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# A Density Functional Study of Uranyl Monocarboxylates

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We studied uranium(VI) monocarboxylate complexes by a relativistic density functional method using simple carboxylic acids as ligands, i.e. $[UO_2(OOCR)]^+$ (R = H, $CH_3$, $CH_2CH_3$). These complexes exist in aqueous solution and, for R = $CH_3$ and $CH_2CH_3$, may also be considered as models of uranyl complexated by humic substances. We investigated mono- and bidentate coordination modes. Short-range solvent effects were accounted for explicitly via aqua ligands of the first hydration shell and long-range electrostatic interactions were described via a polarizable continuum model. The calculated results for the uranyl U=O bond, the bond to aqua ligands, and the averaged uranium distances to equatorial oxygen atoms, U–$O_{eq}$, agreed quite well with EXAFS-derived interatomic distances. However, the uranyl-carboxylate bond was calculated to be notably shorter than the experimentally determined value. Experimental differences between mono- and bidentate coordination, obtained mainly from crystal structures, were qualitatively reproduced for the U–C distance but not for the average bond length, U–$O_{eq}$. We discuss these discrepancies between calculated and experimental results in some detail and suggest changes in the coordination number rather than variations of the coordination geometry as the main source of the experimentally observed variation of the U–$O_{eq}$ distance.

## Introduction

Complexation of actinides by biological decomposition products such as humic substances plays an important role in the migration and retardation of actinides in natural systems.[1,2] Thus, understanding the interaction of actinide species with humic substances is an essential ingredient of safety analysis for radioactive waste management, including long-term storage.[3,4] Carboxylic groups are considered to be the functional groups of humic substances which are mainly responsible for the complexation of metal ions at low pH values because of their strong actinide-complexing ability;[1,5,6] in addition, phenolic, enolic, and aliphatic OH groups as well as amino sites and possibly other functional groups may also be important in this context. Therefore, actinide complexes with various carboxylate ligands have been investigated experimentally by X-ray diffraction (XRD) and extended X-ray absorption fine structure spectroscopy (EXAFS).[7−15] Pertinent theoretical studies are still rare, restricted to uranyl triacetate[16] as a benchmark, as well as uranyl malonate and oxalate complexes.[16,17]

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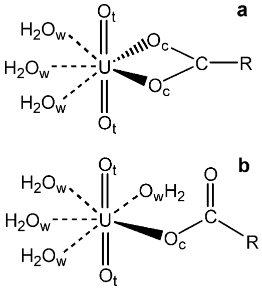

**Figure 1.** Schematic structure of uranyl monocarboxylate complexes $[UO_2(OOCR)(H_2O)_n]^+$ (R = H, $CH_3$, $CH_2CH_3$). The carboxylate ligands are coordinated in (a) bidentate and (b) monodentate fashions to the uranyl ion. Additionally, three and four aqua ligands are coordinated in the equatorial plane to yield pentagonal coordination of the uranium center.

Realistic models for carboxylate complexes are difficult to construct because, even for simpler systems, a variety of possible species, differing in number and coordination type of the carboxylate ligands, have been reported depending on the actinide element, metal and ligand concentrations, as well as on the pH value.[4,18] Most available information refers to uranyl. A carboxylate group can coordinate to an actinide in bi- or monodentate fashion (Figure 1); pseudobridging coordination (i.e., monodentate coordination accompanied by a hydrogen bond between the free carboxylate oxygen and an aqua ligand of the uranyl) has also been suggested.[19] The $U-O_c$ bond between an uranium center and the oxygen atoms of a carboxylic group (Figure 1) and the distance U−C to the carbon center of the carboxylic group are commonly used as indicators for the coordination mode of the carboxylate ligand to an uranyl moiety, when one evaluates X-ray data on crystals and EXAFS results for solution.[8,9,18,20]

For some time, quantum chemistry studies of actinide compounds were scarce because the required simultaneous treatment of relativistic effects and electron correlation presented a great challenge. Recent developments of quantum chemistry methods[21−28] rendered relativistic electronic structure calculations possible even for large complexes of heavy elements and opened a computational route, complementing experimental efforts, to many properties of these complexes. In addition, actinide chemistry is complicated by the fact that solvation is essential. Short-range solvent effects can be modeled by explicit treatment of the hydration sphere in the quantum chemical model,[27−33] while long-range electrostatic interactions with the bulk solvent are well described via a polarizable continuum model (PCM).[17,25,34] These computational methods have been successfully applied in studies of the coordination environment of solvated actinyls $AnO_2^{n+}$ (An = U, Np, Pu) and the stabilization energies of these complexes.[27,28,31−38]

The density functional (DF) investigation reported here explored the structure and energetics of monocarboxylate model complexes of uranyl with formiate, acetate, and propionate ligands in solution, $[UO_2(OOCR)]^+$ (R = H, $CH_3$, and $CH_2CH_3$). We compared bi- and monodentate coordination of a carboxylic group, and we investigated short- and long-range solvation effects. These complexes are known to exist in solution at appropriate conditions;[10,18,19,39] on the other hand, they may serve as simple models of complexing sites of humic substances. Thus, in the spirit of both these views, we have compared our results to structural information from the EXAFS experiments. Previous efforts to clarify the structural aspects of complex heavy-element systems, like heterogeneous catalysts,[40] have provided us with the experience that it is very useful to supplement EXAFS-derived information by accurate computational results. In addition, to assess the quality of our computational approach, we also calculated uranyl triacetate, $[UO_2(OOCCH_3)_3]^-$, as a benchmark system with a well-characterized first ligand shell.[7−10,15,19,39]

## Computational Method

We carried out scalar-relativistic all-electron calculations with the LCGTO-FF-DF (linear combination of Gaussian-type orbitals fitting function density functional) method[41] as implemented in the parallel code ParaGauss.[42,43] The relativistic density functional method applied is based on the second-order Douglas−Kroll−Hess (DKH) approach to the Dirac−Kohn−Sham problem.[22,44] We

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refrained from including spin–orbit interaction because all species examined feature U(VI) centers and a closed-shell electronic structure.

We employed two exchange-correlation functionals: the local-density approximation (LDA) as parametrized by Vosko, Wilk, and Nusair (VWN)[45] and the gradient-corrected functional (generalized gradient approximation, GGA) suggested by Becke and Perdew (BP).[46,47] Structures were optimized at the LDA level, invoking a quasi-Newton algorithm and analytical forces.[48] LDA often yields more accurate results for molecular geometries and frequencies, whereas gradient-corrected functionals yield improved binding energies.[49,50] Therefore, we applied the GGA-BP functional self-consistently to calculate binding energies in a "single-point fashion" at structures that had been optimized at the LDA-VWN level. The symmetric uranyl stretching frequency was determined via numerical second derivatives, keeping other degrees of freedom frozen. On the basis of tests for uranyl monocarboxylate complexes in the gas phase, we estimate deviations from a complete frequency analysis to be less than 5 $cm^{-1}$.

The Kohn–Sham orbitals were represented by flexible Gaussian-type basis sets, contracted in a generalized fashion using appropriate atomic eigenvectors. For U, we used a basis set of the size (24s, 19p, 16d, 11f),[51] contracted to [10s, 7p, 7d, 4f]. The light atoms were described by standard basis sets:[52] (9s, 5p, 1d) → [5s, 4p, 1d] for C and O[52a,b] and (6s, 1p) → [4s, 1p] for H.[52a,c] In the LCGTO-FF-DF method, the classical Coulomb contribution to the electron–electron interaction is evaluated via an approximate representation of the electron density using an auxiliary basis set.[41] The exponents of the corresponding s- and $r^2$-type "fitting functions" were generated from the orbital basis by a standard procedure;[41] we added five p-, d-, and f-type "polarization exponents" each as geometric series with a progression of 2.5, starting with 0.1, 0.2, and 0.3 au, respectively. Thus, the auxiliary charge density basis sets were (24s, 9$r^2$, 5p, 5d, 5f) for U, (9s, 5$r^2$, 5p, 5d) for C and O, and (6s, 1$r^2$, 5p) for H. A comparison with results of other DF calculations confirmed the accuracy of the current FF approach for actinide complexes.[53] Extension of the auxiliary basis of U by a set of five g exponents, constructed according to the procedure given above, confirmed the accuracy of the selected auxiliary basis set. For instance, with g exponents, the bond lengths of uranyl monoformiate in monodentate coordination changed by less than 0.002 Å, and the total energy changed less than 4 kJ $mol^{-1}$.

Long-range electrostatic solvation effects were taken into account using a PCM variant, the COSMO (conductor-like screening model) method[54] as implemented in ParaGauss.[34] In the COSMO approach, as in all continuum models, the solute is placed in an empty cavity of a dielectric medium. The solute cavity for the electrostatic part of the solute–solvent interaction was constructed from atomic spheres of van der Waals radii,[55] scaled by 1.2 (except for H); additional spheres were created according to the GEPOL algorithm.[56,57] The dielectric constant of water was taken as $\epsilon = 78.39$. In addition to the original COSMO model, the ParaGauss solvent module also accounts for short-range nonbonding solvent effects (cavitation energy, etc.) via a force field.[34]

## Experimental Background and Models

Our choice of structural models for uranyl monocarboxylate complexes in aqueous solution has been guided by pertinent X-ray crystal structure data and EXAFS results. For that reason and to provide a basis for the subsequent discussion of the results, we summarize the experimental background, including structural characteristics that are commonly invoked to distinguish between bi- and monodentate coordination modes of the carboxylate group (Figure 1).

Only X-ray crystal structures provide definite information on the coordination type of carboxylate ligands. According to an overview of several crystalline uranyl carboxylate complexes[20] bidentate coordination is generally characterized by two $U-O_c$ distances of 2.48 ± 0.05 Å, associated with one U–C distance of 2.86 ± 0.05 Å per carboxylate ligand (Figure 1a); the U–C distance does not represent a direct bond, of course. On the other hand, distinctly shorter $U-O_c$ distances, 2.39 ± 0.05 Å, were found for monodentate coordination (Figure 1b);[20] the corresponding U–C distance of 3.5 ± 0.1 Å is clearly elongated.[8,11] Distances to oxygen centers, $U-O_w$, of the first hydration shell, 2.42 ± 0.06 Å, are similar to the $U-O_c$ distances in the monodentate case.[20] Bi- and monodentate coordination yield similar distances to terminal oxygen centers of uranyl, $U{=}O_t$, 1.76 ± 0.03 Å.[20]

The interpretation of the corresponding EXAFS data is normally based on a comparison with typical distances derived from X-ray diffraction on crystal structures. However, in the EXAFS spectra, it is often not possible to differentiate various types of U–O distances because $U-O_w$ distances are comparable to $U-O_c$ distances of monodentate and sometimes even of bidentate carboxylate ligands. Therefore, only average equatorial distances $U-O_{eq}$ can be derived.

Various EXAFS data in solution have been obtained on uranyl complexation by carboxylic ligands such as acetate and glycolate.[10,14] Accordingly, bidentate coordination is characterized by $U-O_c$ distances of 2.43–2.50 Å associated with U–C distances of 2.84–2.91 Å; these results are similar to previously discussed data in crystalline systems. For bidentate coordination, equatorial oxygen distances $U-O_{eq}$ are 2.42 ± 0.04 Å on average.[10,14,58] Definitive EXAFS data for monodentate coordination in solution

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are rare: average $U-O_{eq}$ values are ~2.38 ± 0.04 Å.[10,14] When U−C distances of ~2.9 Å (indicative of bidentate coordination) are absent, then these $U-O_{eq}$ distances are generally assigned to monodentate carboxylate ligands.[8,9] Typical $U-O_w$ distances in solution of 2.38 ± 0.02 and 2.41±0.01 Å have been reported for $[UO_2(CH_3COO)]^+$ and $[UO_2(H_2O)_5]^{2+}$, respectively; they indeed are similar to reported $U-O_{eq}$ values.[10,35,58]

EXAFS data both on the complexation of actinides by natural and synthetic humic acids, from crystalline compounds and in solution, indicate predominantly monodentate coordination, based on average $U-O_{eq}$ distances of 2.37−2.39 Å and missing U−C distances near ~2.9 Å.[9,20,59,60] However, it is unclear why only monodentate complexation of actinides should occur, considering the complex structure of humic substances and the predominance of carboxylic groups as complexing sites.

To contribute to the discrimination of mono- and bidentate complexes, we decided to study different coordination modes in model complexes of uranyl with formiate, acetate, and propionate ligands, $[UO_2(OOCR)]^+$ (R = H, $CH_3$, and $CH_2CH_3$). In these models, we accounted for the strong short-range solvent effects by adding explicit aqua ligands in the first hydration sphere, three for bidentate and four for monodentate coordination. In this way, the typical pentagonal coordination of an uranyl moiety is achieved (Figure 1).[11,14,61] Hexagonal coordination has been suggested for some uranyl carboxylate complexes.[10]

To reduce the computational effort, we applied $C_s$ symmetry constraints in all our models, except for the bidentate coordination mode with R = H ($C_{2v}$). In the monodentate systems $[UO_2(OOCR)]^+$, we chose the equatorial uranyl plane, spanned by O centers of the carboxylate ligand ($O_c$) and the aqua ligands ($O_w$), as the symmetry plane (Figure 1b). For the bidentate systems, we considered the equatorial plane as well as a plane perpendicular to it which includes the uranyl moiety (Figure 1a). In the following, we will discuss only results from the energetically more stable conformers which feature the equatorial plane as a mirror plane. In general, the differences between the two bidentate models are small (i.e., distances, angles, and total energies differ by less than 0.02 Å, 2°, and 10 kJ $mol^{-1}$, respectively).

## Results

**Uranyl Triacetate as a Benchmark.** To assess the accuracy of our computational approach, we first studied uranyl triacetate, $[UO_2(OOCCH_3)_3]^-$, as a benchmark system, assuming bidentate coordination of all three ligands and $C_{3v}$ symmetry (Figure 2a). This complex is suited as a test case because, on one hand, experimental data confirming our structural model are available for comparison;[7−10,15,19] on the other hand, the uranium coordination sphere of $[UO_2(OOCCH_3)_3]^-$ is saturated by three acetate ligands and thus there are no short-range solvent effects via aqua ligands directly coordinated to the metal center. To investigate the influence of aqua ligands in the second hydration shell, we also examined the solvated model species $[UO_2(OOCCH_3)_3(H_2O)_3]^-$ (Figure 2b) where three water molecules were added in the uranyl equatorial plane to account for hydrogen bonds to the carboxyl groups.

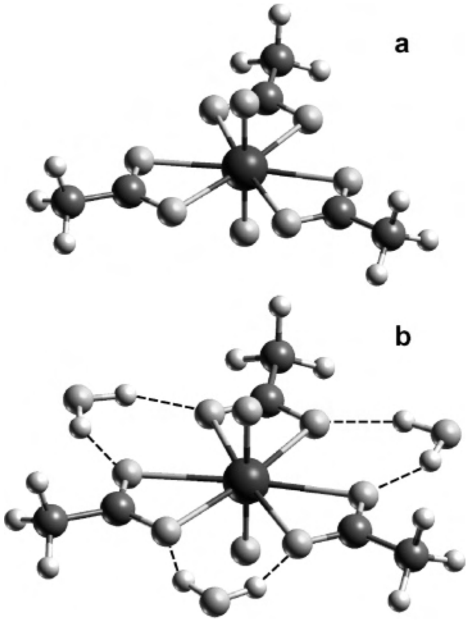

**Figure 2.** Optimized structures of uranyl triacetate complexes $[UO_2(OOCCH_3)_3]^-$ (a) without and (b) with three additional water molecules to simulate hydrogen bonding of the solvent to the carboxylate groups (dashed lines).

**Table 1.** Calculated Structural Parameters (LDA, Å) and Symmetric Uranyl Stretching Frequency, $\nu_s$ ($cm^{-1}$), of Uranyl Triacetate, $[UO_2(OOCCH_3)_3]^-$, for Bidentate Coordination in Comparison to Experimental Data from Solution (sol) and Crystals (cryst) as well as Other Calculated Results (calcd)[a]

| $[UO_2(OOCCH_3)_3]^-$ | $U{=}O_t$ | $U-O_c$ | U−C | $U-CH_3$ | $\nu_s$ |
|---|---|---|---|---|---|
| GP | 1.792 | 2.449 | 2.816 | 4.315 | 837 |
| PCM | 1.803 | 2.424 | 2.817 | 4.299 | 811 |
| GP + $3H_2O$ | 1.783 | 2.459 | 2.848 | 4.337 | 857 |
| PCM + $3H_2O$ | 1.792 | 2.438 | 2.849 | 4.323 | 831 |
| | | exptl | | | |
| sol[b] | 1.78(2) | 2.44(2) | − | 4.34 | 823 |
| cryst[c] | 1.78(1) | 2.48(2) | 2.88(3) | − | − |
| | | calcd[d] | | | |
| GP | 1.81 | 2.51 | − | 4.38 | − |
| PCM | 1.81 | 2.50 | − | 4.38 | − |

[a] Given are results from gas phase (GP) and solvation (PCM) calculations, as well as results including three water molecules to simulate hydrogen bonding to the carboxylate groups (+$3H_2O$). For the designations of atoms, see Figure 1. [b] Refs 15 and 19. [c] Average from refs 7, 8, 9, and 10. [d] ZORA GGA, ref 16.

In Table 1, we present computational results on uranyl triacetate both from the gas-phase (GP) and solvation (PCM) calculations. Both sets of results are quite similar. As the main difference, we note that the $U-O_c$ distance is slightly shorter in solution, by 0.025 Å; other pertinent bond distances differ at most by 0.02 Å. The elongation of the $U{=}O_t$ bond (0.01 Å) in the PCM calculation is reflected in a slightly reduced uranyl stretching frequency, which is calculated 26 $cm^{-1}$ lower than that for the corresponding complex in the gas phase. Models with three explicit water molecules in the second coordination shell yield slightly longer equatorial bond distances. Both in the gas phase and in solution (PCM), the $U-O_c$, U−C, and $U-CH_3$ distances increase about the same amount (0.01 Å, 0.03 Å, and 0.02 Å, respectively)

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because of the aqua ligands in the second hydration shell (Table 1). As expected, the formation of hydrogen bonds between the aqua ligands and the $O_c$ centers of the carboxylate groups weakens the uranium carboxylate bonds $U-O_c$. Concomitant with this weakening of the equatorial U−O bonds, the terminal $U=O_t$ bonds become stronger, as reflected in the shorter bond, by 0.01 Å, and the larger symmetric stretching frequency, 20 $cm^{-1}$ (Table 1).

The most elaborate model ($PCM + 3H_2O$, Table 1) includes solvation effects via three explicit aqua ligands in the second coordination shell and a PCM treatment. Of all models, its structure agrees best with the EXAFS data for solution.[15] Deviations are less than 0.01 Å for the bonds $U=O_t$ and $U-O_c$, less than 0.02 Å for the $U-CH_3$ distance, and only 8 $cm^{-1}$ for the symmetric uranyl stretching frequency. These results illustrate the accuracy of our computational models; their quality is rather typical for actinide complexes.[38,53,62]

In Table 1, we also included computational results for uranyl triacetate from a previous study[16] where a similar computational approach (scalar-relativistic DF calculations with the GGA-PW91 functional, solvent effects via a PCM treatment) had been used. The results of these earlier calculations are almost identical for gas phase and PCM models: interatomic distances agree to 0.01 Å or better. However, compared to experimental data in solution, all pertinent distances of that earlier study are too long (i.e., $U=O_t$ by 0.03 Å, $U-O_c$ by 0.06 Å, and $U-CH_3$ by 0.04 Å).[16] With a corresponding DKH GGA-BP PCM optimization, we corroborated this overestimation of bond distances (within 0.01 Å) as typical for gradient-corrected exchange-correlation functionals, and we confirmed our choice of the local density approximation.[49,50]

**Geometry of Bidentate Uranyl Carboxylate Complexes.** Table 2 summarizes results for bidentate complexation of the uranyl complexes $[UO_2(OOCR)(H_2O)_3]^+$ with R = H, $CH_3$, and $CH_2CH_3$ (i.e., with formiate, acetate, and propionate ligands (Figure 3)). As stated before, solvation effects were taken into account by three explicit aqua ligands of the first hydration sphere, supplemented by a PCM treatment.

The calculated structural parameters of these complexes vary only slightly for the three residues R. While the distances for the acetate and propionate complexes differ by at most 0.01 Å, somewhat larger deviations are found for formiate, pointing toward a weaker bonding of the latter ligand (Table 2). Compared to the former, larger ligands, the $U-O_c$ bond is 0.02 Å longer and the aqua ligands are a little closer to the center. This results in the shortest uranyl bond $U=O_t$ and the strongest uranyl symmetric stretching frequency in the series. These trends, albeit faint, are confirmed by energetic considerations and are also obtained for monodentate carboxylate coordination (see below).

**Table 2.** Calculated Structural Parameters (Å) and Symmetric Uranyl Stretching Frequency, $\nu_s$ ($cm^{-1}$), of $[UO_2(OOCR)(H_2O)_n]^+$ (R = H, $CH_3$, $CH_2CH_3$) Exhibiting Bidentate (bi, $n = 3$) and Monodentate (mono, $n = 4$) Carboxylate Coordination in Comparison with Experimental Data for Aqueous Solution (sol) and Crystals (cryst)[a]

| | R | $U=O_t$ | $U-O_c$ | U−C | $U-O_w$ | $U-O_{eq}$ | $\nu_s$ |
|---|---|---|---|---|---|---|---|
| bi | H | 1.783 | 2.394 | 2.770 | 2.356 | 2.371 | 860 |
| | $CH_3$ | 1.787 | 2.371 | 2.769 | 2.360 | 2.364 | 858 |
| | $CH_2CH_3$ | 1.786 | 2.369 | 2.768 | 2.369 | 2.369 | 853 |
| | $\Delta H_2O$ av | 0.03 | 0.11 | 0.10 | − | 0.16 | −57 |
| | ΔPCM av | 0.01 | 0.04 | 0.03 | −0.06 | −0.02 | −24 |
| exptl | $CH_3$ sol[b] | 1.78(1) | 2.50(2) | 2.91(2) | 2.38(2) | 2.43(2) | 861 |
| | sol[c] | 1.78(1) | 2.46(4) | 2.87(4) | 2.40(4) | 2.42(4) | − |
| | cryst[d] | 1.76(3) | 2.48(5) | 2.86(5) | 2.36(4) | 2.42(6) | − |
| mono | H | 1.788 | 2.221 | 3.400 | 2.415 | 2.376 | 851 |
| | $CH_3$ | 1.790 | 2.201 | 3.401 | 2.421 | 2.377 | 846 |
| | $CH_2CH_3$ | 1.790 | 2.201 | 3.401 | 2.421 | 2.377 | 849 |
| | $\Delta H_2O$ av | 0.03 | 0.14 | −0.01 | − | 0.37 | −55 |
| | ΔPCM av | 0.01 | 0.04 | 0.03 | −0.04 | −0.02 | −22 |
| | Δbi av | 0.00 | 0.17 | −0.63 | −0.06 | −0.01 | 9 |
| exptl | sol[c] | 1.78(1) | − | − | − | 2.38(4) | − |
| | cryst[d] | 1.76(3) | 2.39(5) | 3.5(1) | 2.42(6) | 2.36(2) | − |

[a] Solvent effects are included via explicit aqua ligands and a PCM treatment. Also given are average changes, $\Delta H_2O$, from the addition of the aqua ligands to the corresponding bare complexes $[UO_2(OOCR)]^+$ in the gas phase, and ΔPCM from the embedding of the complexes $[UO_2(OOCR)(H_2O)_n]^+$ in a PCM environment. Average changes Δbi are calculated for complexes in solution with monodentate coordination of the carboxylate ligands with respect to the corresponding bidentate complexes. For the designations of atoms, see Figure 1. [b] Refs 10, 19, and 39. [c] Average values from refs 10, 14, and 58. [d] Average values from refs 9, 10, and 20.

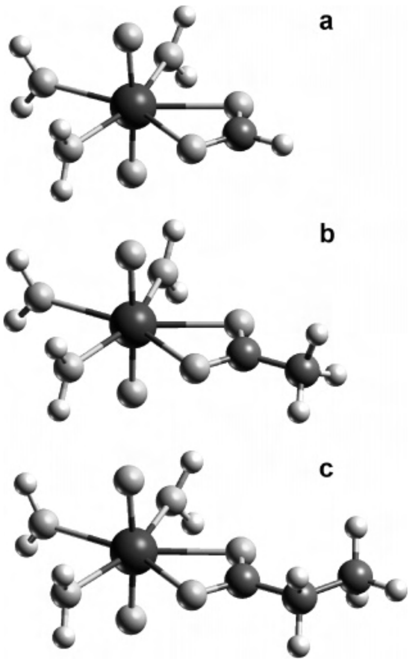

**Figure 3.** Optimized structures of uranyl monocarboxylate complexes $[UO_2(OOCR)(H_2O)_3]^+$, R = (a) H, (b) $CH_3$, and (c) $CH_2CH_3$, with bidentate coordination of the carboxylate group.

For a detailed investigation of solvation, we simulated short-range and long-range effects in two consecutive steps. First, we determined the changes, $\Delta H_2O$ (Table 2), caused by the addition of three explicit aqua ligands to a bare uranyl carboxylate complex $[UO_2(OOCR)]^+$ which was calculated in the gas phase; then, we embedded such an aqua complex $[UO_2(OOCR)(H_2O)_3]^+$ in a PCM environment, resulting in changes ΔPCM. All differences, Δ, listed in Table 2 represent average values for all three types of carboxylate complexes; deviations from these averages are less than 0.01 Å for distances and 6 $cm^{-1}$ for the uranyl stretching frequency.

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Explicit consideration of aqua ligands leads to a distinct elongation of the uranium carboxylate distances U−O$_c$ and U−C by 0.11 Å and 0.10 Å, respectively (Table 2). The U═O$_t$ distance elongated slightly, by 0.03 Å, while the O$_t$═U═O$_t$ angle decreased from 176° to 172°. These bond elongations resulted from increased bonding competition with the aqua ligands at the uranium center. The weaker uranyl bonds were reflected in a reduction of the uranyl stretching frequency, by ~57 cm$^{-1}$ on average. These observed strong effects caused by the coordination of aqua ligands confirm previous findings,[34,38] namely, that aqua ligands of the first hydration shell interact rather strongly with the uranium center.

Long-range solvent effects further elongated the distances U−O$_c$, U−C, and U═O$_t$, by 0.04, 0.03, and 0.01 Å, respectively (Table 2). Screening of polar bonds via polarization by the solvent leads to these ΔPCM increments. The weakening of the uranyl bond is reflected in a further reduction of the uranyl stretching frequency by ~24 cm$^{-1}$. On the other hand, uranium−water distances decrease by ~0.06 Å because of the PCM treatment. Overall, one notes that the solvent effects described by the PCM model are noticeably smaller than the changes due to aqua ligands of the first solvation shell.

Because only limited experimental structure data are available for systems assigned as monocarboxylate species, we compare our results also to averaged data of complexes with more than one carboxylate ligand and a total of 5−6 equatorial O centers in solution (sol) as well as in crystals (cryst) (Table 2). The uranyl moieties are calculated to feature terminal uranium−oxygen distances, U═O$_t$, of 1.78−1.79 Å and slightly bent O$_t$═U═O$_t$ moieties with angles of 174−177°. The calculated U═O$_t$ distances are typical for small uranyl complexes and agree very well with the experimental data for uranyl acetate, 1.78(1) Å,[10] and the average data for bidentate complexes in solution, 1.78(1) Å.[10,14] Concomitant with the accurate results for U═O$_t$, the calculated symmetric uranyl stretching frequencies, $\nu_s$, of 853−860 cm$^{-1}$ also match the experimental value of 861 cm$^{-1}$ for R = CH$_3$.[19] The average uranium−aqua distances, U−O$_w$, of 2.36 Å are in satisfactory agreement with experimental data for acetate, 2.38(2) Å,[10] as well as with the averages of the experimental data, ~2.40(4) Å.[10,58] The values for U═O$_t$, U−O$_w$, and $\nu_s$ are also quite similar to the results calculated for the solvated uranyl ion $[UO_2(H_2O)_5]^{2+}$: 1.78 Å, ~2.36 Å, and 866 cm$^{-1}$, respectively. As for the other data discussed here, that calculation of the solvated uranyl ion applied $C_s$ symmetry and a PCM treatment of solvation effects. Thus, a bidentate carboxylate group affects the uranyl moiety in much the same way as two aqua ligands.

The uranium carboxylate bond is characterized by U−O$_c$ and U−C distances of 2.37−2.39 and 2.77 Å, respectively (Table 2). However, these distances are distinctly shorter, more than 0.1 Å, than the corresponding EXAFS data for R = CH$_3$, namely, 2.50(2) Å for U−O$_c$ and 2.91(2) Å for U−C.[10] Only slightly smaller differences occur in comparison to solution data for bidentate coordination, where average values of 2.46(4) and 2.87(4) Å have been obtained for U−O$_c$ and U−C, respectively.[10] Concomitantly, the average distance, U−O$_{eq}$, from uranyl to neighboring oxygen atoms is underestimated by ~0.05 Å. These discrepancies are significantly larger than typical errors of DF calculations; thus, they may point to an overestimation of the uranium carboxylate bond distances in our models. On the other hand, the rather long experimental interatomic distances between U and the carboxylate for R = CH$_3$[10] in comparison to averaged data for complexes with two or three bidentate carboxylate ligands (Table 2) is hard to rationalize, if one considers that carboxylate ligands bind more strongly than aqua ligands (see below). Still, from these experimental data it has been concluded that uranium is coordinated by 6 (±25%) equatorial oxygen atoms.[10] A comparison of our results for uranyl complexes with one and three acetate ligands shows that both distances, U−O$_c$ and U−C, are reduced by 0.05 Å for the monoacetate, while the corresponding data in ref 10 for monoacetate exceed even the experimental results for triacetate (Table 1).[7−10,15]

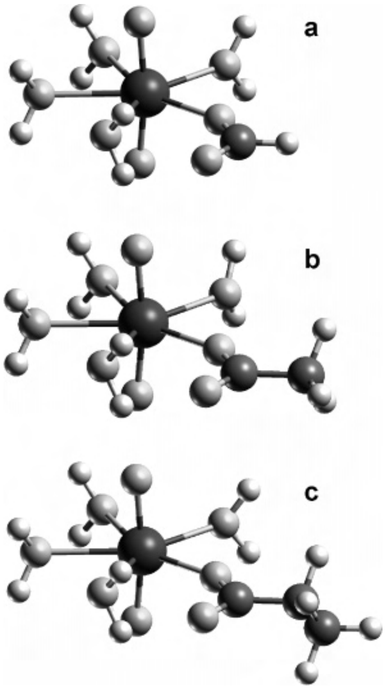

**Figure 4.** Optimized structures of uranyl monocarboxylate complexes $[UO_2(OOCR)(H_2O)_4]^+$, R = (a) H, (b) CH$_3$, and (c) CH$_2$CH$_3$, with monodentate coordination of the carboxylate group.

**Geometry of Monodentate Uranyl Carboxylate Complexes.** We now turn to the corresponding calculations for monodentate coordination in $[UO_2(OOCR)(H_2O)_4]^+$ with R = H, CH$_3$, and CH$_2$CH$_3$ (Table 2, Figure 4). Solvation effects were taken into account as before; however, to reach pentagonal coordination of the uranyl moiety, four explicit aqua ligands were added to the complexes. In addition to a general discussion, we will compare our results to those for the corresponding bidentate complexes (Δbi in Table 2).

Again, all complexes feature similar optimized structural parameters. Terminal uranium−oxygen distances, U═O$_t$, 1.79 Å, were the same as those calculated for bidentate coordination. With O$_t$═U═O$_t$ angles of ~172°, the uranyl moieties were bent slightly more, and uranyl stretching frequencies, 846−851 cm$^{-1}$, were slightly smaller than in the corresponding bidentate carboxylate complexes. Also the differences between the formiate complex and its two congeners with larger ligands are similar: U−O$_c$ is 0.02 Å longer for formiate, while the aqua ligands are a little closer. These indications of a weaker carboxylate bond agreed with the finding that the formiate complex showed the shortest U=O$_t$ distance and the largest uranyl stretching frequency of the series (Table 2). In agreement with qualitative conclusions from the analysis of experimental data,[20] the U−O$_c$ distances were calculated to be notably shorter (2.21 Å) and the U−C distances were significantly longer (3.40 Å) than the corresponding parameters of bidentate complexes: U−O$_c$ = 2.38 Å and U−C = 2.77 Å. Uranium−aqua distances, 2.42 Å, were determined to be longer than those in the bidentate complexes (Δbi = −0.06 Å, Table 2). This finding can be rationalized by bonding competition with four, instead of three aqua ligands; apparently, a monodentate carboxyl ligand binds at least as strong as a bidentate ligand.

As before, we analyzed solvent effects by a stepwise buildup of the models. Comparing the explicit coordination of aqua ligands and bare complexes without PCM treatment (Δ$H_2O$, Table 2), we note distinct elongations of the U−O$_c$ (0.14 Å) and U=O$_t$ (0.03 Å) distances caused by bonding competition with the four equatorial aqua ligands. As discussed for bidentate coordination, incorporation of aqua ligands reduced the uranyl stretching frequency by ∼55 cm$^{-1}$ (Table 2). However, U−C distances were hardly affected (Δ$H_2O$ = −0.01 Å on average), despite the distinct elongation of the U−O$_c$ bonds. This surprising finding results from the reduction of the U−O$_c$−C angle from 160° in the bare complex to 147° in the complex with aqua ligands. This distinct change of the bond angle can be rationalized by the attraction between the “free” negatively charged O$_c$ center of the carboxylic group and the positively charged H centers of adjacent aqua ligands (Figure 4). Subsequent embedding in a PCM environment resulted in smaller corrections (ΔPCM, Table 2) which are comparable to those calculated for the bidentate complexes. Because of screening, U−O$_c$, U−C, and U=O$_t$ distances are elongated by 0.04, 0.03, and 0.01 Å, respectively. The U−O$_w$ distance decreased by 0.04 Å, and the uranyl stretching frequency was reduced by ∼22 cm$^{-1}$ because of the slightly elongated uranyl bonds (Table 2).

A comparison with available experimental data reveals that terminal uranium−oxygen distances, U=O$_t$, 1.79 Å, are in good agreement with the corresponding average experimental value, 1.78(1) Å.[10,14] Also the bond lengths of the aqua ligands, 2.42 Å, are in line with typical experimental values (e.g., 2.40(4) Å).[10,58] The characteristic parameters of the carboxylate bonds, U−O$_c$ (2.21 Å) and U−C (3.40 Å), were found to be considerably shorter than experimental results derived from crystals,[10,11,59] by ∼0.2 Å and 0.1 Å, respectively. Although these differences may be somewhat smaller for complexes in solution, we expect a clear underestimation, as in the case of bidentate coordination (see above). Furthermore, our result calculated for the average U−O bond length in the equatorial plane, U−O$_{eq}$ = 2.38 Å, agrees well with available experimental results for solutions, 2.38 Å (Table 2).[10,14] However, as the present calculations show, the U−O$_{eq}$ distance is of limited value as key indicator of the coordination mode because it averages the widely differing quantities U−O$_c$ and U−O$_w$ (0.2 Å, Table 2). In favorable cases, EXAFS measurements should be able to resolve two such bond distances when a carboxylate ligand is coordinated in monodentate fashion.

**Table 3.** Ligand Abstraction Energies, $\Delta E_{carb}$ (eq 1) and $\Delta E_{aqua}$ (eq 2) (in kJ mol$^{-1}$), of Complexes $[UO_2(OOCR)(H_2O)_n]^+$ (R = H, $CH_3$, $CH_2CH_3$) for Bidentate (bi, $n = 3$) and Monodentate (mono, $n = 4$) Coordination[a]

| | | $\Delta E_{carb}$ | | $\Delta E_{aqua}$ | |
|---|---|---|---|---|---|
| | R | GP | PCM | GP | PCM |
| bi | H | 1128 | 203 | 414 | 249 |
| | $CH_3$ | 1157 | 225 | 395 | 241 |
| | $CH_2CH_3$ | 1151 | 223 | 390 | 238 |
| mono | H | 975 | 130 | 527 | 302 |
| | $CH_3$ | 994 | 144 | 513 | 296 |
| | $CH_2CH_3$ | 990 | 143 | 509 | 296 |

[a] Results are given for systems in the gas phase (GP) and for the PCM solvation models, applying the GGA-BP exchange-correlation functional in a single-point fashion at the LDA-VWN optimized structures.

We calculated the U−C distances of monodentate ligands to be 0.63 Å longer than those for bidentate ligands; despite the deviations of absolute values, this trend is in good agreement with the experimental estimate of 0.6(1) Å for solvated complexes (Table 2). It is not easy to assess the calculated difference of the U−O$_c$ distances (0.17 Å longer for bidentate coordination) because experimental values are restricted to crystal data from which one estimates that difference at 0.1 Å (Table 2). In agreement with experiment, we calculated the bonds from U to the aqua ligands slightly shorter in the bidentate case. Our calculated results for the average value U−O$_{eq}$ are at variance with the experimental trend that this structural characteristic is ∼0.04 Å longer for bidentate coordination. Rather, one infers a slight shortening from the calculations, by 0.01 Å (Table 2). Note, however, that intervals of the experimental results for both coordination modes overlap (Table 2).

**Energetics.** Finally, we will consider energetic aspects of uranyl monocarboxylate species. We will compare bidentate (bi, with $n = 3$ aqua ligands) and monodentate complexes (mono, with $n = 4$ aqua ligands), preserving the equatorial coordination number of uranyl at five. In the following, we will use formal reactions to estimate the strength of metal−ligand bonds. We model long-range solvation effects via PCM and account explicitly for the aqua ligands of the uranyl moiety because they are moderately strongly bound, but we neglect weaker hydrogen bonds. In these models (see below), we forgo thermodynamic corrections to the energetics.

As a rough measure of metal−ligand bonding in uranyl monocarboxylate complexes, we calculated the ligand abstraction energies $\Delta E_{carb}$ and $\Delta E_{aqua}$ of the carboxylate ligand and the aqua ligands, respectively (Table 3)

$$[UO_2(OOCR)(H_2O)_n]^+ \rightarrow [UO_2(H_2O)_n]^{2+} + [RCOO]^- \quad (1)$$

$$[UO_2(OOCR)(H_2O)_n]^+ \rightarrow [UO_2(OOCR)]^+ + nH_2O \quad (2)$$

**Table 4.** Fragmentation Energies, $\Delta E_{frag}$ (eq 3), and Ligand Substitution Energies, $\Delta E_{sub}$ (eq 4) (in kJ mol$^{-1}$), of Complexes $[UO_2(OOCR)(H_2O)_n]^+$ (R = H, $CH_3$, $CH_2CH_3$) for Bidentate (bi, $n = 3$) and Monodentate (mono, $n = 4$) Coordination[a]

| | | $\Delta E_{frag}$ | | $\Delta E_{sub}$ | |
|---|---|---|---|---|---|
| | R | GP | PCM | GP | PCM |
| bi | H | 1940 | 595 | −835 | −75 |
| | $CH_3$ | 1970 | 617 | −864 | −97 |
| | $CH_2CH_3$ | 1964 | 615 | −858 | −95 |
| mono | H | 1970 | 602 | −865 | −82 |
| | $CH_3$ | 1989 | 616 | −883 | −96 |
| | $CH_2CH_3$ | 1985 | 615 | −879 | −95 |

[a] Results are given for calculations in the gas phase (GP) and with PCM solvation models, applying the GGA-BP exchange-correlation functional in single-point fashion at the LDA-VWN optimized structures.

For the gas phase (GP), as well as in solution (PCM), the carboxyl abstraction energies $\Delta E_{carb}$ confirm that formiate binds more weakly than the larger ligands (Table 3). This finding is related to the electron-donating character of alkyl substituents compared to the H in formiate and was also inferred from the structure data (see above). Carboxyl ligands are strongly bound in the gas phase, by about 1150 kJ mol$^{-1}$ for bidentate and 1000 kJ mol$^{-1}$ for monodentate coordination, because of the strong Coulomb attraction of the charged fragments. These differences are considerably reduced in aqueous solution. The abstraction energy of monodentate carboxylate is estimated at ~140 kJ mol$^{-1}$ and the bond is stronger for bidentate coordination, ~220 kJ mol$^{-1}$. Solvation effects also reduce the abstraction energy of the aqua ligands. One estimates the average binding energy per aqua ligand at 80 kJ mol$^{-1}$ for bidentate and at 75 kJ mol$^{-1}$ for monodentate carboxyl coordination. However, overall corresponding complexes of both coordination modes are expected to be comparable in energy because the energy gain of ~80 kJ mol$^{-1}$ in case of bidentate carboxylate coordination is essentially compensated by the loss of one aqua ligand (Table 3).

To further examine the stability of the complexes for different coordination modes, we determined the total energies, $\Delta E_{frag}$, of fragmentation of the solvated complexes into uranyl, carboxylate, and aqua ligands for R = H, $CH_3$, and $CH_2CH_3$ as reaction energies of the following transformation

$$[UO_2(OOCR)(H_2O)_n]^+ \rightarrow [UO_2]^{2+} + [RCOO]^- + nH_2O \quad (3)$$

Results from the gas phase and solvation calculations are summarized in Table 4. All complexes are stable with respect to fragmentation both in the gas phase and in aqueous solution. In the gas phase, because of the unfavorable charge separation, eq 3, fragmentation energies are very high: ~1960 kJ mol$^{-1}$ for bidentate complexes and ~1980 kJ mol$^{-1}$ for monodentate complexes. Again, the formiate complex is calculated to be slightly less stable than the complexes with larger carboxyl substituents. In solution (PCM treatment), the fragmentation energies drop to about one-third of these values: ~610 kJ mol$^{-1}$ for bi- and monodentate complexes. The rather weak preference of monodentate coordination vanishes if solvation is taken into account. The reduction of fragmentation energies can be rationalized by the large solvation energy of the small, charged uranyl moiety (−1245 kJ mol$^{-1}$) which stabilizes the fragmentation products. Solvation of the carboxylate ion (~ −270 kJ mol$^{-1}$) contributes to a smaller extent. The fragmentation energies of bi- and monodentate complexes in solution are essentially the same (Table 4). We thus conclude again that the binding energy of a bidentate carboxyl ligand is close to that of a monodentate carboxyl ligand and an additional aqua ligand, corroborating the preceding analysis based on ligand abstraction energies.

In addition, we examined the competition between the aqua und carboxylate ligands via the formal substitution of aqua ligands of the solvated uranyl ion $[UO_2(H_2O)_5]^{2+}$ by a carboxylate ligand

$$[UO_2(H_2O)_5]^{2+} + [RCOO]^- \rightarrow [UO_2(OOCR)(H_2O)_n]^+ + (5 - n)H_2O \quad (4)$$

The corresponding reaction energies, $E_{sub}$, are also listed in Table 4. For all complexes considered, formation of bi- and monodentate species by substituting aqua by carboxylate ligands is favored both in the gas phase and in solution, in agreement with the known complexing propensity of carboxylate ligands in aqueous solution.[1] In the gas phase, the substitution energies, $E_{sub}$, are much larger (by absolute value), ~ −845 kJ mol$^{-1}$ for bidentate complexes and ~ −875 kJ mol$^{-1}$ for monodentate complexes. Substitution is strongly exothermic because oppositely charged moieties are combined. In aqueous solution, the reactants are strongly stabilized, hence the reaction energies are significantly smaller (by absolute value), about −90 kJ mol$^{-1}$ for bi- and monodentate complexes. Again, the slight preference for monodentate coordination, calculated for the gas phase, vanishes in solution.

Note the rather similar substitution energies of the bi- and monodentate complexes (Table 4), despite the fact that an additional aqua ligand is released in the former case. Therefore, in aqueous solution, there is no clear energetic preference for any of the two coordination modes when solvation effects are accounted for. One expects a slight thermodynamic preference for bidentate coordination when zero-point energies and entropy effects are taken into account.

## Discussion

The discrepancies between calculated structures of uranyl monocarboxylate complexes and EXAFS data, as just described, are rather large and noteworthy if one recalls the overall good agreement of density functional results for uranyl complexes with experimental structure data,[24,34,53] including our benchmark system uranyl triacetate (see above). In the following discussion, we will summarize how our calculated results for uranyl monocarboxylates differ from experimental data for various uranyl carboxylates. We also will point out uncertainties which hamper a direct and more detailed comparison.

The main deviations from experimentally based information are related to the U$-$O$_c$ distances of mono- and bidentate coordination. These values are calculated too short by about 0.2 and 0.1 Å, respectively. Note, however, that the experimental value for the monodentate case refers to a crystalline system where uranyl is coordinated by more than one carboxylate ligand (Table 2). Moreover, separation of equatorial U$-$O distances into different shells is not easy by EXAFS spectroscopy if bond distances are very similar.[18] Calculated and experimentally derived U$-$C distances differ by up to 0.1 Å for either coordination mode; the calculations again yield shorter values. On the other hand, the U$=$O$_t$ uranyl bonds as well as the U$-$O$_w$ distances to the oxygen centers of aqua ligands agree well with experiment. Yet, the averaged value, U$-$O$_{eq}$, satisfactorily matches the experimental value only for monodentate complexes. For bidentate complexes, the calculations underestimate this quantity by $\sim$0.05 Å. This latter discrepancy is somewhat larger than typical experimental error bars. The more pronounced differences calculated for the uranyl$-$carboxylate distances, U$-$O$_c$ and U$-$C, are obviously outside experimental uncertainties.

The differences between experimental structures of mono- and bidentate complexes are qualitatively reproduced by the calculations, but the calculated change of U$-$O$_c$ is larger than in the experiment. In particular, the longer U$-$O$_{eq}$ distance suggested by experiment for bidentate coordination is not reproduced by the calculations.

A crucial approximation of our study is the use of models with $C_s$ symmetry constraints. To check the consequences, we examined the structures of uranyl monoacetate by reoptimization without symmetry constraints, confirming all resulting minima by a normal-mode analysis. For bidentate coordinated species, bond lengths relaxed less than 0.005 Å, hence changes were negligible. As expected, stronger effects were determined for monodentate coordination, but it is important to note that they did not reduce *pertinent* discrepancies with experiment. These structure changes are due to the rotation of the aqua ligand adjacent to the uncoordinated carboxylate oxygen (Figure 4b), resulting in a pseudobridging coordination with a hydrogen bond to this O atom. Concomitantly, the U$-$O$_c$ bond elongates by 0.09 Å and the U$-$C, as well as U$-$O$_w$, distances decrease by about 0.05 Å. Hence, the U$-$O$_c$ bonds of monodentate and bidentate complexes are now underestimated by the same amount, 0.1 Å (Table 2). Nevertheless, the average distance, U$-$O$_{eq}$, of the monodentate complex remains essentially unchanged at 2.36 Å, still in good agreement with the experimental value of 2.38(4) Å (Table 2) and the corresponding value of the bidentate complex (2.37 Å). Thus, the main discrepancies to the experiment for U$-$O$_c$ and U$-$O$_{eq}$ exist also for models without symmetry constraints.

The experimental situation is complicated by the fact that the number of carboxylate ligands and their coordination modes depend strongly on pH and the relative concentration with respect to uranyl. In addition, different uranyl carboxylate complexes can coexist.[14,18,39] While EXAFS spectroscopy provides an average over such ensembles, vibrational spectroscopy yields direct evidence.[19,39] A recent EXAFS study suggested that the prevailing coordination mode in a sample may change on the time scale of months,[18] on the basis of the observation of a slight increase of U$-$O$_{eq}$ and coordination number. Despite all these complications, rather small changes in geometric parameters and coordination number, as provided by fits of EXAFS data, are frequently attributed to changes of the predominant coordination mode and the number of carboxyl ligands.[14,18,20]

In agreement with experimental indications that the coordination mode apparently changes with slight modifications of the pH, concentration, ligand type etc.,[10,14,18] our calculated results suggest that mono- and bidentate coordination exhibit similar stability. However, calculated structure differences exceed the uncertainties of EXAFS determinations discussed above. These discrepancies can, at least partially, be attributed to the fact that in the experiment it is not easy to exclude the presence of complexes with more than a single carboxyl ligand. This is in accordance with the geometric differences calculated for mono- (coordination number 5) and triacetate (coordination number 6) complexes in solution. For instance, the calculated distances U$-$O$_c$ and U$-$O$_{eq}$ increase by more than 0.05 Å on going from uranyl mono- to triacetate (Tables 1 and 3). Thus, the longer U$-$O$_{eq}$ distance of bidentate triacetate complexes in solution found experimentally (0.06 Å relative to monodentate complexes) can be mainly attributed to an in increase of the coordination number from 5 to 6. Because EXAFS studies yield the coordination number $N_{eq}$ corresponding to U$-$O$_{eq}$ with an uncertainty of 15$-$25%,[10,14,18] such a change cannot be excluded. Also, the experiments may have been carried out for an ensemble of monodentate (or pseudobridging) and bidentate complexes.

The discussion so far did not furnish a coherent rationalization of calculated and experimental findings; therefore, we will now address further aspects of our models. Our computational models are based on pentagonal coordination of uranyl because it was found to be preferred in general in various experimental[35,58] and computational studies.[28,32] Our own computational work[34,38] as well as a recent review[63] confirmed this conclusion for uranyl complexes in aqueous solution of low pH. However, other structures of the first coordination shell (with 4 or 6 aqua ligands) have also been discussed.[10,35,58] Additional aqua ligands would increase the bonding competition at the uranium center, hence result in longer equatorial U$-$O bonds. In fact, we have calculated for $[UO_2(H_2O)_n]^{2+}$ in aqueous solution that the U$-$O$_w$ distance elongates from 2.31 to 2.36 and 2.41 Å, for $n = 4$, 5, and 6, respectively. Also uranyl carboxylate crystal structures demonstrate that U$-$O$_{eq}$ distances vary with coordination number. From the database assembled in ref 20, one derives average U$-$O$_{eq}$ values of 2.39 ± 0.04 and 2.48 ± 0.03 Å for coordination numbers 5 and 6, respectively. From EXAFS data on complexes in solution with coordination assigned according to reported coordination numbers as well as speciation,[10,14,15] one derives a smaller

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(63) Den Auwer, C.; Simoni, E.; Conradson, S.; Madic, C. *Eur. J. Inorg. Chem.* **2003**, *21*, 3843$-$3859.

difference, namely, 2.39 ± 0.03 Å for $N_{eq} = 5$ and 2.43 ± 0.03 Å for $N_{eq} = 6$. These latter values have to be taken with due caution because of the error bars of $N_{eq}$ (see above).

In contrast to the strong changes of $U-O_w$ for different coordination numbers, the calculated average values of $U-O_{eq}$ are very similar for monocarboxylates with mono- and bidentate coordination (Table 2). However, calculated U−C distances, which are also used to identify the coordination mode, are in qualitative agreement with the experimental values (Table 2). For coordination number 5, this indifference of $U-O_{eq}$ to the coordination mode of the carboxylate ligand can be rationalized by the concept of bonding competition between aqua and carboxyl ligands. The stronger $U-O_c$ bond of a monodentate carboxylate (144 kJ $mol^{-1}$, Table 3) compared to a bidentate complex (112 kJ $mol^{-1}$ per bond) results in weaker and concomitantly longer aqua ligand bonds. The average binding energy of aqua ligands was calculated at ∼74 kJ $mol^{-1}$ for monodentate carboxylate complexes, compared to ∼80 kJ $mol^{-1}$ for bidentate complexes (Table 3). Thus, the experimentally observed change of $U-O_{eq}$ on going from mono- to bidentate complexes is more likely to be the result of an accompanying alteration of the average coordination number than a rearrangement of the first coordination shell at a fixed coordination number.

Furthermore, one may consider improving the models by simulating hydrogen bonds between the negative oxygen centers of the carboxylate groups and water molecules of the second hydration shell. Such hydrogen bonds are expected to reduce the uranium−carboxylate interaction resulting in longer $U-O_c$ bonds. However, three further water molecules in our model of uranyl triacetate (see above) increased the $U-O_c$ distance by only 0.01 Å. For complexes in solutions of low pH, one may also consider protonation of a carboxylate group.

Uranyl is known to form various hydrolysis species, with increasing pH, which could exhibit significantly changed structure parameters.[64−66] The presence of carboxylate ions suppresses the formation of hydroxide complexes in solution; speciation calculations did not yield any evidence for larger amounts of these species together with carboxylates, at least at lower pH values and low temperatures.[18] On the other hand, also a small fraction of pure hydroxide complexes or mixed complexes with carboxylates could affect ensemble averages of structure parameters, if the geometric parameters of these alternative complexes would considerably deviate from those of pure carboxylate complexes.

All the arguments apply equally well to the more complicated case of a comparison with the EXAFS results of humic acids.[9,20,59,60] There, one has to take into account that complexing sites other than carboxyl groups may affect the EXAFS spectra. Most probable candidates would be sites offering chelate-type complexation. Thus, the straightforward interpretation of those EXAFS results as indication for monodentate complexation of uranyl by humic acids, on the basis of a comparison with small carboxylic acids, needs further discussion.

To clarify open questions raised above, further experimental efforts to discriminate different equatorial U−O contacts are desirable, although this is known to be a difficult task.[18] Also, it will be helpful to extend computational modeling beyond the symmetric structures treated in the present work and, in addition, to account for the effects of the hydrogen-bonded network of further solvation shells. Such work is in progress in our group.

## Conclusions

We started our density functional modeling of uranyl monocarboxylate complexes with uranium triacetate $[UO_2(OOCCH_3)_3]^-$ to establish the accuracy of calculated structures. For this benchmark system, we were able to reproduce experimental data very well; pertinent bond distances deviated less than 0.03 Å. This agreement improved (deviations less than 0.02 Å) when three additional water molecules of the second hydration shell were included in the model to account for hydrogen bonding to the carboxylate groups.

The main goal of the present investigation was to construct models of uranyl monocarboxylate complexes. For this purpose, we first compared bi- and monodentate structures, suitably complemented with aqua ligands to achieve pentagonal coordination in the equatorial plane of the uranyl moiety. As in previous studies,[34,38,62] solvation effects due to explicitly coordinated aqua ligands turned out to be strong, whereas solvation modeling via a polarizable continuum model (PCM) yielded only smaller corrections. Comparing calculated and EXAFS-derived distances, as well as calculated and measured uranyl stretching frequencies, we found that our models seem to overestimate the carboxylate bonding to the uranyl moiety (i.e., the U−O bonds to the carboxylate groups were calculated too short by at least 0.1 Å). Geometric parameters such as the uranyl bonds $U{=}O_t$, the bond distances from uranyl to the aqua ligands, and the average $U-O_{eq}$ distance of monodentate carboxylate complexes, as well as other qualitative differences between the coordination modes, agree with experiment.

Our calculations did not provide a clear energetic preference among bi- and monodentate uranyl monocarboxylate complexes in aqueous solution. The sum of the ligand-binding energies is very similar for both types of coordination. U−O bonds to carboxylates were calculated stronger (100−140 kJ $mol^{-1}$) than bonds to aqua ligands (75−85 kJ $mol^{-1}$). Bond competition between these two types of ligands resulted in average $U-O_{eq}$ values that, at fixed coordination *number*, are almost independent of the coordination *mode*.

From our discussion of various sources for the discrepancies between EXAFS results and our calculated structures, we conclude that straightforward interpretations of spectra of complexes in solution by reference to structures from crystals seems to be questionable in the case of carboxylates. Pertinent uncertainties are the number and type of species

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present in solution at the same time and the geometric details of their coordination. On the basis of evidence from our calculations on uranyl triacetate and monocarboxylates, as well as the solvated uranyl ion, we suggest that variations of average U−O$_{eq}$ distances derived in EXAFS investigations are more probably caused by changes of the coordination number than by frequently invoked variations of the coordination geometry. This holds independent of the results for U−C which more clearly indicate the coordination mode.

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