

Water versus Acetonitrile Coordination to Uranyl. Effect of Chloride Ligands

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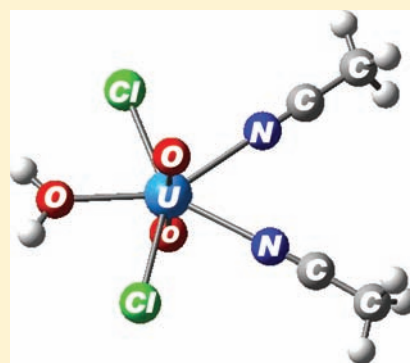
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S Supporting Information

ABSTRACT: Optimizations at the BLYP and B3LYP levels are reported for the mixed uranyl chloro/water/acetonitrile complexes $[\text{UO}_2\text{Cl}_n(\text{H}_2\text{O})_x(\text{MeCN})_{5-n-x}]^{2-n}$ ($n = 1-3$) and $[\text{UO}_2\text{Cl}_n(\text{H}_2\text{O})_x(\text{MeCN})_{4-n-x}]^{2-n}$ ($n = 2-4$), in both the gas phase and a polarizable continuum modeling acetonitrile. Car–Parrinello molecular dynamics (CPMD) simulations have been performed for $[\text{UO}_2\text{Cl}_2(\text{H}_2\text{O})(\text{MeCN})_2]$ in the gas phase and in a periodic box of liquid acetonitrile. According to population analyses and dipole moments evaluated from maximally localized Wannier function centers, uranium is less Lewis acidic in the neutral UO_2Cl_2 than in the UO_2^{2+} moiety. In the gas phase the latter binds acetonitrile ligands more strongly than water, whereas in acetonitrile solution, the trend is reversed due to cooperative polarization effects. In the polarizable continuum the chloro complexes have a slight energetic preference for water over acetonitrile ligands, but several mixed complexes are so close in free energy ΔG that they should exist in equilibrium, in accord with previous interpretations of EXAFS data in solution. The binding strengths of the fifth neutral ligands decrease with increasing chloride content, to the extent that the trichlorides should be formulated as four-coordinate $[\text{UO}_2\text{Cl}_3\text{L}]^-$ ($\text{L} = \text{H}_2\text{O}, \text{MeCN}$). Limitations to their accuracy notwithstanding, density functional calculations can offer insights into the speciation of a complex uranyl system in solution, a key feature in the context of nuclear waste partitioning by complexant molecules.



1. INTRODUCTION

Driven by the quest for ever better separation of radionuclides in nuclear waste, the study of actinide speciation in nonaqueous media is an active area of research. The use of ionic liquids (ILs) is gaining popularity for this purpose,¹ and the coordination chemistry in organic solvents can often be a useful reference for the environments present in ILs. For example, a uranyl trinitrate complex, which is unknown in water, can be observed in acetonitrile and in an IL,² and zwitterionic carboxyl ligands remain coordinated to uranyl in acetonitrile and an IL, but not in water.³ It has also long been known that complex formation with crown ethers can depend notably on the environment: e.g., inclusion complexes between uranyl triflate and 18-crown-6 are only formed in acetonitrile, not in water.⁴ The different redox properties of uranium in nonaqueous solvents, as compared to that in water, has broken the ground for a blossoming chemistry of pentavalent uranium(V) compounds.⁵ Intimately related to these findings is the fact that actinides, uranyl in particular, display quite different affinities toward water and organic solvents as ligands. In a recent EXAFS study of uranyl(VI) chloride complexes in acetonitrile, for instance (by Hennig et al.),⁶ the parent uranyl pentahydrate $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ appeared to be preferred over a corresponding acetonitrile complex, $[\text{UO}_2(\text{NCMe})_5]^{2+}$, even though acetonitrile, the solvent, is present in a large excess over

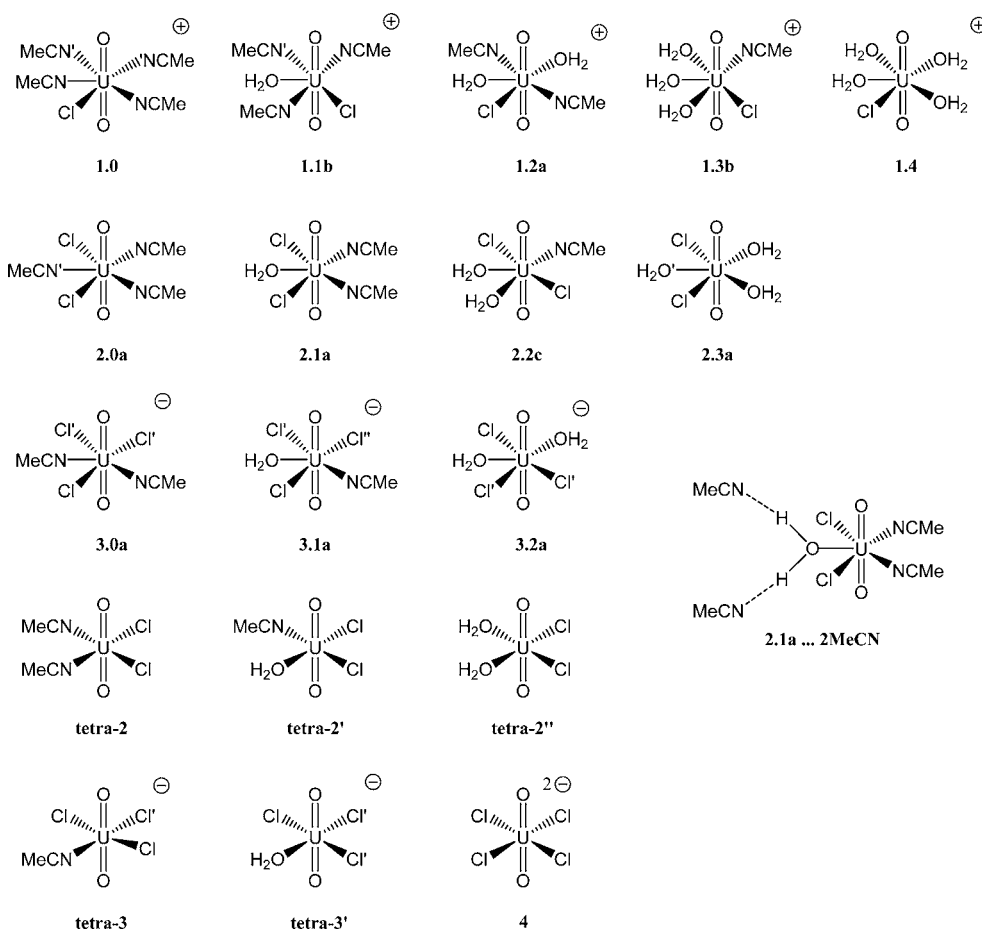
water (coming from the uranyl precursor). This kind of preferential first-shell solvation may be a potential problem when working in organic solvents or ILs, because it may be difficult to strictly exclude all traces of water if the solvent is hygroscopic.

The EXAFS analysis by Hennig et al. suggested that, in the case of uranyl, this preferential binding of water over acetonitrile is strongly dependent on the nature and concentration of potentially coordinating counterions, chloride in this case. While uranyl binds chloride only weakly in aqueous solution,⁷ there is evidence from UV–vis spectroscopy that in acetonitrile all $[\text{UO}_2\text{Cl}]^+$, $[\text{UO}_2\text{Cl}_2]$, $[\text{UO}_2\text{Cl}_3]^-$, and $[\text{UO}_2\text{Cl}_4]^{2-}$ species are successively populated with increasing chloride concentration.⁶ At the same time, EXAFS suggests the presence of both U–N(CMe) and U–O(H₂) bonds in the mono- and dichlorides and just U–N bonds in the trichloride.⁶ The dichloride was tentatively assigned to the complex $[\text{UO}_2\text{Cl}_2(\text{H}_2\text{O})(\text{MeCN})_2]$, which had been characterized in the solid state.⁸ It thus appears that without chloride uranyl has a clear preference for water ligands, with one or two chlorides attached there is little discrimination between water and

Received: October 19, 2011

Published: January 10, 2012

Chart 1. Investigated Four- and Five-Coordinated Complexes; the Latter are Labeled According to the Number of Chloro (First Digit) and Aquo Ligands (Second Digit)^a



^aPositional isomers are labeled with letters a–c. Only the most stable isomer (in the continuum) is shown in each case; for all isomers see Scheme S1 in the Supporting Information.

acetonitrile, and with three chlorides acetonitrile is the preferred ligand.

Computational actinide chemistry is well advanced. The arsenal of methods that can be applied comprises both static quantum-chemical calculations⁹ and dynamic approaches based on fully classical potentials or on those derived by density functional theory (DFT).¹⁰ In a recent study (hereafter named paper 1),¹¹ we have used such static and dynamic DFT tools to rationalize the preference of the uranyl dication to coordinate water vs acetonitrile in solution. This preference was rationalized in terms of polarization of the coordinated water, which is cooperatively enhanced through specific interactions with the solvent (OH...NCMe hydrogen bonds). In order to rationalize the observed speciation in the EXAFS experiment, we now apply the same DFT methodology to study the differential affinities of uranyl chloride complexes to water and acetonitrile ligands. Special attention is called to the change in the cooperative polarization on going from uranyl to uranyl chloride complexes, which may have implications beyond the uranyl case, e.g. for the general affinity of M^{n+} ions toward water in condensed phases as a function of charge and/or other coligands.

2. COMPUTATIONAL DETAILS

Essentially the same methods and basis sets as in paper 1 were employed.¹¹ Nonperiodic geometry optimizations were performed in the gas phase using the BLYP¹² functional, the small-core Stuttgart–Dresden relativistic ECP together with its valence basis set on U¹³ (from which the most diffuse s, p, d, and f functions were each omitted, affording a [7s6p5d3f] contraction),¹⁴ standard 6-31G(d,p) basis for all other elements, and a fine integration grid (75 radial shells with 302 angular points per shell), denoted SDD. The minimum character of each stationary point was verified by computation of the harmonic vibrational frequencies, which were all real. The geometries were reoptimized with the same methods and basis sets using the PCM implementation of Tomasi and co-workers¹⁵ (employing the united-atom UFF radii and the parameters of acetonitrile), denoted PCM. To model the changes in entropy for the condensed phase, reflected in the changes between corresponding ΔE and ΔG values (denoted δE_G), the standard expressions from statistical thermodynamics have been evaluated in the gas phase at a pressure of 1354 atm¹⁶ (at $T = 298$ K). Refined single-point energies were evaluated both in the gas phase and in the continuum at the BLYP/SDD(+) level: i.e., using the geometries optimized in the respective medium, the same SDD ECP and valence basis on U, and the 6-311+G(d,p) basis¹⁷ on all other elements (the resulting energies in the continuum are denoted E_{solv}). Following the recommendation by Ho, Klamt, and Coote,¹⁸ free energies in solution, $\Delta G(\text{PCM})$, have been obtained from $E_{\text{solv}} + \delta E_G + \delta G_{\text{nes}}$, where G_{nes} denotes the sum of nonelectrostatic contributions: i.e., cavitation and dispersion–repulsion interactions.¹⁹ In addition, estimates for the basis-set

Table 1. Mean Optimized or Simulated^a U–X Distances (in Å; X = Cl, N, O_{eq}), Evaluated for Selected Complexes in the Gas Phase, a Polarizable Continuum, or an Explicit Acetonitrile Solution

complex	dist	B3LYP gas	BLYP		CP-opt gas	CPMD		exptl
			gas	PCM		gas	soln	
1.1b	U–Cl	2.59	2.60	2.66				
	U–N	2.58	2.59	2.57				
	U–N'	2.62	2.64	2.60				
	U–O _{eq}	2.56	2.58	2.45				
2.1a	U–Cl	2.69	2.70	2.72	2.70	2.71(7)	2.69(7)	2.66 ^b
	U–N	2.64	2.66	2.61	2.65	2.68(7)	2.72(16)	2.51–2.56 ^b (mean 2.54)
	U–O _{eq}	2.54	2.57	2.53	2.59	2.66(15)	2.54(12)	2.46 ^b
	(O)H...N						1.93(19) ^c	<i>d</i>
2.1a+2MeCN	U–Cl			2.72	2.71	→2.1a+2MeCN		2.66 ^b
	U–N			2.63	2.70			2.51–2.56 ^b (mean 2.54)
	U–O _{eq}			2.46	2.48			2.46 ^b
	(O)H...N			1.84	1.98			<i>d</i>
2.1b	U–Cl	→tetra-2'+MeCN	tetra-2'+MeCN	2.71	2.63	→tetra-2+H ₂ O		2.70(6)
	U–N			2.64	2.72			2.66(13)
	U–O _{eq}			2.52	2.74			2.51(8)
	(O)H...N							1.94(20)
tetra-2'	U–Cl	2.61	2.62	2.66				
	U–N	2.61	2.62	2.56				
	U–O _{eq}	2.56	2.58	2.42				
3.1a	U–Cl	2.87	2.93	2.79				
	U–Cl'	2.72	2.71	2.77				
	U–Cl''	2.69	2.70	2.74				
	U–N	2.66	2.68	2.63				
	U–O _{eq}	2.61	2.64	2.58				
tetra-3	U–Cl	2.69	2.71	2.70	2.70			
	U–Cl'	2.65	2.67	2.69	2.68			
	U–N	2.65	2.66	2.57	2.67			
tetra-3'	U–Cl	2.76	2.79	2.71	2.77			
	U–Cl'	2.65	2.66	2.71	2.65			
	U–O _{eq}	2.62	2.65	2.45	2.70			
4	U–Cl	2.75 ^e	2.77 ^e	2.73	2.72 ^e	2.76(8) ^e	2.72(10)	2.68(2)

^aAverages over the last picosecond of MD; U–X distances of all complexes from Chart 1 are reported in Tables S1–S3 in the Supporting Information. ^bSolid state; ranges for the two molecules in the unit cell are given (from ref 8). ^cFor the persistent H...N bond (see text). ^dNo H atoms refined. ^eFrom ref 37; box length 13 Å.

superposition error (BSSE) of individual bonds were included, which were computed for complex 2.1a using the Counterpoise method,²⁰ employing the BLYP functional, SDD(+) basis, and the BLYP/SDD geometry optimized in the continuum. These corrections (denoted E_{BSSE}), which are summarized in Figure S1 of the Supporting Information, were evaluated from separate two-body decompositions of the different ligands in 2.1a and were subsequently used for the same bond types in the other complexes.²¹

The BLYP functional was chosen for direct comparison with the Car–Parrinello molecular dynamics (CPMD) simulations (see below), which employed it for compatibility with our previous simulations of aqueous solutions,^{10b,c} where this functional performs better than most other standard GGAs for describing the properties of liquid water.²² Gas-phase BLYP structures were reoptimized at the B3LYP/SDD^{23,12b} level. Selected atomic charges were obtained from Mulliken and natural population analysis (NPA)²⁴ using the default partitioning scheme.²⁵ These calculations were performed with the Gaussian 03²⁶ suite of programs.

CPMD²⁷ simulations were performed using the BLYP functional and norm-conserving pseudopotentials that had been generated according to the Troullier and Martins procedure²⁸ and transformed into the Kleinman–Bylander form.²⁹ For uranium, the semicore (or small-core) pseudopotential was employed that had been generated and validated in ref 10b. Periodic boundary conditions were imposed using cubic supercells with a lattice constant of 15 Å. Kohn–Sham

orbitals were expanded in plane waves at the Γ point up to a kinetic energy cutoff of 80 Ry. Simulations were performed in the NVT ensemble using a single Nosé–Hoover thermostat set to 320 K (frequency 1800 cm⁻¹), a fictitious electronic mass of 600 au, and a time step of 0.121 fs. In order to maintain the time step, hydrogen was substituted with deuterium. The somewhat higher temperature was chosen to increase solvent mobility and improve the sampling. For the solutions, the boxes contained the UO₂ moiety with the necessary number of coordinated water molecules, as well as a total of 36 acetonitrile molecules. Long-range electrostatic interactions were treated with the Ewald method. Simulations of solutions started from pre-equilibrated classical MD snapshots using the AMBER force field³⁰ (200 ps with frozen solute) and were continued for 3 ps in each case; data were collected for analysis during the last picosecond. According to the indicators detailed in paper 1 (radial distribution functions, acetonitrile diffusion coefficient), the simulated solutions remained liquid-like throughout.

Selected geometries were optimized in the gas phase using the same setup as described above until the maximum gradient was less than 5×10^{-4} au (denoted CP-opt). The resulting charge distributions were analyzed by transforming the Kohn–Sham MOs into maximally localized Wannier functions characterized by their centers.³¹ For dynamic ensembles, Wannier centers were evaluated for 50 snapshots taken during the last picosecond. The structure of solid 2.1a+2MeCN was also optimized, starting from the heavy-atom coordinates as

deposited in the Cambridge Structure Database (refcode SAZDOM).⁸ A simple orthorhombic cell with lattice constants fixed to the experimental values ($a = 14.891 \text{ \AA}$, $b = 6.733 \text{ \AA}$, $c = 15.931 \text{ \AA}$) was used, containing four formula units. Hydrogen atoms were placed on the water oxygen atoms pointing toward adjacent N atoms and were placed arbitrarily on the methyl C atoms. Atomic positions were relaxed using 1, 2, and 1 k points along the reciprocal a , b , and c axes, respectively.³² The use of more k points along the b axis resulted in no further changes in the geometrical parameters and only very minor changes (less than 1 kcal/mol) in the total energy. All CP-*opt* computations and CPMD simulations were performed with the CPMD program.³³

3. RESULTS

3.1. Structures. The structures of the complexes investigated in this study are displayed in Chart 1. Geometries have been optimized in the gas phase and in a polarizable continuum (PCM) modeling bulk acetonitrile. Geometric parameters are collected in Table 1 for selected, representative complexes. Some were not stable at all levels (denoted by an arrow and the dissociation products upon attempted optimization or CPMD simulation).

Similar to what had been found for the dicationic, mixed aquo/acetonitrile complexes in paper 1,¹¹ the U–O_{eq} distances to the water ligands are quite sensitive to solvation and decrease considerably on going from the gas phase to the bulk, by 0.04–0.2 Å for static minima and a PCM model (compare e.g. BLYP gas and BLYP PCM data for **tetra-3'** in Table 1), and by 0.12 Å for dynamic ensembles with explicit solvation (compare CPMD gas and CPMD solution data for **2.1a** in Table 1). The U–Cl and U–N distances are usually much less affected by solvation, but the extent of this effect tends to increase with the number of chlorides present (see in particular **3.1a**).

Apart from the tetrachloro species **4**, the only structure that can be directly compared to experiment is **2.1a**. The solid analyzed by X-ray diffraction contains two cocrystallized acetonitrile molecules, H-bonded to the water ligand as in **2.1a·2MeCN**. In a gas-phase CPMD simulation of this microsolvated complex, the two additional acetonitrile molecules are very labile, rapidly (within 0.9 ps) detaching from the complex. In solution, the water ligand is solvated by one to two acetonitrile molecules in the second solvation sphere; see the first peak in the H_{H₂O}⋯N_{MeCN} radial distribution function (RDF, dashed curve in Figure 1). Visual inspection of the trajectories reveals that dynamic exchange takes place during the dynamics, where the two original solvating molecules are displaced by two others (see Figure S2).³⁴ Integration of the RDF up to the first minimum at $r \approx 2.7 \text{ \AA}$ indicates that each H_{H₂O} atom is solvated by 0.8 MeCN molecule on average (over the last 2 ps of MD). In contrast, two persistent H bonds were observed for [UO₂(MeCN)₄(H₂O)]²⁺, where the corresponding RDF shows a much higher first peak that integrates to 1.0 MeCN molecules in H-bonding distance (see solid red curve in Figure 1).

To assess the difference in solvation between the two complexes, we considered eq 1, where the two MeCN

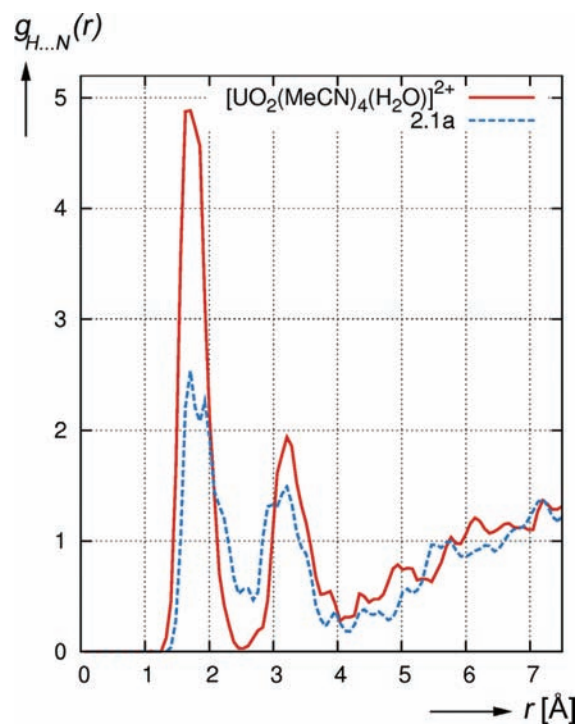
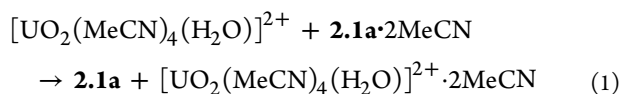


Figure 1. Radial distribution function $g(r)$ for **2.1a** (dashed, blue) and [UO₂(MeCN)₄(H₂O)]²⁺ (solid, red) in acetonitrile solution between the H atoms of the coordinated water ligand and the N atoms of the solvent MeCN molecules.

molecules in the second shell are transferred from **2.1a** to [UO₂(MeCN)₄(H₂O)]²⁺.

The corresponding $\Delta E(\text{BLYP}/\text{PCM})$ value is -4.8 kcal/mol , indicating that the dicationic complex is better solvated than the neutral species, in accord with CPMD(solution) results.

In comparison to the structure in the solid, the U–N distances in the optimized or simulated complexes **2.1a** are significantly elongated, by up to 0.18 Å for CPMD(solution) (see Table 1).³⁵ Part of this discrepancy may be due to the different environments in the crystal and in solution, possibly exacerbated by a shallow U–N stretching potential. When the coordinates of solid **2.1a·2MeCN** are reoptimized at CP-*opt*/BLYP (for a fixed unit cell), U–N distances of 2.54 and 2.59 Å are obtained: i.e., much closer to experiment and with a degree of overestimation that is quite common for metal–ligand distances obtained with this functional.³⁶

As expected, on going from five- to four-coordinate complexes, the distances between U and each donor atom decrease significantly (see BLYP/PCM data in Table 1, e.g. between **2.1a** and **tetra-2'**). The U–Cl distances for **4** in acetonitrile, e.g. 2.72 Å at CPMD(solution), are very similar to the corresponding values in water, e.g. 2.71 Å at CPMD(aq).³⁷

3.2. Energetics. We now assess the relative stability of water vs acetonitrile chloro complexes via energies for cumulative ligand displacement reactions according to eqs 2–4.

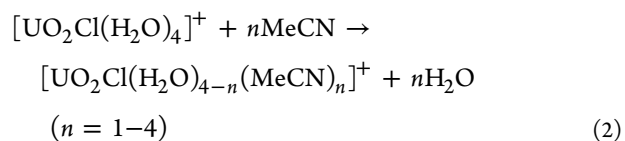


Table 2. Reaction Energies ΔE and Free Energies ΔG for the Successive Displacement of Aquo Ligands with Acetonitrile According to Eqs 2–4 (in kcal/mol)^a

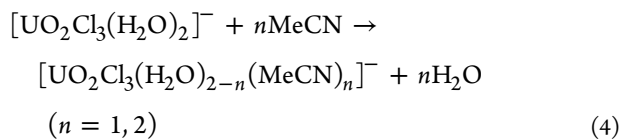
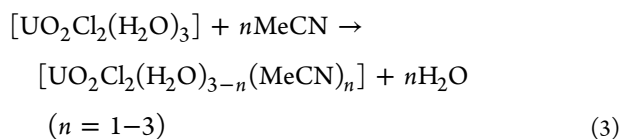
reaction	B3LYP			BLYP			ΔG	
	ΔE_{gas}	ΔE_{gas}	$\Delta E_{\text{soln}}^{\text{PCM}}$	δG_{nes}	δE_{G}	δE_{BSSE}	gas	PCM
Complexes without Chloride								
0.5 + MeCN \rightarrow [UO ₂ (H ₂ O) ₄ (MeCN)] ²⁺ + H ₂ O	-12.4 ^b	-13.2 ^b	2.3 ^b	1.0	0.0	-1.2 ^b	-14.5	1.9
0.5 + 5MeCN \rightarrow [UO ₂ (MeCN) ₅] ²⁺ + 5H ₂ O	-46.8 ^b	-51.4 ^b	16.9 ^b	5.8	-4.8	-6.0 ^b	-62.1	12.0
Monochloride Complexes								
1.4 + MeCN \rightarrow 1.3b + H ₂ O	-5.0	-5.2	2.1	1.0	-0.5	-1.0	-6.8	1.6
1.4 + 2MeCN \rightarrow 1.2a + 2H ₂ O	-9.2	-9.1	5.6	2.0	-1.4	-2.0	-12.5	4.2
1.4 + 3MeCN \rightarrow 1.1b + 3H ₂ O	-12.1	-12.6	8.1	3.2	-3.2	-3.0	-18.8	5.1
1.4 + 4MeCN \rightarrow 1.0 + 4H ₂ O	-14.6	-15.0	11.9	4.5	-4.4	-4.0	-23.3	8.0
Dichloride Complexes								
2.3a + MeCN \rightarrow 2.2c + H ₂ O	1.7	1.0	2.9	1.0	-1.9	-1.0	-1.9	1.1
2.3a + 2MeCN \rightarrow 2.1a + 2H ₂ O	4.9	4.4	5.7	2.2	-3.1	-2.0	-0.7	2.8
2.3a + 3MeCN \rightarrow 2.0a + 3H ₂ O	9.8	8.4	8.9	3.3	-5.2	-3.0	0.3	4.0
tetra-2'' + MeCN \rightarrow tetra-2' + H ₂ O	0.4	0.6	4.3	1.0	-2.4	-1.0	-2.8	1.9
tetra-2'' + 2MeCN \rightarrow tetra-2 + 2H ₂ O	1.6	2.0	9.1	2.2	-3.3	-2.0	-3.3	6.0
Trichloride Complexes								
3.2b + MeCN \rightarrow 3.1a + H ₂ O	dissoc	dissoc	2.6	1.0	dissoc	-1.0	dissoc	dissoc
3.2b + 2MeCN \rightarrow 3.0a + 2H ₂ O	dissoc	dissoc	6.3	2.0	dissoc	-2.0	dissoc	dissoc
tetra-3' + MeCN \rightarrow tetra-3 + H ₂ O	7.5	7.2	3.9	1.1	-2.8	-1.0	3.3	1.1

^a $\Delta G(\text{gas}) = \Delta E(\text{gas}) + \delta E_{\text{G}} + \delta E_{\text{BSSE}}$ and $\Delta G(\text{PCM}) = \Delta E_{\text{soln}}(\text{PCM}) + \delta G_{\text{nes}} + \delta E_{\text{G}} + \delta E_{\text{BSSE}}$; see Computational Details for definitions of these terms. *dissoc* indicates that one ligand dissociates from one of the reaction partner during gas-phase optimizations. ^bFrom ref 11; 0.5 denotes [UO₂(H₂O)₅]²⁺.

Table 3. Computed Driving Forces for H₂O Dissociation (Energies in kcal/mol)^a

reaction	B3LYP			BLYP			ΔG	
	ΔE_{gas}	ΔE_{gas}	$\Delta E_{\text{soln}}^{\text{PCM}}$	δG_{nes}	δE_{G}	δE_{BSSE}	gas	PCM
Dichloride Complexes								
2.1a \rightarrow tetra-2 + H ₂ O	12.4	9.7	6.6	2.3	-8.6	-1.9	-0.8	-1.5
2.2c \rightarrow tetra-2' + H ₂ O	14.5	11.6	4.5	2.3	-8.9	-1.9	0.8	-4.0
2.3a \rightarrow tetra-2'' + H ₂ O	15.8	12.1	3.2	2.4	-8.4	-1.9	1.7	-4.8
Trichloride Complexes								
3.1a \rightarrow tetra-3 + H ₂ O	5.2	3.7	0.7	2.5	-8.4	-1.9	-6.6	-7.2
3.2a \rightarrow tetra-3' + H ₂ O	8.0	dissoc	0.1	2.5	dissoc	-1.9	dissoc	dissoc

^a $\Delta G(\text{gas}) = \Delta E(\text{gas}) + \delta E_{\text{G}} + \delta E_{\text{BSSE}}$ and $\Delta G(\text{PCM}) = \Delta E_{\text{soln}}(\text{PCM}) + \delta G_{\text{nes}} + \delta E_{\text{G}} + \delta E_{\text{BSSE}}$. *dissoc* indicates that one ligand dissociates from one of the reaction partner during gas-phase optimizations.



The results are summarized in Table 2. Again, only the data for the most stable of each isomer is given. In general, the relative energies of different stereoisomers are closely spaced, typically within 1 kcal/mol or less (see Scheme S1 in the Supporting Information). Some representative values for dicationic complexes from ref 11 are included for comparison (first two entries).

For the cationic chloride-free and monochloride complexes, there is a greater energetic affinity for acetonitrile than for water in the gas phase, whereas it is the other way around in the continuum. For the neutral dichloride, water is the preferred ligand throughout. The same appears to be the case for the anionic trichloride, at least for the four-coordinate forms (last entry in Table 2); the five-coordinate complexes were not stable in the gas phase (see below). When the raw PCM energies are corrected for BSSE, enthalpic, and entropic contributions to yield the final estimates for ΔG (last column in Table 2), little discrimination between water and acetonitrile ligands is predicted for most of the chloride complexes. Although water is indicated to be the stronger ligand in all cases, this preference markedly decreases with higher chloride content. In particular, acetonitrile complexes of the type 1.3, 2.2, and tetra-3 are less than 2 kcal/mol higher in ΔG than their all-aqua counterparts. Because this difference is certainly within the error of the method, it is quite possible that all these

species are populated under the experimental conditions, in particular in acetonitrile solution, where this reaction partner is present in large excess. Thus, our results are in full qualitative accord with the interpretation of the EXAFS data, which suggest exclusive binding of water without chloride, but mixed water–acetonitrile coordination in the presence of chloride.⁶

To probe for the preference of five-coordination (as found in **2.1a**)⁸ over four-coordination (as in **4**),³⁸ selected driving forces for ligand dissociation have been evaluated. Those for water ligands are collected in Table 3, and those for acetonitrile and chloride are deposited in Tables S4 and S5 in the Supporting Information.

After BSSE corrections (i.e., taking the sum of ΔE and δE_{BSSE} values in Table 3), BLYP/PCM-computed ligand binding energies are rather low: typically just a few kcal/mol for the dichloride complexes. With our protocol, this weak binding is offset by the gain in entropy upon dissociation, so that all di- and trichloride complexes should be four-coordinate according to the BLYP level (cf. the negative ΔG values in Table 3). Somewhat stronger bonds are found with B3LYP (at least in the gas phase; compare B3LYP/gas and BLYP/gas entries in Table 3), so that the actual driving force for dissociation should be less pronounced. For the trichlorides, the intrinsic binding energies of a fifth ligand are so small, both at BLYP and B3LYP, that entropy will clearly favor four-coordination.

For completeness, we have also evaluated affinities of uranyl toward chloride according to eq 5 so that relative energies of all species can be compared on a uniform scale. Salient data are collected in Table S6 in the Supporting Information, and estimated ΔG values are plotted in Figure 2. Because of the

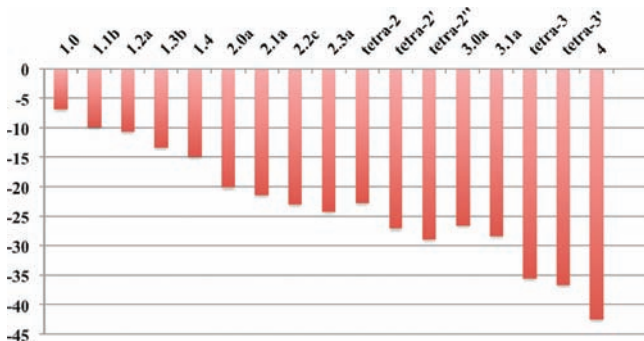
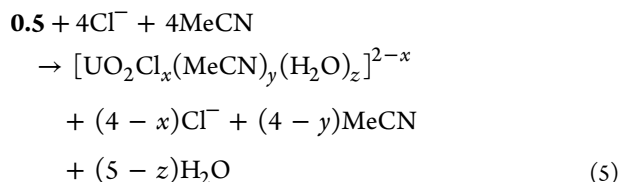


Figure 2. Free energies of formation (kcal/mol) of the complexes from $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ (**0.5**), MeCN, and Cl^- in acetonitrile solution, according to eq 5. ΔG values are computed at the BLYP/PCM level (see Table S6 for details).

limitations of the simple PCM approach (see Discussion), the results obtained for eq 5 are likely to be associated with large errors, but qualitatively, the computed driving forces for formation of higher chloride complexes are consistent with their observation in acetonitrile.



3.3. Charge Distributions. We now turn to the question of how the presence of chloride ions in the coordination sphere

tunes the affinity of uranyl toward other ligands. The NPA charges of the most stable aquo chloro complexes are collected in Table 4 (BLYP/PCM level; for Mulliken and gas-phase results see Table S7 in the Supporting Information).

Table 4. Atomic Charges from Natural Population Analysis (NPA)^a

atom(s)	0.5	1.4	2.3a	3.2a
U	+1.52	+1.27	+1.09	+0.95
UO_2^{2+}	+0.71	+0.40	+0.17	-0.01
$\text{O}_{\text{H}_2\text{O}}$	-0.85	-0.85	-0.86	-0.86
$\text{H}_{\text{H}_2\text{O}}$	+0.55	+0.55	+0.54	+0.53
H_2O	+0.26	+0.25	+0.22	+0.20
Cl^-		-0.34	-0.41	-0.46

^aBLYP/PCM level (6-311+G** basis).

As expected, there is significant charge transfer from the equatorial ligands to uranyl, and this charge transfer is much more pronounced for Cl^- than for H_2O (cf. the deviation of the values for H_2O and Cl^- from their pristine charges of 0 and -1, respectively; last two entries in Table 4). The overall positive charge of the uranyl moiety decreases with an increasing number of chloride ligands. How does the expected, concomitant reduction of the Lewis acidity affect the differential binding of other ligands to uranyl? To address this question, charge distributions were further analyzed in terms of localized Wannier functions, focusing on complex **2.1a**. Assuming that the electronic charge is concentrated in points located on the centers of the Wannier functions (corresponding to electron pairs of bonds or lone pairs; see paper 1), dipole moments of fragments within a molecule or a periodic array of molecules can be calculated.³⁹ This approach has been used successfully to evaluate the dipole moments of individual water molecules in bulk water⁴⁰ and to reproduce the experimental dipole moments of pristine H_2O and MeCN molecules.¹¹ The results are collected in Table 5.

Table 5. Dipole Moments D (in Debye) of the H_2O and MeCN Ligands in Selected Uranyl Complexes

moiety	CP-opt ^a		CPMD ^b	
	gas	gas	gas	MeCN soln
H_2O	1.84 ^c			2.20(12)
H_2O in 2.1a	2.76	2.73(24)		3.76(38) ^d
H_2O in tetra-3'	2.55			
H_2O in $[\text{UO}_2(\text{MeCN})_4\text{H}_2\text{O}]^{2+}$	3.49 ^c	3.44 ^c		4.45(35) ^c
MeCN	4.01 ^c			5.06(19)
MeCN in 2.1a	5.75			5.66(17)
MeCN in tetra-3	5.19			
MeCN in $[\text{UO}_2(\text{MeCN})_4\text{H}_2\text{O}]^{2+}$	7.62 ^c	7.36 ^c		7.33(48) ^c

^aEquilibrium value in the gas phase. ^bAverage over the last picosecond of MD; standard deviations in units of the last digit are given in parentheses. ^cFrom ref 11. ^dCP-opt value for **2.1a-2MeCN**: 3.83 D.

Similar values are obtained for static minima and the dynamic average over the corresponding CPMD trajectory (compare CP-opt gas and CPMD gas values in Table 5). The dipole moment of the water ligand in pristine **2.1a** appears to be significantly smaller than that in $[\text{UO}_2(\text{H}_2\text{O})(\text{MeCN})_4]^{2+}$, by ca. 0.7 D. For acetonitrile this effect is even more pronounced, as its dipole moment differs by ca. 1.9 D between the two

complexes. As expected, the charge donation from the negative chloride ligands makes the uranium center less electrophilic, thus causing less polarization in the coordinated ligands. This trend is continued in the trichlorides, four-coordinate variants of which are included in Table 5. The dipole moments of their neutral water and acetonitrile ligands are noticeably smaller than those in the dichloride **2.1a**.

Turning to the change of the dipole moments upon solvation, that of water ligands increases upon solvation (compare gas-phase and CPMD solution data in Table 5). The extent of this increase is remarkably similar for **2.1a** and $[\text{UO}_2(\text{H}_2\text{O})(\text{MeCN})_4]^{2+}$: ca. 1 D. In contrast, the dipole moment of the acetonitrile ligands in both complexes is rather insensitive to the environment. The sensitivity of the dipole moments of uranyl-coordinated neutral ligands is thus indicated to be rather independent of the number of chlorides that are present.

4. DISCUSSION

Before discussing our results in more detail, a brief word on the expected accuracy of the BLYP/PCM level is in order. Even though it tends to overestimate metal–ligand bond distances significantly,³⁶ for energies of uranyl complexes BLYP usually performs very similar to other, more popular gradient-corrected functionals such as PBE or BP86,⁴¹ which have been used successfully in many performance tests and applications.^{9a,42} In some cases hybrid functionals or massively parametrized meta-GGAs can be more accurate.^{9a,43} In keeping with the general tendency of DFT to underestimate metal–ligand binding energies,⁴⁴ stabilities of four-coordinate complexes (Table 3) are likely to be overestimated at the BLYP level, possibly by up to 5 kcal/mol.^{41,45} This problem is compounded by uncertainties in the computed free energies, because entropic contributions for such dissociative processes in solution are notoriously difficult to model with the underlying ideal-gas/harmonic-oscillator approximation.⁴⁶ Even larger errors may be associated with reaction energies involving free chloride (eq 5), because the huge differential solvation effects involved are a massive challenge for simple continuum models.⁴⁷ On the other hand, the computed driving forces between complexes with the same charge and coordination number about uranyl (eqs 2–4, Table 2) should be reliable, due to favorable error cancellation (in that case, there is also a very small functional dependence; cf. the gas-phase BLYP and B3LYP energies in Table 2). We thus discuss preferentially results pertaining to such “unproblematic” processes.

The main finding transpiring from the results in Table 2 is that, energetically, MeCN is preferred over water as a ligand only in the gas phase and only if less than two chlorides are present. In all other cases, and in particular in the continuum throughout, water is computed to bind more strongly than MeCN. This energetic preference in solution is small, however, and is indicated to be offset by enthalpic and entropic contributions, to the extent that in some cases the estimated free energies (last column in Table 2) show little discrimination between the two neutral ligands. It is thus conceivable that mixed acetonitrile/aquo/chloro species can be populated in solution, consistent with the interpretation⁴⁸ of the EXAFS data.⁶ In the latter study, complex **2.1a** was proposed as a representative model for these mixed complexes, because it has been characterized by X-ray crystallography. According to our results, the corresponding dihydrate, **2.2c**, is slightly more stable than **2.1a** by 1.7 kcal/mol (see entries 7 and 8 in Table

2). While this preference is too small to be considered significant with our methodology, it is interesting to note that the crystal of **2.1a** used in the X-ray structure determination was reported to be stable only at low temperatures.⁸ Apparently, **2.1a** was prepared from uranyl chloride and acetonitrile, but the actual reaction conditions and the source of water in the experiment are unclear; there may just have not been enough water present to form larger quantities of aquo complexes such as **2.2**.

Clearly, the presence of chloride in the coordination sphere of uranyl affects the binding of other ligands. According to simple population analysis, there is significant charge transfer from chloride to uranyl in the pentacoordinate complexes (Table 4). The same had been found for bare UO_2Cl_2 (ca. 0.8e at the B3LYP level), which has led to the suggestion of “some covalent character” for the U–Cl bond.⁴⁹ In a recent topological analysis of the experimental electron density in solid $\text{Cs}_2[\text{UO}_2\text{Cl}_4]$, the U–Cl bonds have been described as “incipient covalent interactions”.⁵⁰

Whatever the nature of the U–Cl bonds, they appear to diminish the Lewis acidic character of the uranyl moiety. Thus, the water ligand is less strongly polarized in **2.1a** than in $[\text{UO}_2(\text{H}_2\text{O})(\text{MeCN})_4]^{2+}$, as revealed by the analysis of the water dipole moments (Table 5). This decreased polarization in the dichloride is consistent with the slightly less strong solvation compared to $[\text{UO}_2(\text{H}_2\text{O})(\text{MeCN})_4]^{2+}$ or $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ (**0.5**): while in solutions of the last two species, each water ligand forms two $\text{OH}^-\cdots\text{NCMe}$ hydrogen bonds, which are persistent for several picoseconds, there are already exchange processes observed for **2.1a** during that time. The different extent of solvation of the water ligands between UO_2^{2+} and UO_2Cl_2 complexes is clearly seen in the RDFs in Figure 2, which show a much higher first peak for **0.5** than for **2.1a**. This apparent difference in solvation strength notwithstanding, the cooperative enhancement of the water dipole moment due to the solvent (the main finding in paper 1)¹¹ is remarkably similar for $[\text{UO}_2(\text{H}_2\text{O})(\text{MeCN})_4]^{2+}$ and **2.1a**, where it amounts to an increase of ca. 1 D. The dipole moments of the acetonitrile ligands, in contrast, are essentially unaffected by the solvent, again irrespective of the number of chlorides. These findings are fully consistent with the optimized or simulated U–O_{eq} and U–N distances in Table 1 (notable contraction upon solvation for the former, less effect for the latter). That the extent (or absence) of cooperative ligand polarization is essentially the same for a dicationic UO_2^{2+} and a neutral UO_2Cl_2 fragment is an important result, inviting further studies for other metal centers.⁵¹

Further studies should also be directed toward the question of whether such differential polarization effects can lead to a switch in relative affinities toward competing ligands. For the $\text{UO}_2^{2+}/\text{H}_2\text{O}/\text{MeCN}$ system, such effects apparently help to drive the preference from acetonitrile in the gas phase toward water in solution. For the $\text{UO}_2\text{Cl}_2/\text{H}_2\text{O}/\text{MeCN}$ system, where there is an energetic preference for water throughout, the additional reinforcement of the binding of water in solution is indicated to be rather small (cf. the BLYP/gas vs BLYP/PCM values in Table 2, e.g. from 1.0 to 2.9 kcal/mol for **2.3a** vs **2.2c**). Other factors, such as entropic contributions from the complex and the surrounding solvent cage, may be dominating in this case.

The “speciation histogram” in Figure 2 shows distinct steps toward negative free energies with increasing chloride content. The height of these steps, i.e. the driving force for chloride

binding, is almost certainly overestimated at the simple PCM level. In water, chloride is known to bind very weakly to uranyl, with an affinity toward the first chloride of only $\Delta G^0 = -0.2$ kcal/mol.⁵² A much more exergonic value, $\Delta G = -11.5$ kcal/mol, is computed at the BLYP/PCM level using the parameters of water.⁵³ Using those of acetonitrile, the computed driving force is considerably larger: $\Delta G = -15.0$ kcal/mol (Table S6). While this enhanced affinity is in qualitative agreement with the observation of all chloride complexes up to 4 in acetonitrile via UV/vis spectroscopy⁶ (the tetrachloride is not observed in pure water), quantitatively it may be in error by more than 10 kcal/mol (judging from comparison with experiment in water). Inclusion of explicit solvent molecules or, ultimately, constrained free-energy simulations in the full solvent would be required for increased accuracy, but such calculations are a formidable task beyond the scope of the present paper.

The same holds for the question of the coordination number about uranyl. The raw BLYP/PCM data would predict dichlorides and higher chlorides to be four-coordinate throughout (Table 3). Some dichlorides and most of the trichlorides are not stable at all in five-coordination but spontaneously lose one ligand during attempted optimization or CPMD simulation. The same had been found for the aquo/chloro complexes in water,³⁷ but as mentioned above, these results are less reliable because of the known DFT deficiencies. In this context it is interesting to note, however, that a recent high-energy X-ray scattering study of uranyl–chloro complexes $[\text{UO}_2\text{Cl}_n(\text{H}_2\text{O})_x]^{2-n}$ in aqueous solution has afforded mean coordination numbers of 5, 4.3, and 4 for $n = 1-3$, respectively.⁵⁴ That is, already for the dichloride in water the fifth ligand is very weakly bound (in apparent excellent agreement with predictions from CPMD),³⁷ and the trichloride shows a clear preference for four-coordination. On these grounds, together with the large driving force for ligand dissociation (Table 3, even if it is overestimated), it is safe to assume that the trichloro species will be predominantly four-coordinated also in acetonitrile. According to our BLYP/PCM results, it is slightly more likely to have water than acetonitrile as the fourth ligand (last entry in Table 2), whereas the EXAFS data have been interpreted in terms of an exclusive presence of N donors in the trichloride.⁶

In all comparisons with experiment we tacitly assume that thermodynamic equilibrium has been achieved throughout. From known kinetic data for ligand exchange processes at uranyl, there is indeed little evidence to doubt this assumption. For instance, the free activation energy for water exchange in aqueous uranyl has been determined as $\Delta G^\ddagger = 9.1$ kcal mol⁻¹.⁵⁵ Rapid ligand exchange is also observed in nonaqueous systems: e.g. DMSO exchange in $\text{UO}_2(\text{acac})_2(\text{DMSO})$, $\Delta G^\ddagger = 14.3$ kcal mol⁻¹.⁵⁶ There is thus no evidence for kinetic hindrance in such systems and our discussion of complex mixtures in terms of relative free energies should be well justified.

5. CONCLUSION

We have used DFT to chart the rich potential energy surface of uranyl complexes with a ternary set of ligands, namely chloride, water, and acetonitrile. A total of 25 complexes were screened at a “static” BLYP level including bulk solvation effects through a simple polarizable continuum model. In general, the discrimination between water and acetonitrile as additional ligands becomes less pronounced with increasing chloride content. For the dichloride, at least three complexes with different composition (and more with different stereo-

chemistry) are indicated to be rather close in free energy, so that all of them can be populated at ambient temperature. This finding corroborates interpretations of EXAFS data of aqueous uranyl chloride in acetonitrile. Intrinsically (i.e., in the gas phase at 0 K), there is a switch from the preference of acetonitrile to water on going from the dicationic UO_2^{2+} without chloride to the UO_2Cl_2 system. Entropy and solvation effects tend to attenuate this preference in solution. For the dichloride, $\text{UO}_2\text{Cl}_2(\text{MeCN})(\text{H}_2\text{O})_2$ (2.2c) is predicted to be the most stable five-coordinate species. On the basis of careful assessment of the PCM data against recent experiments for uranyl chlorides in water, the trichloride in aqueous acetonitrile is predicted to be present as a mixture of $[\text{UO}_2\text{Cl}_3(\text{H}_2\text{O})]^-$ and $[\text{UO}_2\text{Cl}_3(\text{MeCN})]^-$.

With increasing chloride content, uranyl becomes less Lewis acidic and polarizes the neutral acetonitrile and water ligands less strongly than dicationic UO_2^{2+} . This effect has been quantified for the first time through evaluation of dipole moments for the complexed ligands from localized orbitals. The cooperative polarization of water ligands due to solvent molecules in the second solvation sphere is indicated to be remarkably invariant to the number of chlorides present. Further studies involving other metal–ligand systems are in progress. The competition between water and putative ligands (including counterions) can have important consequences, for instance for metal complexation and extraction by hydrophobic extractant molecules. Uranyl and plutonyl cations, for example, are usually extracted by organic O donors from nuclear waste solutions that contain an excess of anions (nitrates and others);⁵⁷ the precise way how each of these ligands, if coordinated to the metal, affects the affinity toward the others is far from being understood.⁵⁸

Even though present-day approximate DFT may not always be quantitatively accurate, its critical application can furnish valuable insights into the speciation of complex mixtures of uranyl species, insights that can corroborate, complement, and, eventually, precede experiments.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, and figures giving additional structures and data, a full citation of ref 26, and optimized coordinates of 1.0–4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENTS

This work was supported by EaStChem via the EaStChem Research Computing facility and a local Opteron PC cluster maintained by Dr. H. Früchtl. N.S. thanks the UJF/CNRS for funding. A.C. and W.G. are grateful to the IDRIS, CINES, the Université de Strasbourg, and GDR CNRS PARIS for computer resources.

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- (39) This procedure affords a very simple point-charge model, where the positive atomic charges (screened by the core if present) are placed at the nuclear positions and negative charges of –2 at the positions of the Wannier centers. The total dipole moment is then calculated from this distribution of point charges.
- (40) See: Silvestrelli, P. L.; Parrinello, M. *J. Chem. Phys.* **1999**, 111, 3572–3580 and references cited therein.

(41) E.g. for the water-exchangereaction in uranyl hydrate: Wahlin, P.; Danilo, C.; Vallet, V.; Real, F.; Flament, J.-P.; Wahlgren, U. *J. Chem. Theor. Comput.* **2008**, *4*, 569–577.

(42) E.g.: Moskaleva, L. V.; Matveev, A. V.; Krüger, S.; Rösch, N. *Chem. Eur. J.* **2006**, *12*, 629–634.

(43) Austin, J. P.; Burton, N. A.; Hillier, I. A.; Sundarajan, M.; Vincent, M. A. *Phys. Chem. Chem. Phys.* **2009**, *11*, 1143–1145.

(44) See for instance: Rotzinger, F. R. *J. Phys. Chem. B* **2005**, *109*, 1510–1527.

(45) See also the binding of water in $[\text{UO}_2\text{F}_4(\text{H}_2\text{O})]^{2-}$: Bühl, M.; Sieffert, N.; Wipff, G. *Chem. Phys. Lett.* **2009**, *467*, 287–293.

(46) The ad hoc pressure correction from ref 16 may not be a panacea, even though it has been shown to work well in certain cases, e.g.: Sieffert, N.; Bühl, M. *Inorg. Chem.* **2009**, *48*, 4622–4624.

(47) PCM results can also be very sensitive to methodological details, in particular the definition of the cavity: Wahlin, P.; Schimmelpfennig, B.; Wahlgren, U.; Grenthe, I.; Vallet, V. *Theor. Chem. Acc.* **2009**, *124*, 377–384. We have chosen the particular PCM variant and cavity definition (default in Gaussian 03) for compatibility with our previous studies. Using the setup that is now the default in Gaussian 09 (IEF-PCM, spheres on all atoms) seems to result in somewhat worse results: e.g., for the chloride affinity of uranyl hydrate in water, $0.5 + \text{Cl}^- \rightarrow 1.4 + \text{H}_2\text{O}$, our setup yields $\Delta G(\text{PCM}) = -15.0$ kcal/mol (Table S11). Switching from the G03 to the G09 defaults increases the computed driving force by another -8.7 kcal/mol, thus worsening the agreement with experiment; $\Delta G^0 = -0.2$ kcal/mol.

(48) We note in passing that this EXAFS analysis assumes no binding of perchlorate. However, according to an FT-IR study of uranyl perchlorate in anhydrous acetonitrile, only 37% of perchlorate is uncoordinated; the rest is bound in either a mono- or bidentate fashion. Cf.: Bunzli, J. C. G.; Metabanzoulou, J. P. *Helv. Chim. Acta* **1994**, *77*, 140–149.

(49) Clavaguéra-Sarrio, C.; Hoyau, S.; Ismail, N.; Marsden, C. J. *J. Phys. Chem. A* **2003**, *107*, 4515–4525.

(50) Zhurov, V. V.; Zhurova, E. A.; Pinkerton, A. A. *Inorg. Chem.* **2011**, *50*, 6330–6333.

(51) Dipole moments of coordinated water ligands in aqueous M^{3+} hydrates have been reported to be greater than that of bulk water, but no effects of cooperativity have been studied yet, Cf. $\text{M} = \text{La}$: (a) Terrier, C.; Vitorge, P.; Gaigeot, M.-P.; Spezia, R.; Vuilleumier, R. *J. Chem. Phys.* **2010**, *133*, 044509. Cf. $\text{M} = \text{Cm}$: (b) Atta-Fynn, R.; Bylaska, E. J.; Schenter, G. K.; de Jog, W. A. *J. Phys. Chem. A* **2011**, *115*, 4665–4677.

(52) Extrapolated to standard conditions, a value of $\log \beta_1^0 = 0.17 \pm 0.02$ has been recommended for the equilibrium constant in the aqueous system $\text{UO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}^+$ in ref 7.

(53) For the reaction $0.5 + \text{Cl}^- \rightleftharpoons 4.1 + \text{H}_2\text{O}$, taken as BLYP $\Delta E^{\text{CP}}/\text{SDD}(+)/\text{PCM} + (\Delta E/\text{PCM} - \Delta G/\text{PCM})$ from Table 2 in reference 37.

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(55) Calculated from the ΔH^\ddagger and ΔS^\ddagger values given in: Farkas, I.; Bányai, I.; Szabó, Z.; Wahlgren, U.; Grenthe, I. *Inorg. Chem.* **2000**, *39*, 799.

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(57) Paiva, A. P.; Malik, P. J. *Radioanal. Nucl. Chem.* **2004**, *261*, 485–496.

(58) Counterions could also impact on the amount of water coordinated to rare-earth ions and their complexes, thereby markedly affecting their luminescence properties; see e.g.: Samikkanu, S.; Mellem, K.; Berry, M.; May, P. S. *Inorg. Chem.* **2007**, *46*, 7121–7128.