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Structure of $[UO_2Cl_4]^{2-}$ in Acetonitrile

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The complex formation of uranyl UO_2^{2+} with chloride ions in acetonitrile was studied by UV–vis and U L_{III} EXAFS spectroscopy. The investigations unambiguously point to the existence of a $[UO_2Cl_4]^{2-}$ species in solution with D_{4h} symmetry. The distances in the U(VI) coordination sphere are U–O_{ax} = 1.77 ± 0.01 Å and U–Cl = 2.68 ± 0.01 Å.

In the past, optical properties of the uranyl chloride complexes in the solid state have been extensively studied. Crystals of the type $M_2UO_2Cl_4$ with M = Cs^+, K^+, Rb^+, NH_4^+, etc. have been investigated thoroughly by the groups of Denning, Tanner, Flint, and Görller-Walrand.[1−4] Thermodynamic data of U(VI) aquo chloro complexes have been reported in comprehensive reviews by Grenthe et al.,[5] as well as their complex structures in aqueous solution by Allen et al.[6] and Hennig et al.[7] In contrast, little is known on U(VI) chloride complexation in nonaqueous solution. Therefore, in this paper, UV−vis and EXAFS spectroscopy are used to determine the Cl coordination of uranyl in acetonitrile.

Acetonitrile was used as a solvent because solutions in acetonitrile are stable for a longer time compared with those in acetone. To reduce the water content, acetonitrile was dried on molecular sieves. $UO_2(ClO_4)_2 \cdot xH_2O$ (50 mM) was mixed with tetrabutylammonium chloride (NBu_4Cl) in acetonitrile in uranyl-to-chloride ratios of 1:0 to 1:6.[8] When a ratio higher than 1:4 is reached, no further changes are observed in the spectra. To obtain the spectrum of the free uranyl ion, we used a solution of $UO_2(ClO_4)_2 \cdot xH_2O$ (50 mM) in acetonitrile.[9] UV−vis spectra were recorded at room temperature on a Varian Cary 5000 spectrophotometer in the wavelength interval between 600 and 300 nm. For the EXAFS measurements, we used a solution that contains 50 mM $UO_2(ClO_4)_2 \cdot xH_2O$ and 0.25 M NBu_4Cl in acetonitrile. EXAFS measurements were performed in transmission mode using a Si(111) double-crystal monochromator on the Rossendorf Beamline[10]

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(8) Various hydrates of uranyl perchlorate $UO_2(ClO_4)_2 \cdot xH_2O$ (x = 0, 1, 2, 3, 5, 6, 7) have been reported in the literature. The treatment of the initial solid probably governs the degree of hydration. However, it is very difficult to determine the exact number of water molecules in the uranyl perchlorate salt due to its hygroscopic behavior. Even if we determine the exact number of water molecules, it is always an estimation. Therefore, to have more or less an idea about the uranyl concentration in our samples, we use the molecular weight of the hexahydrate for calculating concentrations (MW 577.02 g/mol). Comparison of the ϵ values for 5, 6, or 7 water molecules in the uranyl perchlorate salt yields an error of about 3%.

(9) Per definition, the free uranyl ion is observed in a solution of a strongly dissociated salt, like uranyl perchlorate. By dissolving $UO_2(ClO_4)_2 \cdot xH_2O$, the perchlorate ions are removed from the first coordination sphere. Perchlorate ions are known for their weakly coordinating properties. In reality, the free uranyl ion is a hydrated ion. The hydrated uranyl ion present in the solid perchlorate pentahydrate is $[UO_2(H_2O)_5]^{2+}$. When we dissolve $UO_2(ClO_4)_2 \cdot xH_2O$ in acetonitrile, the perchlorate ions are replaced by acetonitrile in the first coordination sphere. We call this also the free uranyl ion. We can conclude that a "bare" UO_2^{2+} does not exist. However, with the free uranyl ion, we mean the uranyl ion surrounded by only solvent molecules and no ligands.

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at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Higher harmonics were rejected by two Pt-coated mirrors. The uranium L_{III}-edge spectra were collected using argon-filled ionization chambers at ambient temperature and pressure. Data were collected in equidistant k-steps of 0.05 $Å^{-1}$ across the EXAFS region. An Y metal foil (first inflection point at 17038 eV) was used for energy calibration. The U L_{III} threshold energy, $E_{k=0}$, was defined as 17185 eV. EXAFS data were extracted from the raw absorption spectra by standard methods including a spline approximation for the atomic background using the program EXAFSPAK.[11] Theoretical phase and amplitude functions were calculated with FEFF 8.2.[12] Scattering phases and amplitudes were calculated using a hypothetical cluster based on the structure of $Cs_2UO_2Cl_4$.[13] The amplitude reduction factor, S_0^2, was defined as 0.9 in the FEFF calculation and fixed to that value in the data fits.

Görller-Walrand et al. have investigated the complexation of the uranyl ion UO_2^{2+} with chloride ions in acetone by UV−vis spectroscopy.[14] With a metal-to-ligand ratio higher than 1:4, the main features in the spectrum remain constant, which indicates that the uranyl complex reached the maximal coordination of Cl^- ions in the equatorial plane. On the basis of the similarity between single crystals of the type $M_2UO_2Cl_4$, which have been thoroughly studied by Denning et al.,[1f] and solution, we can conclude that a $[UO_2Cl_4]^{2-}$ complex with D_{4h} coordination symmetry is present in solution (acetone).[14]

The UV−vis spectrum in acetonitrile exhibits the same vibrational fine structure as in acetone. Consequently, a complex with four equatorial chloride ligands (D_{4h}) is also formed in acetonitrile. The UV−vis spectrum of the tetrachloro complex $[UO_2Cl_4]^{2-}$ in acetonitrile is shown in Figure 1. For comparison, the spectrum of the free uranyl ion in acetonitrile is also included.

Presently, the derived energy levels of UO_2^{2+} in $[UO_2Cl_4]^{2-}$ and their positions are generally accepted. The transitions in the spectrum mainly arise from electronic configurations of the type $(\sigma_u^+)^2 \rightarrow \sigma_u^+\delta_u$ and $(\sigma_u^+)^2 \rightarrow \sigma_u^+\phi_u$.[1f,3] In an intermediate coupling scheme, this corresponds with $\Sigma_g^+ \rightarrow \Pi_g$, $\Sigma_g^+ \rightarrow \Delta_g$, $\Sigma_g^+ \rightarrow \Phi_g$ and $\Sigma_g^+ \rightarrow \Delta_g$ for $(\sigma_u^+)^2 \rightarrow \sigma_u^+\delta_u$.[1f,3] Table S1 of the Supporting Information lists the transitions we assign for $[UO_2Cl_4]^{2-}$ in acetonitrile, as well as an overview of the energy values of the $Cs_2UO_2Cl_4$ single crystal, studied in great detail by Denning et al.[1f] in D_{4h} symmetry. For comparison, the energy values calculated with ab initio methods by K. Pierloot are also included.[15] All calculated values correspond to their experimental value for $Cs_2UO_2Cl_4$ single crystals[1f] and $[UO_2Cl_4]^{2-}$ in solution.[14]

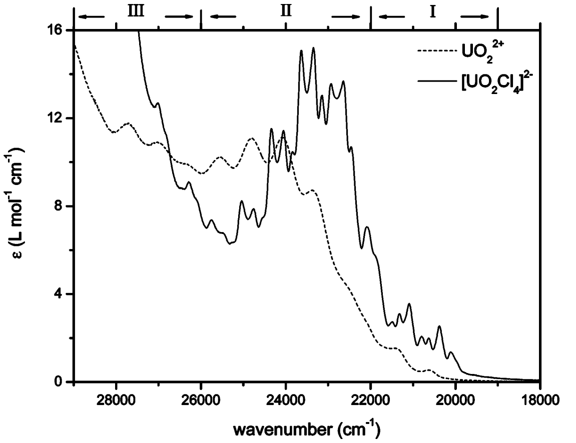

Figure 1. UV−vis spectrum of free UO_2^{2+} (dashed line) and $[UO_2Cl_4]^{2-}$ (solid line) in acetonitrile at room temperature. Concentrations are $[UO_2^{2+}] = 50$ mM and $[Cl^-] = 0.25$ M.

The centrosymmetric coordination symmetry D_{4h} implies that the spectrum is purely vibronic in nature, which means that intensity can only be induced by coupling of vibrations with ungerade symmetry.[1e] The symmetric stretching vibration ν_s (a_{1g}) of the uranyl ion itself is always superimposed on each vibronic transition. Besides this gerade vibration, three ungerade, intensity inducing vibrations are coupled to the electronic transitions, namely the asymmetric stretching vibration ν_a (a_{2u}) and the bending vibration ν_b (e_u) of the axial oxygens of the uranyl ion and mainly one vibration of the equatorial ligands, ν_{10} (b_{1u}). The U−Cl out-of-plane bending, b_{1u}, is coupled to the first electronic transition $\Sigma_g^+ \rightarrow \Pi_g$ ($A_{1g} \rightarrow E_g$) and one component of the transition $\Sigma_g^+ \rightarrow \Delta_g$ ($A_{1g} \rightarrow B_{2g}$ in D_{4h}).[1f,14]

The U L_{III}-edge k^3-weighted EXAFS spectra and the corresponding Fourier transforms (FT) are shown in Figure 2, and structural parameters of the standard EXAFS shell fitting including phase correction are summarized in Table 1. Multiple-scattering paths $U-O_{ax1}-U-O_{ax2}$ and $U-O_{ax}-Cl$ were included in the curve fit (MS, Figure 2) by constraining their Debye−Waller factors and effective path lengths.

The Fourier transform shows two significant peaks which arise from two axial oxygen atoms (O_{ax}) at 1.77 ± 0.01 Å and four equatorial chloride atoms at 2.68 ± 0.01 Å. The determination of the coordination number may have a high error due to its strong correlation with the Debye−Waller factor and three theoretical amplitude modifying functions, but the estimated equatorial coordination number is in good agreement with the UV−vis results. The determination of atomic distance has a comparably low error of ±0.01 Å. This allows a correlation of weak changes in bond lengths with geometrical effects of the ligand arrangement. In aqueous solution, the Cl coordination competes with H_2O. There, the coordination number of the equatorial shell $N_{Oeq} + N_{Cl}$ is 5.[7] For different species in aqueous solution ($UO_2(H_2O)_4Cl^+$, $UO_2(H_2O)_3Cl_2^0$, and $UO_2(H_2O)_2Cl_3^-$) it has been shown that the U−Cl bond length is 2.71 Å.[7] It seems that the equatorial coordination number is always 5 if a H_2O molecule is present, and 4 if the equatorial coordination shell consists merely of Cl. A reduction of the coordination

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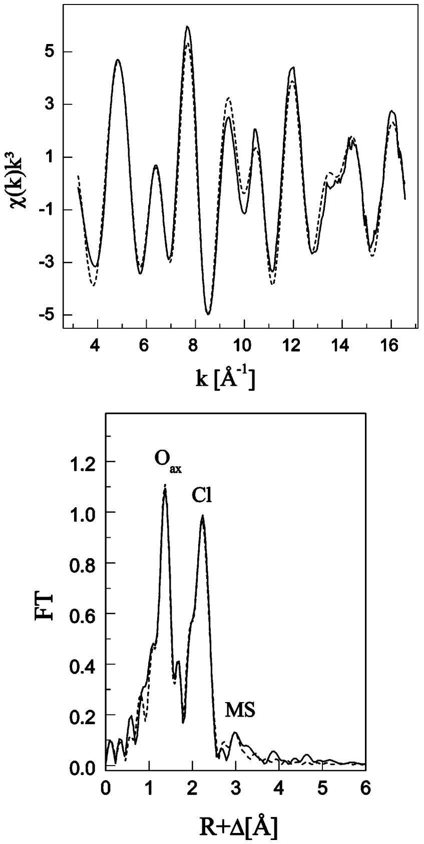

Figure 2. U L_{III}-edge k^3-weighted EXAFS data and corresponding Fourier transforms taken over $k = 3.2-16.6$ Å^{-1}, experimental data as line and theoretical curve fit as dots.

Table 1. EXAFS Structural Parameters of the $[UO_2Cl_4]^{2-}$ Polyhedron[a]

U−O$_{ax}$			U−Cl			
R [Å]	*N*	σ^2 [Å^2]	*R* [Å]	*N*	σ^2 [Å^2]	ΔE_0 [eV]
1.77	2.1	0.0015	2.68	3.7	0.0044	−1.8

[a] Errors in distances, *R*, are ±0.01 Å, errors in coordination numbers, *N*, are ±10%.

number from 5 to 4 is obviously related with a shortening of the bond length from 2.71 to 2.68 Å.

The bond length of $[UO_2Cl_4]^{2-}$ in nonaqueous solution is in close agreement with structural parameters obtained previously for the solid compound $Cs_2UO_2Cl_4$.[13] The use of crystalline reference compounds is not always useful because distances can be influenced by interactions with the next higher neighbors.[16] The environment in a crystal is different from the environment in solution. A comparison with the U−Cl bond lengths of solid $Cs_2UO_2Cl_4$ yields the same bond lengths because the $[UO_2Cl_4]^{2-}$ units are isolated in the crystal structure.

The FT shows a weak peak between the main O_{ax} and Cl peaks and an asymmetry of the Cl shell. These features are described completely by using only a two-shell fit. An inclusion of an additional oxygen shell leads to a unphysical long U−O_{eq} distance of around 2.6 Å.[17] A similar effect was observed for the U(VI) aquo chloro complexes and ruled out by factor analysis.[7] A $[UO_2Cl_4]^{2-}$ species, obtained by DOWEX extraction, revealed a similar weak peak between the main O_{ax} and Cl peaks despite the absence of any oxygen in the coordination shell.[6] Therefore, these features can be indicated as peak overlap effects.

In conclusion, we have shown that both UV−vis and EXAFS spectroscopy point unambiguously to the formation of a $[UO_2Cl_4]^{2-}$ coordination polyhedron in acetonitrile. The striking vibrational fine structure in the UV−vis spectrum and the short U−Cl bond length are characteristic for the existence of a $[UO_2Cl_4]^{2-}$ species in nonaqueous solution.

Acknowledgment. The EXAFS measurements were performed at the Rossendorf Beamline at the ESRF. K.S. is a research assistant and R.V.D. is a postdoctoral fellow of the Fund for Scientific Research, Flanders (Belgium) (F.W.O.-Vlaanderen). We thank the FWO−Vlaanderen and the NWO for providing access to the DUBBLE facility at the ESRF (Grenoble, France) from which beamtime had been exchanged with the ROBL beamline for these experiments. We thank Peter Nockemann for drawing the crystal structure of $Cs_2UO_2Cl_4$ (Table of Contents).

Supporting Information Available: Listings of UV−vis data of $[UO_2Cl_4]^{2-}$ in acetonitrile at room temperature (S1); discussion of the inclusion of a hypothetic oxygen shell corresponding to equatorial H_2O (S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Furthermore, XRD reflection intensities are mainly determined by the heavy uranium scatterers, and light scatterers contribute only weak (the heavy-atom problem). This may lead to inaccuracies in bond length determinations by XRD. See: Hennig, C.; Reck, G.; Reich, T.; Rossberg, A.; Kraus, W.; Sieler, J. *Z. Kristallogr.* **2003**, *218*, 37−45.

(17) A discussion of a hypothetic oxygen shell corresponding to equatorial H_2O is given as Supporting Information.