Coordination of the Neptunyl Ion with Carbonate Ions and Water: A Theoretical Study

Gagliardi, Laura; Roos, Björn O.

Inorg. Chem. **2002**, *41*, 1315–1319

Coordination of the Neptunyl Ion with Carbonate Ions and Water: A Theoretical Study

Laura Gagliardi*,† and Björn O. Roos‡

Dipartimento di Chimica G. Ciamician, Università di Bologna, Via F. Selmi 2, 40126 Bologna, Italy, and Department of Theoretical Chemistry, Chemical Center, P.O. Box 124, S-221 00 Lund, Sweden

Received October 17, 2001

The results of a study on the ground-state of monocarbonate, bicarbonate, and tricarbonate complexes of neptunyl using multiconfigurational second-order perturbation theory (CASSCF/CASPT2) are presented. The equilibrium geometries of the complexes corresponding to neptunium in the formal oxidation state (V) have been fully optimized at the CASPT2 level of theory in the presence of an aqueous environment modeled by a reaction field Hamiltonian with a spherical cavity. Some water molecules have been explicitly included in the calculation. This study is consistent with the hypothesis that the monocarbonate complex has a pentacoordinated structure with three water molecules in the first coordination shell and that the bicarbonate complex has a hexacoordinated structure, with two water molecules in the first coordination shell. The typical bond distances are in good agreement with experimental results. The tricarbonate complex was studied with explicit counterions, which resulted in somewhat longer Np–carbonate bond distances than experiment indicates.

1. Introduction

The use of computational chemistry has substantially increased the understanding of actinide chemistry in the past few years. Neptunium is of radiological concern because it is highly soluble under typical groundwater conditions[1] and its sorption on common minerals is relatively low.[1,2] Under most environmental conditions, Np will be present as the pentavalent trans dioxo (neptunyl) cation, NpO_2^+. Carbonate is an important natural ligand because of its relatively high concentration and strong actinide-complexing ability.[3,4] Therefore, carbonato complexes of Np(V) are expected to play an important role in the fate and transport of Np in natural aquatic environment.

Our work was inspired by two papers by Clark et al.[5,6] in which the carbonate complexation of neptunyl was investigated. Solutions containing $[NpO_2(CO_3)]^-$ (Figure 1), $[NpO_2(CO_3)_2]^{3-}$ (Figure 2), and $[NpO_2(CO_3)_3]^{5-}$ (Figure 3) were prepared, and the solution species were studied using various spectroscopic techniques, such as EXAFS, Raman, ^{13}C nuclear magnetic resonance, and near-infrared electronic absorption spectroscopies. These studies made it possible to determine the molecular structure of the carbonate complexes, the temperature dependence of carbonate complexation, and the solution conditions under which each species can be prepared.

We are mainly interested in the molecular structure of the complexes and the explicit coordination of water molecules. Clark et al.[5] consider almost definitive the structure of $[NpO_2(CO_3)_3]^{5-}$, while they seem more uncertain about the structures of $[NpO_2(CO_3)]^-$ and $[NpO_2(CO_3)_2]^{3-}$. This uncertainty concerns the number of water molecules bound to the complexes. They suggest that *the structural information reported in their work may enable more accurate modeling of neptunyl carbonate reactivity*. We have previously studied with quantum chemical methods the ground state of the tricarbonato complex of dioxouranate and determined the equilibrium geometry in several oxidation states.[7] We have

* To whom correspondence should be addressed. E-mail: laura.g@ciam.unibo.it.
† Università di Bologna.
‡ Department of Theoretical Chemistry, Chemical Center.

(1) Nitsche, H.; Lee, S. C.; Gatti, R. C. *J. Radioanal. Nucl. Chem.* **1988**, *124*, 171.
(2) Triay, I. R.; Robinson, B. A.; Mitchell, A. J.; Overly, C. M.; Lopez, R. M. *Mater. Res. Soc. Symp. Proc.* **1993**, *294*, 797.
(3) Clark, D. L.; Hobart, D. E.; Neu, M. P. *Chem. Rev.* **1995**, *95*, 25.
(4) Nash, K. L.; Cleveland, J. M.; Rees, T. F. *J. Environ. Radioact.* **1988**, *7*, 131.
(5) Clark, D. L.; Conradson, S. D.; Ekberg, S. A.; Hess, N. J.; Neu, M. P.; Palmer, P. D.; Runde, W.; Tait, C. D. *J. Am. Chem. Soc.* **1996**, *118*, 2089.
(6) Clark, D. L.; Ekberg, S. A.; Hess, N. J.; Conradson, S. D.; Janecky, D. R.; Neu, M. P.; Palmer, P. D.; Tait, C. D. *New J. Chem.* **1996**, *20*, 211.
(7) Gagliardi, L.; Grenthe, I.; Roos, B. O. *Inorg. Chem.* **2001**, *40*, 2976.

10.1021/ic011076e CCC: $22.00
Published on Web 02/14/2002

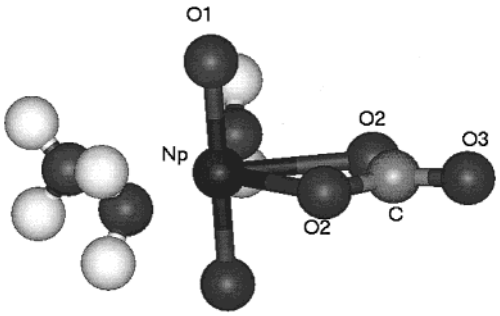

Figure 1. Structure of $[NpO_2(CO_3)_2]^{-}\cdot 3H_2O$.

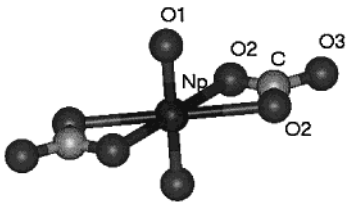

Figure 2. Structure of $[NpO_2(CO_3)_2]^{3-}$.

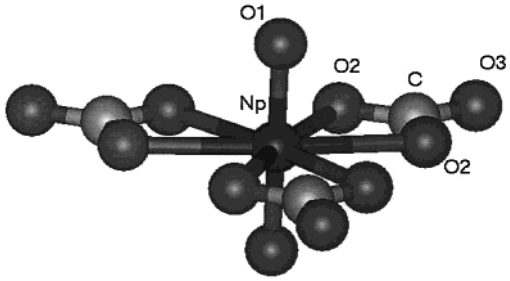

Figure 3. Structure of $[NpO_2(CO_3)_3]^{5-}$.

also used quantum chemistry to study several uranium compounds in both their ground and excited electronic states.[8,9] In this paper we present the results of a study on the ground state of neptunyl mono-, bi-, and tricarbonato complexes in water solution. From now on they will be indicated as NpMono, NpBis, and NpTris, respectively. The structure of these systems has been determined, and the water coordination has been investigated. The isolated neptunyl ion corresponding to three oxidation states of Np, namely, Np(VII), Np(VI), and Np(V), has also been studied.

2. Details of Calculations

The calculations have been performed at the complete active space (CAS) SCF[10] level of theory, with dynamic electron correlation added using second-order perturbation theory, CASPT2.[11,12] The presence of an aqueous environment has been taken into account by a reaction field Hamiltonian with a spherical cavity. The size of the spherical cavity was optimized pointwise for the structures, and it has a radius of 5.92 Å for NpMono with three explicit water molecules, 5.40 Å for NpBis, and 5.82 Å for NpTris. In addition, calculations on NpTris were run in the presence of counterions, without any spherical cavity.

The relativistic effects due to the high atomic number of the neptunium atom are taken into account implicitly through the use of effective core potentials (ECPs) derived from highly accuracy relativistic calculations on atoms. The energy-adjusted neptunium ECPs of Küchle et al. were used for this purpose.[13] The accompanying basis sets of the neptunium ECPs were used to describe the valence electron density.[14] On the carbon and oxygen atoms the atomic natural orbital, ANO-S, 4s3p2d basis sets[15] were used (indicated as BS-1 in the following). Basis set effects on the CASPT2 results for some uranium compounds have been investigated in a previous paper.[8] In this study we have repeated the calculations on NpBis with one extra *g*-type function in the valence basis of Np (exponent 1.223 67) and the atomic natural orbital, ANO-L, 4s3p2d1f basis sets[16] on the carbon and oxygen atoms (indicated as BS-2 in the following). Our previous studies of uranium compounds indicated that spin−orbit coupling is not vital for the description of the molecular structure of these compounds, and it was not included in the present study.

All calculations were performed with the MOLCAS-5 quantum chemistry software.[17]

Preliminary CASSCF calculations with dynamic electron correlation added using second order perturbation theory, CASPT2, were performed with an active space formed by two electrons in the seven 5f Np orbitals (2/7). More extended active spaces were then investigated by initially considering the bare Np trans dioxo cations, corresponding to Np(VII), Np(VI), and Np(V). In the NpO_2^{3+} closed-shell case, with ground state $^1\Sigma_g^+$, we assumed that the most important orbitals would be the neptunyl O 2p orbitals and the strongly correlated orbitals of the same symmetry centered on neptunium. This gives an active space of twelve electrons in twelve active orbitals (12/12). For the NpO_2^{2+} doublet, with a $^2\Phi_u$ ground state, one extra electron has to be added to a neptunium 5fϕ orbital, giving an active space of (13/13). Finally for NpO_2^{+} with a ^3H_g ground state, the addition of one more electron in a 5fδ orbital gives (14/14). The 14/14 active space should then be used in all calculations on the carbonate complexes corresponding to Np(V). This means 626 655 configuration state functions for $[NpO_2(CO_3)_3]^{5-}$ in C_{2v} symmetry. Such calculations become rather lengthy, and possibilities to reduce the active space without losing any chemical information were therefore investigated. Inspection of the occupation numbers shows that it is possible to remove four electrons and two active orbitals, which gives a final active space of (10/12). This active space, corresponding to 70 900 configuration state functions (for $[NpO_2(CO_3)_3]^{5-}$ in C_{2v} symmetry), has been used in most of the calculations on the carbonate complexes.

(8) Gagliardi, L.; Roos, B. O. *Chem. Phys. Lett.* **2000**, *331*, 229.
(9) Gagliardi, L.; Roos, B. O.; Malmqvist, P.-Å.; Dyke, J. M. *J. Phys. Chem. A* **2001**, *105*, 10602.
(10) Roos, B. O. In *Advances in Chemical Physics; Ab Initio Methods in Quantum Chemistry—II*; Lawley, K. P., Ed.; John Wiley & Sons: Chichester, England, 1987; Chapter 69, p 399.
(11) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.
(12) Andersson, K.; Roos, B. O. In *Modern electron structure theory*; Yarkony, R., Ed.; Advanced Series in Physical Chemistry, Vol. 2; World Scientific Publishing:: Singapore, 1995; Part I, p 55.
(13) Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1994**, *100*, 7535−7542.
(14) Institut für Theoretische Chemie, Universität Stuttgart. ECPs and corresponding valence basis sets at http://www.theochem.uni-stuttgart.de/.
(15) Pierloot, K.; Dumez, B.; Widmark, P.-O.; Roos, B. O. *Theor. Chim. Acta* **1995**, *90*, 87.
(16) Widmark, P.-O.; Malmqvist, P.-Å.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291.
(17) Andersson, K.; Bernhardsson, A.; Blomberg, M. R. A.; Boussard, P.; Cooper, D. L.; Fleig, T.; Fülscher, M. P.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Neogrády, P.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Schimmelpfennig, B.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Stålring, J.; Thorsteinsson, T.; Veryazov, V.; Wahlgren, U.; Widmark, P.-O. *MOLCAS*, version 5.0; Department of Theoretical Chemistry, Chemical Center, University of Lund: Lund, Sweden, 2000.

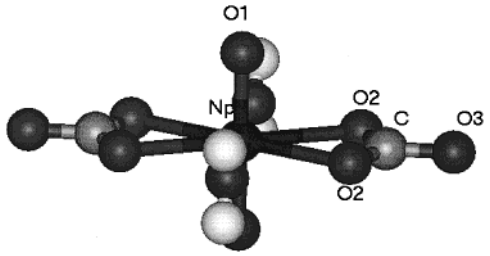

Figure 4. Structure of $[NpO_2(CO_3)_2]^{3-}\cdot 2H_2O$.

Table 1. Typical Bond Distances, Å, and Angles, deg in $NpO_2(CO_3)_2^{3-}$ (See Figures 2, 4 for the Atom Numbering), Obtained at CASPT2 Level with Different Active Spaces (2/7 and 10/12) and Basis Sets (BS-1 and BS-2)[a]

	2/7, BS-1	10/12, BS-1	10/12, BS-2	$2H_2O$;[b] 10/12, BS-1	exptl[c]
R_{NpO1}	1.854	1.850	1.817	1.854	1.85 ± 0.02
R_{NpO2}	2.532	2.548	2.565	2.548	2.48 ± 0.03
R_{NpC}	2.954	2.970	2.986	2.891	2.93 ± 0.03
R_{NpO3}	4.275	4.290	4.295	4.244	4.18 ± 0.03
R_{CO2}	1.311	1.310	1.295	1.269	
R_{CO3}	1.322	1.320	1.310	1.352	
∠O2NpO2	52	51	52	52	
∠O2CO2	117	118	117	123	

[a] When some water molecules are explicitly added, this is specified. All results were obtained in the presence of the reaction field Hamiltonian. [b] Np−water distance is 2.585 Å. [c] Reference 5.

The neptunyl bond was optimized pointwise at the CASPT2 level in the bare cations. Geometry optimizations were also performed for NpMono, NpBis, and NpTris at the CASPT2 level. Five degrees of freedom were optimized pointwise using a five-dimensional grid (21 points distributed on a sphere with a radius of 0.05 au plus one point in the center): the Np−O neptunyl bond distance R_{NpO1}, the Np−O carbonate bond distance R_{NpO2}, the two typical carbon oxygen bond distances R_{CO2} and R_{CO3}, and the equatorial O2NpO2 angle (see Figures 1−3 for the numbering of the atoms). NpMono, NpBis, and NpTris were assumed to have C_{2v}, D_{2h}, and D_{3h} symmetry, respectively. Since MOLCAS works in subgroups of D_{2h}, the calculations on the three systems were performed in C_{2v}, D_{2h}, and C_{2v}, respectively.

NpMono was optimized in the presence of three water molecules, and NpBis was optimized both alone and in the presence of two water molecules (Figure 4). The Np−water bond distance was always optimized when water was present, assuming a fixed internal structure for the water molecules (equal to the structure of the free water).

The force constants were obtained by fitting the points to a second-order polynomial. These points were obtained in a second set of calculations where the center of the sphere was at the computed equilibrium geometry.

3. Results and Discussion

In Table 1 the typical bond distances and angles obtained for NpBis (Figures 2, 4) are reported. The 2/7 and 10/12 active spaces give similar results, all in agreement with experimental results. The 10/12 bonds are ca. 0.015 Å longer than the 2/7 bonds, with the exception of the neptunyl bond, which is 0.005 Å shorter. The Np−O3 bond is slightly longer than experimental results with both active spaces, while all the other bonds are within the experimental range. The 10/12 calculation was repeated with the large basis set, BS-2. The neptunyl bond becomes 0.033 Å shorter, and the Np−O2 distance increases by 0.017 Å. In our previous studies on uranium oxides,[8,9] the inclusion of one or two *g* functions on uranium and the use of ANO-L instead of ANO-S on oxygen decreased the U−O bond ca. 0.02−0.03 Å, in line with what we obtain here. The inclusion of two water molecules (Figure 4) in the 10/12 calculation does not seem to affect the Np−O1 and Np−O2 bonds.

The C−O2 and C−O3 bonds become respectively shorter and longer than in the water-free calculation, and overall, Np−O3 becomes shorter. One would intuitively expect the C−O3 bond to be shorter because the external oxygen should acquire some double bond character because of the polarization of the negative charge toward the neptunyl ion. This is also what was found in our previous study of the uranyl compound.[7] An effect competing with the neptunyl polarization could be the solvent polarization, which could be responsible for the C−O3 elongation. We thus repeated the optimization of C−O2 and C−O3 for NpBis·$2H_2O$ without the reaction field Hamiltonian, and we obtained the reverted situation, with an internal C−O2 bond of 1.32 Å and an external C−O3 bond of 1.29 Å.

The Np−O(water) distance was also optimized at the CASPT2 level, and a value of 2.585 Å was obtained. The orientation of the water molecules with respect to the central neptunyl was kept fixed throughout the optimization. The water molecules lie perpendicularly to the equatorial plane, and the water oxygens form an angle of 90° with the Np−C−O3 axis. This is clearly an arbitrary choice, but it ensures that the interaction between the water hydrogens and carbonate oxygens is approximately constant at each step of the optimization. Structurewise the inclusion of water does not seem to have any dramatic effect. However, some energetic considerations show that NpBis·$2H_2O$ is ca. 50 kcal/mol lower in energy than NpBis with no explicit water. The binding energy for one water molecule is thus estimated to be about 25 kcal/mol.

For NpMono (Figure 1) the calculations were performed with the 10/12 active space. The bare complex with no explicit water molecules is rather unbalanced because of the presence of only one carbonate group on the equatorial plane, and the neptunyl becomes bent on the side opposite the carbonate. Instead, we considered a structure formed by NpMono and three water molecules. The water molecules were placed perpendicularly to the equatorial plane, at a fixed angle with respect to the Np−C−O3 axis. The Np−water distance was optimized, and a value of 2.565 Å was obtained. The results are presented in Table 2. The structural agreement with experimental results is already good with BS-1 and is improved further by using BS-2; the neptunyl bond becomes shorter and the Np−O2 distance longer, as for NpBis. This confirms the hypothesis that the NpMono is pentacoordinated in the plane with three water molecules in the first coordination sphere. It is surprising to notice that while in NpBis the internal C−O bond (C−O2) is always shorter than the external C−O bond (C−O3) in the presence of the reaction field Hamiltonian; they are reverted in NpMono.

The system that we found most problematic to describe was NpTris (Figure 3). We initially followed the same recipe as for NpMono and NpBis and optimized the structure at

Table 2. Typical Bond Distances, Å, and Angles, deg, in $[NpO_2(CO_3)]^-$ with Three Water Molecules (See Figure 1 for the Atom Numbering), Obtained at CASPT2 Level with the 10/12 Active Space and BS-1 and BS-2 Basis Sets[a]

	$3H_2O$;[b] 10/12, BS-1	$3H_2O$;[c] 10/12, BS-2	exptl[d]
R_{NpO1}	1.855	1.836	1.84 ± 0.02
R_{NpO2}	2.456	2.475	2.49 ± 0.03
R_{NpC}	2.953	2.933	2.94 ± 0.03
R_{NpO3}	4.218	4.212	4.24 ± 0.03
R_{CO2}	1.345	1.317	
R_{CO3}	1.265	1.279	
∠O2NpO2	54	53	
∠O2CO2	111	114	

[a] All results were obtained in the presence of the reaction field Hamiltonian. [b] Np−water distance is 2.565 Å. [c] Np−water distance is 2.570 Å. [d] Reference 5.

the CASPT2 level starting from a CASSCF(10/12) wave function, in the presence of the reaction field Hamiltonian. To our surprise, we found that the central neptunyl was not bound to the carbonate groups. While the typical neptunyl bond was within the experimental range, the Np−O carbonate distance was more than 3 Å, which is much longer than the predicted experimental value of 2.53 ± 0.03 Å. We then repeated the calculation with the largest active space, namely, 14/14, but this did not affect the result. We explored the possibility of the complex not being D_{3h} and studied a distorted structure with D_3 symmetry, following what we did in the previous $[UO_2(CO_3)_3]^{5-}$ study.[7] It was, however, found to lie higher in energy than the D_{3h} structure. We also considered the possibility of Jahn−Teller distortion and performed a calculation on a complex in which the three carbonate groups were not equivalent (no symmetry restrictions were imposed in this calculation), but again, we obtained an increased energy compared to the D_{3h} structure. We finally considered the isomerization from the D_{3h} to the C_3 structure, in which the carbonates lie parallel to neptunyl, but the D_{3h} structure still resulted as the lowest in energy among them all.

The only possible explanation for this behavior that we could find was that with such a highly negative charge (−5) the rather simplified solvent model used was not able to keep the complex bound. We optimized the structures of $[NpO_2(CO_3)_3]^{3-}$ and $[NpO_2(CO_3)_3]^{4-}$, corresponding to Np(VII) and Np(VI), respectively, and they turned out to be bound (see Table 3). The neptunyl bond distance is shorter than for the −5 complex because of the presence of less

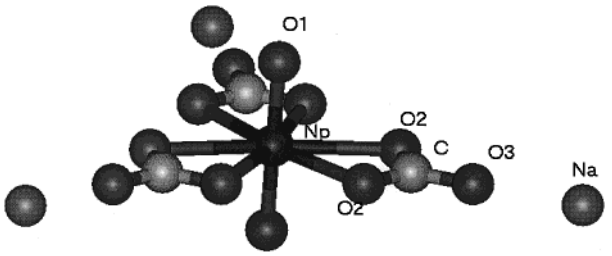

Figure 5. Structure of $[NpO_2(CO_3)_3]^{5-}\cdot 3Na^+$.

negative charge on the Np atom. The Np−O carbonate bond distance is shorter than the experimental value for $[NpO_2(CO_3)_3]^{3-}$, while it is in exact agreement with the experimental value for $[NpO_2(CO_3)_3]^{4-}$. However, experimentally the Np(V) complex is detected and not Np(VI).

We thus decided to repeat the calculations on $[NpO_2(CO_3)_3]^{5-}$ in the presence of some counterions, hoping that this could be a more realistic model for the real system. We optimized the system $[NpO_2(CO_3)_3]^{5-}\cdot 3Na^+$, with a total charge of −2 (Figure 5).

We arbitrarily placed the counterions along the Np−C−O3 axis. In this case a reaction field Hamiltonian was not used, the reason being that the supersystem formed by neptunyl tricarbonate and three counterions is very big. (The Np−Na distance is about 6.6 Å.) A cavity containing all this would thus be so large to have hardly any effect on the description of the system. The calculations were performed at the CASPT2 level starting from a CASSCF(2/7) and CASSCF(10/12) wave function. The results are reported in Table 3. The neptunyl bond is within the experimental range in both cases and does not vary in going from 2/7 to 10/12. The Np−O carbonate bond is still longer than the experimental bond, but it is considerably reduced compared to the calculation without counterions. It has a value of 2.618 Å in the 2/7 calculation and 2.598 Å in the 10/12 calculation. The active space increase does not seem to have a dramatic effect. The internal C−O2 bond is shorter than the external C−O3. The counterions now polarizes the C−O bonds in the opposite direction, increasing the negative charge on O3. This polarization is clearly stronger than the polarization from neptunyl.

A comparison with the structure of $[UO_2(CO_3)_3]^{5-}$ determined in our previous study[7] shows that the neptunyl bond distance of 1.876 Å in $[NpO_2(CO_3)_3]^{5-}$ is ca. 0.05 Å shorter than the uranyl bond distance of 1.929 Å in $[UO_2(CO_3)_3]^{5-}$,

Table 3. Typical Bond Distances, Å, and Angles, deg (See Figures 3, 5 for the Atom Numbering), for $[NpO_2(CO_3)_3]$ (−5), (−4), and (−3), Obtained at CASPT2 Level with Different Active Spaces with BS-1 Basis Set[a]

	$NpTris^{5-}\cdot 3Na^+$, 2/7	$NpTris^{5-}\cdot 3Na^+$, 10/12	$NpTris^{4-}$, 13/13	$NpTris^{3-}$, 12/12	exptl[b]
R_{NpO1}	1.879	1.876	1.805	1.791	1.86 ± 0.02
R_{NpO2}	2.618	2.598	2.533	2.326	2.53 ± 0.03
R_{NpC}	2.997	2.974	2.979	2.782	2.98 ± 0.03
R_{NpO3}	4.346	4.361	4.305	4.058	4.22 ± 0.03
R_{CO2}	1.286	1.295	1.304	1.314	
R_{CO3}	1.349	1.386	1.326	1.276	
R_{O3Na}	2.394[c]	2.309			
∠O2NpO2	51	52	52	56	
∠O2CO2	121	121	115	113	

[a] The results for 4^- and 3^- compounds are obtained in the presence of the reaction field Hamiltonian. [b] Reference 5. [c] This distance was not optimized in the 2/7 case.

Table 4. CASPT2 Bond Distance, Å, for the Cations[a]

system	NpO_2^+	NpO_2^{2+}	NpO_2^{3+}
active space	14/14	13/13	12/12
R_{Np-O}	1.765	1.707	1.701

[a] All results were obtained in the presence of the reaction field Hamiltonian.

in agreement with experimental results. The Np−O carbonate bond of 2.598 Å is 0.065 Å longer than the U−O carbonate bond of 2.529 Å, while experimentally these two bonds are expected to be very similar (2.53 ± 0.03 for $[NpO_2(CO_3)_3]^{5-}$ and 2.50 ± 0.02 for $[UO_2(CO_3)_3]^{5-}$).

In Table 4 the typical bond distances of NpO_2^+, NpO_2^{2+}, and NpO_2^{3+} obtained with the largest active space are reported. This shows that the Np−O bond distance in the cation alone is shorter than in the presence of the complex. However, the trend in the series of the three cations is very similar to the trend of the neptunyl bond distance in the series $[NpO_2(CO_3)_3]^{5-}$, $[NpO_2(CO_3)_3]^{4-}$, $[NpO_2(CO_3)_3]^{3-}$ (Table 3).

4. Conclusions

We have presented the results of the CASSCF/CASPT2 study of neptunyl carbonate complexes in aqueous solution. This study shows that the structures of neptunyl monocarbonate and bicarbonate complexes obtained at the CASPT2 level are in agreement with what has been determined experimentally by Clark et al.,[5] and it is consistent with the presence of three and two water molecules, respectively, in the first coordination shell. The neptunyl tricarbonate complex has also been investigated. The neptunyl bond distance is obtained within the experimental range, while the neptunium carbonate bond distance turns out to be longer than what has been predicted experimentally. Actually a bound complex can only be obtained by explicitly including counterions in the complex. This can only, in an approximate way, describe the complex dynamic situation in the solvent, and the deviation from experiment is therefore not surprising.

We did not have these difficulties in our recent study of the corresponding uranyl complex.[7] Here also, the structure of the 5− complex was in agreement with the experimental structure without the explicit inclusion of counterions. It seems that the neptunyl ion has less complexing strength than uranyl. There are several indications that this is the case. First, the UO bond in UO_2^+ is lengthened 0.17 Å in the complex, while the corresponding Np−O bond only becomes 0.11 Å longer. Also, the perturbation of the CO_3 units is larger, in particular the lengthening of the C−O2 bond and the corresponding shortening of C−O3. Actually, there are two competing effects that distort the CO_3 unit. One is the polarization due to the cation, which would tend to shorten the C−O3 bond and lengthen C−O2. However, the effect of the solvent will act in the opposite direction. In the uranyl compound $[UO_2(CO_3)_3]^{4-}$, the first effect dominates, leading to a short C−O3 bond (1.16 Å) and a long C−O2 bond (1.38 Å). Here, we see the same effect for NpMono, but for the other compounds the solvent effect seems to dominate. This is confirmed by the fact that in the solvent-free calculation on NpBis C−O3 becomes shorter than C−O2. When explicit counterions are placed close to the O3 atoms, we see a considerable lengthening of the C−O3 bond, as expected.

Acknowledgment. This work was partially supported by the Italian "Ministero dell'Univeristà e della Ricerca Scientifica" and the Swedish Natural Research Council (NFR). The authors thank Professor Ingmar Grenthe for useful discussions. B. O. Roos thanks Cineca Supercomputer Center, Bologna, Italy, for hosting him during the Minos projects.

IC011076E