J. Phys. Chem. A **1999,** *103,* 8257−8264

Structure of Uranium(VI) in Strong Alkaline Solutions. A Combined Theoretical and Experimental Investigation

U. Wahlgren,* H. Moll,[†] I. Grenthe,[†] B. Schimmelpfennig, L. Maron,[‡] V. Vallet,[‡] and O. Gropen[§]

Fysikum, University of Stockholm, P.O. Box 6730, S-11385 Stockholm, Sweden

Received: January 5, 1999

The structures of the $UO_2(aq)^{2+}$ ion and of the uranium(VI) hydroxide complex(es) formed in strongly alkaline solution have been investigated theoretically using molecular-orbital based quantum chemical methods, and experimentally using EXAFS methodology. Relativity was included explicitly through the Douglas−Kroll transformation. The uranium atom was described at the ECP level, using the AIMP methodology. The structures of $[UO_2(H_2O)_5]^{2+}$, and the hydroxide complexes, viz., $[UO_2(OH)_4\cdot(H_2O)]^{2-}$, $[UO_2(OH)_4]^{2-}\cdot(H_2O)$, $[UO_2(O)(OH)_2]^{2-}\cdot2(H_2O)$, and $[UO_2(OH)_5]^{3-}$, were optimized at the SCF level, using gradient techniques, while the relative stabilities were calculated at the MP2 level of approximation. The third structure contains three coordinated ligands, one of which is an oxide ion, in the plane perpendicular to the linear UO_2-unit. Complexes of this type have not been experimentally identified for U(VI); however, they are formed for the iso-electronic Np(VII). The experimental EXAFS data indicates that the complex(es) formed is(are) mononuclear. The number of coordinated ligands in the equatorial plane is 4.5 ± 0.4, while the bond distances are the same within the experimental errors, as in a previous study of $[Co(NH_3)_6{}^{3+}]_2[UO_2(OH)_4{}^{2-}]_3\cdot2H_2O$, by Clark et al. An EXAFS model where the coordination number is fixed to four, is only marginally less precise than the model without constraints on the coordination number. This fact together with the close agreement between experimental and theoretically observed variations in bond distances between the different structure models provides a strong indication for the formation of $[UO_2(OH)_4]^{2-}$ in solution. This is an unusual coordination number for uranium(VI) complexes, previously found in sterically crowded systems such as $UO_2Cl_4{}^{2-}$.

Introduction

It is well-known that actinide chemistry is an area with many important applications, as, for example, reprocessing and nuclear waste management. To take the latter area as an example: the understanding of interactions between spent nuclear fuel and intruding ground water, including radiolysis products, is necessary to analyze the function and the safety of repositories for high-level radioactive waste. This requires prediction of the chemical behavior of actinides, which must have a sound theoretical basis.

The chemistry of 5f-elements represents a challenge for both experimental and theoretical chemists as they are in many aspects very different from the 4f-elements and from the other transition elements. Examples are the large number of chemically accessible oxidation states for the pre-curium elements and the formation of linear dioxo-actinoid (V or VI) ions. It is reasonably easy to obtain quantitative experimental chemical information on thorium and uranium, while special facilities are required for the heavier actinides and especially plutonium. The chemical properties for a given oxidation state are often found to vary in a predictable way. Therefore; one can combine the experimental data collected for just a few of actinides with theoretical results to predict the properties of those systems which are difficult to access by experiment. In this paper we will describe the extension of current quantum chemical methodologies to study the coordination of dioxouranium(VI) in acid and alkaline solutions, including a comparison between experimental and theoretical data.

In quantum chemical studies, several difficulties arise when dealing with actinides. The actinides are very heavy, which means that relativistic effects are important, and must be accurately accounted for. Especially scalar relativistic effects cannot be treated perturbationally. In most of the cases, the electronic structure involves a partly filled f-shell, which means that all complexes except the simplest ones will have a highly complex electronic structure. Furthermore the f-shell is more diffuse than that, for example, in the lanthanides, and can participate in the bond. Another property specific for the actinides is, as pointed out by Pyykkö,[1] that the 6s- and the 6p-atomic orbitals, which in lighter elements normally would be considered as the outer core, are highly polarizable and must be treated as valence orbitals in the calculations. The number of electrons which have to be treated explicitly in a calculation thus becomes quite large and makes accurate calculations using standard correlation methods difficult.

The 5f-participation in the actinide bonding is nicely illustrated by the actinyl(VI) ions, which are symmetric linear di-oxygen ions with a VI-valent actinide at the center. Stable ions of this kind exist for the sequence uranium to americium.

[†] Permanent address: Department of Chemistry, Inorganic Chemistry, The Royal Institute of Technology, Teknikringen 30, 10044 Stockholm, Sweden.

[‡] Permanent address: Laboratoire de Physique Quantique I.R.S.A.M.C, Université Paul Sabatier and CNRS (UMR 5626) 118, route de Narbonne, 31062 Toulouse cedex, France.

[§] Permanent address: Institute of mathematical and physical science, University of Tromsø, N-9037 Tromsø, Norway.

10.1021/jp990042d CCC: $18.00

The increased nuclear charge stabilizes the 5f-orbital along the actinide series. Thorium has a $6d^27s^2$ ground state, and the 5f-orbital is not yet stable enough to form a doubly charged dioxo-ion. The electronic configuration for the atomic ground states are for U $5f^36d^17s^2$, for Np $5f^46d^17s^2$, for Pu $5f^66d^07s^2$, and for Am $5f^76d^07s^2$, showing the gradual stabilization of the 5f-orbital as we move to the right along this series. As the 5f-orbital starts to compete with the 6d-orbital, it mixes into the molecular bonds, giving rise to the characteristic doubly charged dioxo-ions for U–Am. After Am the 5f-orbital has become so stabilized that ions of that type cannot be formed. This stabilization is also demonstrated by the redox properties. Uranyl(VI) is very stable, while it is comparably easier to reduce plutonyl(VI),[2] a fact which is used in the nuclear reprocessing. The AmO_2^{2+} ion is a strong oxidizing agent and only stable in a nonreducing environment. As the discussion above shows, it is very important to describe the f-orbitals in a satisfactory manner in theoretical calculations on the actinide compounds.

The bonding in actinide complexes differs in other respects from the usual bonding in lighter systems. In contrast to them, relativistic effects tend to stabilize the 7s-orbitals in the actinides and to destabilize the high angular momentum orbitals, which affects the binding properties. For example, in ThO, the bonding takes place primarily between the Th d- and the O p_σ-orbitals whereas the Th 7s-orbital becomes a diffuse lone pair.[3]

The unusual polarizability of the outer core orbitals mentioned above gives rise to technical difficulties in theoretical calculations, at least in the wave function based ones, as the outer core electrons must be included in correlation treatments. As an example, at least 24 electrons (the oxygen 2s- and 2p- and the uranium 6s-, and 6p-orbitals) have to be correlated in UO_2^{2+}, and 26 electrons in PuO_2^{2+}.

Two conclusions emerge from the listed difficulties and unusual properties. The first is the need for simplifications and a candidate could be local density methods. The second is to check carefully the accuracy of the employed approximations. For example, the MP2 and CASPT2[4] methods are fast and easy to use, but there is hitherto little experience on their accuracy for actinide complexes. Additionally, the MP2 and CASPT2 methods suffer from the same drawbacks as ordinary Hartree–Fock methods in the sense that they are limited by requiring the calculation of all two-electron integrals.

Local density methods have been used in calculations on UO_2^{2+} complexes, but again it is difficult to judge the accuracy.[5] In an investigation by Ismail et al.,[6] it is concluded that the hybrid method B3LYP gives reasonable results for spectroscopic constants on uranyl(VI) and plutonyl(VI), while the pure DFT functional BP86 gives a bent uranyl(VI). Screckenbach et al. have studied uranyl(VI) coordinated by four hydroxide ions using B3LYP, and report geometries and vibrational frequencies in reasonable to good agreement with experiments by Clark et al. cited in ref 30. Results published by Gagliardi et al.[7] appear to be promising although they do not use hybrid functionals.

The aim of the present study is to compare predictions made from theory with experimental observations. From the theoretical point of view, this is a necessary process in order to understand the effects of the various approximations used and therefore to establish confidence in the methodology. From the experimental point of view, theory may assist in the interpretation of experimental results, facilitate the choice between different plausible chemical models, and even suggest new experiments.

The examples discussed in the present paper are all related to the coordination chemistry of uranium(VI). In the theoretical part we have used a molecular-orbital based ab initio approach, but decreasing the number of electrons by using an effective core potential to describe the uranium inner core. Relativity is described by a first principles approach, and correlation is estimated at the MP2 level. The experimental data are structure information obtained by EXAFS and X-ray diffraction of $[UO_2(H_2O)_5]^{2+}$ and $[UO_2(OH)_4]^{2-}$ (aq) in solution and in the solid state. The stoichiometry of the uranyl(VI) penta-aquo ion is well established experimentally. However, the information on the preferred orientation of the coordinated water molecules is limited. The available diffraction data from solids containing coordinated water indicate that the water protons are above and below the coordination plane perpendicular to the "UO_2" axis. A more detailed discussion of the properties of the UO_2^{2+} ion will appear in a forthcoming publication. An arrangement where all water molecules, including their hydrogen atoms, lie in the plane perpendicular to the linear UO_2-axis seems less likely from a geometrical point of view, at least some of them should be oriented perpendicular to this plane in order to reduce repulsion between the water hydrogen atoms, in agreement with the experimental observations. An estimate of the energy barrier for rotation is a useful indicator for the dynamics of this system. This will be discussed later on in the geometries section. There is limited experimental information in the literature on the stochiometry of the hydroxide complexes of uranium(VI) in alkaline solution. The predominance of $UO_2(OH)_3^-$ over the pH range from 8.8 to approximately 10 is well documented.[31] Palmer and Nguyen-Trung[25] have proposed that a set of trinuclear complexes are formed over a broad pH range, up to pH = 12. Their own experimental data do not provide strong support for the formation of trinuclear complexes at high pH. A particular problem with the most common experimental method, potentiometry, is that it is not possible to obtain a unique determination of the constitution of the complexes formed. The reason for this is apparent from the following equations:

$$UO_2^{2+} + 4H_2O \rightarrow [UO_2(OH)_4]^{2-} + 4H^+ \qquad (1)$$

$$UO_2^{2+} + 3H_2O \rightarrow [UO_2O(OH)_2]^{2-} + 4H^+ \qquad (2)$$

The stoichiometry of the complexes formed is deduced from measurements of the free hydrogen ion concentration in water solutions of known total concentration of protons and uranium(VI). As four protons are released in both equations the two different stoichiometries cannot be distinguished by this method. Other experimental methods, such as EXAFS, may be used, but theory also offers interesting possibilities. The formation of Np(VII) complexes containing coordinated oxo-ions is well documented. As U(VI) and Np(VII) are iso-electronic it is of interest to explore if species like $[UO_2O(OH)_2]^{2-}$ might form.

Detailed information of the chemical bonding in actinide systems seems only possible through the use of theory. It is well known from many experimental investigations[8] that the axial "yl"-ligands are substitution inert, except in photochemically excited states and in some hydroxide complexes. The equatorial ligands are much more reactive, where the rate of substitution also may increase in the photochemically excited states. The strength of the bonding of axial and equatorial ligands in photochemically excited states is an issue that could be addressed by theory.

The two complexes under investigation have different structures. In the first one, uranyl coordinates four hydroxide ions in a square bipyramid type structure. The other possibility is a coordination with two hydroxide ions and one "oxo"-type oxygen in a trigonal bipyramid configuration. The latter complex is predicted due to the ability of the open 5f-shell to form further bonds. In order to obtain comparable iso-electronic systems in the calculations, one (respectively two) water molecules were added. This minimizes errors associated with the computational procedures used. We also made calculations on UO_2^{2+}(aq) in an acid solution, using $[UO_2(H_2O)_5]^{2+}$ as a model. Uranyl complexes with nitrate and sulphate ligands have been studied previously using ECP, MP2 and DFT,[5] and different conformers of the four-coordinated $[UO_2(OH)_4]^{2-}$ complex have been studied by Screckenbach et al. using relativistic ECPs and the hybrid B3LYP method.[30]

Clark et al.[9] have suggested, from EXAFS experiments, that the uranyl(VI) ion may coordinate five rather than four hydroxide ions in a strong alkaline solution. The coordination number obtained from EXAFS experiments is based on a number of assumptions and is comparatively uncertain. We have investigated this possibility, and we find strong indications that the coordination number is four, not five. This conclusion is supported by a recent solubility study by Yamamura et al.,[32] who identified $[UO_2(OH)_4]^{2-}$ as the limiting complex in the pH range 12−14.

The structure of $[UO_2(H_2O)_5]^{2+}$ in acid solution was known at the beginning of the present study,[27] but no information on the structure of the complexes formed in strongly alkaline solutions was available. Later EXAFS experiments have been successfully carried out also in that case, resulting in structural information.

Experimental Investigation and Computational Details

The EXAFS Measurements. *Sample Preparation.* The U(VI) perchlorate stock solutions were prepared as described earlier.[10,11] One test solution was prepared from this stock solution and perchloric acid to give a final concentration of approximately 0.05 M in UO_2^{2+} and 0.1 M $HClO_4$. Two other test solutions were prepared from the appropriate amounts of $UO_2(NO_3)_2{\cdot}6H_2O$ (MERCK) and tetra-methyl-ammonium hydroxide (TMA-OH) to get a final concentration of approximately 0.05 M UO_2^{2+}, and 1 and 3 M TMA-OH, respectively. In the EXAFS experiments we used a path length of 13 mm, which gave an edge jump of ∼1.0 across the U L_{III} absorption edge.

EXAFS Measurements. The EXAFS spectra were collected at HASYLAB in Hamburg. The data were collected in transmission mode and room temperature at the beamline Al, using a Si(311)-double-crystal monochromator. The incident beam flux was reduced to ∼50% of its maximum. Three EXAFS scans were collected from each sample and then averaged. For energy calibration of the sample spectra, the spectrum from a foil of yttrium was recorded simultaneously. The ionization energy of the U L_{III} electron, E_0, was arbitrarily defined as 17166 eV. The data were treated using the WinXAS software.[12] Theoretical back scattering phase and amplitude functions used in data analysis were calculated for the model compound α-$UO_2(OH)_2$[13] using the FEFF7[14] program. The MS path O−U−O (four-legged path) of the linear UO_2^{2+} unit was included in the model fitting. The EXAFS oscillations were isolated using standard procedures for preedge subtraction, spline removal and data normalization.[15] The amplitude reduction factor, S_0^2, was held constant at 1.0 for all the fits.

Computational Details. All the theoretical calculations were carried out using the *MOLCAS*-4[16] program package. Scalar relativistic effects (i.e., all first order relativistic effects except spin−orbit coupling) were described using the no-pair equation deduced from the Douglas−Kroll transformation.[17] The implementation of this formalism was done using the procedure outlined by Hess.[18]

In order to reduce the size of the problem the calculations on the uranyl(VI) complexes in solution were done using the AIMP method suggested by Huzinaga, Seijo, and Barandiaran.[19,20] The AIMP method is an ECP-method of the Huzinaga type, where the exchange integrals are obtained from atomic exchange integrals projected onto the molecular basis set, and the Coulomb integrals are fit to a sum of Gaussians. The parameters were determined for the ground state of the neutral uranium atom. The relativistic effects were included at the full DK level by adding the DK operators directly to the AIMP Hamiltonian (no relativity is included in the AIMP Hamiltonian except for the fact that relativistic core orbitals are used in the parameter determination). The technique is described in detail in ref 21. The geometry optimizations were done at the SCF level using gradient techniques, with symmetry constraints. The gradients were calculated using relativistic densities but nonrelativistic integrals. The final energies for the various configurations were calculated at the MP2 level, including relativistic effects, at the optimized SCF geometries.

At the all-electron level, we used the primitive 24s, 19p, 14d, and 11f functions optimized by Faegri.[22] For the uranium-AIMP, the 1s−4s, 2p−4p, 3d−4d, and 4f atomic orbitals were considered as core, leaving 32 valence electrons in neutral uranium. The AIMP basis set was constructed by a least-squares fit, based on the all-electron AOs, using 15s, 12p, 10d, and 7f, contracted to 5s, 5p, 4d, and 3f within the Rafenetti contraction scheme.[23] Oxygen and hydrogen were described at the all-electron level. For oxygen we used the primitive 9s, 5p basis set suggested by Huzinaga,[24] augmented by one diffuse p-function and one d-function and contracted to 3s, 4p, and 1d using the Rafenetti scheme. Hydrogen, finally, was described by Huzinaga's 5s basis contracted to 3s,[24] with one diffuse p-function.

Results and Discussion

Experimental Results. The nonlinear least-squares curve fits were done over the range 3-13.5 Å^{-1} for UO_2^{2+} in 0.1 M $HClO_4$, and 3.8−15.1 Å^{-1} for UO_2^{2+} in TMA-OH on the raw EXAFS data. The bond length and coordination numbers obtained are summarized in Table 1. The EXAFS spectra measured and the corresponding FTs are shown in Figure 1. The EXAFS oscillations of U(VI) in 1 M TMA-OH and 3 M TMA-OH are very similar, while the uranyl sample in the acidic pH region shows a different oscillation pattern. These differences are more apparent in the FTs. The FTs are not corrected for the EXAFS phase-shift so that peaks appear at shorter distances ($R+\Delta$), relative to the true near-neighbor distances (R). The most intensive first peak in Figure 1 corresponds to the two axial oxygen atoms O_{ax} of the linear uranyl unit. The following peak represents the coordinated oxygen atoms O_{eq} in the equatorial plane perpendicular to the linear "yl"-axis. No significant intensity from U−U interactions at higher R-values could be observed in any of the spectra. These results show clearly that only mononuclear species are formed under high alkaline conditions in TMA-OH, which contrasts reports of the formation of trinuclear U(VI) hydroxide species based on interpretation of solution chemical studies in ref 25. There is a significant increase in the uranium−"yl" oxygen distance and a shortening of the U−O_{eq} distance, between to the U(VI) aquo cation and the species present in alkaline solution. A lengthening of the uranium−"yl" oxygen distance was also observed in U(VI) oxide precipitates prepared at pH values above 7.[26] The coordination numbers and bond distances for the U(VI) aquo ion determined by EXAFS are consistent with results obtained

TABLE 1: EXAFS Structure Results Measured for UO_2^{2+} in Acidic Solution and UO_2^{2+} in Highly Alkaline Solutions Compared with Structural Parameters Determined by Quantum Chemical Calculations and Large Angle X-ray Scattering Experiments

sample	scattering path	*N*	*R*(Å)[a]	σ^2(Å^2)	ΔE_0(eV)	ref
0.05 M UO_2^{2+} in 0.1 M $HClO_4$	U−O_{ax}	2.0 f[d]	1.78_3	0.0015	−6.7[b]	this work
	U−O_{eq}	4.5 ± 0.4	2.41_3	0.0062		
1 M UO_2^{2+} in 0.1 M $HClO_4$	U−O_{ax}	2.0	1.702			27
	U−O_{eq}	5.0	2.421			
$[UO_2(H_2O)_5]^{2+}$ ab initio quantum chemical calcd	U−O_{ax}	2.0	1.750			this work
	U−O_{eq}	5.0	2.570			
0.055 M UO_2^{2+} in 1 M TMA-OH	U−O_{ax}	2.0 f	1.82_2	0.0015	3.7	this work
	U−O_{eq}	5.0 ± 0.5	2.24_7	0.0056		
0.055 M UO_2^{2+} in 3 M TMA-OH	U−O_{ax}	2.0	1.82_2	0.0014	3.5	this work
	U−O_{eq}	5.2 ± 0.5	2.24_1	0.0055		
$[UO_2(OH)_4]^{2-}\cdot H_2O$ ab initio quantum chemical calcd	U−O_{ax}	2.0	1.800[c]			this work
	U−O_{eql}	2.0	2.430			
	U−O_{eq2}	2.0	2.470			
$[UO_2(OH)_4]^{2-}$ ab initio quantum chemical calcd	U−O_{ax}	2.0	1.80[c]			this work
	U−O_{eql}	2.0	2.360			
	U−O_{eq2}	2.0	2.380			

[a] Uncertainty of ±0.005 to ±0.01 Å. [b] E_0 defined as 17185 eV. [c] Corrected values, see text. [d] f: parameter fixed during the fit.

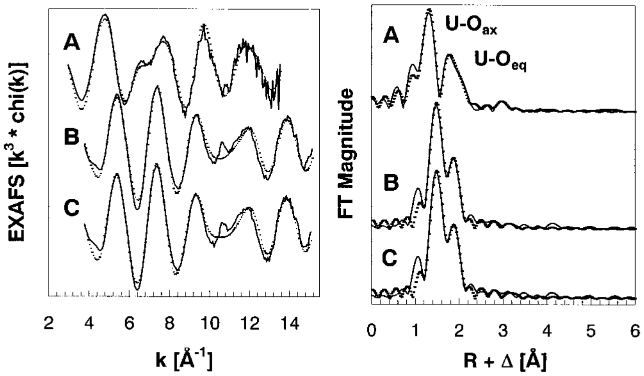


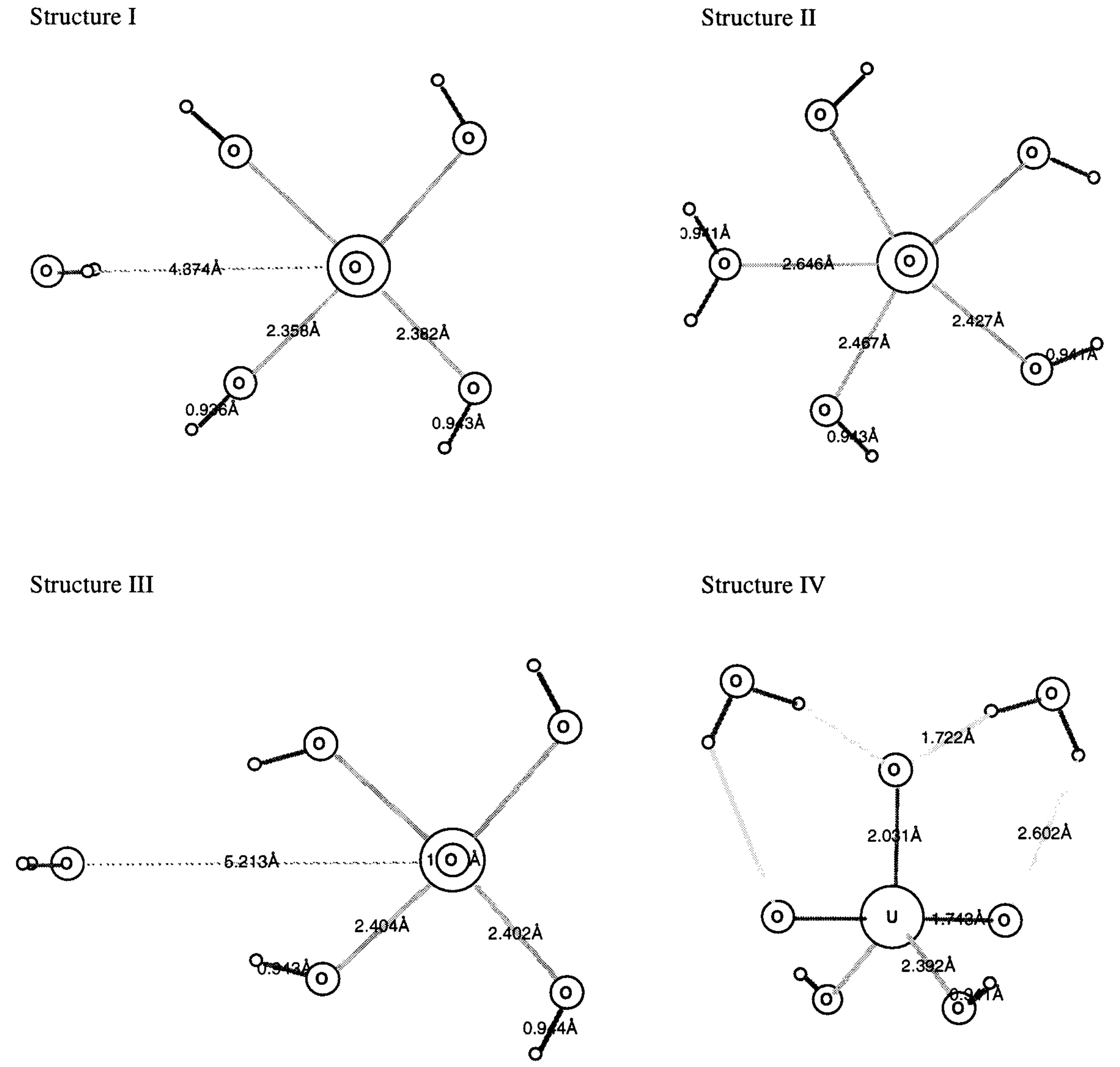
Figure 1. Raw L_{III}-edge k^3-weighted EXAFS data and corresponding FT's measured for (A) 0.05 M UO_2^{2+} in 0.1 M $HClO_4$, (B) 0.055 M UO_2^{2+} in 1 M TMA-OH, and (C) 0.055 M UO_2^{2+} in 3 M TMA-OH. The solid line is the experimental data, and the dashed line represents the best theoretical fit of the data.

by X-ray diffraction experiments.[27] The EXAFS analysis of the TMA-OH samples yielded 5 ± 0.5 oxygen atoms at 2.25 Å for the UO_2^{2+}.

A preliminary report of these data was presented as a poster at Actinide XAS 98.[28] The results from the alkaline solution agree with results presented at the Actinides'97 conference by Clark et al.,[9] who reported an U−OH distance of 2.258 Å in the crystal $[Co(NH_3)_6]_2[UO_2(OH)_4]_3\cdot 2H_2O$. This solid contains discrete $UO_2(OH)_4^{2-}$ units, where U(VI) is surrounded by four OH^- ligands at very near the same distance as in the alkaline solutions. In EXAFS experiments the bond distances in the first coordination shell are determined with a much higher precision than the coordination number. When comparing structure data more reliance should therefore be placed on measured bond distances. It is well-known that an increase in the coordination number around a given metal ion results in an increase in the average bond length. This suggests that the coordination number should be the same and equal to four. Hence, we suggest that the alkaline solutions contain the complex $UO_2(OH)_4^{2-}$, despite the higher coordination number indicated by the EXAFS data. This point will be elaborated by ab initio quantum chemical calculations where we have compared the bond distances for $UO_2(OH)_4^{2-}$ and $UO_2(OH)_5^{3-}$. A coordination number of five might also be a result of the coordination of a water to $UO_2(OH)_4^{2-}$. We have therefore tested also this possibility in the quantum chemical calculations. The formation of $UO_2(OH)_4^{2-}$ results in a lengthening of the U−O_{ax} bond distance of about 0.04 Å, compared to that of the U(VI) aquo ion. We have compared also this experimental finding with quantum chemical calculations, including geometry optimization on $UO_2(H_2O)_5^{2+}$. The results show that the bond distance is 0.044 Å longer in $UO_2(OH)_4^{2-}$ than that in $UO_2(H_2O)_5^{2+}$, in excellent agreement with the EXAFS data. We also made theoretical calculations on bond distances and geometries for the five-coordinated complex $UO_2(OH)_4^{2-}\cdot H_2O$, c.f. Table 1. The calculations showed that only the average bond distance for the model with the noncoordinated water is compatible with the experimental observations. The distances obtained from the ab initio calculations differ systematically from the experimental values; the reasons for this are known and discussed in the geometry section. The calculations also showed a shortening of the average U−O_{eq} bond distance of about 0.19 Å in $[UO_2(OH)_4]^{2-}$, compared to that of the U(VI) aquo ion. The experimental value is 0.17 Å, so the agreement between the two values is very satisfactory. Both EXAFS measurements and ab initio quantum chemical calculations support the formation of the mononuclear species $UO_2(OH)_4^{2-}$ as the dominant complex in strong alkaline solutions. The calculations also showed that $UO_2O(OH)_2^{2-}$ is not formed. From solution chemical experiments using potentiometry one cannot distinguish between $UO_2O(OH)_2^{2-}$ and $UO_2(OH)_4^{2-}$. The calculations also indicated that the preferred coordination geometry around uranium is octahedral, this is an unusual coordination geometry for uranium(VI). The coordination of a water molecule to $UO_2(OH)_4^{2-}$ results in a lengthening of the U−O_{eq} distance (see Table 1) which is not consistent with the experimental observations.

Structures and Relative Stabilities. The theoretical calculations were carried out on isolated ions, without any stabilizing external medium representing the bulk of the solution. This is a rather crude model of the complex in solution but the relative energies should nevertheless provide a solid guideline to the relative stability of the complexes. However, one should not put too much emphasis on absolute numbers. Although all calculated bond distances are too long by up to 0.1 Å, observed trends are well reproduced by the theoretical calculations. The error in the experimental determination of coordination numbers is fairly large. Hence, theoretical calculations may provide important additional information when selecting the "best" model. EXAFS techniques can provide precise bond distances and are therefore important for model validation.

The CI effects on the internal dioxouranium bond distance is quite large, a lengthening of 0.05−0.07 Å, but test calculations



Structure I

Structure II

Structure III

Structure IV

Figure 2. Optimized structures for uranyl complexes.

at the MP2 level showed only small effects on the properties of the complexes (except for the expected lengthening of the dioxouranium bond).

Initially, the problem we addressed was if UO_2^{2+} in a strong alkaline solution would coordinate four hydroxide ions and one water molecule in an essentially pentagonal bipyramid structure or if an oxo-oxygen and two hydroxide ions in an essentially trigonal bipyramid structure were more stable. The investigation was undertaken prior to the experimental work by Moll et al.[28] on UO_2^{2+} in strong alkaline solutions. They determined the distances between the uranium atom in UO_2^{2+} and the coordinated hydroxide-, water, or oxo-oxygen using EXAFS techniques. Experimentally, a coordination number of about five at the same equatorial distance was found. The experimental results seem to contradict a trigonal bipyramid coordination, in which case at least two distances should be seen. Thus the two most likely possibilities appear to be either a uranyl(VI) in a square bipyramid configuration, coordinating four hydroxides, or a pentagonal bipyramid geometry with five hydroxide ions, or four hydroxide ions and one water molecule. Since the experimental coordination number is uncertain, it is difficult to decide between these possibilities using only EXAFS data.

All geometries were optimized using gradient techniques, with the over all symmetry constrained to C_{2v} in all cases. The hydroxide hydrogens were constrained to lie in the equatorial plane. We did not investigate any other orientation of the hydrogens, as the distances make it very likely that the rotational barrier of the coordinated hydroxide ions should be low. Considering that our model is rather crude these approximations and restrictions are reasonable. Our assumption that the barrier to internal rotation of the hydroxide hydrogens is small has been confirmed in a very recent DFT study on $[UO_2(OH)_4]^{2-}$ by Schreckenbach et al.[30]

Three different structures of the $[UO_2(OH)_4H_2O]^{2-}$ were investigated. In the first one the hydrogens of the water molecule are pointing towards the dioxo-uranium(VI) oxygens (structure **I**) and are therefore out of the equatorial plane. In structure **II**, both the oxygen and the hydrogens of the water molecule are in the equatorial plane with the hydrogens pointing towards the neighboring hydroxide ions. In structure **III**, the oxygen is pointing towards the uranium in the equatorial plane with the hydrogens perpendicular to this plane. The optimized geometries of these three structures are shown in Figure 2, together with the optimized trigonal bipyramid complex (structure **IV**).

Structures **I** and **III** are clearly four coordinated, with one water molecule at very long distance, whereas structure **II** is pentacoordinated in the equatorial plane. Comparing the energies at the SCF level of these three structures, **I** is the lowest, followed by structure **II** (Table 2). The energetic order of the structures is so clear that we expect it not to be changed by

TABLE 2: Relative Energies in kcal mol^{-1}

complex	relative energy (SCF)	relative energy (MP2)
I	0.0	0.0
II	11.83	6.87
III	16.40	17.55
IV	5.43	−9.23

TABLE 3: Calculated and Experimental Bond Distances in $[UO_2(OH)_4{\cdot}H_2O]^{2-}$ Optimized at the SCF Level[a]

structure	$r(U-O_{uranyl})$	$r(U-O_{hydrox})$	$r(U-O_{water})$	$r(O-H_{water})$
I	1.72 (1.80)	2.36−2.38	4.37	0.94
II	1.72 (1.80)	2.43−2.47	2.65	0.94
III	1.72 (1.80)	2.40	5.21	0.94
ref 30	1.84−1.85	2.33−2.34		
EXAFS exptl this work	1.82	2.24		
exptl 30	1.80	2.21		

[a] Distances in angstroms. The $U-O_{uranyl}$ bond distances have been corrected for the lack of correlation and (within parentheses) for the error in the AIMP.

TABLE 4: Calculated and Experimental Bond Distances in $[UO_2(H_2O)_5]^{2+}$ Optimized at the SCF Level[a]

	$r(U-O_{uranyl})$	$r(U-O_{water})$
this work	1.67 (1.75)	2.57
EXAFS exptl (this work)	1.78	2.41
exptl 27	1.70	2.42

[a] Distances in angstroms. The $U-O_{uranyl}$ bond distances have been corrected (within parentheses) for the lack of correlation and for the error in the AIMP.

TABLE 5: Rotational Barrier in $[UO_2(H_2O)_5]^{2+\ a}$

configuration	rotational barrier
D_{5h}	0.0
R-1	−0.36
R-2	0.96
R-5	22.01

[a] D_{5h} means that all water molecules are oriented perpendicular to the equatorial plane, R-l, R-2, and R-5 refer to structures with one, two, and five water molecules oriented in the equatorial plane. All energies in kcal mol^{-1}.

lifting the geometry constraints. In conclusion, the model where $[UO_2(OH)_4H_2O]^{2-}$ turns out to be four-coordinated in strong alkaline solutions is the most stable one.

However, at the most sophisticated level (MP2), the calculations predict the lowest structure to be a trigonal bipyramid with two water molecules which bind to the dioxouranium and the oxo-oxygen (structure **IV**). The two water molecules in $[UO_2O(OH)_2]^{2-}{\cdot}2H_2O$ stabilize the system by about 50 kcal mol^{-1}, compared to $[UO_2O(OH)_2]^{2-} + 2H_2O$ at long distance. There are four hydrogen bonds in $[UO_2O(OH)_2]^{2-}{\cdot}2H_2O$ (see Figure 2), giving an energy contribution of 12−13 kcal mol^{-1} per hydrogen bond. This is a very strong stabilization induced by the two water molecules. This could be explained by the fact that the water molecule is a dipole and the cluster is negatively charged. Indeed, using the experimental value of the dipole moment of the water molecule and assuming the charge of the complex to be centered on uranium, the attraction turns out to be about 20 kcal/mol for one water molecule.

The distances between the water molecules and the UO_2^{2+} ion are quite large for structures **I**, **II**, and **IV** (4.4 Å for structure **I**, 5.2 Å for structure **III**, and 4.0 Å for structure **IV**). The abnormally large stabilization then indicates that our model is not balanced enough to describe the difference in hydration energy for $[UO2(OH)_4]^{2-}$ and $[UO_2O(OH)_2]^{2-}$. Explicit inclusion of more water molecules in the complexes would certainly improve the model and probably make the artificial stabilization of complex **IV** ($[UO_2O(OH)_2]^{2-}$) less pronounced. We do not have to consider the unrealistic energy of this complex in the further discussion. This is also supported by the experimental results which rule out the trigonal bipyramid.

Geometries. The calculated geometries for $[UO_2(OH)_4H_2O]^{2-}$ and $[UO_2(H_2O)_5]^{2+}$, optimized at the SCF level, are shown in Tables 3 and 4, together with experimental results from ref 28. Let us first consider the bond distance in the uranyl(VI) unit. A glance at Tables 3 and 4 shows that the U−O bond optimized at the SCF level is much too short compared to experiments. This is of course not surprising since the bond distance in an isolated uranyl(VI) is 1.65 Å at the SCF level and 1.71 Å at the correlated level (see ref 29). However, the calculated change in the internal uranyl bond distance between acid and alkaline solutions is well described by the calculations. The theoretical shift is 0.05 Å compared to the experimental value of 0.04 Å.

Since the difference in bond distance between the uranyl unit and the equatorial ligands is fairly large in both $[UO_2(OH)_4H_2O]^{2-}$ and $[UO_2(H_2O)_5]^{2+}$, we can assume the correlation effect on the internal uranyl bond to be similar for the complexes and for the isolated uranyl(VI) ion. We can correct the bond lengths in the complexes with the bond increase of 0.06 Å found in the gas phase. In addition, the AIMP approximation gives a dioxouranium bond distance which is too short by 0.02 Å for the isolated ion, and it is reasonable to correct the internal uranyl distances in the complex for this deficiency as well. Adding these two corrections (0.08 Å) leads to results in good agreement with experiment. Indeed, the corrected calculated bond distances are too short by 0.02 Å for $[UO_2(OH)_4H_2O]^{2-}$ and by 0.03 Å for $[UO_2(H_2O)_5]^{2+}$.

Several orientations of the water molecules in the $[UO_2(H_2O)_5]^{2+}$ complex were investigated: all water molecules oriented perpendicular to the equatorial plane (D_{5h}), one water molecule in the equatorial plane (R-1), two (nonadjacent) water molecules in the equatorial plane (R-2), and finally all five water molecules in the equatorial plane (R-5). Results obtained at the MP2 level are included in Table 5. The calculated rotational barriers are very small, below 1 kcal mol^{-1}, for one and two rotated water molecules, and it is likely that these rotations are essentially free, while the energy cost for orienting all five water molecules in the equatorial plane is appreciable, 22 kcal mol^{-1}. All comparisons between the hydroxide complexes and $[UO_2(H_2O)_5]^{2+}$ have been done for an aqua ion with all the water molecules oriented perpendicular to the equatorial plane.

Let us now turn to the bond distances between the uranium and the equatorial oxygens. In this case the calculated distances are too long by 0.12−0.15 Å, which is substantial. This is also probably due to an oversimplified theoretical model. However, the calculated shift in the bond distances in going from the aqua ion to the hydroxide complexes is in reasonably good agreement with experiment. The calculations give a shortening of 0.20 Å for the equatorial bond $U-O_{eq}$ and a lengthening of 0.05 Å for the internal uranyl U−O distance, using our model. The change in the equatorial bond distance can be explained by the role of the f-functions. The total f-population is 2.3 in $[UO_2(H_2O)_5]^{2+}$ and 2.1 in $[UO_2(OH)_4]^{2-}$, showing an increased f-stabilization in the uranyl bond of the former systems.

Screckenbach et al.[30] have studied different conformers of $[UO_2(OH)_4]^{2-}$ at the DFT level, using relativistic ECPs and the hybrid functional B3LYP. They find the most stable conformer to be a structure with bent U−O−H bonds, where two of the hydrogens above and two below the equatorial plane in a trans-type configuration. The bond lengths between uranium and the

TABLE 6: Calculated and Experimental Bond Distances of the Five-Coordinated Complex $[UO_2(OH)_5]^{3-}$ Optimized at the SCF Level[a]

	$r(U-O_{uranyl})$	$r(U-O_{eq})$	Δr
five-coordinated	1.72 (1.80)	2.50	0.07
four-coordinated	1.72 (1.80)	2.36−2.38	0.19−0.21
EXAFS exptl (this work)	1.82	2.24	0.17

[a] Distances in angstroms. The $U-O_{uranyl}$ bond distances have been corrected for the lack of correlation and (within parentheses) for the error in the AIMP. We also compare with the geometries obtained in the four-coordinated case. Δr is the difference in the $U-O_{water}$ bond length between the acid and the alkaline cases.

equatorial oxygens (2.33, Å, see Table 2) are shorter than the ones obtained by us (2.37 on the average) by 0.04 or 0.09 Å longer than experiment (2.24 Å). In contrast, the internal uranyl bond (1.84 Å) is longer than our uncorrected result (1.72 Å) by 0.12 Å and by 0.04 Å compared to our corrected value (1.80 Å). The experimental value is 1.82 Å (present work). The geometries reported in ref 30 were optimized for nonplanar structures and for the isolated $[UO_2(OH)_4]^{2-}$ complex, while we optimized $[UO_2(OH)_4H_2O]^{2-}$ constraining all the hydroxides to be in the equatorial plane. However, the energy difference between structures with different orientations of the hydroxide ions (all up, three up one down, two up two down in a cis configuration) is less than 1.5 kcal/mol in ref 30, and the bond length is in all cases 2.33 Å. In a previous all electron calculation we have found $UO_2(OH)_2$ to be linear, and from this we conclude that the planar structure must be close in energy to the ones in ref 30 and that the uranium−hydroxide bond distances must be similar. We thus attribute the differences in uranium−hydroxide bond distances to the different methods used, where Schrekenbach et al. have included exchange and correlation in the geometry optimizations through the DFT functional. At any rate, the agreement between our results and the results of Screckenbach et al. is fair. Screckenbach et al. also present calculated symmetric vibrational frequencies for the uranyl unit, 739 cm^{-1}, in good agreement with experiment, 784−786 cm^{-1}. Ismail et al.[6] report a symmetric stretch frequency of 1072 for uranyl using B3LYP and a relativistic ECP.

Clark et al.[9] have suggested that the uranyl(VI) ion may coordinate five rather than four hydroxide ions in a strongly alkaline solution. We have presented our structure chemical arguments why a model with four coordinated hydroxide ions should be preferred. We have also carried out a geometry optimization on uranyl(VI) coordinated by five hydroxide ions $[UO_2(OH)_5]^{3-}$. We are aware that such a highly negative charged system is stabilized in solution by counter ions. However, it is complicated to include them in the calculations. Anyway, the optimized geometries should be at least qualitatively compatible with the corresponding results for the doubly negative ions. They are presented in Table 6. We also tried to start the calculation from a distorted geometry in which one of the $U-O_{hydrox}$ was arbitrarily lengthened by 0.1 Å. In the final structure this hydroxide is still coordinated to the uranium, which means that such structure is possible.

The internal uranyl bond distance does not change when a hydroxide ion is added to the four-coordinated complex, while the uranium−hydroxide distance increases by 0.13 Å on the average, 0.26 Å longer than experiment. We expected longer bond distances as the negative charge on the complex has increased. However, the bond lengths were already too long by 0.12−0.14 Å in the four-coordinated complex (structure **I**). So, an additional large prolongation induced by the fifth hydroxide ion is, although not a conclusive proof, a strong indication that the complex found in solution is four- and not five-coordinated.

A much stronger indication is provided by the geometrical shifts observed between $[UO_2(H_2O)_5]^{2+}$ and $[UO_2(OH)_4]^{2-}$. The changes in the bond length found by comparing the water complex and the four-coordinated hydroxide complex were in excellent agreement with experiment. Concerning the internal uranyl distance, we end up with the same difference in all cases, i.e., 0.05 Å. However, the corresponding shift for the $U-O_{eq}$ distance is 0.07 Å for the five-coordinated complex compared to 0.20 Å for the four-coordinated species and 0.17 Å experimentally. Hence, we conclude that the coordination number of uranyl(VI) ion in strongly alkaline solution is four, not five, in agreement with the conclusions of Yamamura et al.[32] This is further supported by an EXAFS model with the coordination number fixed to four. The residual obtained with this model is 23 as compared to 21 in a model with no restrictions.

Acknowledgment. This work was supported by the Grant V6414 from the Norwegian VISTA foundation. L.M. and V.V. are grateful to participate to the program of “cotutelle de Thèse” financed by the French Government. B.S. would like to thank the Deutsche Forschungsgemeinschaft and the Norwegian research council for financial support. We also would like to acknowledge the REHE program of the ESF to have provided collaborations to promote quantum relativistic studies. This work has received support from The Research Council of Norway (Program of Supercomputing) through a grant of computing time. The experimental work was supported by the European Commission within the Training and Mobility of Researcher (TMR) Program under contract number ERBFMBICT972296. A part of the measurements were done at SSRL which is operated by the U.S. Department of Energy. The other experiments were performed at HASYLAB. The help of Melissa A. Denecke with the treatment of the EXAFS spectra is gratefully acknowledged. The Swedish Nuclear Fuel and Waste Management Co. (S.K.B.) provided financial assistance.

Note Added in Proof. Since this paper was accepted a more detailed discussion of the stoichiometry of the complex(es) formed in strongly alkaline solution has been given by Clark et al. in *Inorg. Chem.* **1999**, *38*, 1456. The authors discuss the possibility of an equilibrium between $UO_2(OH)_4{}^{2-}$ and $UO_2(OH)_5{}^{3-}$, but the evidence for this is not conclusive. There is no isosbestic point in the visible spectrum, and the evidence relies on the emission spectrum at liquid nitrogen temperature. It is not clear at this point how this information can be transferred to data at 25 °C. We still believe that the practically identical EXAFS data of $UO_2(OH)_4{}^{2-}$ in solid phase and the spectrum of lacalice U(VI) solutions is a very strong indicator that the stoichiometry is the same in both phases.

References and Notes

(1) Pyykkö, P. *Inorg. Chim. Acta* **1987**, *139*, 989.

(2) Vallet, V.; Maron, L.; Schimmelpfennig, B.; Leininger, Th.; Teichteil, Ch.; Gropen, O.; Grenthe, I.; Wahlgren, U. *J. Phys. Chem.* In press.

(3) Marian, C. M.; Wahlgren, U.; Gropen, O.; Pyykkö, P. *J. Mol. Struct.* (*Theochem*) **1988**, 339.

(4) Andersson, K.; Malmqvist, P-A.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483.

(5) Craw, J. S.; Vincent, M. A.; Hillier, I. H.; Wallwork, A. L. *Phys. Chem.* **1995**, *99*, 10181.

(6) Ismail, N.; Heully, J-L.; Saue, T.; Daudey, J-P.; Marsden, C. J. *Chem. Phys. Lett.*

(7) Cagliardi, L.; Willets, A.; Skylaris, C-K.; Handy, N. C.; Spencer, S.; Ioannou, A. G.; Simper, A. M. **1998**.

(8) Jung, W.; Ikeda, K.; Tomiyasu, H.; Fukutomi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2317.

(9) Clark, D. L.; Conradson, S. D.; Keogh, D. W.; Neu, M. P.; Palmer, P. D.; Rogers, R. D.; Runde, W.; Scott, B. L.; Tait, C. D. Coordination chemistry of actinide ions under highly alkaline conditions. Presented at the Actinides '97 International Conference, Germany, 21−26 Sept, 1997.

(10) Ciavatta, L.; Ferri, D.; Grenthe, I.; Salvatore, F. *Inorg. Chem.* **1981**, *20*, 463.

(11) Grenthe, I.; Lagerman, B. *Acta Chem. Scand.* **1991**, *45*, 231.

(12) Ressler, T. *J. Synchrotron Rad.* **1998**, *5*, 122.

(13) Taylor, J. C. *Acta Crystallogr.* **1971**, *B27*, 1088.

(14) Zabinski, S. I.; Rehr, J. J.; Ankudinov, A.; Albers, R. C.; Eller, M. J. *Phys. Rev. B* **1995**, *52* (4), 2995.

(15) Koningsberger, D. E., Prins, R., Eds. *X-ray Absorption: Principles, Applications, Techniques for EXAFS, SEXAFS and XANES*; Wiley-Interscience: New York, 1988.

(16) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Lindh, R.; Malmqvist, P-A.; Neogrády, P.; Olsen, J.; Roos, B. O.; Sadlej, M.; Schütz, A. J.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Widmark, P.-O. *MOLCAS-4 program package*; Lund University: Sweden, 1997.

(17) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89.

(18) Hess, B. A. *Phys. Rev. A* **1986**, *33*, 3742.

(19) Huzinaga, S.; Seijo, L.; Barandiarán; Klubokowski, M. *J. Chem. Phys.* **1987**, *86*, 2132.

(20) Huzinaga, S.; Seijo, L.; Barandiarán *J. Chem. Phys.* **1989**, *91*, 7011.

(21) Wahlgren, U.; Schimmelpfennig, B.; Jusuf, S.; Strømsnes, H.; Gropen, O.; Maron, L. *Chem. Phys. Lett.* **1998**, *287*, 525.

(22) Faegri, K. Oslo University. Private communication.

(23) Raffenetti, R. C. *J. Chem. Phys.* **1973**, *58*, 4452.

(24) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(25) Palmer, D. A.; Nguyen-Trung, C. *J. Sol. Chem.* **1995**, *24* (12), 1281.

(26) Allen, P. G.; Shuh, D. K.; Bucher, J. J.; Edelstein, N. M.; Palmer, C. E. A.; Silva, R. J.; Nguyen, S. N.; Marquez, L. N.; Hudson, E. A. *Radiochim. Acta* **1996**, *75*, 47.

(27) Åberg, M.; Ferri, D.; Glaser J.; Grenthe, I. *Inorg. Chem.* **1983**, *22*, 3986.

(28) Moll, H.; Denecke, M. A.; Farkas, I.; Jalivehvand, F.; Sandström, M.; Szabo, U.; Wahlgren, S.; Grenthe, I. Presented at Actinide XAS 98, 1998.

(29) Vallet, V.; Schimmelpfennig, B.; Maron, L.; Teichteil, C.; Leininger, T.; Gropen, O.; Grenthe, I.; Wahlgren, U. *Chem. Phys.* **1999**, *244*, 185.

(30) Schrekenbach, J.; Hay, P. J.; Martin, R. L. *Inorg. Chem.* **1998**, *37*, 4442.

(31) Grenthe, I.; Fuger, J.; Konings, R. J. M.; Lemire, R. J.; Muller, A. B.; Nguyen-Trung, C.; Wanner, H. Chemical Thermodynamics of Uranium; North Holland; Amsterdam, 1992.

(32) Yamamura, T.; Kitamura, A.; Fukui, A.; Nishikawa, S.; Yamamota, T.; Moriyama, H. *Radiochim. Acta* **1998**, *83*, 139.