynamic evidence for a significant covalent contribution to lanthanide−nitrogen bond formation. Microcalorimetric experiments on some representative lanthanide systems validate the use of the van't Hoff method for the determination of the complexation enthalpy in systems of this type.

Concerning the americium results, the measured Am−ADPTZ complexation enthalpy is, for the first time in homogeneous conditions, consistent with a greater degree of covalence in the actinide−nitrogen bonds as compared to lanthanide−nitrogen bonds. Complex formation is more exothermic for the americium(III)−ADPTZ complex than for the corresponding lanthanide complex, lending greater stability to the actinide complex. DFT calculations globally support the experimental results. Moreover, orbital population calculations attribute the covalency preferentially to a charge transfer from the σ orbitals of the ligand to the 6d and 5f orbitals of the actinide cation. Experimental thermodynamic data on other actinide(III)−ADPTZ complexes, structural data on the complexes in solution, and other studies on similar systems capable of probing the electronics of the metal−ligand bond may shed additional light on the origins of the selectivity of soft donor ligands for the actinide cations.

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(43) Guillaumont, D. *J. Phys. Chem. A* **2004**, *108*, 6893.