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EXAFS Determinations of Uranium Structures: Uranyl Complexed with Tartaric, Citric, and Malic Acids

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Synopsis

ULIII - edge EXAFS were measured for 1:1 mixtures of uranyl with tartaric, malic, and citric acids. The room temperature EXAFS of these mixtures demonstrate the characteristic uranium-oxygen interactions of the uranyl ion UO$_2^{2+}$, and also show a U-U interaction at 3.92 Å, indicating the presence of a uranyl dimer. Based on models proposed by earlier potentiometric titration experiments by Martell et al., it is concluded that the dimer is the ligand bridged species, (UO$_2$)$_2$(L)$_2$, in which bridging occurs through the α-hydroxyl groups of the polycarboxylate ligands.
EXAFS Determinations of Uranium Structures:
Uranyl Complexed with Tartaric, Citric, and Malic Acids

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Abstract

The uranium LIII-edge extended x-ray absorption fine structure (EXAFS) was measured for 1:1 mixtures of uranyl with tartaric, malic, and citric acids. The room temperature EXAFS of these mixtures at pH = 3 show the characteristic short uranium-oxygen interactions of the uranyl ion, UO22+, at 1.80 Å along with ~5 oxygen near neighbors around the uranyl equator at 2.40 Å. In addition, the EXAFS of each solution reveal a U-U interaction at 3.92 Å, indicating the presence of a uranyl dimer structure. Based on models proposed by earlier potentiometric titration experiments, it is concluded that the dimer is the ligand bridged species, (UO2)2(L)2, in which bridging occurs through the α-hydroxyl groups of the polycarboxylate ligands.
Introduction

Studies of the coordination chemistry of uranium in aqueous solutions are increasingly important for understanding the behavior of uranium in the environment.\textsuperscript{1-7} Actinide speciation information is essential for assessing and developing long-term strategies addressing problems such as migration in nuclear waste repositories or improvements in the processing of nuclear waste and materials. Relative to the latter, one method for removing uranium contamination from soils involves extraction using a chelating agent such as Tiron, or citrate.\textsuperscript{8} These types of extractants are quite efficient at binding uranyl and thus are suitable for removing uranium contamination when it is in the hexavalent uranyl ion form. Martell \textit{et al.}\textsuperscript{9,10} and Markovitz \textit{et al.}\textsuperscript{11} have published a series of articles detailing the complexation of uranyl with tartaric, malic, and citric acids as a function of pH. Using the functional dependencies of potentiometric titration results, they showed that in the pH range 2-4, the uranyl ion forms a 2:2 dimeric species, (UO$_2$)$_2$(L)$_2$, where L= tartrate, malate, or citrate ligands. In considering the possible 2:2 structures shown in Figure 1, both which involve the $\alpha$-hydroxyl group of the ligands for bridging of the uranyl ions, Martell \textit{et al.} stated a preference for the structure in Figure 1b.\textsuperscript{10} However as Martell \textit{et al.} state, it is not possible from the titration data alone to directly distinguish between the structures shown in Figure 1 as well as other plausible 2:2 structures.

With the advent of the structural technique, extended x-ray absorption fine-structure spectroscopy (EXAFS),\textsuperscript{12} we have reinvestigated the solution structures of the uranyl complexes formed in these systems. Using the local environment information derived from the EXAFS of these complexes in solution (i.e., bond lengths and near neighbor types), it is possible to directly determine the dimeric structure that was inferred by earlier potentiometric titrations. Additionally, the results are applicable to models for U complexation with organic acids present in the environment such as humic acids.
Experimental Section

Solution and EXAFS Sample Preparation. Materials used were reagent grade. Double-distilled deionized water was used in all preparations. A 0.08 M stock solution of the UO$_2^{2+}$ ion was prepared by mixing uranyl nitrate, UO$_2$(NO$_3$)$_2$· 6 H$_2$O (B & A, Allied Chemical & Dye Corp.), in a solution of 0.1M nitric acid. Separate 1:1 mixtures of uranyl with each ligand were prepared by mixing 10 ml of the uranyl nitrate stock solution with 10 ml of 0.2 M stock solutions of the dibasic salts K$_2$(tartrate) · 0.5 H$_2$O (Merck), Na$_2$(malate) · H$_2$O (Aldrich), and tribasic salt Na$_3$(citrate) · 2 H$_2$O (Mallinckrodt) and diluting to 25 ml. The final pH readings of the uranyl tartrate, malate, and citrate solutions were 2.2, 2.0, and 3.8, respectively. Aliquots of 3 ml each mixture were placed inside flexible polyethylene bags. Polyethylene frames (with a 5 x 20 mm open slot for x-ray transmission) were placed in the bags to give rigidity to the assembly and to provide an appropriate path length for the EXAFS measurements. The resultant ~5 mm path length and the final 0.08 M uranyl concentration yielded an edge jump ~0.5 across the uranium L$_{III}$ absorption edge. The primary polyethylene containers were heat-sealed and surrounded by a second, heat-sealed bag for safety purposes.

EXAFS Data Acquisition and Analysis. Uranium L$_{III}$-edge x-ray absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on wiggler beamline 4-3 (unfocused) under dedicated ring conditions (3.0 GeV, 50-100 mA) using a Si (220) double-crystal monochromator. Rejection of higher order harmonic content of the beam was achieved by detuning $\theta$, the angle between crystals in the monochromator, so that the incident flux was reduced to 50% of its maximum (>95% harmonic is rejected). All spectra were collected in the transmission geometry using Ar-filled ionization chambers and a vertical slit of 0.5 mm. Three EXAFS scans were collected from each solution at ambient temperature, and the results were averaged. The spectra were energy calibrated by simultaneously measuring the spectrum from a
reference solution of 0.2 M UO$_2$Cl$_2$ which was placed between the second and third ionization chambers. The first inflection point of the absorption edge for the reference was defined as 17166 eV. EXAFS data reduction was performed by standard methods described elsewhere,$^{12}$ using the suite of programs EXAFSPAK developed by G. George of SSRL. Data reduction included pre-edge background subtraction followed by spline fitting and normalization (based on the Victoreen falloff) to extract the EXAFS data above the threshold energy, $E_0$, defined as 17185 eV. Curve-fitting analyses were performed using EXAFSPAK to fit the raw $k^3$-weighted EXAFS data. The theoretical EXAFS modeling code, FEFF6, of Rehr et al.$^{13}$ was employed to calculate the backscattering phases and amplitudes of the individual neighboring atoms for the purpose of modeling the data.

Results and Discussion

Figure 2 shows the raw $k^3$-weighted EXAFS data for the uranyl tartrate, malate, and citrate solutions. Based solely on the raw data, the U polycarboxylate spectra show a strong similarity. There is close agreement among the three samples in the phase as well as the amplitude of all the features in k-space. Similarly, the R-space plots of the Fourier transformed EXAFS shown in Figure 3 are also in close agreement. The Fourier transforms (FTs) represent a pseudo-radial distribution function of the uranium near-neighbor environment, and the peaks appear at lower R values relative to the true near neighbor distances as a result of the EXAFS phase shifts which are different for each neighboring atom ($\alpha$=0.2-0.5 Å). The FTs illustrate that the EXAFS is dominated by scattering from the O atoms of the linear UO$_2^{2+}$ group (peak at 1.30 Å) and scattering from the O atoms lying in the equatorial plane of the UO$_2^{2+}$ ion (peak at 1.90 Å). In addition, the FTs show the presence of another interaction at ca 3.75 Å which is reproduced in each solution. The portion of the FT above 4 Å can be used to gauge the noise level in the EXAFS signal. Considering the fact that the FT above 4 Å is featureless and smooth, the 3.75 Å peak is the result of a real interaction, rather than an experimental artifact.
Modeling and curve-fitting analyses were performed on the raw EXAFS data to determine the bond lengths and coordination numbers, and to examine the origin of the peak at 3.75 Å. The data range used in the fitting procedure was 3-14 Å\(^{-1}\) for the tartrate and malate solutions, and 3-12 Å\(^{-1}\) for the citrate solution. The structural results are summarized in Table 1. Each sample shows ~2 O at 1.78 Å indicative of axial oxygen atoms on the uranyl group. A relatively weak multiple scattering interaction at 3.56 Å originating from the 4-legged path along the O–U–O vector (twice the U–Oax distance) was included in the fits as a variable linked directly to floating bond lengths (R) and coordination number (N) values of the axial oxygen atoms.\(^{14}\) The equatorial plane around the uranyl group contains ~5 O at ca 2.40 Å in each of the samples. The tartrate and malate data sets extended out to higher k-values which permitted the resolution of the equatorial O shell into two components with different U–O distances. The fits also show 2 C atoms at ca 2.9 Å. The presence of C neighbors in the EXAFS confirms ligation directly to the tartrate, malate, and citrate ligands at the carboxylate groups or the α-hydroxyl groups. The observation of at least two unique equatorial O bond lengths results from the presence of different U–O bond lengths for oxygens in the the carboxylate groups, the α-hydroxyl groups, and water molecules—each of which may be present in the equatorial plane of the uranyl.

In an investigation of the nature of the 3.75 Å peak, this contribution was isolated by taking the difference between the uranyl tartrate data and a fit which included only the near-neighbor contributions mentioned above.\(^{15}\) The residual obtained by this procedure contains only those contributions unaccounted for in the fit—specifically the interaction appearing at 3.75 Å. The residual EXAFS signal was Fourier-filtered over the range of 3.2–4.2 Å to remove noise in the fit,\(^{12}\) and is shown in Figure 4. Even at this level of analysis, the increasing EXAFS amplitude as a function of k is a signature of backscattering from an atom of relatively high Z. The corresponding single U shell fit (Figure 4) confirms this assignment. The only other possible source of this peak would be scattering along paths involving the low Z ligands C or O centers. Low Z atoms are not normally detected in room temperature solutions at R > 3 Å, unless a multiple scattering enhancement of the amplitude is operative. Examples for uranium systems have been
observed when ligands like carbonate or nitrate adopt a symmetric bidentate geometry where the distal O atom is collinear with the absorbing atom and the C or N atoms.\textsuperscript{14,16} Thus, the most plausible alternative explanation for the peak at 3.75 Å is bidentate ligation of the carboxylate groups (i.e., a U–C–C path). However, the phase and amplitude derived from a U–C–C path does not match that shown in Figure 4 and was therefore rejected as a possible model.

The fitting results obtained by the inclusion of a U–U interaction along with the O and C shells contributions described above are summarized in Table 1. The fits to the EXAFS data and FTs of each are shown in Figures 2 and 3, respectively. Combining the results with those of Martell \textit{et al.},\textsuperscript{9,10} it should now be possible to more definitively assign a structure to the 2:2 dimer present in these solutions. The structure in 1b is ruled out on the basis that a U–U interaction at 3.9 Å, if configurationally allowed, would be not be detected due to dynamic disorder in the solution. Another relevant dimeric structure that can be discounted has been observed by x-ray diffraction in solid vanadium and antimony compounds that contain a distinct M\textsubscript{2}(tartrate)\textsubscript{2} unit.\textsuperscript{17,18} In these examples, the V–V and Sb–Sb distances are 4.24 and 5.08 Å, respectively. Thus, in an identical arrangement of the tartrate ligands with the uranyl groups, a U–U distance of 3.95 Å, which is substantially shorter than the analogous V–V and Sb–Sb distances, would not be possible.\textsuperscript{19}

Apart from the structure shown in Figure 1a, the only other structure that could possess a U–U interaction at 3.95 Å would be a hydrolysis product, (UO\textsubscript{2})\textsubscript{2}(OH)\textsubscript{2}\textsuperscript{2+}.\textsuperscript{20} However, equilibrium calculations using the computer code HYDRAQL\textsuperscript{21} and considering the numerous equilibria involved show that the concentrations of (UO\textsubscript{2})\textsubscript{2}(OH)\textsubscript{2}\textsuperscript{2+} and other hydrolysis products are several orders of magnitude smaller than the concentration of (UO\textsubscript{2})\textsubscript{2}(L)\textsubscript{2}. In contrast, the calculations indicate that the amount of the free uranyl aquo ion, UO\textsubscript{2}\textsuperscript{2+}, is significant at low pH. For the uranyl tartrate and malate solutions at pH=2, the molar ratio of UO\textsubscript{2}\textsuperscript{2+} to (UO\textsubscript{2})\textsubscript{2}(L)\textsubscript{2} is 2:1. For the uranyl citrate solution at pH=3.8, the ratio is 1:20. Since EXAFS is an atomic property and is averaged over the total U present in each species, the calculated value for the U coordination number, N\textsubscript{U}, would be 0.5 at pH=2 and 1.0 at pH=3.8. This result is supported by
the curve-fitting results in Table 1 which give $N_U = 0.5, 1.3$ for the tartrate and citrate solutions, respectively. Although the Debye-Waller factors, $\sigma$, are correlated in the fitting results ($\sigma$ gets larger with $N$), the integrated amplitudes$^{22}$ of the U–U contributions from the tartrate and citrate solutions remain in a constant 1:2 ratio. Thus, the equilibrium calculations further rule out certain structures and confirm the type of structure depicted in Figure 1a for the formation of $(\text{UO}_2)_2(\text{L})_2$ dimers.

Acknowledgment

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References


(19) In this arrangement, the tartrates are quadridentate and bridging. There is bidentate coordination to a metal atom at each end of the tartrate using a single oxygen atom from each of the hydroxyl and carboxylate groups. For uranyl to adopt this geometry, the two linear UO$_2^{2+}$ groups would have to align end-to-end, which seems implausible. Additionally, the same quadridentate ligation is not possible for the malate or citrate ligands.


(22) The integrated amplitude is calculated from the integral $\int N*exp(-\sigma^2k^2)$ taken over a given k-range and is used as a measure of the relative magnitudes of the EXAFS components.
Table 1. EXAFS Structural Results for (UO$_2$)$_2$(L)$_2$ Complexes.

<table>
<thead>
<tr>
<th></th>
<th>(UO$_2$)$_2$(tartrate)$_2$ R(Å)$^a$</th>
<th>CN$^b$</th>
<th>$\sigma^2$ (Å)$^c$</th>
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<td>U-O$_{ax}$</td>
<td>1.78</td>
<td>2.3</td>
<td>0.0027</td>
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<tr>
<td>U-O$_{eq1}$</td>
<td>2.35</td>
<td>3.1</td>
<td>0.0035</td>
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<tr>
<td>U-O$_{eq2}$</td>
<td>2.47</td>
<td>2.3</td>
<td>0.0045</td>
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<tr>
<td>U-C</td>
<td>2.92</td>
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<tr>
<td>U-U</td>
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<td>0.5</td>
<td>0.0020</td>
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<th>CN</th>
<th>$\sigma^2$ (Å)</th>
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<td>1.78</td>
<td>2.3</td>
<td>0.0022</td>
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<tr>
<td>U-O$_{eq1}$</td>
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<td>2.7</td>
<td>0.0034</td>
</tr>
<tr>
<td>U-O$_{eq2}$</td>
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<td>2.7</td>
<td>0.0045</td>
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<tr>
<td>U-C</td>
<td>2.94</td>
<td>2.0</td>
<td>0.0047</td>
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<tr>
<td>U-U</td>
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<td>0.7</td>
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<th>CN</th>
<th>$\sigma^2$ (Å)</th>
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<td>1.78</td>
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<tr>
<td>U-U</td>
<td>3.93</td>
<td>1.3</td>
<td>0.0070</td>
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**a.** Errors in distances (±0.02 Å) and coordination numbers (± 15%) are estimated from the deviation between fitting results from models of known structure and their true values.

**b.** Coordination number

**c.** $\sigma$=Debye-Waller factor
Figure Captions

Figure 1 Possible structural models for the uranyl tartrate dimer having the empirical formula (UO$_2$)$_2$(L)$_2$ where L=tartrate; (a) uranyl groups are bridged by α-hydroxyl groups, (b) no bridging occurs through the α-hydroxyl groups.

Figure 2 Raw U L$_{III}$-edge $k^3$-weighted EXAFS data for 1:1 mixtures of uranyl with tartrate, malate, and citrate ligands at low pH. The solid line is the experimental data, and the dashed line is the best theoretical fit of the data.

Figure 3 Fourier transforms of U L$_{III}$ EXAFS for 1:1 mixtures of uranyl with tartrate, malate, and citrate ligands at low pH. Transforms were taken over the range of the data shown in Figure 2. The solid line is the experimental data, and the dashed line corresponds to the best theoretical fit of the data. The U–U peak at 3.75 Å (uncorrected for phase shift) is evidence for the dimeric structure described in the text.

Figure 4 The Fourier-filtered U–U EXAFS signal (solid line, —) and the corresponding single shell fit (dotted line, ····) obtained by the procedure described in the text. The increasing EXAFS amplitude as a function of k is characteristic of backscattering from U.