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Systematic DFT Study of Gas Phase and Solvated Uranyl and Neptunyl Complexes $[AnO_2X_4]^n$ (An = U, Np; X = F, Cl, OH, $n = -2$; X = H_2O, $n = +2$)

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The six-valent uranyl and neptunyl complexes $[An^{VI}O_2X_4]^n$ (An = U, Np; X = F, Cl, OH, $n = -2$; X = H_2O, $n = +2$) have been studied within the framework of density functional theory. The relative stabilities of the cis and trans isomers, structural properties, charge distribution, and ligand binding energies have been determined using the modified Perdew–Burke–Ernzerhof functional at the all-electron scalar relativistic level. Uranyl and neptunyl complexes with different ligands have been compared in a systematic fashion, demonstrating close similarity of these actinides in oxidation state VI. In addition, the effect of an aqueous solution has been taken into account with the polarizable continuum model COSMO. Computed averaged ligand binding energies permit one to rationalize the observed different stabilities of the title species in aqueous media.

1. Introduction

Secure storage of radioactive waste continues to be an important issue involving environmental molecular science, which requires a thorough understanding of the chemistry of actinides in aqueous media.[1] Therefore, the chemical behavior of these compounds, such as their stability or solubility in water or their tendency to form complexes with readily available ligands,[2] draws attention from researchers. In addition to experimental work, first-principles quantum chemistry calculations, enhanced by models of solvent effects, permit one to study the geometric, electronic, and energetic properties of actinide compounds of interest.[3−5] In many cases, such theoretical studies represent a readier and certainly safer way to acquire the desired information. Several theoretical investigations have already focused on modeling the behavior of actinide species in aqueous solution, either considering some of the surrounding water molecules explicitly[6−11] or representing the solvent environment with a dielectric continuum.[12−21]

Experimentally characterized actinyl species, AnO_2^{2+}, assume a linear or nearly linear arrangement, O−An−O. The number of ligands coordinated in the equatorial plane of the

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linear actinyl moiety depends on the nature of the bonds and the size of the coordinated species but, in general, varies between four[13,22−35] and six,[36−40] with five often being dominant.[13,26,35−44] In the present work, we are mainly interested in actinyl complexes formed with small anionic and aqua ligands. As the experimentally observed coordination number of complexes involving Cl^- and OH^- is four (see below), we have chosen to study tetracoordinated species for all anionic as well as for aqua ligands to render a comparison between them straightforward. Whereas experimental information on uranyl complexes is readily available in many cases,[5,12−44] there is only a limited number of experimental studies on the analogous neptunyl complexes.[20,41,45−48]

This motivated us to extend this computational work in a systematic fashion to the analogous tetracoordinated species of neptunium to achieve a consistent comparison of structures and binding energies within the series [AnO_2X_4]^n (An = U, Np; X = F, Cl, OH, $n = -2$; X = H_2O, $n = +2$). Uranyl complexes of this type have been the target of a number of computational investigations.[10,12,14,49−52] Yet, the picture resulting from these studies is rather fragmented because different theoretical approaches have been employed for different uranyl complexes, and long-range solvent effects have not always been taken into account. Theoretical studies on neptunyl complexes are quite scarce, and those on complexes of the type [NpO_2X_4]^n are limited to a neptunyl tetrahydroxo complex.[6,20]

In this paper, we report on a study of the hexavalent uranyl (UO_2^{2+}) and neptunyl (NpO_2^{2+}) species and their tetracoordinated fluorides, chlorides, hydroxo, and aqua complexes using an all-electron scalar relativistic density functional (DF) method based on a gradient-corrected exchange-correlation functional (PBEN). The geometries were optimized for the complexes in the gas phase as well as in aqueous solution. The geometric parameters, relative stability of the isomers, binding energies of the various ligands, and electronic structure-related considerations are presented and discussed.

In particular, we focused on the relative stability of the cis and trans isomers of the above complexes. Here, the designation “trans” refers to complexes with the common linear uranyl unit and “cis” to complexes with a nonlinear uranyl moiety. The existence of stable cis isomers had been established in an earlier systematic gas-phase study[3] on anionic fluoro, chloro, and hydroxo complexes of UO_2^{2+}; the study was based on calculations with relativistic effective core potentials (ECP) and a frozen-core quasi-relativistic (FCQR) method, employing several gradient-corrected functionals. These calculations had shown that cis complexes were only 13−30 kcal/mol less stable than their trans isomers. This interesting finding has implications for the chemistry of U(VI); for instance, cis structures may play an important role as intermediates in intramolecular oxygen ligand exchange.[49]

Our current study is extended to complexes with four aqua ligands and to the analogous NpO_2^{2+} complexes. In view of the fact that environmental chemistry is dominated by processes in aqueous medium, we examined solvent effects via the polarizable continuum model COSMO.[53] In addition, we rationalized the experimentally observed different stabilities of the uranyl complexes associated with the chemical nature of the coordinated ligands.[54]

This work is the first *systematic all-electron* study of the title uranyl and neptunyl complexes in the gas phase and aqueous solution. A comparison of the neptunyl complexes

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to their uranium congeners reveals many similarities between these actinides in oxidation state VI.

2. Computational Details

For the chemistry of actinide species, consideration of relativistic effects is essential, even in approximate computational approaches. To include them, either (i) all electrons are explicitly considered and a relativistic calculation is performed, or (ii) one invokes an implicit relativistic treatment of the core electrons, either via a frozen-core approximation (FC)[55,56] or a pseudopotential approach.[57−62]

In the present work, we used the Douglas−Kroll−Hess (DKH) transformation[63−65] to decouple electronic and positronic degrees of freedom in the relativistic Dirac−Kohn−Sham equation.[3,66,67] We used the corresponding scalar relativistic variant of the Gaussian-type orbitals fitting-function density functional method[68] (LCGTO-FF-DF) as implemented in the parallel code ParaGauss.[69]

Three different exchange-correlation functionals were evaluated to identify the one most suitable for describing the systems of interest. These test calculations were done on the hexafluorides, UF_6 and NpF_6,[78] for which reliable experimental gas-phase data are available. Bond lengths, frequencies, and the enthalpy of the $UF_6 \rightarrow U + 3F_2$ reaction were calculated with the local density functional of Vosko, Wilk, and Nusair (VWN),[70] as well as with two gradient-corrected functionals within the generalized gradient approximation (GGA): the one proposed by Becke and Perdew (BP)[71,72] and another GGA functional, introduced by Perdew, Burke, and Ernzerhof and modified by Hammer and Nørskov (PBEN).[73] LDA functionals are well-known for yielding accurate bond lengths of medium and heavy atoms, in contrast to GGA functionals, which tend to slightly overestimate bond distances.[74,75,78] On the other hand, results obtained with LDA functionals for binding energies strongly overestimate these energies, while GGA results are generally fairly good.[76,77]

The VWN, BP, and PBEN results[78] for the bond lengths, vibrational frequencies, and binding energies of the UF_6 and NpF_6 species calculated with uncontracted basis sets, together with the experimental data available in the literature,[74,79−82] reflected, not surprisingly, that the LDA distances are more accurate (average deviation from experiment ±0.003 Å) than the GGA ones (+0.04 Å) but that the LDA binding energies are overestimated by ∼200 kcal/mol. We thus chose to use a GGA functional for the present study, more adequate for our purposes, and we decided on the PBEN functional. As a consequence, one has to accept somewhat less accurate computed structure parameters than an LDA functional would give. However, with this study we are not aiming for perfect agreement with experimental data; instead, we want to carry out a consistent systematic comparison of uranyl and neptunyl complexes with specified ligands, aiming at accurate binding energies, relative stabilities of isomers, and the long-range effects of solvation.

The performance of the actinide orbital basis sets suggested by Minami and Matsuoka,[83] (24s, 19p, 16d, 11f), as well as an enlarged version (24s, 21p, 17d, 13f, 2g) was tested on the six-, five-, and four-valent oxocations, AnO_2^{2+}, AnO_2^{+}, and AnO_2, and on the halides, AnF_6 and $AnCl_6$ (An = U, Np).[78] The light elements (O, F, Cl, H) have been described by standard basis sets,[84] (6s, 1p) → [4s, 1p] for H, (9s, 5p, 1d) → [5s, 4p, 1d] for O, F, and Cl, contracted in a generalized fashion. For all species, optimized geometric parameters were obtained, along with vibrational frequencies and binding energies. With the (24s, 19p, 16d, 11f) basis, bond lengths were well reproduced, and the variations in distances caused by the addition of the 2 p, 1 d, 2 f, and 2 g functions were very small, 0.002−0.009 Å (0.1−0.5%). The improvement resulting from the larger (24s, 21p, 17d, 13f, 2g) basis set for frequencies was also small, at most 1.5%. Only when binding energies were considered, were greater differences encountered (0.3 eV, 4%), but they could in no way justify the extra cost of the larger basis set.

As the second step, the (24s, 19p, 16d, 11f) basis sets for U and Np were contracted, (24s, 19p, 16d, 11f) → [10s, 7p, 7d, 4f], in a generalized fashion using atomic eigenvectors determined from scalar relativistic calculations. Tests were performed to see if these contracted basis sets yield the same results as the uncontracted ones, taking the actinide oxides and hexahalides mentioned above as probe systems. The deviations caused by the contraction (24s, 19p,

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16d, 11f) → [10s, 7p, 7d, 4f] were almost insignificant: less than 0.25% for distances and less than 1% for vibrational frequencies and binding energies. We thus chose this contraction as standard for the systematic study after we had also tested other contraction schemes. The smaller contraction (24s, 19p, 16d, 11f) → [9s, 7p, 6d, 4f] rendered substantial deviations from the behavior obtained with the "standard" contraction, while the larger contraction (24s, 19p, 16d, 11f) → [10s, 7p, 7d, 5f] showed no significant improvement over the results already obtained with the scheme chosen to be standard.

The grid for the numeric integration of the exchange-correlation functional consisted of about 26 000 points for U, 16 000 points for Cl, 9900 points for O, 8500 points for F, and 8900 points for the H centers.

In the geometry optimizations, the total energy and elements of the density matrix were required to converge to 10^{-8} au; the convergence criteria for the largest component of the displacement gradient vector and the update step length were set to 10^{-5} au. For computational efficiency, the highest applicable symmetry constraint was applied during optimization.

Solvation effects were taken into account using the COSMO[85−88] approach as implemented in ParaGauss.[53] In this model, the solute molecule is placed into a cavity of the solvent, which is simulated by a dielectric continuum with the dielectric constant $\epsilon = 78.39$. The molecular cavity is constructed as a set of overlapping spheres according to the GEPOL algorithm. Detailed information has been provided elsewhere.[53]

3. Results and Discussion

Figure 1 shows the structures of the cis and trans isomers of the actinyl complexes studied in this work with fluoro (Figure 1a), chloro (Figure 1b), hydroxo (Figure 1c), and aqua (Figure 1d) ligands. Trans isomers assume a square bipyramidal distribution of two axial actinyl oxygens and four equivalent equatorial ligands. These structures exhibit D_{4h} symmetry for X = F, Cl, and H_2O. The aqua ligands are coordinated perpendicular to the equatorial plane of the actinyl (Figure 1d, left panel). For X = OH, the *trans*-$[AnO_2(OH)_4]^{2-}$ species with alternating "up" and "down" hydroxo groups shows D_{2d} symmetry[49] (Fig, 1c, left panel). This conformer corresponds to the "trans 2 up, 2 down" structure found by Schreckenbach et al.[49] as most stable and also assumed by Vallet et al.[13] and Bolvin et al.[20] in their theoretical studies. The cis isomers do not maintain the perfect square bipyramidal distribution; the observed distortion depends on the nature of the ligands. For these isomers we will differentiate between ligands that lie approximately in the plane defined by the actinyl moiety, "equatorial" or X_e, and those that are out of this plane,"out-of-plane", "axial", or X_a. For X = F, Cl, and H_2O, the cis complexes feature C_{2v} symmetry, with the 2-fold rotational axis bisecting the angle formed by an actinyl moiety. We considered only the lowest-energy cis isomer of $[AnO_2(OH)_4]^{2-}$ identified in refs 3 and 49, which has a symmetry as low as C_s.

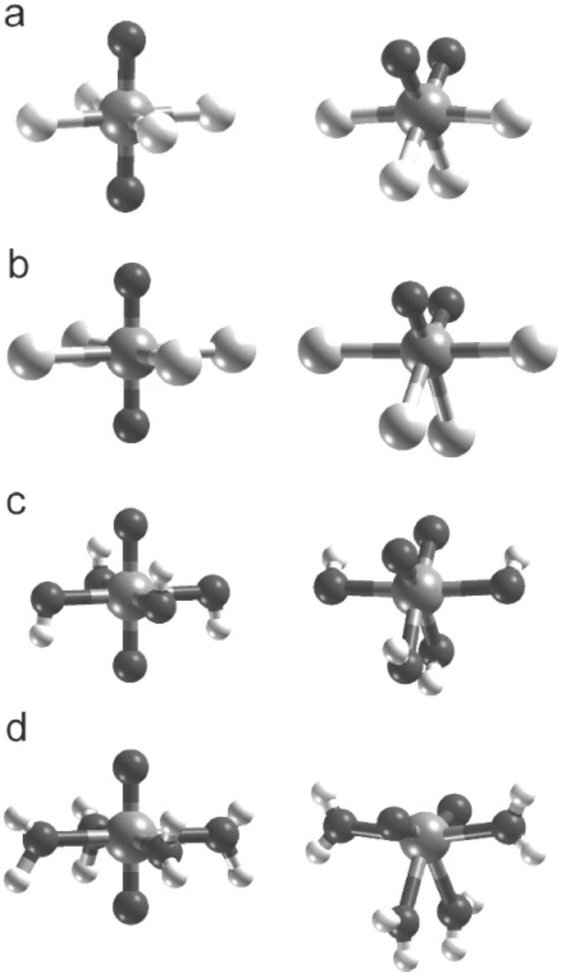

Figure 1. Calculated structures of trans and cis isomers of fluoro (a, $n = -2$), chloro (b, $n = -2$), hydroxo (c, $n = -2$), and aqua (d, $n = +2$) actinyl complexes $[AnO_2X_4]^n$ in the gas phase.

3.1. Structures. Full geometry optimizations were performed for cis and trans isomers of all actinyl complexes of interest, without and with inclusion of solvation effects. Before describing each complex in detail, we point to some general features observed. As can be seen from Tables 1−4, computed bond distances are systematically about 0.05 Å longer than the experimental values, a consequence of having chosen the exchange-correlation functional PBEN (see above).[76] To explicitly demonstrate this, we performed a VWN optimization of the *trans*-$[UO_2Cl_4]^{2-}$ species, and we obtained shorter bond lengths both for the U=O (1.790 vs 1.806 Å with the PBEN functional) and U−Cl distances (2.677 vs 2.773 Å). Despite this known limitation, the PBEN functional is adequate for a systematic study, with respect to both structural and energetic aspects. Earlier works provide sufficient evidence in this direction.[15,53,89,90] The variation of the geometry caused by long-range solvation effects within the VWN description is similar to that obtained with the PBEN functional.

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Table 1. Geometric Parameters of the trans and cis Isomers of $[UO_2F_4]^{2-}$ and $[NpO_2F_4]^{2-}$ in the Gas Phase and in Aqueous Solution (aq, values in italics)[a]

trans

		An═O	An−F
U	calcd	1.856	2.254
		1.854	*2.229*
	calcd[b]	1.823	2.259
	calcd[c]	1.870	2.276
	calcd[d]	1.847	2.205
	calcd[e]	1.762	2.207
	calcd[f]	1.754	2.258
	exptl, cryst[g]	1.779−1.804	2.244 (terminal)
			2.368 (bridging)
	exptl, aq[h]	*1.80*	*2.26*
Np	calcd	1.839	2.234
		1.835	*2.207*

cis

		An═O	$\mathrm{An{-}F_e/An{-}F_a}$	O═An═O	$\mathrm{F_e{-}An{-}F_e/}$ $\mathrm{F_a{-}An{-}F_a}$
U	calcd	1.906	2.206/2.256	95	87/187
		1.903	*2.176/2.230*	*95*	*87/185*
	calcd[b]	1.887	2.177, 2.266		
	calcd[c]	1.932	2.207, 2.290		
	calcd[d]	1.895	2.168, 2.202		
Np	calcd	1.893	2.180/2.240	95	87/188
		1.888	*2.151/2.214*	*95*	*88/187*

[a] Distances in angstroms; angles in degrees. [b] Hay-Wadt ECP, B3LYP, ref 3. [c] Hay-Wadt ECP, BLYP, ref 3. [d] FCQR BLYP, ref 3. [e] Hay-Wadt ECP, HF, ref 52. [f] Stuttgart ECP, HF, ref 12. [g] XRD, $[U_2O_4F_8]^{4-}$ dimer, ref 94. [h] EXAFS, $[UO_2F_4(H_2O)]^{2-}$ in aqueous solution, ref 12.

Table 2. Geometric Parameters of the trans and cis Isomers of $[UO_2Cl_4]^{2-}$ and $[NpO_2Cl_4]^{2-}$ in the Gas Phase and in Aqueous Solution (aq, values in italics)[a]

trans

		An═O	An−Cl
U	calcd	1.806	2.773
		1.810	*2.726*
	calcd[b]	1.780	2.784
	calcd[c]	1.826	2.811
	calcd[d]	1.799	2.730
	calcd[e]	1.80	2.68
	exptl, cryst[f−p]	1.72−1.81	2.62−2.71
	exptl, aq[q]	*1.760(6)*	*2.67(1)*
Np	calcd	1.789	2.755
		1.793	*2.706*

cis

		An═O	$\mathrm{An{-}Cl_e/An{-}Cl_a}$	O═An═O	$\mathrm{Cl_e{-}An{-}Cl_e/}$ $\mathrm{Cl_a{-}An{-}Cl_a}$
U	calcd	1.857	2.736/2.776	98	88/178
		1.861	*2.688/2.730*	*98*	*88/180*
	calcd[b]	1.813	2.746/2.818	122	
	calcd[c]	1.874	2.747/2.839	107	
	calcd[d]	1.843	2.702/2.734	98	
Np	calcd	1.843	2.712/2.767	99	89/176
		1.846	*2.672/2.718*	*98*	*89/174*

[a] Distances in angstroms; angles in degrees. [b] Hay-Wadt ECP, B3LYP, ref 3. [c] Hay-Wadt ECP, BLYP, ref 3. [d] FCQR BLYP, ref 3. [e] ZORA,VWN, ref 51. [f] XRD, $[N(CH_3)_4]$ $[UO_2Cl_4]$, refs 27, 28. [g] XRD, $Rb_2[UO_2Cl_4]{\cdot}2H_2O$, ref 27. [h] XRD, $[Ca(OH_2)_3(15\text{-crown-}5)][UO_2Cl_4]$, ref 30. [i] XRD, $[(H_5O_2)(H_9O_4)(\text{benzo-15-crown-5})_2][UO_2Cl_4]$, ref 31. [j] XRD, $[(H_5O_2)_2(18\text{-crown-}6)][UO_2Cl_4]$, ref 31. [k] XRD, $[K(18\text{-crown-}6)]_2[UO_2Cl_4]$, ref 32. [l] XRD, $[Na(15\text{-crown-}5)]_2[UO_2Cl_4]$, ref 32. [m] XRD, $[Li(12\text{-crown-}4)]_2[UO_2Cl_4]$, ref 32. [n] XRD, $[C_3N_2H_5^+]_2[UO_2Cl_4]^{2-}$, ref 33. [o] XRD, $[LH]_2[UO_2Cl_4]{\cdot}2H_2O$ (L = 2,6-diacetylpyridine-bisphenyl hydrazone), ref 27. [p] XRD, $Cs_2[UO_2Cl_4]$, refs 27, 34. [q] EXAFS, ref 35.

Longer An═O and shorter An−X distances than those in the corresponding trans isomers are common for all cis isomers. Deviations from perfect orthogonality in the actinyl angle O═An═O and the X_e−An−X_e angle between the in-plane ligands observed in cis isomers are also interesting. For anionic ligands, the angle O═An═O exceeds 90° at most by 15°. The X_e−An−X_e and X_a−An−X_a angles do not deviate from 90° and 180°, respectively, by more than ±10°. For the complexes with neutral aqua ligands, the behavior is different as we will discuss later in more detail. The O═An═O angle opens considerably (145−147°), while the X_e−An−X_e and X_a−An−X_a angles are smaller in comparison to other cis isomers. Modeling long-range effects from the presence of an aqueous environment (with the COSMO approach) results in shorter An−X bond distances for both types of isomers. With the inclusion of solvation in the models, the An═O almost do not vary for X = F, Cl, OH, and elongate for X = H_2O (<2.5%).

Neptunyl complexes follow the general trends of uranyl complexes. The similarity of the geometries is striking indeed: An═O and An−X distances of neptunyl complexes are only 1% shorter than those of their uranyl congeners. Our results are consistent with almost identical values for the ionic radii of U and Np in oxidation state VI, 0.87 and 0.86 Å, respectively.[91] The close similarity between U and Np complexes can be rationalized with the character of the orbital occupied by the additional f electron of Np. This is essentially an atomic f orbital which for symmetry reasons does not overlap with the orbitals of ligands in a pseudo-octahedral arrangement. The HOMO orbital of the neptunyl complexes, where the extra electron is located, always has at least a 90% f_{Np} character, as shown by an analysis of the effective electronic configuration of the $[AnO_2X_4]^n$ species. This unpaired electron, consequently, does not participate directly in the bonding, hence it does not affect the geometries.

3.1.1. Fluoro Complexes, $[AnO_2F_4]^{2-}$. $[UO_2F_4]^{2-}$. The geometric parameters of *trans*- and *cis*-$[UO_2F_4]^{2-}$ are collected in Table 1 (Figure 1a). Bending of the O═U═O angle, which leads to the cis species, is associated with an elongation of the U═O bonds by 0.05 Å with respect to the trans isomer. Concomitantly, the U−F_e distances shrink by about the same amount, whereas the U−F_a distances remain practically unchanged. The cis isomer (Figure 1a, right) has the shape of a slightly distorted octahedron, with O═U═O and F_e−U−F_e angles of 95 and 87°, respectively. The F_a−U−F_a angle is 173° and is bent toward the two F_e ligands. Solvation effects hardly change bond angles; they shorten the U═O bonds of the cis and trans isomers very slightly, by 0.002−0.003 Å, and U−F distances more noticeably, by 0.025−0.030 Å. Overall, solvation affects distances by at most 1.5%.

A direct comparison to experiment is hampered by the fact that the uranyl coordination number of fluorides is five.

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Table 3. Geometric Parameters of the trans and cis Isomers of $[UO_2(OH)_4]^{2-}$ and $[NpO_2(OH)_4]^{2-}$, in the Gas Phase and in Aqueous Solution (aq, values in italics)[a]

trans

		An═O	An−O(H)	O−H	An−O−H
U	calcd	1.879	2.321	0.975	100
		1.880	*2.288*	*0.973*	*109*
	calcd[b]	1.842	2.334		
	calcd[c]	1.892	2.360		
	calcd[d]	1.867	2.302		
	calcd[e]	1.841	2.309	0.965	
	calcd[f]	1.763	2.336	0.941	112
		1.768	*2.299*	*0.951*	*118*
	exptl, cryst[g]	1.82(1)	2.26(2)		
	exptl, aq[h]	*1.82(2)*	*2.24(1)*		
	exptl, aq[i]	*1.83(0)*	*2.26(5)*		
Np	calcd	1.858	2.316	0.975	99
		1.857	*2.282*	*0.974*	*106*
	calcd[j]	1.74	2.31		
		1.74	*2.27*		
	calcd[k]	1.83	2.29		
		1.83	*2.25*		
	calcd[l]	1.86	2.29		
	exptl, aq[m]	*1.82(2)*	*2.21(3)*		

cis

		An═O	An−O_e/An−O_a	O−H_e/O−H_a	O═An═O	O_e−An−O_e/O_a−An−O_a	An−O_e−H/An−O_a−H
U	calcd	1.930, 1.924	2.275, 2.287/2.323	0.977, 0.974/0.974	104	81/172	98, 96/99
		1.927, 1.933	*2.245, 2.222/2.293*	*0.976, 0.973/0.973*	*102*	*83/177*	*104, 111/109*
	calcd[b]	1.874, 1.870	2.267, 2.320/2.349		128		
	calcd[c]	1.923, 1.918	2.301, 2.345/2.374		126		
	calcd[d]	1.926, 1.894	2.271, 2.237/2.299		104		
Np	calcd	1.913, 1.910	2.253, 2.257/2.309	0.978, 0.975/0.975	100	85/176	98, 96/98
		1.912, 1.918	*2.218, 2.216/2.277*	*0.977, 0.974/0.973*	*96*	*86/179*	*104, 110/108*

[a] Distances in angstroms; angles in degrees. [b] Hay-Wadt ECP, B3LYP, refs 3, 49. [c] Hay-Wadt ECP, BLYP, ref 3. [d] FCQR, BLYP, ref 3. [e] Stuttgart ECP, B3LYP, ref 14. [f] Stuttgart ECP, HF, CPCM solvation effects in parentheses, ref 12. [g] XRD, ref 26. [h] EXAFS, ref 23. [i] EXAFS, ref 24. [j] Stuttgart ECP, ROHF, CPCM solvation effects in parentheses, ref 20. [k] Stuttgart ECP, B3LYP, CPCM solvation effects in parentheses, ref 20. [l] ZORA, B3LYP, ref 6. [m] EXAFS, ref 47.

Table 4. Geometric Parameters of the trans and cis Isomers of $[UO_2(H_2O)_4]^{2+}$ and $[NpO_2(H_2O)_4]^{2+}$, in the Gas Phase and in Aqueous Solution (values in italics)[a]

trans

		An═O	An−O(H)	O−H	An−O−H
U	calcd	1.768	2.458	0.980	127
		1.783	*2.402*	*0.978*	*126*
	calcd[b]	1.746	2.479		
		1.748	*2.428*		
	calcd[c]	1.776	2.430		
Np	calcd	1.752	2.432	0.980	127
		1.771	*2.335*	*0.980*	*126*

cis

		An═O	An−O_e/An−O_a	O−H_e/O−H_e	O═An═O	O_e−An−O_e/O_a−An−O_a	An−O_e−H/An−O_a−H
U	calcd	1.774	2.540/2.512	0.980, 0.978/0.980, 0.978	145	70/166	116, 138/125, 129
		1.794	*2.456/2.451*	*0.977, 0.978/0.977, 0.977*	*145*	*67/166*	*118, 135/125, 128*
Np	calcd	1.768	2.536/2.500	0.980, 0.980/0.980, 0.978	147	70/175	117, 137/125, 129
		1.785	*2.449/2.437*	*0.977, 0.977/0.977, 0.977*	*148*	*67/177*	*119, 134/124, 128*

[a] Distances in angstroms; angles in degrees. [b] Hay-Wadt ECP, BLYP, U═O distances were not optimized, ref 18. [c] Hay-Wadt ECP, B3LYP, ref 7.

Thus, the formal $[UO_2F_4]^{2-}$ species in solution actually contains an aqua ligand in the first coordination shell,[12] $[UO_2F_4(H_2O)]^{2-}$. In the experimentally characterized structures of solid fluoride systems, the coordination number is five, as well;[92−94] crystal structures often contain coordinated (inner sphere) water or bridging F atoms connecting UO_2F_5 pentagonal bipyramids, like in the dimer $[U_2O_4F_8]^{4-}$ occurring in $(C_4N_2H_{12})UO_2F_4$·$3H_2O$ molecular phases.[94] We can nevertheless compare our calculated U−F bond lengths to the terminal ones of the $[U_2O_4F_8]^{4-}$ dimer and also to the EXAFS values for $[UO_2F_4(H_2O)]^{2-}$ in aqueous solution, which agree with each other within 0.02 Å. Our computed

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U═O distances are too long by 0.06 Å; the U−F distances are only slightly overestimated, by 0.01−0.02 Å. (This finding does not go against the tendency of the PBEN functional to overestimate bond lengths because a longer bond is expected for pentacoordinated uranyl compared to tetracoordinated systems.)

The theoretical field offers several studies on square bipyramidal *trans*-$[UO_2F_4]^{2-}$ for direct comparison (Table 1). Data from HF pseudopotential calculations[12,52] show that the U═O distances were significantly underestimated, as expected for this method. Schreckenbach et al.[3] computed the geometry of both isomers in the gas phase with pseudopotential approaches employing large-core pseudopotentials proposed by Hay and Martin[57,59] (HMLC B3LYP and HMLC BLYP) and a frozen-core quasi-relativistic[55,56] FCQR BLYP. The FCQR BLYP method was shown on other complexes to give the best agreement with experimental geometric parameters;[3] still, the bond lengths predicted with this approach seem to be overestimated even more than by the current PBEN calculations.

$[NpO_2F_4]^{2-}$. The structures of *trans*- and *cis*-$[NpO_2F_4]^{2-}$ are not very different from those of $[UO_2F_4]^{2-}$. As shown in Table 1, relevant distances are only 1% shorter than in $[UO_2F_4]^{2-}$ and bending of the O−Np−O angle is again associated with an elongation of the Np═O bonds (0.054 Å) relative to the trans isomer. Np−F_a bonds elongate slightly, while the Np−F_e bonds shrink by 0.054 Å. The O−Np−O and F_e−Np−F_e angles in the cis species are 95° and 87°, respectively, the same as those obtained for the analogous uranyl complex. The F_a−Np−F_a angle is close to 180°, with a slight bending in the direction of the equatorial fluoro ligands.

Solvation has an almost negligible effect on the Np═O distances; they shorten by 0.004−0.005 Å. The Np−F distances decrease by 0.026−0.029 Å. Overall the changes in the bond distances caused by solvation are never more than 1.5%.

We did not find any experimental or theoretical data on the $[NpO_2F_4]^{2-}$ species. We expect that our computed bond lengths are overestimated by ∼0.05 Å because of the PBEN functional.

3.1.2. Chloro Complexes, $[AnO_2Cl_4]^{2-}$. $[UO_2Cl_4]^{2-}$. Table 2 compares the current results to the relevant experimental and theoretical values for the $[UO_2Cl_4]^{2-}$ structure from the literature. Most experimental structure data derive from X-ray analysis of crystal structures. In these structures the U═O and the U−Cl distances vary within wide ranges, between 1.72−1.81 and 2.62−2.71 Å, respectively. Compared to other anionic ligands, F^- and OH^-, the U−Cl distances are about 20% longer, consistent with the larger radius of Cl. As shown by our calculations, the O═U═O angle of *cis*-$[UO_2Cl_4]^{2-}$ is 3° larger than that in the fluoro complex, but the Cl_a ligands bend further toward the uranyl oxygens, reducing the steric repulsion. When the cis and trans isomers of the chloro complex are compared, the U═O distances of the former are again longer, by 0.051 Å. Just like in the fluoro complexes, the axial U−Cl distances, U−Cl_a, are about the same as the U−Cl distances of the trans isomer, while the equatorial bonds, U−Cl_e, are 0.037 Å shorter in the cis isomer.

The inclusion of solvation effects through a continuum model weakly elongates the U═O bonds (0.004 Å) and shortens the U−Cl bonds by 0.046−0.048 Å for both isomers, but the obtained distances are 0.05 Å longer than those found experimentally for aqueous solutions of $[UO_2Cl_4]^{2-}$. This discrepancy can again be attributed to a systematic overestimation of distances by the PBEN functional. The LDA functional VWN gives the gas-phase U═O and U−Cl distances at 1.790 and 2.687 Å in very good agreement with values found experimentally for this species in aqueous solution.

Other theoretical values are available from refs 3 and 51. Schreckenbach et al.[3] provide HMLC B3LYP, HMLC BLYP, and FCQR BLYP data on both isomers in the gas phase. As for the $[UO_2F_4]^{2-}$ species, the bond lengths of the ECP calculations are slightly longer (HMLC B3LYP) or shorter (HMLC BLYP) than our calculated results, while the FCQR BLYP results are in quite good agreement with ours. Bond lengths computed by Bridgeman and Cavigliasso,[51] with VWN and ZORA, agree best with the experimental values in aqueous solutions.

$[NpO_2Cl_4]^{2-}$. To our knowledge, no theoretical or experimental data for the $[NpO_2Cl_4]^{2-}$ species have been reported to date. The results of our calculations, Table 2, show a 1% shortening upon going from U to Np, as observed above for the analogous fluoro complex. As for uranyl complexes, the Np−Cl distances are 20% longer than the corresponding values for the anionic F^- and OH^- ligands. When going from the trans to the cis isomer, Np═O bonds elongate by 0.054 Å, while Np−Cl_e bonds contract by 0.043 Å, and the Np−Cl_a bonds slightly elongate. Solvation induces a minimal elongation of Np═O distances (0.003−0.004 Å) and shortens Np−Cl bonds by ∼0.05 Å.

3.1.3. Hydroxo Complexes, $[AnO_2(OH)_4]^{2-}$. $[UO_2(OH)_4]^{2-}$. EXAFS measurements[23,24,26] and quantum chemical calculations[13,14,23] support the formation of a tetracoordinated $[UO_2(OH)_4]^{2-}$ in strong alkaline solutions.

In *trans*-$[UO_2(OH)_4]^{2-}$, the hydroxyl oxygens bonded to the uranium atom are located on the equatorial plane, but the H atoms can orient themselves in different directions (Figure 1c, left). Pyykkö et al.[52] chose to study the trans D_{4h} conformer, where the U, O, and H were located on a line. Such a linear M−O−H arrangement is not common for transition metal complexes, although for some complexes of uranium, $[UO_2(H_2O)_4(OH)]^+$,[16] $UO(OH)^{2+}$, and $U(OH)_2^{2+}$,[15] a linear U−O−H fragment was predicted theoretically. Yet, unconstrained optimization of the U−O−H angle in tetrahydroxo complexes, $[UO_2(OH)_4]^{2-}$, renders this fragment bent.[14,23,49]

Schreckenbach et al.[49] studied four conformers of the trans isomer that differed by the relative positions of the H atoms with respect to the equatorial plane, defined by the corresponding four oxygen centers: "2 up, 2 down" with two OH groups pointing up adjacent (cis) or located across the diagonal (trans), "3 up, 1 down", and "all up". Their HMLC B3LYP results indicate that the most stable conformers correspond to the two “2 up, 2 down” species, among which the “across” conformer (Figure 1c, left) is only 0.1 kcal/mol more stable than the “adjacent” conformer (not shown in Figure 1).[49] This difference of stability is so small that before choosing one or the other, we decided to optimize both of them in the gas phase. Our all-electron relativistic PBEN results predicted the “across” conformer (D_{2d}) to be 3.5 kcal/mol more stable than the “adjacent” conformer. One can easily rationalize this result by a larger electrostatic dipole repulsion between the neighbor OH groups in the “adjacent” conformer. The geometric parameters of these two conformers are very similar, except for the differently orientated OH groups. Therefore, we will restrict the following discussion to the “across” isomer.

For the cis isomer, we decided to study the conformation predicted in ref 49 to be more stable by at least 1.2 kcal/mol with respect to other cis structures (Figure 1c, right). This conformer exhibits C_s symmetry.

Table 3 summarizes our optimized geometries along with other theoretical results and experimental data obtained from crystal structures or measured in aqueous solutions. Calculated distances again show an elongation of the U═O bonds by 0.03−0.05 Å when going from the trans to the cis isomer. The U−O(H) distances follow the same trend as the U−F and U−Cl bonds in $[UO_2F_4]^{2-}$ and $[UO_2Cl_4]^{2-}$. The U−O$_a$ distances in the cis isomer remain almost unchanged with respect to the U−O(H) distances of the trans isomer, whereas the U−O$_e$ distances shrink by ~0.04 Å. The O═U═O angle of the cis species, 104°, is larger than in the corresponding fluro and chloro complexes. Inclusion of solvation results in a minimal change of the U═O distances and a notable shortening, 0.03−0.07 Å, of the U−O(H) distances.

A comparison to available experimental data of $[UO_2(OH)_4]^{2-}$ in aqueous solution confirms the by now familiar overestimation of distances associated with the functional employed. Our calculated U═O distances are 0.05−0.06 Å too long, and the U−O(H) distances are also overestimated, by 0.03−0.05 Å.

Earlier theoretical work on the cis and trans complexes was done by Schreckenbach et al.,[3,49] whose gas-phase results obtained with various density functionals and with a large-core pseudopotential basis for U, also seem to overestimate the bond lengths. A more recent study of a trans complex by the same group,[14] employing a small-core RECP and a B3LYP functional, showed a significantly improved agreement with experiment.

While most computational studies ignored effects of solvation, Vallet et al.[12] computed the D_{2d} *trans*-$[UO_2(OH)_4]^{2-}$ species employing the COSMO model.[87] In their work, the geometry optimization was performed at the HF level, employing the small-core Stuttgart pseudopotential for the uranium atom.[60] The resulting solvation effects comprise an elongation of the U═O bond by 0.005 Å, a shortening of the U−O(H) bond by 0.037 Å, an elongation of the O−H distance by 0.010 Å, and an opening of the U−O−H angle by ~6°. The two first values, as well as the opening of the U−O−H angle, agree very well in magnitude and sign with the effects of solvation found in this work for the *trans*-$[UO_2(OH)_4]^{2-}$ species. With respect to the O−H distance, the elongation of 0.010 Å calculated by Vallet et al. contrasts strongly with our results, which predict a slight shortening of 0.002 Å.

$[NpO_2(OH)_4]^{2-}$. In analogy to tetrahydroxouranyl, the $[NpO_2(OH)_4]^{2-}$ species were optimized with the D_{2d} and C_s symmetry constraints for the trans and the cis isomers, respectively. Experimentally, tetracoordinated *trans*-$[NpO_2(OH)_4]^{2-}$ was characterized by EXAFS[47] and by quantum-chemical calculations.[20] Our calculated distances (Table 3) are 0.04−0.07 Å longer than the experimental values. The best agreement with experiment is achieved at the small-core ECP B3LYP level.[20] Solvation has a minimal effect on the Np═O distances and shortens the Np−O(H) distances by 0.03−0.04 Å for the two isomers, similar to what was found for the uranyl congener. The effects of solvation observed for the trans isomer in the present work agree with the results of Bolvin et al.,[20] where solvation leaves the Np═O distances unaffected and shortens the Np−O(H) distances by ~0.04 Å. The similarity between the computed structures of $[UO_2(OH)_4]^{2-}$ and $[NpO_2(OH)_4]^{2-}$ is also evident when one compares the ECP B3LYP results,[14,20] which show a slight shortening (<1%) of the bond lengths in the tetrahydroxoneptunyl relative to the corresponding uranyl complex. Comparing the cis and trans isomers, we again observe an elongation of the Np═O distance by ~0.05 Å and a shrinking of Np−O$_e$ distances by ~0.06 Å in the cis isomers. The O═Np═O angle (100°) of the cis isomer is larger than that in the corresponding fluoro and chloro complexes, as in *cis*-$[UO_2(OH)_4]^{2-}$.

3.1.4. Aqua Complexes, $[AnO_2(H_2O)_4]^{2+}$. $[UO_2(H_2O)_4]^{2+}$. Despite established crystal structures with pentacoordinated uranyl,[43,95] several EXAFS measurements of $[UO_2(H_2O)_n]^{2+}$ in solution predicted coordination numbers below five.[23,95] However, one may argue that the coordination number cannot be determined with high precision in EXAFS.[23] Neuefeind et al.[42] recently reported an X-ray scattering measurement, where the electron density on the equatorial ligands could be best interpreted assuming an equilibrium between four and five coordinated aqua ligands. Thus, although $[UO_2(H_2O)_5]^{2+}$ is likely to be the dominating species, the tetracoordinated complex $[UO_2(H_2O)_4]^{2+}$ probably coexists in aqueous solutions at a small percentage (6−21%).[42] These equatorial aqua ligands are labile and interchange with the aqueous media, whereas the two oxygen centers of uranyl are inert with respect to substitution.[96,97]

Quite a few theoretical studies[7−9,15−18,53] computed the effects of hydration on UO_2^{2+} considering 4, 5, and 6 water molecules in the equatorial plane. On the basis of solvation energetics, several authors identified the pentacoordinated complex as energetically preferred.[8,10,15,16] Here, we focus on tetracoordinated uranyl, although we are not able to

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directly compare experimental and theoretical geometries for this complex.

In contrast to the anionic ligands, OH^-, F^-, and Cl^-, considered above, aqua ligands are electrostatically neutral, and therefore, one expects the complexes to feature different properties. Indeed, the uranyl U═O distances (Table 4) only elongate by 0.006 Å when going from the trans to cis isomer, almost an order of magnitude less than for the anionic ligands (Tables 1−3). The uranyl angle of the cis isomer deviates considerably more from 90°. The cis structure appears to be quite distorted from the square-bipyramidal geometry, with an O═U═O angle of 145°, now being much closer to the standard linear motif. The aqua ligands lie at larger distances from the uranium atom than the OH ligands, and the elongation of the U−O(H_2) bond from the trans to the cis isomer is considerable, 0.054 and 0.082 Å. When solvation is taken into account via a continuum model, U═O distances elongate more, 0.015−0.020 Å, than in complexes with anionic ligands, where the elongation did not exceed 0.005 Å. In contrast, U−O(H_2) distances are notably shortened, by 0.05−0.08 Å.

$[NpO_2(H_2O)_4]^{2+}$. Similarly to the uranyl tetra-aqua complexes, significant differences are observed in this cationic species with respect to the complexes with anionic ligands. Whereas Np═O distances elongate only by 0.016 Å when comparing the cis to the trans isomer, the distances between the oxygen atom of the water molecules and the neptunium center elongate by either 0.068 or 0.104 Å for axial or equatorial ligands, respectively. As indicated for *cis*-$[UO_2(H_2O)_4]^{2+}$, the O═Np═O angle (147°) of *cis*-$[NpO_2(H_2O)_4]^{2+}$ deviates significantly from a right angle, in contrast to the cis isomers with anionic ligands where it was 95−100° (Table 4). Solvation elongates the Np═O distances by about the same amount as in the uranyl complexes, 0.017−0.0019 Å. The Np−O(H_2) distances are notably shortened because of solvation: the *cis*-Np−O_a(H_2), *cis*-Np−O_e(H_2), and *trans*-Np−O(H_2) distances shrink by 0.063, 0.087, and 0.097 Å, respectively.

3.1.5. Comparison of Geometries. In general, one observes some notable differences between the geometric trends of anionic complexes and complexes with neutral aqua ligands. Particularly, in cis isomers of anionic complexes, the O═U═O angle remains close to 90°, whereas in the aqua complexes it opens to 145°. Also, note the lengthening of the An═O bond, <0.02 Å, from the trans to cis isomer of $[AnO_2(H_2O)_4]^{2+}$ compared to ∼0.05 Å in the case of $[AnO_2X_4]^{2-}$ complexes. The An−O(H_2) bonds in aqua complexes are 0.1−0.2 Å longer than in the corresponding hydroxo compounds. All of these features are directly related to a considerably weaker binding of the neutral aqua ligands than that of the anionic ligands, F^-, Cl^-, and OH^-, see section 3.3.

3.2. Relative Stability of the Cis and Trans Isomers. It is well-known from theory and experiment that uranyl, UO_2^{2+}, in contrast to the isoelectronic ThO_2, has a linear structure because of the different relative ordering of the 5f and 6d levels.[98] In the present context, one may very well ask whether the presence of ligands can stabilize a bent (cis) geometry of the UO_2^{2+} moiety. Schreckenbach et al.[3] have shown that cis complexes of uranyl, $[UO_2X_4]^{2-}$, X = F, Cl, OH, are stable local minima, 10−30 kcal/mol above the corresponding trans isomers. Our results corroborate that finding: we found that all trans isomers, for uranium as well as for neptunium, were more stable than the corresponding cis isomers, regardless of the nature of the ligand, anionic or neutral. The cis−trans energy differences range from 13 to 31 kcal/mol (Table 5).

Table 5. Calculated Relative Stability of *cis*- Compared to *trans*-$[AnO_2X_4]^n$ Complexes in the Gas Phase and in Aqueous Solution (aq)[a]

		F	Cl	OH	H_2O
n		−2	−2	−2	+2
$[UO_2X_4]^{2+/2-}$	gp	13.2	20.6	13.6	30.9
	aq	13.0	19.4	12.9	24.1
	ECP B3LYP[b,c]	23.5	30.3	18.0	
	ECP BLYP[c]	14.7	20.5	10.8	
	FCQR BLYP[c]	13.7	20.7	15.3	
$[NpO_2X_4]^{2+/2-}$	gp	14.5	21.1	8.5	29.2
	aq	14.3	19.7	6.6	30.0

[a] Energies in kilocalories per mole. [b] Ref 49. [c] Ref 3.

Inspection of the results in the gas phase reveals that the energy difference between the trans and cis isomers depends more on the nature of the ligand than on the actinide atom. For aqua ligands, the cis−trans difference of stability is 1.7 kcal/mol smaller for the neptunyl complexes than for the uranyl complexes. In contrast, for the F^- and Cl^- ligands, the cis−trans difference is 0.5−1.2 kcal/mol larger for neptunyl than for uranyl. The only large cis−trans difference was found for OH^- ligands, which for the neptunyl is 5 kcal/mol in the gas phase and 6 kcal/mol in solution smaller than that for uranyl.

Effects of solvation were not considered previously. We found that solvation hardly affects the cis−trans stability difference. The solvation energies of the cis and trans structures differ by less than 1 kcal/mol; small differences are due to the fact that trans structures have no dipole moment at all because of symmetry, whereas the cis structures may have one causing a small increase of solubility with respect to the trans structures. The An(VI) centers of the complexes have charges of ∼1 e in anionic complexes (∼1.5 e in aqua complexes), while the rest of the charge is almost equally distributed over the actinyl oxygens and the ligands, leading to a charge distribution with low dipole and multipole moments. Table 5 shows that in solution, the cis−trans difference decreases only slightly for anionic ligands, from 13.2 to 13.0 kcal/mol for $[UO_2F_4]^{2-}$, from 20.6 to 19.4 kcal/mol for $[UO_2Cl_4]^{2-}$, and from 13.6 to 12.9 kcal/mol for $[UO_2(OH)_4]^{2-}$. The corresponding changes of values for neptunyl complexes from solvation are, for anionic ligands, from 14.5 to 14.3 kcal/mol for $[NpO_2F_4]^{2-}$, from 21.1 to 19.7 kcal/mol for $[NpO_2Cl_4]^{2-}$, and from 8.5 to 6.6 kcal/mol for $[NpO_2(OH)_4]^{2-}$. That difference is the largest for the aqua complexes, ∼30 kcal/mol in the gas phase. The

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Table 6. Calculated Average Binding Energies[a] Per Ligand of Actinyl Complexes $[AnO_2X_4]^n$ in the Gas Phase and in Aqueous Solution (aq)[b]

n			F −2	Cl −2	OH −2	H_2O +2
trans	$[UO_2X_4]^{2+/2-}$	gp	190	142	194	57
		aq	71	34	78	26
	$[NpO_2X_4]^{2+/2-}$	gp	190	142	193	57
		aq	73	35	77	28
cis	$[UO_2X_4]^{2+/2-}$	gp	187	137	191	49
		aq	68	29	74	20
	$[NpO_2X_4]^{2+/2-}$	gp	187	137	191	50
		aq	69	30	76	21

[a] Determined according to the reaction $[AnO_2X_4]^n \rightarrow AnO_2^{2+} + X^{(n-2)/4}$. [b] Energies in kilocalories per mole.

effect of solvation on the cis−trans difference is small for $[NpO_2(H_2O)_4]^{2-}$, 0.7 kcal/mol, but more substantial for $[UO_2(H_2O)_4]^2$, −6.8 kcal/mol.

3.3. Average Ligand Binding Energies. The average binding energies per ligand, calculated according to

$$[AnO_2X_4]^{2+/2-}{}_{(aq)} \rightarrow AnO_2{}^{2+}{}_{(aq)} + 4\,X^{0/-}{}_{(aq)} \qquad (1)$$

are given in Table 6 along with the corresponding values for the reaction in the gas phase. The first important observation, consistent with the cis−trans differences discussed above, is that the binding energies of the cis complexes are about 4−27% smaller than the corresponding binding energies for the trans isomers. The second and perhaps even more important point is the effect of solvation on the binding energies. Gas-phase data indicate that F^- and OH^- ligands have approximately the same average binding energies, 190 kcal/mol, followed by Cl^- ligands, 140 kcal/mol. Aqua ligands were found to bind weaker, with energies of ∼55 kcal/mol, consistent with the expected additional charge separation energy if X is negatively charged in eq 1. Solvation drastically changes these values. Whereas for OH^- and F^- the binding energies reduce to almost a third of their gas-phase values, about 70 kcal/mol, the Cl^- binding energies reduce to a fourth of their gas-phase value, 33 kcal/mol. In the case of water, the average binding energies reduce to half of their value in the gas phase, about 25 kcal/mol.

This large reduction of binding energies for anionic ligands in aqueous solution is the result of the fact that free anions are stabilized in solution by hydration energies of ∼100 kcal/mol, whereas neutral water molecules gain only a few kcal/mol. Thus, reaction 1 becomes significantly less endothermic in solution for $X = F^-$, Cl^-, and OH^-. Ligand bonds of chloride ions are the most dramatically weakened because the U−Cl distance (Table 2) and thus the effective radius of the complex are larger; hence the solvation energy of $[UO_2Cl_4]^{2-}$ is smaller. The order of stabilities, $OH^- > F^- \gg Cl^-$, obtained in our work agrees with that determined experimentally on the basis of the stability constants of these species.[54] Last, the substitution of U by Np does not significantly affect the binding energies per ligand, at most 2−3 kcal/mol.

3.4. Charge Distribution. We briefly comment on the general qualitative characteristics common to the uranyl and neptunyl cis and trans complexes considered. The charge distributions of the complexes, derived with a Mulliken analysis, are presented in Table 7 along with the atomic charges of the free UO_2^{2+} and NpO_2^{2+} species. Fluorine, chlorine, and hydroxyl ligands accumulate a negative charge, −0.43 e to −0.57 e. The O atoms of the actinyl moieties also exhibit negative charges, −0.38 e to −0.52 e. The charges of the actinide center depend strongly on the nature of the ligands. Actinide centers in hydroxo complexes exhibit a lower charge (0.79 e) than in complexes with fluoro ligands (0.98 e). Cl^- ligands withdraw the largest amount of electron density; thus, the actinide center carries a higher charge, 1.07 e, than in the F^- and OH^- complexes.

Table 7. Comparison of Mulliken Charges (e) in trans and cis Actinyl Complexes $[AnO_2X_4]^n$, An = U, Np; $X = F^-, Cl^-, OH^-, H_2O$[a]

	X	*q*(An)	*q*(O)	*q*(X), *q*(X_e)/*q*(X_a)
UO_2^{2+}		2.03 *2.32*	−0.01 *−0.16*	
NpO_2^{2+}		1.98 *2.25*	0.01 *−0.13*	
trans-$[UO_2X_4]^{2+/2-}$	F^-	0.96 *0.92*	−0.49 *−0.49*	−0.46 *−0.49*
	Cl^-	1.08 *0.99*	−0.35 *−0.36*	−0.60 *−0.57*
	OH^-	0.79 *0.80*	−0.50 *−0.52*	−0.45 *−0.44*
	H_2O	1.56 *1.62*	−0.20 *−0.28*	0.21 *0.23*
trans-$[NpO_2X_4]^{2+/2-}$	F^-	0.97 *0.92*	−0.49 *−0.49*	−0.50 *−0.49*
	Cl^-	1.04 *0.94*	−0.34 *−0.35*	−0.59 *−0.56*
	OH^-	0.81 *0.81*	−0.49 *−0.51*	−0.46 *−0.45*
	H_2O	1.51 *1.56*	−0.18 *−0.28*	0.21 *0.25*
cis-$[UO_2X_4]^{2+/2-}$	F^-	0.98 *0.94*	−0.54 *−0.55*	−0.46/−0.50 *−0.44/−0.49*
	Cl^-	1.11 *1.00*	−0.42 *−0.43*	−0.53/−0.60 *−0.49/−0.58*
	OH^-	0.78 *0.79*	−0.53, −0.54 *−0.56, −0.57*	−0.41, −0.42/−0.45 *−0.40, −0.36/−0.44*
	H_2O	1.64 *1.74*	−0.20 *−0.29*	0.20/0.19 *0.23/0.20*
cis-$[NpO_2X_4]^{2+/2-}$	F^-	0.99 *0.94*	−0.53 *−0.54*	−0.46/−0.51 *−0.44/−0.50*
	Cl^-	1.07 *0.96*	−0.40 *−0.42*	−0.53/−0.60 *−0.48/−0.58*
	OH^-	0.79 *0.80*	−0.53, −0.53 *−0.56, −0.57*	−0.42, −0.41/−0.45 *−0.37, −0.40/−0.45*
	H_2O	1.61 *1.68*	−0.18 *−0.26*	0.19/0.18 *0.22/0.19*

[a] Values in italics correspond to solvated species.

The charge distributions of the aqua complexes are qualitatively different. Most of the positive charge is located on the actinide center, 1.60 e, with some positive charge distributed to the aqua ligands, 0.20 e. Although the actinyl oxygen centers accumulate partial negative charges, −0.20 e, their absolute values are smaller than in complexes with anionic ligands. In fact, the charge distributions of actinyl moieties of aqua complexes resemble the situation determined for free actinyl species more than they resemble the charge distributions obtained for complexes with anionic ligands, see Table 7.

For a given isomer or a given set of ligands, analogous complexes of uranium and neptunium have rather similar charge distributions; atomic charges differ by at most 5%. This is again a consequence of the quasi-atomic (nonbonding) character of the additional f electron on Np. Switching between the cis and trans isomers of a given complex affects the charges of the ligands and of the actinyl oxygen centers in a more notable fashion. This statement mainly refers to the cis isomers of the chloro and hydroxo complexes, where the actinyl oxygen centers gain up to 15% electron population compared to the corresponding trans isomers.

Solvent polarization changes the charge distribution in complexes with anionic ligands only slightly. The charges of the actinide center decrease for the F^- and Cl^- complexes and remain almost unaffected for OH^- complexes. For complexes with aqua ligands, the actinide center has the highest positive charge, which becomes even more positive with the inclusion of solvation in the model, whereas the charges associated with the actinyl oxygen centers become more negative.

4. Conclusions

We presented a systematic study of tetracoordinated fluoro, chloro, hydroxo, and aqua complexes of uranyl and neptunyl employing a scalar relativistic gradient-corrected density functional method as implemented in the program ParaGauss.[69] We calculated models for complexes in the gas phase and in aqueous medium to determine the effects of solvation on structures, charge distribution, and binding energies. We also discussed the relative stabilities of the cis and trans isomers in the gas phase and in solution.

The geometric effects of solvation were rather moderate. The An═O bond length of the complexes with anionic ligands hardly changes because of solvation, less than 0.4%. In contrast to this small effect, the An−X ligand bonds typically decrease by 1−2% in an aqueous environment. The effects of solvatation are slightly stronger in neptunyl complexes than they are in their uranyl congeners. Aqua complexes are more affected by the solvent than the anionic complexes: An═O bonds change ∼1.2% and $U-O(H_2)$ distances change up to 4%. This is easy to rationalize because the aqua ligands are more weakly bound, and thus the bond lengths are more easily perturbed by an external Coulomb field.

As expected, the trans isomers in all cases have been shown to be energetically favored over the corresponding cis isomers. The difference of stability primarily depends on the nature of the ligand: it is smaller for complexes with anionic ligands F^-, Cl^-, and OH^- than that for aqua complexes. Solvation reduces the cis−trans energy difference, as well as the average ligand binding energies. For Cl^- ligands, this reduction of the binding energy is particularly strong, in agreement with the low stability found experimentally for $[AnO_2Cl_4]^{2-}$ species in water.[54]

The average binding energies per ligand show how important it is to take a polarizable medium into account. Gas-phase data indicate that F^- and OH^- ligands have approximately the same average binding energy, followed by Cl^- ligands. Aqua ligands were determined to be bound 3.5−4 times less strongly. Solvation changes these values drastically. Ligand binding energies of the anionic complexes are reduced by about 110−120 kcal/mol; the average ligand binding energies of the aqua complexes are reduced by about 30 kcal/mol to half of their gas-phase values. Thus, solvated chloride complexes are expected to easily interchange ligands with an aqueous medium because the binding energies of the chloride ions and the aqua ligand are quite close.

A comparison between the uranyl and neptunyl complexes showed similar behavior qualitatively and quantitatively, revealing the close similarity of these actinides in oxidation state VI.

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