

## DFT Studies of Uranyl Acetate, Carbonate, and Malonate, Complexes in Solution

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The aim of this work is to demonstrate that theoretical chemistry can be used as a complementary tool in determining geometric parameters of a number of uranyl complexes in solution, which are not observable by experimental methods. In addition, we propose plausible structures with partial geometric data from experimental results. A gradient corrected DFT methodology with relativistic effects is used employing a COSMO solvation model. The theoretical calculations show good agreement with experimental X-ray and EXAFS data for the triacetato–dioxo–uranium(VI) and tricarbonato–dioxo–uranium(VI) complexes and are used to assign possible geometries for dicalcium–tricarbonato–dioxo–uranium(VI) and malonato–dioxo–uranium(VI) complexes. The results of this exercise indicate that carbonate bonding in these complexes is mainly bidentate and that hydroxo bridging plays a critical role in the stabilization of the polynuclear uranyl complexes.

## 1. Introduction

Uranium fluxes in aqueous systems are mainly controlled by the redox state of the system and by the presence of oxygen containing ligands. Uranium(VI) is more soluble and therefore more mobile than uranium(IV), and the uranyl cation is a hard ion with a tendency to build strong complexes with oxygen containing ligands such as carbonate, phosphate, and low molecular weight organic ligands such as acetate and malonate.

There is a wealth of data concerning the thermodynamics of uranium and the main stoichiometries that conform uranium speciation in natural water systems.<sup>1–3</sup> This has been the result of a large effort in developing and applying solution chemical and spectroscopic methods. In the last years, there

has been a substantial development in the use of sensitive spectroscopic techniques to gain structural information regarding the main aqueous species. In this context, extended X-ray absorption fine structure (EXAFS) techniques have been successfully used to ascertain the composition and structure of some uranyl complexes.<sup>3–5</sup>

Theoretical chemistry techniques can be used to complement the determined stoichiometric and structural data in order to distinguish among plausible structures and to support the information obtained by spectroscopic means, notably by EXAFS spectroscopy.<sup>6–9</sup> Although actinides present a

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(1) Clark, D. L.; Hobart, D. E.; Neu, M. P. *Chem. Rev.* **1995**, *95*, 25.

(2) 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.

(3) Nitsche, H.; Silva, R. J.; Brendler, V.; Geipel, G.; Reich, T.; Teterin, Y. A.; Thieme, M.; Baraniak, L.; Bernhard, G. Actinide Speciation in High Ionic Strength Media. *Experimental and modeling approaches to predict actinide speciation and migration in the subsurface*; Reed, D. T., Clark, S. B., Rao, L., Eds.; Kluwer Academic/Plenum Publishers: New York, 1999.

(4) Reich, T.; Denecke, M. A.; Pompe, S.; Bubner, M.; Heise, K.; Schmidt, M.; Brendler, V.; Baraniak, L.; Nitsche, H.; Allen, P. G.; Bucher, J. J.; Edelstein, N. M.; Shuh, D. K. *Synchrotron Radiation Techniques in Industrial, Chemical and Materials Science*; D'Amico, K., Ed.; Plenum: New York, 1996.

(5) Bernhard, G.; Geipel, G.; Reich, T.; Brendler, V.; Amayri, S.; Nitsche, H. *Radiochim. Acta* **2001**, *89*, 511.

(6) Randall, S. R.; Sherman, D. M.; Ragnarsdottir, K. V.; Collins, C. R. *Geochim. Cosmochim. Acta* **1999**, *63*, 2971.

(7) Ladeira, A. C. Q.; Ciminelli, V. S. T.; Duarte, H. A.; Alves, M. C. M.; Ramos, A. Y. *Geochim. Cosmochim. Acta* **2000**, *65*, 1211.

challenge to theoretical chemistry due to the large relativistic effects and the role of the 5f orbitals in the molecular bonding, there are several examples in the literature dealing with successful applications of DFT and other ab initio calculations for the uranyl ion and its complexes.<sup>9–35</sup>

The objective of this work is to demonstrate the validity of the theoretical DFT approach in order to complement and validate structural and solution chemical data. In addition, we will discuss the most probable structures that conform the proposed stoichiometries from solution chemical and spectroscopic data. The work is performed in a two-step approach: First, triacetato–dioxo–uranium(VI)  $[\text{UO}_2(\text{CH}_3\text{COO})_3]^-$  and tricarbonato–dioxo–uranium(VI)  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  complexes are studied to test the validity of the theoretical methodology on relatively simple cases where there is enough experimental information to calibrate the computational results. Second, we propose plausible structures for calcium uranyl carbonate and uranyl malonate complexes in solution based on a combination of DFT calculations and the available EXAFS experimental data. Uranium(VI) acetate and malonate complexes are relevant in understanding the mobility of uranium in surface environments. They also have been chosen as a chemical model for the polyfunctional humic acid complexation. Humic acids,

as well as low molecular weight organic molecules, like acetate and malonate, are present in soils, waters, and sediments and are important ligands for the migration/retardation of uranium and other metal ions in natural systems.<sup>36,37</sup>

## 2. Computational Details

All the calculations were carried out by using the Amsterdam Density Functional Program (ADF 2002), developed by Baerends et al.<sup>38,39</sup> The numerical integration scheme used in the calculations was developed by te Velde et al.<sup>40,41</sup> and the geometry optimization algorithms were implemented by Versluis and Ziegler.<sup>42</sup> Functionals used were VWN<sup>43</sup> together with the Perdew–Wang 1991 exchange–correlation correction, PW91xc.<sup>44</sup> A gradient corrected methodology has been chosen due to the inaccuracy of the local density approach (LDA) for some metal-containing systems.<sup>45</sup> All the complexes have been fully optimized without any geometrical or symmetrical constrain.

Two basis sets (named basis set I and II) have been used and compared. Basis set I consists of a triple- $\zeta$  with double polarization for all. Basis set II is a triple- $\zeta$  with polarization for uranium and a double- $\zeta$  with polarization basis set for the rest of the atoms. The frozen core approximation is used in both basis set: 1s–5d electrons for U and 1s electrons for the rest of heavy atoms. First-order ZORA<sup>46–48</sup> scalar relativistic corrections were added for all systems as they should be included for the f-block atoms.<sup>49</sup>

The solvent effects were included by means of the COSMO model<sup>50–52</sup> as implemented in ADF.<sup>53</sup> The solvent accessible surface (SAS) of the solvent cavity was determined using the GEPOL93 algorithm.<sup>54</sup> A value of 78.4 was used for the dielectric constant of water.

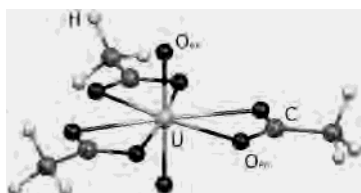
## 3. Results and Discussion

### 3.1. Complex 1. Triacetato–Dioxo–Uranium(VI), $[\text{UO}_2(\text{CH}_3\text{COO})_3]^-$ .

This complex was selected to calibrate the DFT calculations based on the already existing comprehensive experimental X-ray<sup>55,56</sup> and EXAFS<sup>3</sup> data. The spectroscopic data indicated that the oxygen atoms of the

- (8) Morris, L.; Williams, D. E.; Kaltsoyannis, N.; Tocher, D. A. *Phys. Chem. Chem. Phys.* **2001**, *3*, 132.
- (9) Pykkö, P.; Li, J.; Runeberg, N. *J. Phys. Chem.* **1994**, *98*, 4809.
- (10) Craw, J. S.; Vincent, M. A.; Hillier, I. H.; Wallwork, A. L. *J. Phys. Chem. A* **1995**, *99*, 10181.
- (11) Craw, J. S.; Vincent, M. A.; Hillier, I. H.; Wallwork, A. L. *J. Phys. Chem. A* **1998**, *102*, 3773.
- (12) Schreckenbach, G.; Hay, P. J.; Martin, R. L. *Inorg. Chem.* **1998**, *37*, 4442.
- (13) Schreckenbach, G.; Hay, P. J.; Martin, R. L. *J. Comput. Chem.* **1999**, *20*, 70.
- (14) Ismail, N.; Heully, J.-L.; Saue, T.; Daudey, J.-P.; Marsden, C. J. *Chem. Phys. Lett.* **1999**, *300*, 296.
- (15) Vallet, V.; Schimmelpfennig, B.; Maron, L.; Teichteil, C.; Leininger, T.; Gropen, O.; Grenthe, I.; Wahlgren, U. *Chem. Phys.* **1999**, *244*, 185.
- (16) Tsushima, S.; Suzuki, A. *THEOCHEM* **1999**, *487*, 33.
- (17) Spencer, S.; Gagliardi, L.; Handy, N. C.; Ioannou, A. G.; Skylaris, C.-K.; Willetts, A.; Simper, A. M. *J. Phys. Chem. A* **1999**, *103*, 1831.
- (18) Hay, P. J.; Martin, R. L.; Schreckenbach, G. *J. Phys. Chem. A* **2000**, *104*, 6259.
- (19) Tsushima, S.; Suzuki, A. *THEOCHEM* **2000**, *529*, 21.
- (20) Hemmingsen, L.; Amara, P.; Ansoborlo, E.; Field, M. J. *J. Phys. Chem. A* **2000**, *104*, 4095.
- (21) Tsushima, S.; Yang, T.; Suzuki, A. *Chem. Phys. Lett.* **2001**, *334*, 365.
- (22) Tsushima, S.; Reich, T. *Chem. Phys. Lett.* **2001**, *347*, 127.
- (23) Gagliardi, L.; Grenthe, I.; Roos, B. O. *Inorg. Chem.* **2001**, *40*, 2976.
- (24) Vallet, V.; Wahlgren, U.; Schimmelpfennig, B.; Moll, H.; Szabo, Z.; Grenthe, I. *Inorg. Chem.* **2001**, *40*, 3516.
- (25) Semon, L.; Boehme, C.; Billard, I.; Hennig, C.; Lutzenkirchen, K.; Reich, T.; Rossberg, A.; Rossini, I.; Wipff, G. *ChemPhysChem* **2001**, *2*, 591.
- (26) Vallet, V.; Wahlgren, U.; Schimmelpfennig, B.; Szabo, Z.; Grenthe, I. *J. Am. Chem. Soc.* **2001**, *123*, 11999.
- (27) De Jong, W. A.; Harrison, R. J.; Nichols, J. A.; Dixon, D. A. *Theor. Chem. Acc.* **2001**, *107*, 22.
- (28) Tsushima, S.; Uchida, Y.; Reich, T. *Chem. Phys. Lett.* **2002**, *357*, 73.
- (29) Majumdar, D.; Balasubramanian, K.; Nitsche, H. *Chem. Phys. Lett.* **2002**, *361*, 143.
- (30) Vallet, V.; Wahlgren, U.; Szabó, Z.; Grenthe, I. *Inorg. Chem.* **2002**, *41*, 5126.
- (31) Oda, Y.; Aoshima, A. *J. Nucl. Sci. Technol.* **2002**, *39*, 647.
- (32) Schreckenbach, G. *Inorg. Chem.* **2002**, *41*, 6560.
- (33) Kaltsoyanis, N. *Inorg. Chem.* **2000**, *39*, 6009.
- (34) Vallet, V.; Moll, H.; Wahlgren, U.; Szabó, Z.; Grenthe, I. *Inorg. Chem.* **2003**, *42*, 1982.
- (35) Coupez, B.; Wipff, G. *Inorg. Chem.* **2003**, *42*, 3693

- (36) Choppin, G. R.; Allard, B. Complexes of actinides with naturally occurring organic compounds. *Handbook of the physics and chemistry of the actinides*; Freeman, A. J., Keller, C., Eds.; Elsevier Science Publisher: Amsterdam, 1985.
- (37) Choppin, G. R. *Radiochim. Acta* **1988**, *44/45*, 23.
- (38) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.
- (39) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1988**, *99*, 391.
- (40) te Velde, G.; Baerends, E. J. *J. Comput. Chem.* **1992**, *99*, 84.
- (41) Boerrigter, P. M.; te Velde, G.; Baerends, E. J. *Int. J. Quantum Chem.* **1988**, *33*, 87.
- (42) Versluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322.
- (43) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
- (44) Perdew, J. P.; Wang, Y. *Phys. Rev. B.* **1992**, *45*, 13244.
- (45) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.
- (46) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597.
- (47) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1994**, *101*, 9783.
- (48) van Lenthe, E.; Ehlers, A. E.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943.
- (49) Pykkö, P. *Chem. Rev.* **1988**, *88*, 563.
- (50) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans.* **1993**, *2*, 799.
- (51) Klamt, A. *J. Phys. Chem.* **1995**, *99*, 2224.
- (52) Klamt, A.; Jones, V. *J. Chem. Phys.* **1996**, *105*, 9972.
- (53) Pye, C. C.; Ziegler, T. *Theor. Chem. Acc.* **1999**, *101*, 396.
- (54) Pascual-Ahuir, J. L.; Silla, E.; Tuñon, I. *J. Comput. Chem.* **1994**, *15*, 1127.



**Figure 1.** Complex 1, triacetate-dioxo-uranium(VI),  $[\text{UO}_2(\text{CH}_3\text{COO})_3]^-$ .

**Table 1.** Relevant Distances (Å) of Complex 1

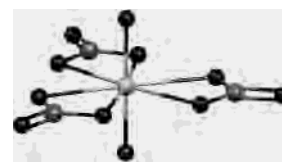
	$R_{\text{U}-\text{O}_{\text{eq}}}$	$R_{\text{U}-\text{O}_{\text{ax}}}$	$R_{\text{U}-\text{C}}$
X-ray <sup>56</sup>	2.48	1.76	4.34
EXAFS <sup>3</sup>	2.44	1.78	4.34
solvent, basis I	2.50	1.81	4.38
solvent, basis II	2.50	1.81	4.38
gas-phase, basis II	2.51	1.81	4.38

uranyl group are in axial position while the three acetate ligands coordinate the uranium in the equatorial plane. Carboxyl groups are bonded in a bidentate fashion with 1:3 stoichiometry. Figure 1 shows the optimized geometry for this complex, and Table 1 reports the experimentally obtained parameters together with the result of the present theoretical calculations. The results from X-ray and EXAFS determinations are quite similar, indicating that complex 1 has the same geometry in the solid-state and in aqueous solution.

The EXAFS results show that the uranium atom is surrounded by 2 axial oxygen atoms at 1.78 Å and 6 equatorial oxygen atoms at a medium value of 2.44 Å. Normally, light elements such as C and O are not detected by EXAFS at distances longer than 3 Å. However, in this case, the EXAFS results clearly indicated the existence of 3 equatorial carbon atoms at 4.34 Å, detected due to their linear U–C–C arrangement.

The calculations performed in aqueous medium and in the gas-phase gave the same results for complex 1. The calculated distances, although slightly longer than the observed ones, are in agreement with the experimental data. Moreover, the smaller basis set II yields quite a similar geometry than the high level basis set I. We also attempted to optimize complex 1 with the acetate groups bound in a monodentate fashion. This structure resulted in being 36 kcal·mol<sup>-1</sup> less stable than the one assuming bidentate coordination, and the calculated distances did not match the experimentally determined ones. This is a confirmation that the theoretical calculations are sensitive enough to reproduce the observed geometries and discriminate between the various structural arrangements.

**3.2. Complex 2. Tricarbonato-Dioxo-Uranium(VI),  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ .** The stoichiometry and structure of complex 2 has been largely investigated as it constitutes one of the predominant uranyl species in aquatic systems. EXAFS studies in aqueous solution<sup>5</sup> show that the three carbonate groups are bound in a bidentate mode, to the uranyl ion in the equatorial plane in a geometry similar to that of complex 1, previously described. They also show the same coordina-



**Figure 2.** Complex 2, tricarbonato-dioxo-uranium(VI),  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ .

**Table 2.** Relevant Distances (Å) of Complex 2

	$R_{\text{U}-\text{O}_{\text{eq}}}$	$R_{\text{U}-\text{O}_{\text{ax}}}$	$R_{\text{U}-\text{O}_{\text{dist}}}$	$R_{\text{U}-\text{C}}$
solvent MBPT2 <sup>23</sup>	2.41	1.88	4.11	2.84
EXAFS <sup>5</sup>	2.44	1.80	4.20	2.89
solvent, basis I	2.48	1.86	4.21	2.93
solvent, basis II	2.46	1.85	4.16	2.90
gas-phase, basis II	2.56	1.85	4.29	3.01

tion number and quite similar distances for U–O<sub>ax</sub> and U–O<sub>eq</sub>. This arrangement is also observed in X-ray studies of  $\text{UO}_2(\text{CO}_3)_3$ <sup>57–59</sup> and the bis(dicarbonato-peroxo-uranyl) complex.<sup>60</sup> Figure 2 shows the optimized structure of the uranyl carbonate complex. The experimental observations together with our DFT calculations are summarized in Table 2.

Gas-phase calculations failed to reproduce the observed distances beyond the experimental error. However, the calculated geometry in aqueous solution is in agreement with the results from the EXAFS measurements and is very similar to the previously reported high level ab initio MBPT2 calculations.<sup>23</sup>

As in the previous case, the triacetate-dioxo-uranium(VI) complex, both basis sets I and II, gave similar results for the calculations of complex 2 including solvent effects. The larger difference in the calculated distances was 0.05 Å in the U–O<sub>dist</sub> bond.

**3.3. Complexes 3–6. Dicalcium-Tricarbonato-Dioxo-Uranium(VI),  $[\text{Ca}_2\text{UO}_2(\text{CO}_3)_3]^{10-}$ .** This species has been recently reported to be predominant in the U(VI) speciation in uranium mine effluents in moderate alkaline environments.<sup>61</sup> The stoichiometric and structural characterization of this complex has been performed by using an array of spectroscopic techniques including, time-resolved laser-induced fluorescence spectroscopy (TRLFS), laser-induced photoacoustic spectroscopy (LIPAS), and EXAFS studies.<sup>5</sup> The EXAFS studies of calcium uranyl carbonate in solution indicate that this complex has approximately the same structural arrangement as the uranyl carbonate complex (complex 2). In addition, a new U–Ca interaction is observed at 3.94 Å with a coordination number of 2. This would indicate a similar structural geometry as that of the mineral phase liebigite,  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}$ , where the calcium atoms are located in the equatorial plane between the carbonate groups.

The addition of two calcium atoms to the uranyl carbonate coordination sphere increases the number of possible con-

(57) Coda, A.; Della Giusta, A.; Tazzoli, V. *Acta Crystallogr.* **1981**, B37, 1496.

(58) Mereiter, K. *Acta Crystallogr.* **1986**, C42, 1682.

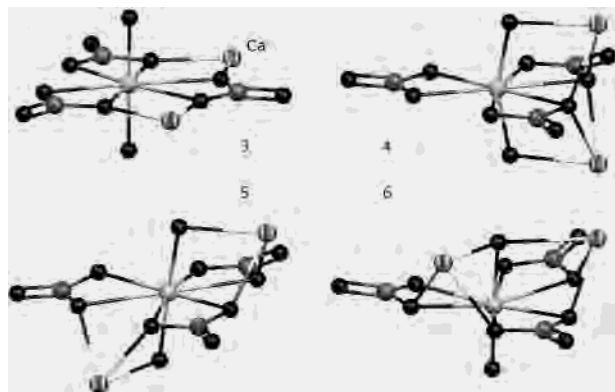
(59) Effenberger, H.; Mereiter, K. *Acta Crystallogr.* **1988**, C44, 1172.

(60) Mikhailov, Yu. N.; Lobanova, G. M.; Shchelokov, R. N. *Zh. Neorg. Khim.* **1981**, 26, 718.

(61) Bernhard, G.; Geipel, G.; Bendler, V.; Nitsche, H. *Radiochim. Acta* **1996**, 74, 87.

(55) Templeton, D. H.; Zalkin, A.; Ruben, H.; Templeton, L. K. *Acta Crystallogr.* **1985**, C41, 1439.

(56) Navaza, A.; Charpin, P.; Vigner, D.; Heger, G. *Acta Crystallogr.* **1991**, C47, 1842.



**Figure 3.** Dicalcium-tricarbonato-dioxo-uranium(VI),  $[\text{Ca}_2\text{UO}_2(\text{CO}_3)_3]^0$ , conformers, complexes 3–6.

**Table 3.** Distances (Å) of Complexes 3–6

	$R_{\text{U}-\text{O}_{\text{eq}}}$	$R_{\text{U}-\text{O}_{\text{ax}}}$	$R_{\text{U}-\text{O}_{\text{dist}}}$	$R_{\text{U}-\text{C}}$	$R_{\text{U}-\text{Ca}}$	$E_{\text{rel}}$ (kcal mol <sup>-1</sup> )
EXAFS <sup>5</sup>	2.44	1.81	4.22	2.90	3.94	
Gas-Phase, Basis II						
3	2.53	1.81	4.27	3.05	3.68	+22.8
4	2.52	1.95	4.23	3.02	3.31	+2.54
5	2.45	1.90	4.14	2.94	3.19	0.0
6						
Solvent, Basis II						
3	2.46	1.83	4.19	2.94	3.86	0.0
4	2.43	1.88	4.14	2.90	3.48	+13.4
5	2.43	1.87	4.14	2.91	3.34	+6.0
6	2.45	1.86	4.17	2.93	3.38	+8.1
Solvent, Basis I						
3	2.46	1.83	4.20	2.94	3.86	0.0
4	2.43	1.86	4.15	2.90	3.46	+12.7
5	2.43	1.86	4.14	2.91	3.35	+6.3
6	2.45	1.86	4.16	2.94	3.38	+9.0

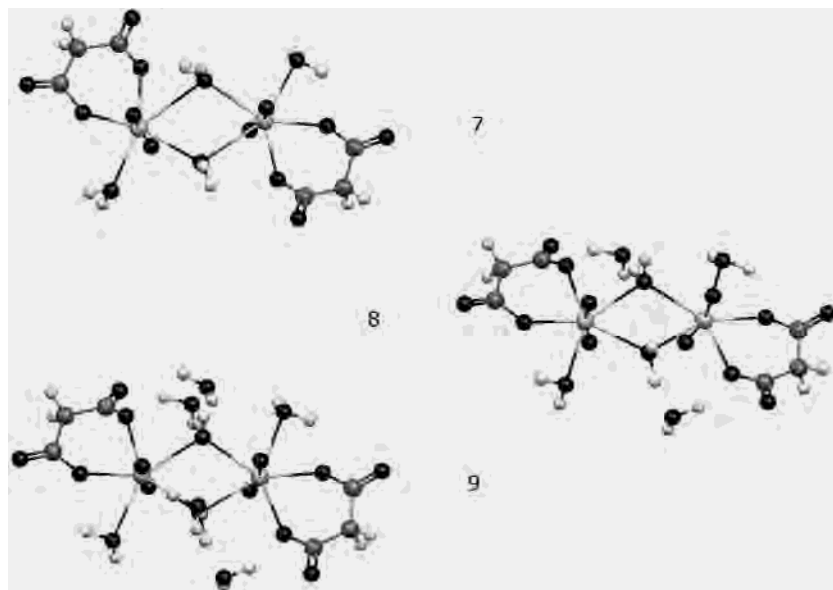
formers. The new calcium atoms can be either inside or outside the equatorial plane defined by the carbonate groups. In order to study this behavior, we have performed a complete conformational study, and we have found four different geometries that are consistent with the existence of three equatorial carbonate groups. These structures are

depicted as complexes 3–6 in Figure 3. In Table 3, we report their relative energy and the relevant distances in the gas-phase and in aqueous solution.

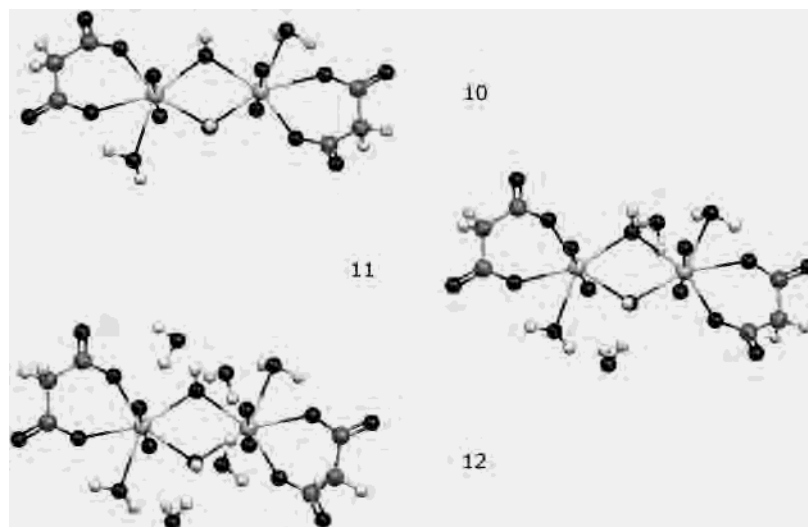
The most stable of the four complexes in aqueous solution is depicted as complex 3. This is ca. 6 kcal·mol<sup>-1</sup> more stable than complex 5, which is the second most stable. The calculated bond distances of complex 3 in aqueous solution are in agreement with the reported EXAFS data and are similar to a recent publication by Tsushima et al.<sup>28</sup> It has the typical  $\text{UO}_2^{2+}$  axial geometry and an equatorial plane containing the three carbonate ligands and the two calcium atoms. The calculated U–Ca distance is 3.86 Å (0.08 Å shorter than the experimental value). None of the other three possible complexes are able to reproduce the observed U–Ca distance. For the gas-phase calculations, the structure depicted as complex 6 is not observed, and complex 5 turns out to be the most stable: 2.5 kcal·mol<sup>-1</sup> more than complex 4, and ca. 23 kcal·mol<sup>-1</sup> more than complex 3. None of the calculated gas-phase geometries is in agreement with the experimental EXAFS data, as indicated by the U–Ca distances.

The inverted energy order obtained when including solvent effects in the calculations can be explained as follows. In the absence of water, the energy gained by the electrostatic interaction of the  $\text{Ca}^{2+}$  ion and the negative charged oxygen atoms is larger than the energy needed to distort the  $\text{UO}_2^{2+}$  cation (note the great U–O<sub>ax</sub> elongation for complexes 4 and 5 in the gas-phase in Table 3 and the distortion of the O<sub>ax</sub>–U–O<sub>ax</sub> angle in Figure 3). In aqueous solution, the  $\text{Ca}^{2+}$ –oxygen electrostatic interactions are not so intense due to the polarizing effect of the water molecules. Consequently, the energy needed to distort the  $\text{UO}_2^{2+}$  cation is larger than the electrostatic compensation.

As in the case of complexes 1 and 2, both basis sets give similar results for the calculated geometries in aqueous solution. These are also in agreement with the experimental data. On the contrary, the calculated gas-phase geometries



**Figure 4.** Complexes 7–9, malonato-dioxo-uranium(VI) complexes with water bridge ligands:  $[(\text{UO}_2)_2(\text{C}_3\text{H}_2\text{O}_4)_2(\text{H}_2\text{O})_{4+n}]^0$  where  $n = 0, 2, \text{ or } 4$ .



**Figure 5.** Complexes 10–12, malonato–dioxo–uranium(VI) complexes with hydroxo bridge ligands:  $[(\text{UO}_2)_2(\text{C}_3\text{H}_2\text{O}_4)_2(\text{OH})_2(\text{H}_2\text{O})_{2+n}]^{2-}$  where  $n = 0, 2, \text{ or } 4$ .

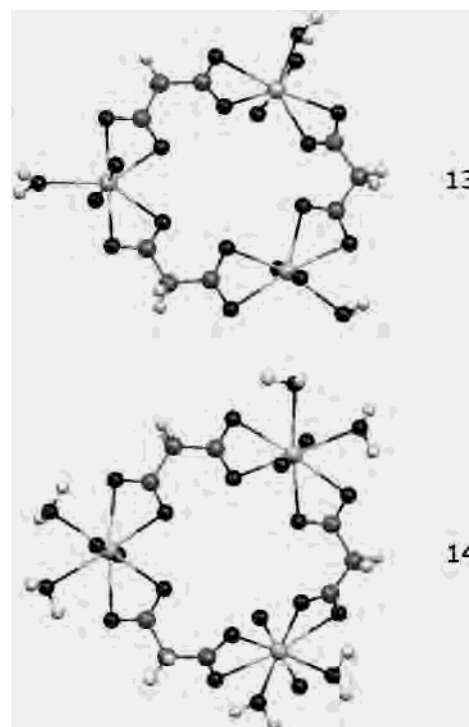
fail to reproduce the EXAFS distances (with errors that are much larger than  $0.1 \text{ \AA}$  for the U–Ca distance). As we have already indicated, the gas-phase calculations give an energetic ordering different from the one from aqueous solvent calculations. According to our DFT calculations, the predicted geometry for the most stable  $[\text{Ca}_2\text{UO}_2(\text{CO}_3)_3]^0$  conformer, depicted as complex 3, in aqueous solution agrees well with the experimental EXAFS values. The calculated structure would suggest that the two calcium atoms are in the equatorial plane between two carbonate ligands, similarly to the structural arrangement of liebigite.

### 3.4. Complexes 7–14. Malonato–Dioxo–Uranium(VI).

As we have discussed in the uranyl complexes previously studied, the performance of the large basis set I is quite similar to that of the smaller basis set II. In addition, solvent calculations reproduced the experimentally determined geometries much better. Therefore, we decided to study the malonato–dioxo–uranium(VI) complex using basis set II only and including solvent effects.

The EXAFS spectra<sup>3</sup> of the malonato–dioxo–uranium(VI) complex show a U–U distance at  $3.96 \text{ \AA}$ . This would indicate that this complex in solution is polynuclear with, at least, two close uranyl groups. Two main features can be observed, the typical U–O<sub>ax</sub> distance at  $1.81 \text{ \AA}$  and a slight decrease in the U–O<sub>eq</sub> distance from  $2.44 \text{ \AA}$  in complex 1 to  $2.37 \text{ \AA}$  in the actual complex. The coordination number of equatorial oxygen atoms decreases from 6 to 5. In this case, the acid groups can chelate the uranium either as bidentate carboxyl ligands, as in the previous cases, or as monodentate carboxyl groups.

We optimized three different “families” of these complexes: two uranyl–malonate moieties bonded by two bridge ligands, either water (Figure 4) or hydroxo (Figure 5) where the malonate ligands act as monodentate ones, bonded to the uranium atom by the two carboxyl groups and a cyclic structure containing three uranyl groups bonded by three bidentate malonate ligands (Figure 6). In principle, hydroxo and oxo bridging are the preferred options for the condensa-



**Figure 6.** Complexes 13 and 14, malonato–dioxo–uranium(VI) cyclic complexes.

tion of metallic cations in aqueous media<sup>62–64</sup> while water rarely constitutes a bridging ligand in aqueous complexes, although there are some exceptions.<sup>65</sup> We tested, however, the hypothesis of  $\text{H}_2\text{O}$  bridging for the sake of completeness.

We also attempted to optimize a binuclear complex where each uranyl cation is bound to two malonate ligands. According to our calculations, the structure is unstable, and

(62) Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley-Interscience: New York, 1976.

(63) Bruno, J. J. *Chem. Soc., Dalton Trans.* **1987**, 2431.

(64) Bruno, J.; Grenthe, I.; Sandström, M.; Ferri, D. J. *Chem. Soc., Dalton Trans.* **1987**, 2440.

(65) Perry, D. L.; Ruben, H.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1980**, *19*, 1067.

**Table 4.** Distances (Å) of Uranyl Malonate Complexes

	$R_{U-O_{sq}}$	$R_{U-O_{ax}}$	$R_{U-U}$
EXAFS <sup>3</sup>	2.37	1.78	3.96
	H <sub>2</sub> O Bridge		
<b>7</b>	2.51	1.80	4.52
<b>8</b>	2.47	1.80	4.34
<b>9</b>	2.46	1.80	4.24
	OH <sup>-</sup> Bridge		
<b>10</b>	2.43	1.81	3.82
<b>11</b>	2.42	1.81	3.92
<b>12</b>	2.41	1.82	3.87
	Cyclic		
<b>13</b>	2.45	1.80	6.86
<b>14</b>	2.52	1.79	7.22

it dissociates in two mononuclear dimalonato-aquo-dioxo-uranium(VI) complexes. Hence, the results of the structural optimization are not reported.

It is interesting to notice that for the structures of the complexes depicted as **7** and **10** in Figures 4 and 5, respectively, the addition of another water ligand to each uranyl coordination sphere results in the motion of the new water molecule from the equatorial positions to form two hydrogen bonds with the bridge ligands. This results in the structures indicated as complexes **8** and **11**, respectively, and has important consequences in the calculated U–U distances as reported in Table 4. This would indicate that the hydrogen bonds and their effect on the overall geometry cannot be properly reproduced by the COSMO continuous solvent model. To further improve these results, we have added two water molecules more to the bridge ligands, obtaining complexes **9** and **12**, to generate four hydrogen bonds. As expected, the addition of this new water ligand affects the geometry of the complexes, but to a lesser extent than the changes from structures: **7** to **8** or **10** to **11**, see Table 4 and Figures 4 and 5. In the case of  $[(UO_2)_2(C_3H_2O_4)_2(H_2O)_{4+n}]^0$ , complexes **7–9** (Figure 4), the U–U distance decreased from 4.52 to 4.34 and 4.24 Å respectively; these values are far from the experimental distance, 3.96 Å. For  $[(UO_2)_2(C_3H_2O_4)_2(OH)_2(H_2O)_{2+n}]^0$ , complexes **10–12** (Figure 5), the U–U distance changes from 3.82 to 3.92 and 3.86 Å, respectively. The last two values of the U–U distance are in good agreement with EXAFS results.

For complexes **13** and **14** (Figure 6), the resulting structures are similar; the only difference resides in the number of equatorial water ligands. In both complexes, the malonate ligand is bonded in a bidentate mode, and they do not lie in the same plane, although the uranyl cation is almost planar. A comparison of the structural information indicates that the calculated U–U distances are too long compared with the experimental value, approximately 7 Å. Hence, we discarded these geometries as not being compatible with the experimental information.

On the other hand, the optimized structures **11** and **12**, containing two hydroxo bridging ligands, reproduce quite accurately the EXAFS data with an acceptable error threshold on all the distances below 0.1 Å. The explicit introduction

of two and four water molecules forming hydrogen bonds with the hydroxo bridges improves the reproducibility of the experimental distances by the theoretical results. This would indicate that polar water molecules have a key role in stabilizing malonato-dioxo-uranium (VI) binuclear complexes in aqueous solution.

#### 4. Conclusions

The performed calculations in this work are in good agreement with experimental EXAFS data for a series of uranyl carboxylate and carbonate complexes. Both the larger basis set I and the smaller basis set II give quite similar results. Gas-phase calculations fail to reproduce in most cases the observed EXAFS distances and coordination numbers. This is the case for the tricarbonato-dioxo-uranium(VI), complex **2**, and the dicalcium-tricarbonato-dioxo-uranium(VI), complexes **3–6**, where the predicted geometry is in disagreement with the experimental observations. These results would indicate that the polarizing effects of the aqueous medium are quite strong for the uranyl carbonate complexes.

In the case of the mononuclear uranyl complexes, solvent calculations give satisfactory results. However, for the dimeric malonato-dioxo-uranium(VI) complex, the explicit addition of water molecules in the calculations largely improves the results due to the formation of hydrogen bonds with the bridging hydroxo ligands. These cannot be correctly reproduced by the solvent continuous models.

The results of this study corroborate the fact that carbonate and carboxylate binding to hard cations, like uranyl, is mainly bidentate and that hydroxo bridging is a key cornerstone in the build up of hydroxo and mixed hydroxo carbonate and carboxylate complexes.

In summary, the calculations presented in this work provided unique geometries for the not well-established calcium uranyl carbonate and uranyl malonate complexes in aqueous solution that complement and help to interpret the results from EXAFS spectroscopy.

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**Supporting Information Available:** Coordinates and total energies of all computed structures with basis set II and solvent effects. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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