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Abstract

We studied the structures of $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$, and $\text{Ba}_2\text{UO}_2(\text{CO}_3)_3^0$ using HF, MP2, and B3LYP methods. We obtained an unusual long uranyl bond for the $\text{UO}_2(\text{CO}_3)_3^{4-}$ complex by ECP calculations. This study shows that it is crucial to explicitly include the counterion(s) and the hydration water molecules in the calculation of the aqueous uranyl tricarbonat complex. The calculated structure of the hydrated $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ has good agreement with the experiment. © 2002 Published by Elsevier Science B.V.

1. Introduction

The actinide carbonate complexation is very important to the radioactive waste disposal because of the high abundance of carbon dioxide and carbonate containing minerals in the geosphere. An excellent review discussing the actinide carbonate complexation was published by Clark et al. in [1]. Carbonate and bicarbonate ions exist in significant concentration in the groundwater especially under high pH condition. At relatively higher pH region, carbonate species will become the major species and govern the solubility of the actinide oxides and the hydroxides.

Theoretical studies of the uranyl tricarbonat were previously reported by Pyykkö et al. [2] at the HF level, and by Gagliardi et al. [3] at the MBPT2 and the CASPT2 levels in the aqueous environment. In paper [3], the authors obtained unusual long U–O_{ax} bond lengths in the uranyl tricarbonat complex at the MBPT2 level and pointed out that the multiconfigurational treatment like CASPT2 fixes this problem. In this Letter, we studied the structure of the uranyl tricarbonat complex at different levels of theory. The role of the solvent and the counterion was discussed in this Letter.

2. Calculation

We used GAUSSIAN 98 package of programs [4] for the calculations. HF, MP2, and B3LYP

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methods were used. Spin–orbit effects were not considered, since they are less important for the geometry optimization of the closed shell system being considered here. We employed relativistic effective core potential (ECP) for uranium. The Los Alamos large core ECP¹ and the Stuttgart large core ECP² and the corresponding basis sets were chosen³. The former does not include the *g* functions while the latter does. The 6-31G*, 6-31+G, 6-31+G*, 6-31++G, and 6-31++G* all electron basis sets were used for carbon, oxygen and hydrogen atoms³. The geometries were fully optimized with no symmetry constraints.

3. Results and discussion

The initial structure of the uranyl tricarbonate, $\text{UO}_2(\text{CO}_3)_3^{4-}$, has six equatorial oxygens directly bonded to uranium atom, forming three four-membered bidentate rings (Fig. 1, (I)). The initial structure of the uranyl pentahydrate, $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$, has five water molecules perpendicular to the equatorial plane forming the D_{5h} symmetry. During the structure optimization, we did not make any symmetry constraints, but the final structures were only slightly different from their initial symmetries. The calculated U–Oax and U–Oeq bond lengths of $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ are given in Table 1. The structures obtained by EXAFS (extended X-ray absorption fine structure) measurements are shown in the same table. At the B3LYP level of theory, by adding a set of diffuse functions to the basis set, we get a small contraction in the uranyl bond up to 0.006 and 0.014 Å for the hydrate and the tricarbonate, respectively. We also get a considerable

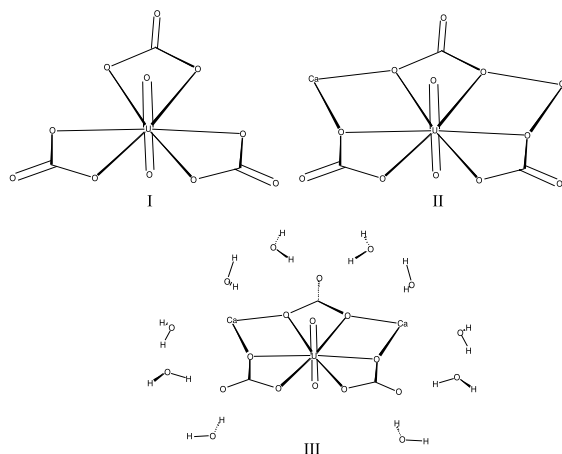


Fig. 1. The structures of $\text{UO}_2(\text{CO}_3)_3^{4-}$ (I), $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ (II), and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0 \cdot 10\text{H}_2\text{O}$ (III).

lengthening of the U–Oeq bond up to 0.02 and 0.03 Å for the hydrate and the tricarbonate, respectively. The addition of polarization function gives more prominent influence on the structure. We get 0.02 Å contraction in the uranyl bond both in the hydrate and in the tricarbonate.

At the B3LYP and MP2 levels, the calculated uranyl bond lengths of $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ are close to the experimental value. For the uranyl tricarbonate, the calculated uranyl bond lengths are clearly overestimated. The equatorial bond lengths are always overestimated both in $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$. The best equatorial bond length was obtained at the MP2 level using the Stuttgart large core ECP for uranium. The Stuttgart large core ECP always gives shorter axial and equatorial bond lengths compared to the Los Alamos large core ECP.

There is one thing that should be noted here. The EXAFS data show that the U–Oax bond lengths of the $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ and the $\text{UO}_2(\text{CO}_3)_3^{4-}$ do not deviate too much. However, the calculated U–Oax bond length differs appreciably between the $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ and the $\text{UO}_2(\text{CO}_3)_3^{4-}$. At the B3LYP level, the difference is about 0.07 Å and does not depend much on the choice of the ECP and the basis set. Clearly, the B3LYP calculation is overestimating the U–Oax bond length of the $\text{UO}_2(\text{CO}_3)_3^{4-}$ complex. Similar observation was also found at the HF and MP2 levels of calcula-

¹ This basis set is unpublished, but their use has been described in J.V. Ortiz, P.J. Hay, and R.L. Martin, *J. Am. Chem. Soc.* 114 (1992) 2736.

² W. Kuechle, unpublished work.

³ Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy.

Table 1

The structures of $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ obtained at various levels of theory (length in Å)

Complex	Method	ECP ^a	Basis set	U–Oax	U–Oeq
$\text{UO}_2(\text{H}_2\text{O})_5^{2+}$	HF	LANL	6-31+G*	1.690	2.556
	HF	SLC	6-31+G*	1.677	2.539
	B3LYP	LANL	6-31G*	1.757	2.512
	B3LYP	LANL	6-31+G	1.775	2.502
	B3LYP	LANL	6-31+G*	1.751	2.532
	B3LYP	SLC	6-31+G*	1.731	2.513
	B3LYP	LANL	6-31++G	1.776	2.502
	B3LYP	LANL	6-31++G*	1.751	2.532
	MP2	LANL	6-31+G*	1.783	2.518
	MP2	SLC	6-31+G*	1.766	2.475
	EXAFS [9]			1.77 ± 0.02	2.40 ± 0.02
$\text{UO}_2(\text{CO}_3)_3^{4-}$	HF	LANL	6-31+G*	1.738	2.575
	HF	SLC	6-31+G*	1.726	2.559
	B3LYP	LANL	6-31G*	1.838	2.564
	B3LYP	LANL	6-31+G	1.844	2.604
	B3LYP	LANL	6-31+G*	1.824	2.592
	B3LYP	SLC	6-31+G*	1.796	2.559
	B3LYP	LANL	6-31++G	1.844	2.604
	B3LYP	LANL	6-31++G*	1.824	2.592
	MP2	LANL	6-31+G*	1.843	2.537
	MP2	SLC	6-31+G*	1.830	2.497
	EXAFS [10]			1.80 ± 0.02	2.43 ± 0.02

^a LANL: Los Alamos large core ECP, SLC: Stuttgart large core ECP.

tions. The largest difference in the uranyl bond length between $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ was found at the B3LYP/6-31G* level (0.081 Å), while the smallest difference was found at the HF/6-31+G* level (0.048 Å). The best U–Oax distance (1.796 Å) was obtained at the B3LYP/6-31+G* using Stuttgart large core ECP. But at the same level of calculation, U–Oax bond length of the $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ was 1.731 Å, being too much underestimated.

In our present calculations, the calculated U–Oeq bond lengths are in surprisingly poor agreement with the experiments both for the hydrate and the tricarbonate. Gagliardi et al. [3] obtained U–Oeq distance 2.426 Å for uranyl tricarbonate at the MBPT2 level gas phase calculations. This equatorial bond distance agrees well with the experimental bond distance of 2.43 Å, but their U–Oax distance (1.894 Å) is too long compared to the experimental distance (1.80 Å). The best U–Oeq distance in our calculations is 2.497 Å obtained at the MP2 level using Stuttgart large core ECP. This bond distance of 2.497 Å is,

however, quite different from 2.426 Å obtained by Gagliardi et al. at the MBPT2 level. The major difference between our calculations and their's is that we used large core ECP for uranium, while they used small core ECP. Schreckenbach et al. [5] argues that the large core ECP-B3LYP calculations generally give reliable U–Oax bond lengths but somewhat overestimated U–Oeq bond lengths. We have had the same found. The small core ECP is probably crucial to get the accurate equatorial bond distances. However, small core ECP drastically increases the computational cost.

One additional explanation for the overestimation of the U–Oeq bond lengths is the neglect of the bulk solvent [6,7]. By adding 10 water molecules in the second hydration shell of $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$, we got 0.05 Å shorter U–Oeq bond length. The U–Oeq bond distance of $\text{UO}_2(\text{H}_2\text{O})_5(\text{H}_2\text{O})_{10}^{2+}$ is 2.465 Å at the B3LYP/6-31G* level. The bond distance got closer to the experimental value, nevertheless it is still overestimated. The bulk solution effect should be more significant for the carbonate, since the distal oxy-

gens have strong hydrogen bonding and the charge transfer with the water molecules in the outer coordination shell. To explicitly consider the interaction of distal oxygens with the outer solvent, we introduced six water molecules which are hydrogen-bonded to the $\text{UO}_2(\text{CO}_3)_3^{4-}$. The U–Oax bond length in the $\text{UO}_2(\text{CO}_3)_3^{4-} \cdot (\text{H}_2\text{O})_6$ is 1.812 Å at the 6-31++G* level, instead of 1.824 Å in the $\text{UO}_2(\text{CO}_3)_3^{4-}$ at the same level of theory. The effect of the solvent was not so significant as we expected. The similar trend was also reported by Gagliardi et al. [3]. In the aqueous phase calculations, they found the shortening of the axial and the equatorial bond lengths of 0.013 Å and 0.019 Å, respectively, compared to the gas phase calculation.

Clark et al. [8] have found that the counterion has an influence on the O=U=O symmetric stretching ν_1 band of the uranyl hydrate in solution. When the NO_3^- counterion is replaced with the Cl^- counterion, there is a shift of ν_1 band for 2 cm^{-1} . This fact indicates that the counterions may situate very close to the uranyl moiety. The uranyl tricarbonate complex, which has high negative charge (−4), is expected to have strong interactions with the counterions. Thus, it is a probable difficulty to calculate the structure of the aqueous $\text{UO}_2(\text{CO}_3)_3^{4-}$ without adding the counterion(s) and/or the hydration water molecules.

We have carried out the structure optimizations of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ (Liebigite), and $\text{Ba}_2\text{UO}_2(\text{CO}_3)_3^0$.

The structure of the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ is given in Fig. 1 (II). In both $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ and $\text{Ba}_2\text{UO}_2(\text{CO}_3)_3^0$, two alkaline earth atoms (Ca or Ba) neutralize the negative charge of the carbonate ligand. The calculated structure of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ and $\text{Ba}_2\text{UO}_2(\text{CO}_3)_3^0$ at the B3LYP/6-31G* level is given in Table 2. By adding two alkaline earth atoms, the U–Oax bond distance has been shortened by $\sim 0.05 \text{ Å}$ compared to the uranyl tricarbonate at the same level of calculations. But the EXAFS measurements give the U–Oax bond length 1.80 Å for the $\text{UO}_2(\text{CO}_3)_3^{4-}$ and 1.81 Å for the aqueous $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$, suggesting that the U–Oax bond lengths are almost equal in these two complexes. The calculated structure of the aqueous $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ does not deviate too much from that obtained by the EXAFS measurements except that the equatorial bond distances are somewhat overestimated. These facts show that the calculated structure of the aqueous $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ has a reasonable accord to the EXAFS data, while the uranyl tricarbonate gives overestimated axial bond distance. It suggests that counterion(s) play very important roles in the electronic and geometric structures of the uranyl tricarbonate complex. Adding 10 hydration water molecules to the Liebigite (forming $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0 \cdot 10\text{H}_2\text{O}$, Fig 1, (III)) gives better agreement with the experiments (Table 2). The only discrepancy between the calculated and the experimental structures is that we obtained an asymmetric distribution of the

Table 2

The structures of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ and $\text{Ba}_2\text{UO}_2(\text{CO}_3)_3^0$ obtained by B3LYP/6-31G* calculations (length in Å)

Method	Complex	U–Oax	U–Oeq	U–C	U–M ^a	U–Odis
EXAFS [11]	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0 \cdot 10\text{H}_2\text{O}^b$	1.81	2.44	2.90	3.94	4.22
B3LYP	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$	1.79	2.36	2.97	3.83	4.19
			2.55	2.97		4.19
			2.84	3.37		4.59
			2.40	2.96		4.13
B3LYP	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0 \cdot 10\text{H}_2\text{O}$	1.80	2.60	2.96	3.99	4.13
			2.72	3.25		4.62
			2.43	2.88		4.19
			2.40	2.94		4.17
EXAFS [11]	$\text{Ba}_2\text{UO}_2(\text{CO}_3)_3^0 \cdot 6\text{H}_2\text{O}^c$	1.80	2.43	2.88	3.91	4.19
B3LYP	$\text{Ba}_2\text{UO}_2(\text{CO}_3)_3^0$	1.80	2.40	2.94	4.17	4.17
			2.49	2.94		4.17
			2.74	3.24		4.48

^a M = Ca or Ba.

^b In solution (0.014 M UO_2^{2+} , 0.028 M Ca^{2+} , 0.042 M CO_3^{2-} at pH = 8.0).

^c Solid synthetic $\text{Ba}_2\text{UO}_2(\text{CO}_3)_3^0 \cdot 6\text{H}_2\text{O}$ at 15 K.

U–Oeq, U–C, and U–Odis atomic distances on the basis of the B3LYP calculations, instead of a symmetric distribution by the EXAFS measurements. The difference between the longest and the shortest bond length of U–Oeq bond is 0.32 Å, which is sufficiently large enough to resolve in the EXAFS analysis. This discrepancy, however, could be justified if we take into account the fact that our calculations did not consider the full orientations of the water molecules in the outer coordination shell.

4. Conclusions

We have studied the structures of the uranyl tricarbonate $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$, and $\text{Ba}_2\text{UO}_2(\text{CO}_3)_3^0$ by B3LYP calculations. The structure of the gas phase $\text{UO}_2(\text{CO}_3)_3^{4-}$ gives too long U–Oax bond length compared to the experimental bond distances in solution. It demonstrates that the calculation of the aqueous tricarbonate complex needs to explicitly consider the counterion(s) and/or hydration water molecules and should not be considered as a bare $\text{UO}_2(\text{CO}_3)_3^{4-}$ ion. Since the counterion(s) situate very close to the uranyl moiety, it is probable that the calculation inclusive of the counterion(s) is very crucial to get the accurate geometry. In fact, we obtained the structure of the hydrated Liebigite $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}$ which has good agreement with experiments.

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