Inorg. Chem. **2008**, *47*, 7983−7991

Inorganic Chemistry
Article

Theoretical Study of the Uranyl Complexation by Hydroxamic and Carboxylic Acid Groups

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Received September 20, 2007

A theoretical study on the complexation of uranyl cation (UO_2^{2+}) by three different functional groups of a calix[6]arene cage, that is, two hydroxamic and a carboxylic acid function, has been carried out using density functional theory calculations. In particular, interaction energies between the uranyl and the functional groups have been used to determine their affinity toward uranyl, whereas pK_a calculations give some information on the availability of the functional groups in the extraction conditions. On the one hand, calculations of the interaction energies have pointed out clearly a better affinity with the hydroxamic groups. The stabilization of this complex was rationalized in terms of a stronger electrostatic interaction between the uranyl cation and the hydroxamic groups. The presence of a water molecule in the first coordination sphere of uranyl does not destabilize the complex, and the most stable complex is obtained with two functional groups and two water molecules, leading to a coordination number of 8 for the central uranium atom. On the other hand, pK_a theoretical evaluation shows that both hydroxamic (deprotonated on the oxygen site) and carboxylic groups are potential extractants in aqueous medium with a preference for carboxylic functions at low pH. Moreover, these data allowed to unambiguously identify the oxygen of the alcohol function as the favored deprotonation site on the hydroxamic function.

1. Introduction

The natural conformational flexibility of calixarenes favors and enhances both their reactivity and natural complexing capabilities with neutral or charged molecules. Moreover, the properties of these cage molecules can be modified by acting on the size of the complexing macrocycle and on the functionalization of lateral groups. During the last decades, their applications in various domains led to numerous experimental studies in the fields of chemical sensing,[2–5] ionic transport,[6] or separation and host−guest chemistry.[7–33] One of these applications concerns the extraction of actinide elements from various media such as tap or seawater,[5,7]

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10.1021/ic7018633 CCC: $40.75

nuclear wastes,[7–29] or even urine to monitor the health of nuclear workers.[30–33] To select an efficient calixarene-based uranophile extractant, three criteria must be taken into account: the size of the cage, the macrocycle structure imposed by the chelating groups, and finally the nature of the functionalized groups on the lower rim. The size of the cage can vary from 4 to 6 basic phenolic units in most cases up to 12 units encompassing two uranyl cations, as evidenced by recent studies.[23–29] From X-ray crystallographic studies, Shinkai et al. showed that a single uranyl cation may adopt either a pseudoplanar penta- or hexacoordinated structure.[11,12] Hence, they proved that these coordination numbers are favored with calix[5]arenes or calix[6]arenes-based complexes. Further studies[13–17] evidenced the high affinity of functionalized calix[6]arenes toward uranyl, bearing either carboxylic or hydroxamic chelating groups, with improved selectivity capabilities. To optimize the selectivity of these molecules, we have recently showed[33] that the 1,3,5-OMe-2,4,6-OCH$_2$CONHOH-*p*-*tert*-butylcalix[6]arene molecule is a highly efficient candidate for the selective extraction of such an ion.

Several theoretical studies have been carried out on uranium and uranyl during the past decade using different modeling techniques, from classical molecular mechanics/molecular dynamics[34–38] to pure ab initio calculations.[39–51] Combined quantum and classical approaches[52–54] and recent applications of first-principles molecular dynamic techniques[55–57] to study the properties of the hydrated cation have to be also mentioned.

As it concerns more specifically the calixarenes, the size of the complexes often prevents a full quantum treatment and, therefore, ab initio calculations were, with few exceptions, restricted to the study of the interaction of uranyl with small chelating or coordinating groups such as, for instance, halides,[39,43,44] nitrates,[40,49,57] acetates,[40] carbonates,[40,49] and hydroxides.[41,42,44] The philosophy behind such studies is based on the hypothesis that the electronic aspects of the complexation phenomena are mainly local in nature so that noteworthy information on the molecule-ligand interaction can be obtained by considering a structural model of the whole system. The few studies of the complexation of uranyl with a whole calix[6]arene were, to the best of our knowledge, carried out with classical molecular dynamics simulations.[34] Unfortunately, some important effects like charge transfers or electronic cloud polarization are missing at this level of theory. In such context, we have carried out, very recently, a first investigation, using semiempirical and Density Functional Theory (DFT) calculations, on the conformational behavior of a calix[6]arene in the gas phase and in solution.[58] In particular, we showed that the *cone* structure, characterized by all the chelating functions on the same side (see Figure 1) is the most stable one, both in the gas phase and in solution.

In this paper, we proceed to the next step, that is, a theoretical analysis of the complexation process of the uranyl for the two different macrocycles previously cited, namely 1,3,5-OMe-2,4,6-OCH$_2$CONHOH-*p*-*tert*-butylcalix[6]arene and 1,3,5-OMe-2,4,6-OCH$_2$COOH-*p*-*tert*-butylcalix[6]arene. We considered only the interaction of the uranyl cation with

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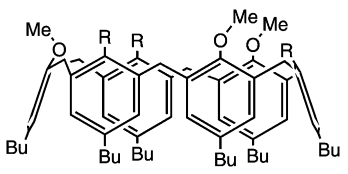

R=OCH_2COOH; $OCH_2CONHOH$

Figure 1. Sketch of the calix[6]arene in its most stable conformation.

three different chelating groups, protonated (R_{iH}) or deprotonated (R_i). These groups correspond to two hydroxamic (i = hydO or hydN, depending on the deprotonation site) and one carboxylic acid (i = carb) functions. Our calculations can give useful indications on the effects ruling the interactions between the uranyl and the ligands, since the main role of the calixarene cage is to support the complexating functions and does not have any significant effects on their electronic structure. Two other processes have been also studied to better simulate the experimental conditions. In particular, solvent effects have been modeled by both explicitly adding water molecules into the first solvation shell of the uranyl and using a continuum dielectric to simulate solvent bulk effects. Furthermore, the pK_a values of the three different chelating groups have been evaluated to simulate their availability in the experimental conditions.

2. Computational Details

All DFT calculations were carried out with the Gaussian code.[59] All the molecules have been fully optimized at the DFT level using the so-called PBE0 "parameter free" hybrid model[60] issuing from the Perdew−Burke−Ernzerhof (PBE) exchange-correlation functional[61] in a hybrid HF/DFT scheme, where the HF exchange ratio (1/4) is fixed a priori.[62] The 6−31+G(2d,2p) basis set[63a] has been used for light atoms (H, N, O, and C) while the relativistic effective core potential (ECP) of the Los Alamos group together with its associated valence basis set has been employed for uranium.[63b] Such basis is characterized by having 78 (out of 92) electrons in the core and a valence basis set with the contraction (10s8p2d4f)/[3s3p2d2f]. The choice of the metal basis set is, of course, crucial for obtaining reliable geometries and interaction energies. Therefore, to verify the convergence of the obtained results, some calculations have been carried out with the small core ECP of the Stuttgart group, in which 60 electrons are frozen and the valence basis set is much larger (contraction (25s17p16d8f)/[8s7p6d4f]).[64] All stationary points have been guaranteed to be minima via inspection of the analytical Hessian.

Electron population analyses have been performed using the Natural Population Analysis (NPA).[65] For the uranium atom, two valence/Rydberg partition schemes have been employed. The first one, [7s5f]/[8s-10s 7p-10p 6d-9d 6f-7f], includes 6d orbitals in the Rydberg part. This is the default partition implemented in the Gaussian code and our reference for the discussion. The second one, [7s5f6d]/[8s-10s 7p-10p 7d-9d 6f-7f], proposed by Clark and co-workers,[66] includes 6d orbitals in the valence part. Total interaction energies were corrected for the basis set superposition errors (BSSE) with the standard counterpoise model.[67]

Solvent effects were evaluated using the Conductor-like Polarizable Continuum Model (CPCM)[68] using the United Atoms Topological Model (UATM)[69] for the molecular cavity determination with the UAKS radii. The solvation free energies determined by such a model were introduced in a standard Born−Haber cycle to compute pK_a values using a standard approach.[70]

3. Results and Discussion

The study of the interaction of uranyl with the chelating ligands of calixarene has been conducted in two steps. The first one concerns the affinity of the three different ligands, the two hydroxamic and the carboxylic acid functions, toward uranyl: the strongest interaction will correspond to the largest affinity. Interactions energies, that is, energy differences between the uranyl-ligands complex and the individual fragments, give some insights on the affinity of the different ligands. The second process is related to the availability of the complexing function at the extraction conditions. Here the limiting step is the deprotonation process of the function, which can be evaluated through the evaluation of the pK_a constant. Of course the two factors, affinity and availability, are in competition, in the sense that the greatest affinity does not correspond, a priori, to the greatest availability. Therefore, our last working hypothesis concerns the fact that all the complexing functions (three at maximum) are potentially available to the uranyl. Finally, we have to note that the ligand coordination to uranyl ion occurs in its equatorial plane, perpendicular to the $O{=}U{=}O$ axis, and that the (equatorial) coordination number is generally 5 or 6[11,12] leading to penta- or hexacoordinated uranyl complexes. Such coordination number will be discussed in the following sections, the corresponding uranium value being larger of 2 units.

3.1. Gas-Phase Pentacoordinated Complexes. As starting point in our investigation, we were interested in the estimation of the gas-phase interaction between different chelating groups and the uranyl cation in the bare pentacoordinated structures. Experimental studies have shown that in the complex formation, two hydrogen atoms are exchanged for a uranyl molecule.[33] Therefore, of the three complexing functions available, two were considered as deprotonated, leading to a coordination number of 5 for the central uranium atom. The reference structures of the three pentacoordinated $[UO_2(R_i)_2(R_{iH})]$ complexes are presented in Figure 2, while the corresponding energetic results are gathered in Table 1.

The largest interaction, -2825 kJ mol^{-1}, was obtained for a structural rearrangement involving three hydroxamic func-

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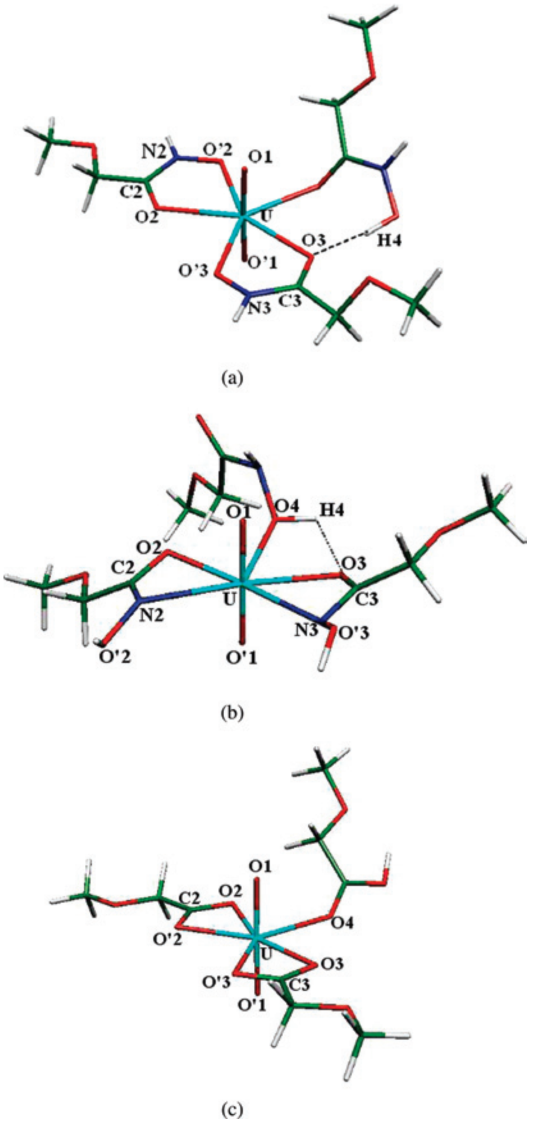

Figure 2. Optimized structures of the three pentacoordinated $[UO_2(R_i)_2(R_{iH})]$ complexes with R_i = hydO (a), hydN (b), and carb (c).

tions, two of them being deprotonated on the oxygen atom of the alcohol group (i.e., i = hydO). A weaker interaction is, instead, found when the deprotonation occurs on the nitrogen site (i.e., i = hydN), the corresponding energy being -2594 kJ mol^{-1}. If the interaction with the three carboxylic functions is taken as reference, the former complexation energy is 130 kJ mol^{-1} lower and the last 101 kJ mol^{-1} higher. Therefore, at least in the gas phase, the hydroxamic function has a higher affinity with the uranyl than the other two groups. To have a reference of the strengths of such interactions, the interaction energy of the hydrated uranyl $[UO_2(H_2O)_5]^{2+}$ is also reported in Table 1. Such energy is more than two times lower than the other (-1048 kJ mol^{-1}), thus suggesting that uranyl prefers to interact with any of the chelating functions rather than with water.

From a structural point of view, a close examination of the selected parameters, reported in the Tables 1–3, helps in rationalizing these energetic results. These parameters have been obtained through a full optimization of all internal coordinates, leading to the most stable local minima characterized on the potential energy surfaces. Other structures have been identified, corresponding to different orientations of the ligand extremities, but, in any case, they are higher in energy.

The obtained complexes are not symmetric, and the structures of the two bidentate ligands are different, thus explaining the differences observed between equivalent atoms, like O2 and O3 or C2 and C3. These ligands are at different distances from the central uranium atom and, on average, the distance range is slightly larger for R_{hydO} bidentate ligands than for R_{carb} and R_{hydN}. For instance, in the first complex $[UO_2(R_{hydO})_2(R_{hydOH})]$, the U−O distances vary from 2.375 to 2.590 Å with a mean distance of 2.454 Å. In the second one, $[UO_2(R_{carb})_2(R_{carbH})]$, they vary from 2.408 to 2.513 Å with a mean distance of 2.441 Å. A similar average distance, 2.460 Å, is found for the last complex (i = hydN). As it concerns the third monodentate ligand, the distance with respect to the uranium atom decreases in the order $R_{hydO} < R_{carb} < R_{HydN}$. This last sequence corresponds to the trend observed for the complexation energies.

It is also interesting to note the small variations for the intramolecular geometrical parameters found in going from the free carboxylic ligand to the complexed ones. Larger changes are, instead, found for the hydroxamic functions (see Tables 2–4, last columns of each table).

In summary, the structure of uranyl is slightly affected by the interactions with any kind of ligands, the intramolecular U−O distance being around 1.76 Å close to the value of the bare uranyl, that is, 1.74 Å.

From a computational point of view, the complexes $[UO_2(R_i)_2(R_{iH})]$ (i = hydN, carb) were also computed using the small-core Stuttgart ECP on uranium and its associated large basis set. The obtained results show that this small-core ECP provides structures which are close to those obtained with the large-core Los Alamos ECP, the largest difference being 0.005 Å. The computed interaction energies are systematically lower by about 75 kJ/mol, leading to a variation of about 3% with respect to that obtained with the small basis set. Similar decreases have been also found for the complexes with one water molecule ($[UO_2(R_i)_2(R_{iH})(H_2O)]$), see below). These variations are in line with those reported in the literature[71] and strengthen the trends of our investigations. Therefore, also because of the large number of systems to be studied, only the large-core ECP has been considered for the other complexes.

As expected, energy and geometrical features can be related to the electron distribution through an NPA analysis. Two valence/Rydberg partition schemes have been used on the metal atom, one including 6d orbitals in the Rydberg part and the other, proposed by Clark and co-workers,[66] including them in the valence part. This formal difference leads to some variations when going from one partition scheme to the other one. In particular, an average gain of

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Table 1. Interaction Energies (Δ*E* in kJ/mol) between the Different Functions (R_i^-, i = hydO, hydN, and carb), Water, and Uranyl (UO_2^{2+})[a]

system	coordination number	hydO	hydN	carb
$[UO_2(R_i)_2(R_{iH})]$	5	−2825 (−130)	−2594 (101)	−2695 (0)
$[UO_2(R_i)_2(H_2O)]$	5	−2799 (−127)	−2684 (−12)	−2672 (0)
$[UO_2(R_i)_2(R_{iH})(H_2O)]$	6	−2819 (−113)	−2668 (38)	−2706 (0)
$[UO_2(R_i)_2(H_2O)_2]$	6	−2840 (−92)	−2755 (−7)	−2748 (0)
$[UO_2(H_2O)_5]$	5		−1048	

[a] In parentheses are reported the relative energies with respect to the carboxylic functions and, for comparison purpose, in the last line the interaction energy of five water molecules with uranyl, computed under the same conditions. All the values have been corrected for BSSE.

Table 2. Selected Bond Distances (Å) and Bond and Dihedral Angles (deg) for Different Uranyl Complexes Involving Hydroxamic Functions Deprotonated on Oxygen Atom (i = hydO)

	$[UO_2(R_i)_2(R_{iH})]$	$[UO_2(R_i)_2(H_2O)]$	$[UO_2(R_i)_2(R_{iH})(H_2O)]$	$[UO_2(R_i)_2(H_2O)_2]$	free ligand/uranyl
UO1/UO′1	1.769/1.762	1.760/1.765	1.764/1.756	1.756/1.764	1.745
UO2/UO3	2.464/2.590	2.435/2.345	2.619/2.667	2.555	
UO′2/UO′3	2.375/2.388	2.435/2.505	2.404/2.486	2.452	
UO4	2.434		2.442		
U−O(W1)		2.576	2.690	2.594	
U−O(W2)				2.594	
C2O2/C3O3	1.258/1.263	1.256/1.254	1.255/1.258	1.253	1.243
C2N2/C3N3	1.309/1.311	1.315/1.317	1.309/1.311	1.314	1.338
N2O′2/N3O′3	1.336/1.322	1.331/1.330	1.333/1.324	1.329	1.309
O3H4	1.657		1.653		
O2C2N2/O3C3N3	120.8/119.5	120.1/120.1	120.4/119.6	119.8	127.2
C2N2O′2/C3N3O′3	119.9/121.4	120.6/120.3	120.4/120.8	120.3	128.2

Table 3. Selected Bond Distances (Å) and Bond and Dihedral Angles (deg) for Different Uranyl Complexes Involving Hydroxamic Functions Deprotonated on Nitrogen Atom (i = hydN)

	$[UO_2(R_i)_2(R_{iH})]$	$[UO_2(R_i)_2(H_2O)]$	$[UO_2(R_i)_2(R_{iH})(H_2O)]$	$[UO_2(R_i)_2(H_2O)_2]$	free ligand/uranyl
UO1/UO′1	1.766/1.759	1.765/1.760	1.770/1.761	1.765/1.765	1.745
UO2/UO3	2.375/2.411	2.430/2.354	2.446/2.447	2.455	
UN2/UN3	2.522/2.535	2.527/2.525	2.551/2.532	2.528	
UO4	2.593		2.263		
U−O(W1)		2.618	2.583	2.641	
U−O(W2)				2.641	
C2O2/C3O3	1.276/1.276	1.277/1.280	1.265/1.274	1.277	1.250
C2N2/C3N3	1.315/1.315	1.312/1.311	1.320/1.313	1.308	1.322
N2O′2/N3O′3	1.397/1.398	1.393/1.396	1.422/1.403	1.395	1.476
O3H4	2.132		2.00		
O2C2N2/O3C3N3	115.5/115.5	115.7/115.5	114.0/114.3	114.6	123.5
C2N2O′2/C3N3O′3	113.0/112.7	113.1/112.8	114.5/113.5	114.1	109.3

Table 4. Selected Bond Distances (Å) and Bond and Dihedral Angles (deg) for Different Uranyl Complexes Involving Carboxylic Functions (i = carb)

	$[UO_2(R_i)_2(R_{iH})]$	$[UO_2(R_i)_2(H_2O)]$	$[UO_2(R_i)_2(R_{iH})(H_2O)]$	$[UO_2(R_i)_2(H_2O)_2]$	free ligand/uranyl
UO1/UO′1	1.763/1.755	1.756/1.758	1.756/1.757	1.756/1.761	1.745
UO2/UO3	2.491/2.441	2.416/2.406	2.430/2.512	2.484	
UO′2/UO′3	2.424/2.408	2.471/2.442	2.467/2.498	2.479	
UO4	2.513		2.737		
U−O(W1)		2.565	2.562	2.571	
U−O(W2)				2.571	
C2O2/C3O3	1.267/1.256	1.267/1.260	1.253/1.264	1.264	1.253
C2O′2/C3O′3	1.256/1.269	1.257/1.266	1.268/1.252	1.256	1.241
O2C2O′2/O3C3O′3	121.1/120.8	120.8/120.9	120.6/120.8	120.9	130.2

1.05 $|e^-|$ is observed on the uranium atom for the non hydrated pentacoordinated complexes while lower variations are found for the uranyl cation. In other words, the partition scheme seems to be more important for the electronic redistribution within the U−O bond in uranyl than in the uranium-ligand interaction. These results, together with those obtained on other actinide complexes,[72,73] induced us to choose the standard NBO partition. However, the trends are similar in the two cases.

From the NPA charges of Table 5, it appears that the charge on the uranyl is similar for the three complexes, and small variations are found for the different ligands. In particular, the charge borne by the uranyl complex is about +1.5, and that on all the bidentate ligands is about −0.80 while the third ligand is almost neutral. Therefore, the electron transfer from deprotonated ligands (formal charge −1) to the uranyl (formal charge +2) is similar for all the considered ligands. This point, together with the proven reliability of the NPA scheme for the description of the bonding interaction in heavy metal complexes,[72] suggests that the difference in interaction energies can be ascribed more to electrostatic factors than to orbital interactions. The

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(72) Adamo, C.; Maldivi, P. *Chem. Phys. Lett.* **1997**, *268*, 61. (a) Petit, L.; Joubert, L.; Maldivi, P.; Adamo, C. *J. Am. Chem. Soc.* **2006**, *128*, 2190.

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Table 5. NPA Atomic Charges in |e$^-$| for the Bare Gas-Phase Complexes[a]

system/atom	hydO	hydN	carb
	penta-coordinated		
$[UO_2(R_i)_2(R_{iH})]$			
U	3.44 | *2.29*	3.32 | *2.31*	3.40 | *2.42*
UO_2^{2+}	1.55 | *1.08*	1.43 | *1.01*	1.54 | *1.14*
O4	−0.79 | *−0.71*	−0.68 | *−0.62*	−0.72 | *−0.65*
L1[b]	−0.77 | *−0.59*	−0.63 | *−0.55*	−0.79 | *−0.62*
L3[c]	0.00 | *0.09*	−0.18 | *0.09*	0.03 | *0.10*
$[UO_2(R_i)_2(H_2O)]$			
U	3.44 | *2.40*	3.33 | *2.31*	3.39 | *2.41*
UO_2^{2+}	1.55 | *1.10*	1.43 | *1.02*	1.53 | *1.14*
L1	−0.79 | *−0.60*	−0.73 | *−0.55*	−0.78 | *−0.62*
H_2O	0.03 | *0.09*	0.03 | *0.09*	0.04 | *0.10*
	hexa-coordinated		
$[UO_2(R_i)_2(R_{iH})(H_2O)]$			
U	3.42 | *2.38*	3.35 | *2.24*	3.39 | *2.37*
UO_2^{2+}	1.57 | *1.10*	1.46 | *0.96*	1.55 | *1.12*
O4	−0.78 | *−0.70*	−0.67 | *−0.61*	−0.81 | *−0.77*
L1[b]	−0.79 | *−0.63*	−0.75 | *−0.56*	−0.80 | *−0.64*
L3[c]	0.00 | *0.09*	0.02 | *0.08*	0.01 | *0.05*
H_2O	0.02 | *0.07*	0.02 | *0.08*	0.04 | *0.11*
$[UO_2(R_i)_2(H_2O)_2]$			
U	3.44 | *2.37* (3.44 | *2.36*)	3.34 | *2.25* (3.35 | *2.26*)	2.35 | *3.40* (2.36 | *3.41*)
UO_2^{2+}	1.57 | *1.09* (1.54 | *1.06*)	1.44 | *0.96* (1.43 | *0.95*)	1.54 | *1.09* (1.54 | *1.08*)
L1	−0.82 | *−0.64* (−0.81 | *−0.63*)	−0.75 | *−0.57* (−0.75 | *−0.57*)	−0.81 | *−0.65* (−0.81 | *−0.65*)
H_2O[d]	0.03 | *0.10* (0.04 | *0.10*)	0.03 | *0.09* (0.03 | *0.09*)	0.04 | *0.10* (0.04 | *0.10*)

[a] The reference values in plain characters are based on the standard valence/Rydberg partition scheme, excluding 6d orbitals from the valence part. In italics are reported other NPA charge values based on an alternate partition scheme[66] including 6d orbitals in the valence shell. For both partition schemes, charges in solvent (ethanol) are reported in parenthesis. [b] Average value for the two bidentate ligands. [c] Value for the monodentate ligands. [d] Average value for the two water molecules.

high interaction energies also support such kind of interaction.

Looking more in detail at the charges on the different atoms, the oxygen atoms of the bidentate R_{hydO} ligands and the oxygen and nitrogen atoms of the R_{hydN} ligand have similar charges (about −0.6). Therefore, the third ligand (monodentate) is responsible for differences in interaction energies between the corresponding complexes. In fact the coordinating oxygen atom (O4, see Figure 2) has a charge of −0.79 in the first complex and of −0.68 in the second one. This last value is closer to the O4 atom of the carboxylic function (−0.72). If a simple Coulomb (electrostatic) model is then applied, using the U−O4 distances reported in Tables 2–4, a trend similar to the variations of the dissociation energies is found, thus, pointing out the electrostatic nature of the interaction.

It is interesting to note that the atomic charges computed for the free ligands are close to those obtained using the whole calix[6]arene in its most stable conformation (cone).[72] For instance the N3 atom in the hydroxamic functions (R_{hydN}) has a charge of −0.38 in the free ligand and −0.39 in the whole calix[6]arene. Similar differences are found for other atoms of the ligands, with the exception, of course, of the terminal atoms of the alkyl chain. These results confirm the validity of our structural model.

Finally, a fine-tuning of the interaction can be related to the formation of a hydrogen bond between a deprotonated and a protonated hydroxamic function, which stabilizes the corresponding complexes. The O3H4 distance increases from 1.657 Å (R_{hydO}) to 2.132 Å (R_{hydN}), in agreement with the respective interaction energies of the corresponding two complexes. No such interaction is observed for the complex involving carboxylic functions.

In summary, electrostatic interactions seem to have a predominant role in ruling the interaction between uranyl and chelating ligand. Although a better point-charge or multipole model[74,75] could provide an improved description of these interactions, it appears clearly that nonbonded interactions should play a key role in the stabilization of these complexes. Nevertheless, these interactions in the hydroxamic functions are fine tuned by acting on the non negligible covalent character through chemical modification (R_{hydO} vs R_{hydN}).

3.2. Penta- vs Hexacoordinated Complexes: the Role of Solvent Molecules. In a second step, the role of the solvent on the complexing properties has been addressed. In particular two questions arise: the role of an eventual competition between the water molecules and acid groups in the first coordination sphere of uranyl and the bulk solvent effects on the interaction energies. Starting with the three reference structures, we can envisage substituting a carboxylic or an hydroxamic function with one water molecule, preserving the same coordination number (here 5). The resulting system will be indicated as $[UO_2(R_i)_2(H_2O)]$. In this case, we note a slight destabilization with a decrease of the absolute interaction energy of about 25 kJ mol^{-1} for the complexes with R_{hydO} and R_{carb} chelating groups. On the other hand, a substantial stabilization (90 kJ mol^{-1}) is observed for the third complex $[UO_2(R_{hydN})_2(H_2O)]$. Therefore, this system becomes more competitive with respect to the corresponding hydrated carboxylate complex, showing similar interaction energies (2684 vs 2672 kJ mol^{-1}, respectively).

From a geometrical point of view, no significant variations are found concerning the structures of the two ligands in all the three complexes, as well as in their distances from the uranium atom. Furthermore, while for the $[UO_2(R_{HydO})_2(H_2O)]$ and $[UO_2(R_{carb})_2(H_2O)]$ complexes the U−OH_2 distance (2.58 and 2.57 Å respectively) is very close to that in the pentahydrated complex, ($[UO_2(H_2O)_5]^{2+}$, 2.51 Å), a larger distance is instead found for the $[UO_2(R_{HydN})_2(H_2O)]$ complex (2.62 Å).

Following this behavior, the electronic distribution is not significantly affected by the substitution of the monodentate ligand with one water molecule, the latter bearing a negligible positive charge.

These results point out, once again, the predominant role of the electrostatic interactions in such complexes. More in general, according to the small interaction energy differences between the reference structures and the hydrated ones and omitting the improbable $[UO_2(R_{hydN})_2(R_{hydNH})]$ complex (see

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(74) Stone, A. J. *Chem. Phys. Lett.* **1981**, *83*, 233.

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the pK_a discussion in section 3.4), we can conclude that only two acid groups are necessary to strongly stabilize the uranyl cation, completing the first coordination sphere with a single water molecule.

The maximum coordination number of uranyl is 6. To reach this coordination, two configurations may be envisaged. The first one is obtained by adding a second water molecule to the previous hydrated pentacoordinated complexes. Indeed, the new structures $[UO_2(R_i)_2(H_2O)_2]$ correspond to hexacoordinated complexes since the uranium−oxygen(water) distance is less than 3 Å, a length close to the other distances found between uranium and the chelating groups. The insertion of the second water molecule stabilizes all the considered systems, with an energy decrease ranging between 41 and 76 kJ mol^{-1} (see Table 1 for details). The final structures are, for all the considered cases, more stable than those with one water molecule $[UO_2(R_i)_2(H_2O)]$ and those with three ligands $[UO_2(R_i)_2(R_{iH})]$. This stabilization is lower for $[UO_2(R_{hydO})_2(H_2O)_2]$ than for $[UO_2(R_{hydN})_2(H_2O)_2]$ and $[UO_2(R_{carb})_2(H_2O)_2]$ complexes. Furthermore, the second water molecule makes $[UO_2(R_{hydN})_2(H_2O)_2]$ competitive with the corresponding carboxylate complex, the interaction energies being 2755 and 2748 kJ mol^{-1}, respectively.

The insertion of a second water molecule has a small effect on the structures of the adducts, making the coordination sphere of the uranium atom symmetric in the final adduct. As a consequence, since the two water molecules are closer to the uranium than in the mono hydrated complex, the ligands are pushed slightly far from the metal atom. Furthermore, these distances are very close in the different ligands, all being around 2.49 Å. In a similar manner, the electronic structure of the complexes does not change in a significant way (see atomic charges in Table 5).

A second way to reach the same coordination number of 6 is to start from the reference complex structures with three chelating groups and add a single water molecule to the first coordination sphere of uranyl. The resulting complex is $[UO_2(R_i)_2(R_{iH})(H_2O)]$. These complexes are in all the three cases less stable than those with two water molecules, and their stabilization energy is comparable to the bare $[UO_2(R_i)_2(R_{iH})]$ systems (see Table 1). To accommodate the water molecule, the systems react in different ways: the ligands are pushed away in R_{hydO} and R_{hydN}, while the structures of the bare and hydrated caboxylate complexes are very similar, because of the smaller size of the ligand. A significant difference is also evident from the water−uranium distance which is shorter in R_{carb} than in the other ligands.

In summary, the conclusions are similar for both penta- or hexacoordinated complexes, that is, the substitution of one acid group by water molecules does not destabilize the systems, and the most stable structures are those characterized by two water molecules, $[UO_2(R_i)_2(H_2O)_2]$. In any case, the strongest metal−ligand interaction is obtained for the hexacoordinated $[UO_2(R_{hydO})_2(H_2O)_2]$ hydroxamic complex.

Finally, to have a rough idea of the strengths of such complexes in solution, we calculated the dissociation energies of a single water molecule in the different complexes envisaged, and we found an order of magnitude similar to the absolute value of the interaction energy for the water dimer. For instance, if we consider the $[UO_2(R_i)_2(R_{iH})(H_2O)]$ hexacoordinated complexes, the corresponding dissociation energy is 20 and 24 kJ mol^{-1} for R_{hydO} and R_{carb} chelating groups, respectively. These values are very close to the absolute interaction energy in water dimer (∼20 kJ mol^{-1}). A last important element strengthens this result. Indeed, we have to remember that the uranyl cation is already strongly hydrated in water, forming a pentacoordinated complex with water molecules.[76] The absolute interaction energy of the five water molecules with the cation is 1048 kJ mol^{-1} and has to be compared to the absolute interaction energies for our three non hydrated reference complexes in Table 1. The ratio ranges between 2.5 and 3 in favor of the acid groups. At the same time, the desolvation energy of the ligands plays a minor role, since the largest interaction energy of a water molecule, corresponding to the water bonded to the deprotoned atom, is only 93 kJ/mol. Lower interaction energies (about 20 kJ/mol) are found for the water molecules bonded to the other hydration site of the ligands. Even if the hydration/dehydration reactions require more detailed studies, possibly carried out using dynamic methods, it is reasonable to argue that calixarene with hydroxamic or carboxylic functions have a greater affinity with uranyl with respect to water.

3.3. Bulk Solvent Effects. As a further investigation on the solvent effects, the reaction field generated by the bulk solvent was introduced using a polarizable continuum model (PCM), choosing ethanol as a model of 1-heptanol, the solvent used during solvent extraction experiment for the organic phase.[77] The structures of the complexes were fully reoptimized in ethanol and the resulting interaction energies were very close to those obtained in the gas phase. For instance, for the three complexes $[UO_2(R_i)_2(H_2O)_2]$, the energy differences vary between 9 and 17 kJ mol^{-1}. In a similar manner, their electronic structure is not affected by interaction with the bulk (see Table 5). As a conclusion, we can deduce that the solvation of these complexes by ethanol has a weak influence in terms of energetic stability.

3.4. Acidity of Complexing Functional Groups. From a general point of view, a cation interacts preferentially with the most basic site of a complexing functional group. The hydroxamic functions are monoacids but they have two possible deprotonation sites, oxygen or nitrogen. For the carboxylic function (R_{carbH}), the OH group is the only possibility for deprotonation. Using a Born−Haber thermodynamic cycle and a standard approach within the PCM solvent approach,[70] the pK_a values of the different functional groups in water can be obtained. The three reactions corresponding to the different deprotonation sites are

$$CH_3OCH_2CONHOH \leftrightarrow CH_3OCH_2CONHO^- + H^+ \quad \text{(hydroxamic function, OH site)} \tag{1}$$

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(76) Hay, P. J.; Martin, R. L.; Schreckenbach, G. *J. Phys. Chem. A* **2000**, *104*, 6259.

(77) Garcia, B.; Ibeas, S.; Hoyuelos, F. J.; Leal, J. M.; Secco, F.; Venturini, M. *J. Org. Chem.* **2001**, *66*, 7986.

Table 6. Deprotonation Gibbs Free Energies (kJ/mol^{-1}) and pK_a Values Determined for Different Functional Acid Groups

functional group	deprotonation site	ΔG_{gaz}, R_{iH}	ΔG_{solv}, R_{iH}	pK_a	pK_a (exp) [a]
hydroxamic	OH	1480	−1430	9.9	9.34
	NH	1442	−1354	17.0	
carboxylic	OH	1375	−1354	5.2	4.76

[a] ref 77.

$$CH_3OCH_2CONHOH \leftrightarrow CH_3OCH_2CON^{-}OH + H^{+} \quad \text{(hydroxamic function, NH site)} \tag{2}$$

$$CH_3OCH_2COOH \leftrightarrow CH_3OCH_2COO^{-} + H^{+} \quad \text{(carboxylic function, OH site)} \tag{3}$$

The corresponding thermodynamic data are collected in Table 6. The deprotonation site of hydroxamic acids has been long debated. Indeed, they may be considered as NH-acids in DMSO or in the gas phase and as OH-acids in water and alcohols.[78,79]

If we first examine the two possible deprotonation sites of the hydroxamic functions, we can note that the Gibbs free energy for the reaction 1 (OH site) is higher than the value obtained for the reaction 2 (NH site). In contrast, when the solvation is taken into account, the values are inverted. These results are in agreement with previous experimental studies showing that hydroxamic acids are NH-acids in gas phase and in DMSO while they are OH-acids in water and in an alcohol media.[33] Finally, it is interesting to point out that the experimental pK_a value (9.34) for hydroxamic functions is very close to the theoretical value corresponding to the deprotonation of OH (reaction 1), that is, 9.9. In contrast, the calculated value for reaction 2 is quite high (pK_a = 17) and not included in the acidity domain of water. These results indicate that the deprotonation of the NH site in water is highly improbable. For the carboxylic function, we find a lower value for the pK_a (5.2), and we are again very close to the experimental value of 4.76. In summary, all the functions studied correspond to weak acids, even if the NH-acids (R_{hydN}) are weaker than the carboxylic ones.

4. Comments

The chemical aspects emerging from our results can be summarized as follows:

(1) The affinity of hydroxamic ligands, deprotonated on the oxygen atom, is higher than those for other chelating ligands thus suggesting a better extractive power. The R_{hydN} function is competitive with the carboxylate, but its availability is very low since the corresponding pK_a is high. Therefore, among the three considered chelating groups, only two, R_{hydO} and R_{carb}, are plausibly available in experimental conditions.

(2) The investigated complexes correspond to different coordination shells for the uranyl, leading to a coordination number between 5 and 6 (i.e., 7 and 8 for uranium). The bare pentacoordinated system, $[UO_2(R_i)_2(R_{iH})]$, is already very stable, more than the hydrated uranyl, thus underlining its extracting power in aqueous solution.

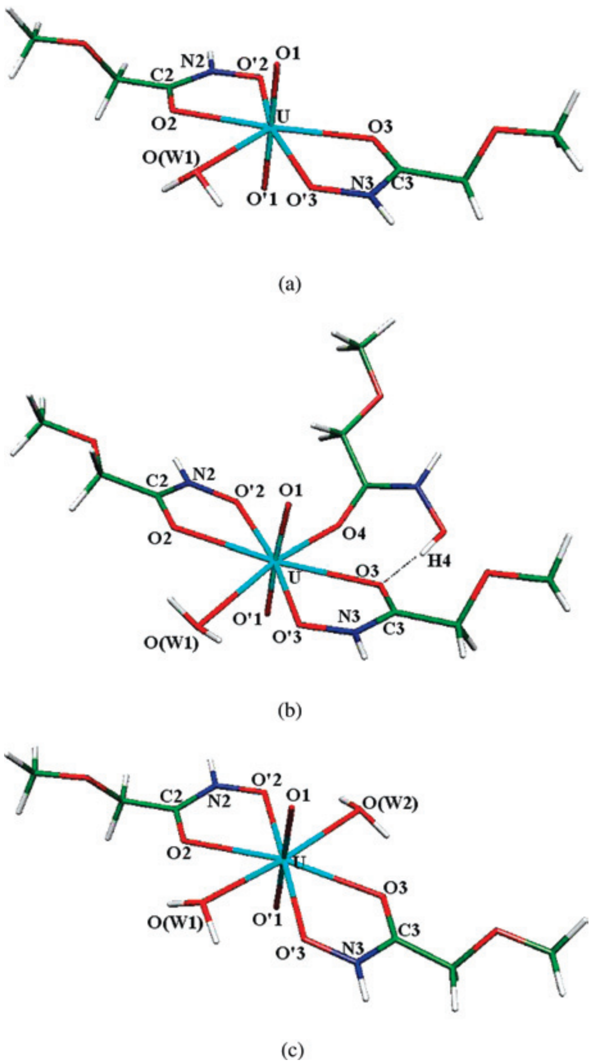

Figure 3. Optimized structures of the three most stable hydrated complexes: $[UO_2(R_{hydO})_2(H_2O)]$ (a), $[UO_2(R_{hydO})_2(R_{hydOH})]$ (b), and $[UO_2(R_{hydO})(H_2O)_2]$ (c).

(3) A water molecule stabilizes this last complex, leading to the $[UO_2(R_i)_2(R_{iH})(H_2O)]$ system, where the coordination number of uranyl is 6 (8 for uranium). An even more stable complex is obtained by replacing the protonated ligand, R_iH, with a second water molecule and still conserving the same (6) coordination number.

(4) The most stable complex, $[UO_2(R_i)_2(H_2O)_2]$, is obtained by explicitly including two water molecules representing the first solvation shell in the calculations. Bulk solvent effects (in ethanol) are instead negligible. More generally, these complexes can be envisioned as the product of a ligand exchange reaction between $[UO_2(H_2O)_5]^{2+}$ and two R_i^{-} acid groups. Such a reaction is exothermic, from a thermodynamic point of view, with reaction energies ranging from −1464 kJ/mol (hydroxamic functions) to −1380 kJ/mol (carboxylic functions).

(5) The hydroxamic ligands lead to the formation of three (out of four) different complexes, namely, $[UO_2(R_i)_2(R_{iH})]$, $[UO_2(R_i)_2(R_{iH})(H_2O)]$, and $[UO_2(R_i)_2(H_2O)_2]$, whose stabi-

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lization energies are within a small range (±10 kJ mol^{-1}). This is not the case for the carboxylate derivatives, where the most stable complex is 42 kJ mol^{-1} lower in energy than the second one. This result suggests that the complexation with hydroxamic functions is favored not only from an energetic point of view (lower complexation energy) but also from an entropic aspect (3 complexes possible out of 4).

(6) pK_a calculations indicate well how the carboxylic ligands are available at lower pH than the hydroxamic one, in agreement with the experimental findings.

(7) From a more technical point of view, NPA charges strongly suggest predominant electrostatic interactions between the metal and the ligands. Furthermore, the partition scheme between valence and Rydberg orbitals of the uranium atom is important only for the description of the electronic distribution in uranyl but not for the interaction between the uranium atom and the functionalized acid groups.

5. Conclusion

In this paper, we presented a detailed theoretical analysis of the complexation of uranyl cation by hydroxamic or carboxylic extractant groups. First, DFT calculations have been carried out to compare the relative stabilities of the different formed complexes and to examine the influence of water molecules in the first coordination sphere. From these results, we can draw some conclusions. During the mixture process of the extraction procedure, the hydrated pentacoordinated uranyl complex is partially or completely dehydrated in its first coordination sphere. The stronger availability of hydroxamic functions (deprotoned on oxygen atoms) favors the formation of penta- or hexacoordinated uranyl complexes with two deprotonated hydroxamic groups and one or two water molecules, respectively. From an energetic point of view, these partially hydrated forms may coexist with a fully dehydrated structure where the uranyl cation is complexed by three acid groups, two of them being deprotonated. However, if we now envisage the real process involving a full calix[6]arene functionalized by hydroxamic functions, the preferential cone configuration of the cage will distort the uranyl complex that will deviate then from the ideal planar structure. Therefore, a stabilizing interaction with three chelating groups is questionable while a conformational structure with only two hydroxamic functions (and a water molecule) seems to be preferable. Further calculations, modeling the whole calix[6]arene cage, are still in progress in our laboratory.

Acknowledgment. The authors thank IDRIS for a grant of computer time within the Project No. 72116. They also thank one of the referees for pointing out the problem of the NPA partition scheme on the uranium atom.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

IC7018633