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The Role of Peripheral Alkyl Substituents: A Theoretical Study of Substituted and Unsubstituted Uranyl Isoamethyrin Complexes

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Relativistic density functional theory has been applied to the uranyl(VI) and uranyl(V) complexes of unsubstituted (**1**) and dodeca-alkyl-substituted (**2**) isoamethyrin (hexaphyrin(1.0.1.0.0.0)). The experimentally observed bent conformation in the uranyl(VI) complex of **2** (Sessler, J. L. et al. *Angew. Chem., Int. Ed.* **2001**, *40*, 591) is reproduced accurately by the calculations. It is entirely due to the external alkyl substitutents; the unsubstituted complexes of **1** are planar. Complex geometry and stability are seen to be the result of two competing factors; aromatic stabilization favors a planar conformation of the macrocycle whereas the bending affords a much better fit between the cavity and the uranyl cation. The uranyl(VI) complex of **2** is more stable than that of **1** as a result; the trend is reversed for the larger uranyl(V) cation. An energy decomposition analysis shows that the differences between U^{VI} and U^{V} originate in the different capabilities of these cations for covalent and/or polarization interactions with the ligands rather than in sterical factors.

1. Introduction

Nuclear waste is a major legacy of over 60 years of nuclear weapons production and civil nuclear technology. Its remediation and safe storage constitutes one of the greatest environmental challenges of our time. Solving the nuclear waste problem requires the ability to selectively extract the radioactive actinide element from mixed solutions, in order to prepare it for eventual safe disposal. Selective extraction is also important in the nuclear fission cycle.

One proposed method for selective extraction of actinide elements involves their coordination with polydentate macrocycles.[1] Such systems are attractive because they can in principle be tuned to provide a specific fit to the target cation by changing the size of the cavity or the nature of the donor atoms. Actinide inclusion complexes of macrocycles have been studied experimentally. These include complexes of calixarenes[2,3] and crown ethers.[3−6] Another promising group of macrocycles are expanded porphyrins and related Schiff-base macrocycles.[7,8]

Sessler and co-workers[9] have synthesized and characterized the uranyl(VI) and neptunyl(V) complexes of hexaphyrin(1.0.1.0.0.0) (isoamethyrin). This expanded porphyrin system is initially obtained only in its neutral, free-base form that contains four NH moieties (out of six pyrrol nitrogens). The situation is similar to that of its isomer amethyrin (hexaphyrin(1.0.0.1.0.0)). The neutral, free-base form of the ring is 24-π-electron anti-aromatic. It can be oxidized during the complexation with some metal cations[10] by removing a pair of hydrogen atoms and adding an extra double bond to the conjugated π system. The oxidation leads to 1:1 in-plane actinyl complexes of an aromatic, 22-π-electron two-NH form of the ligand. (The free-base two-NH form is shown in Scheme 1 for unsubstituted **1** and dodeca-alkyl substituted isoamethyrin **2**.) For the substituted isoamethyrin ligand **2**, neptunyl(V) and uranyl(VI) complexes were obtained and

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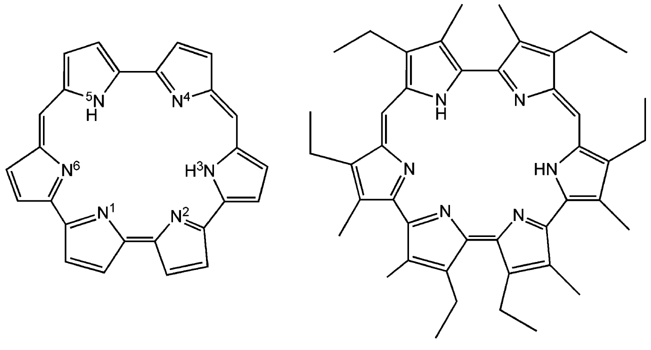
Scheme 1. Schematic Representation of the Unsubstituted (**1**) and Dodeca-alkyl Substituted (**2**) Isoamethyrin Ligands (Oxidized Free-Base Forms of Which Are Shown). The Numeration Scheme for the Nitrogen Donor Atoms Is Shown as Well



1 **2**

characterized by X-ray diffraction.[9] Complexation leads to a significant change in the electronic structure of the ligand. This, in turn, results in a strong change of its UV−vis spectra. Thus, the ring system has been proposed as a colorimetric actinide sensor.[11]

Interestingly, the X-ray structures of the experimentally obtained dodeca-alkyl substituted isoametryrin complexes show a bent conformation of the ligand for both U^{VI} and Np^{V} complexes. In other words, the ring is saddle-type distorted from planarity, even though the ring itself is considered to be aromatic and therefore should be planar. The authors speculate[9] that the bending is "*a result of a need to accommodate a metal center that is slightly too small*." Furthermore, they conclude that the formation of the isoamethyrin complex must be more favorable for the neptunyl(V) cation (due to the larger radius of actinyl(V) ions) because the ligand is less bent than that of the related uranyl(VI) complex.

Theoretical studies of actinide complexes have, for the longest time, been a "*challenge to quantum chemistry*".[12] This is due to the combined difficulties arising from the large number of electrons, correlation effects, and relativity as well as condensed phase (solvent or crystal packing) effects.[13,14] Only recently have accurate methods become available that allow treating realistic (i.e., experimentally relevant) actinide systems by computational methods. Still, the challenge remains, and quantum-chemical studies on actinide systems are far from routine and quite expensive. It is common practice to cut off substituents peripheral to the reaction center, in order to simplify the model compound and decrease computational costs.

Quantum-chemical studies of complexes formed between actinide ions and macrocycles are still rare, precisely because of the mentioned challenges. Liao et al.[15] have investigated actinyl complexes with unsubstituted alaskaphyrin. We have studied the same alaskaphyrin system, together with related macrocyclic complexes,[16] as well as crown ether inclusion complexes of the actinyls.[17,18]

In the current work, we use modern relativistic quantum chemistry in the form of density functional theory (DFT)[19] to study the uranyl(VI) and uranyl(V) complexes of **2** as well as its unsubstituted parent system **1** (isoamethyrin, Scheme 1). We will address the following questions: (i) To what extent can we reproduce the experimental geometry parameters of these complexes? (ii) What are the consequences of simplifications in the model by neglecting the external alkyl substituents of **2** (yielding **1**)? (iii) What is the reason for the observed nonplanar structure of the complexes and how important is ligand planarity for the complex stability? (iv) How do the U^{VI} and U^{V} systems compare?

We should note that, experimentally, Np^{V} complexes have been studied in addition to U^{VI}. It is well-known that, while the relative stabilities of different oxidation states of uranium, neptunium, and plutonium are very different (e.g., the preference of the penta- and hexavalent oxidation states for neptunium and uranium, respectively), the coordination chemistry of all of these elements in a given oxidation state is markedly similar. In the present study we consider coordination-chemistry-related properties of actinyl(VI) and actinyl(V), particularly the binding energies and geometries of the corresponding complexes. Therefore, we will consider U^{V} as a model for Np^{V} and Pu^{V} with regards to the coordination properties of these metals. Likewise, the question as to why macrocycles tend to stabilize the pentavalent oxidation state of the actinide metal relative to the hexavalent oxidation state will not be addressed, but will be the subject of separate future studies.[18] Instead, the focus here is on binding energies between cations and ligands.

2. Computational Details

Scalar relativistic all-electron calculations have been performed using the Priroda code.[20−25] Priroda employs a relativistic method that is based on the full Dirac equation but with spin−orbit effects separated out[26] and neglected. We use energy-optimized all-electron Gaussian basis sets of triple-ζ polarized quality (TZP) for the large component, corresponding kinetically balanced basis sets for the small component, and corresponding Coulomb/exchange optimized fitting basis sets.[24] The particular Gaussian basis sets used in Priroda

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version 3.0 are undocumented.[27] However, we have extensively tested the performance of the Priroda code as compared to that of other, standard programs that incorporate different relativistic approximations. We find that results are consistently similar, provided that all other settings are comparable.[16,28] Moreover, we have also compared different versions of Priroda (versions 3.0, 4.0, and 5.0) that include slightly different basis sets.[24] Again, we find that the results are always very similar, and the minor changes of basis set structure are unimportant for the results.[28]

All calculations were based on approximate DFT in the form of the PBE functional,[29] i.e., a generalized gradient approximation (GGA) version of DFT.[19] Geometry optimizations have been performed without any symmetry or other constraints. Optimized geometries are always verified as minima on the potential energy surface by calculating the harmonic vibrational frequencies at the stationary point. Very tight criteria were used for geometry optimization, self-consistent field (SCF) convergence, and numerical DFT integration. These choices ensure that, even for a very flat potential energy surface, any minima found are true minima and not spurious artifacts resulting from numerical noise. Atomic charges and bond orders are calculated using the Hirshfeld approach[30] and population-based bond orders (Mayer),[31] respectively. The settings are similar to those used in earlier studies on related actinyl complexes where we have shown them to be sensible.[16,18,28,32]

An extended transition state (ETS) analysis[33] was performed on the Priroda-optimized geometries using single-point calculations within the ADF code.[34−36] We have refrained from re-optimizing the structures in the ADF code because of the computational cost involved. This is of course an approximation; however, experience shows that re-optimization does not markedly change the calculated structures and, in particular, any trends in their properties. In these ADF calculations, we use the ZORA method[37−39] to describe the scalar relativistic effects. The ADF-ZORA calculations employed the following all-electron STO standard basis sets: ZORA-TZP for uranium and the donor atoms coordinated to it, ZORA-DZP for the other ligand atoms, and ZORA-DZ for H atoms of the macrocyclic ligand. The PBE XC functional was again used.[29] In the ETS method,[33] the energy of complex formation from the ligand anion and uranyl cation $\Delta E(1)$ is decomposed into a sum of energy of deformation of the fragments from free ions to its geometry in the complex (E_{def}) and the total binding energy (TBE) between these deformed fragments: $\Delta E(1) = E_{\mathrm{def}} + \mathrm{TBE}$. Since we use one code for the geometry optimizations (Priroda) and another for the fragment analysis (ADF), we have calculated two TBE values: TBE(Priroda) is calculated as ($\Delta E(1) - E_{\mathrm{def}}$), and TBE(ADF) is the result of an ADF fragment calculation based on ligand dianion and uranyl cation fragments. The important point is that these two sets of values, despite being calculated by different methods and codes, are close in absolute values and change similarly for different complexes. This gives confidence in our computational procedure. In the ETS analysis scheme, TBE is further decomposed into three terms: E_{Pauli}, which corresponds to the Pauli repulsion between frozen occupied orbitals of the fragments; E_{Elstat}, which corresponds to electrostatic interactions between them; and E_{Orb}, which is the energy of relaxation of the frozen fragment orbitals to the normal self-consistent orbitals of the complex. The latter term corresponds to covalent and polarization-charge-transfer interactions between fragments. Thus, $\mathrm{TBE} = E_{\mathrm{Pauli}} + E_{\mathrm{Elstat}} + E_{\mathrm{Orb}}$.

Most current approximate DFT methods are not able to describe nonbonding interactions in a quantitative fashion. This might be considered to be a problem because a central part of our discussion concerns the interactions between the external alkyl ligands of the substituted isoamethyrin system (see below).[19] These problems apply mostly to attractive dispersion energy terms—dispersion is missing from GGA functionals.[19] In the given context, repulsive interactions between the alkyl ligands are most relevant. They result from the Pauli principle (i.e., the Fermion nature of the electron.) These kinds of interactions should be fairly well described by methods using Slater determinants. (Such as Hartree−Fock or Kohn−Sham DFT including GGA or hybrid functionals. One should keep in mind that the latter two, being DFT methods, model exchange via approximate functionals and that the description of the Pauli repulsion will not be exactly similar to that of the HF exchange. However, computational chemistry practice shows that there is no significant numerical difference between these methods.)

3. Results and Discussion

Geometries and Conformations. Optimized geometries of the $\mathrm{U^{VI}}$ complexes formed with **1** and **2** are shown in Figures 1 and 2, respectively. The $\mathrm{U^{V}}$ complexes have qualitatively similar geometries. Key geometry parameters, uranyl stretching frequencies, energetics, population bond orders, and charges for all four complexes are provided in Table 1.

The calculations show that the macrocycle is practically planar in the complexes of the unsubstituted isoamethyrin $[\mathrm{UO_2}\mathbf{1}]^{m-}$, $m = 0, 1$ (Figure 1; see also the sums of the N−U−N bond angles around uranium which are 360°, Table 1.) As discussed above, this would be expected from the aromaticity of the dianionic form of the ligand because this aromaticity is expected to favor the planar conformation. The alkyl-substituted complexes $[\mathrm{UO_2}\mathbf{2}]^{m-}$ (Figure 2), however, show the experimentally observed bent conformation. This is evident from the sum of the N−U−N angles of 363.7°

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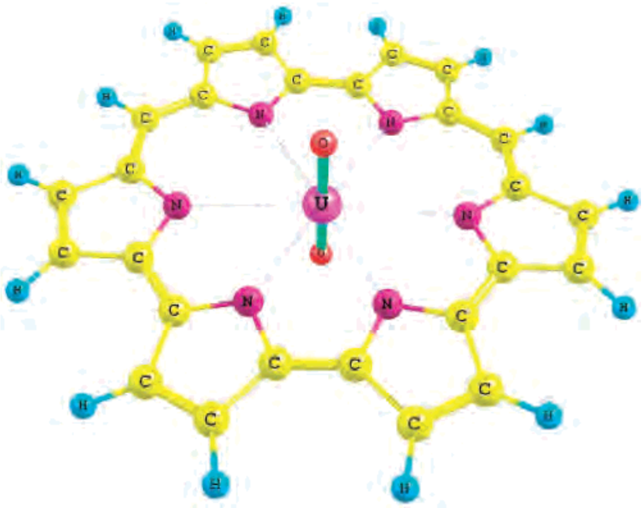

Figure 1. Optimized structure of the uranyl(VI) isoamethyrin **1** complex.

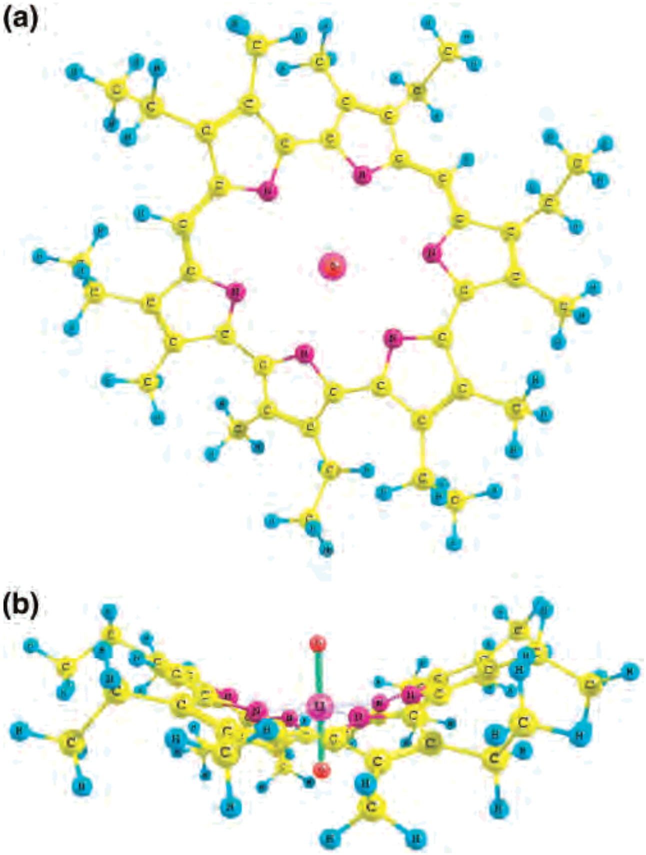

Figure 2. Optimized structure of the uranyl(VI) complex with dodeca-alkyl-substituted isoamethyrin **2**: (a) top view and (b) side view.

and 363.0°, which can be compared to the 366° observed experimentally for uranyl(VI). Thus, while the UO_2^{2+} cation is indeed too small for the ligand cavity (cf. two U−N distances of 2.6 Å vs four U−N distances of 2.8 Å and 2.9 Å), the size of the metal atom cannot be responsible for the experimentally observed bent conformation. The deviation from planarity is instead entirely due to the steric requirements of the external methyl and ethyl ligands that force the system into the nonplanar conformation. Indeed, the optimized structures of the free anionic ligands $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ as well as their free-base neutral forms $H_2\mathbf{1}$ and $H_2\mathbf{2}$ show the same planar and bent conformations, correspondingly. We have also optimized the structure of a corresponding free ring system **3** with external methyl ligands instead of the experimentally used ethyl groups of **2**. This system **3** is bent, but to a lesser degree than that of **2**. Thus, **3** is in-between **1** and **2** with respect to its conformation. Moreover, the charges on the ligand donor atoms do not change significantly from $\mathbf{1}^{2-}$ to $\mathbf{2}^{2-}$ (as shown in Table 2). This means that there is no strong electronic influence from the alkyl groups (that are known to be weak electron donors) in the latter. Thus, the interaction of the metal cation with the ligand is not the main cause of the bending.

The conformational change from planar $[UO_2\mathbf{1}]^{m-}$ to bent $[UO_2\mathbf{2}]^{m-}$ has a dramatic influence on the bond distances (Table 1). Especially the equatorial U−N distances are strongly influenced. Three of these decrease by as much as 0.2−0.3 Å in the U^{VI} complex. The change in the remaining equatorial and axial bond lengths is less dramatic. Going from U^{VI} to U^{V} leads to slight increases in the bond lengths in each case. However, the overall picture is very similar.

Comparison to experiment is possible for the substituted U^{VI} complex. The equatorial bond lengths are still slightly longer than those of experiment, despite the shortening discussed above, and the axial bond length is overestimated by 0.04 Å. This level of reasonable agreement is typical for the PBE functional used,[16,18,28,32] and one should keep in mind that our calculations neglect any condensed phase (solvation or crystal-packing) effects. The slightly longer bonds as compared to experiment are—likely—also the reason for the slightly smaller bending in the theoretical structure (364° vs 366° for the sum of the N−U−N angles). The calculated equatorial bond lengths for uranyl(VI) follow the same trend as the experimental ones in that the cation is situated slightly off-center and closest to N1 and N2 (Scheme 1 and Figure 2).

Finally, regarding geometries and conformations, we need to briefly address the possibility of different binding sites for the metal within the cavity, possibly accompanied by dynamic exchange. Indeed, this is a common feature of complexes formed between d elements and expanded porphyrins.[7] However, we do not expect this to be the case for the given systems, for the following reasons. (i) Actinides in general, and the uranyl(VI, V) cations in particular, are much bigger than these d elements. (ii) Uranium tends to form bonds that are to a large degree ionic and certainly much less covalent than those of typical transition metals. Thus, those bonds are also much less directional. (iii) We have extensively looked at the possibility of different binding sites for other, larger ring systems (such as grandephyrin[40] and pacman[41,42]). Even there, though, we find exactly one binding site per cavity for An^{VI} and An^{V}, respectively

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Table 1. Selected Geometry Parameters (Bond Lengths in Å; Angles in deg), Vibrational Frequencies (cm^{-1}), Energetics (kcal/mol for Energies; kcal/(K mol) for Entropies), Population Bond Orders for U═O and U−N Bonds, and Hirshfeld Charges for the Different Complexes

parameter		UO_2**1**$^-$	UO_2**2**$^-$	UO_2**1**	UO_2**2**	UO_2**2** (exp)[a]
bond lengths	$d_{U═O}$	1.800	1.803	1.790	1.799	1.760(2)
	$d_{U-N1/N2}$	2.628	2.595	2.627	2.590	2.566(2)
	$d_{U-N3/N6}$	2.924	2.808	2.906	2.773	2.677(2)
	$d_{U-N4/N5}$	2.826	2.750	2.786	2.714	2.644(2)
	d_{U-N} (avg)	2.793	2.718	2.773	2.692	2.63(1)
bond angles	N1−U−N2	58.7	59.1	58.2	58.7	
	N2−U−N3	57.6	57.6	57.4	57.5	
	N3−U−N4	62.4	64.0	62.5	64.6	
	N4−U−N5	61.3	60.8	62.0	60.8	
	N5−U−N6	62.4	64.0	62.5	64.6	
	N6−U−N1	57.6	57.6	57.5	57.5	
sum of U−N−U bond angles		360.0	363.0	360.1	363.7	366
uranyl frequencies	ν_{symm}	810	824	860	840	
	ν_{asymm}	931	923	951	931	
bond orders	U═O	2.21	2.19	2.24	2.20	
	U−N1/N2	0.45	0.47	0.44	0.45	
	U−N3/N6	0.26	0.33	0.26	0.33	
	U−N4/N5	0.31	0.35	0.33	0.36	
energies ΔE	reaction 1	−350.38	−348.78	−638.85	−643.21	
	reaction 2	−21.45	−19.67	−25.02	−29.21	
ΔH (298.15 K)	reaction 2	−27.62	−26.05	−29.48	−33.93	
ΔS (298.15 K)	reaction 2	17.20	11.56	18.98	9.49	
ΔG (298.15 K)	reaction 2	−32.75	−29.50	−35.14	−36.76	
Hirshfeld charges	U	0.684	0.656	0.721	0.665	
	O	−0.317	−0.320	−0.292	−0.309	
	UO_2 fragment	0.050	0.015	0.138	0.046	
	N1/N2	−0.129	−0.135	−0.123	−0.130	
	N3/N6	−0.134	−0.133	−0.126	−0.126	
	N4/N5	−0.132	−0.134	−0.127	−0.128	

[a] Sessler et al.[9]

Table 2. Calculated Hirshfeld Charges for the Free Ligand Anions

	N1	N2	N3	N4	N5	N6
1^{2-}	−0.170	−0.174	−0.174	−0.170	−0.170	−0.170
2^{2-}	−0.178	−0.172	−0.175	−0.176	−0.172	−0.178

(An = U, Np, Pu). (iv) Multiple uranyl binding sites or (related) "wandering uranyl units" and dynamic exchange are not known crystallographically, either. Overall, we have strong reasons to believe that competing binding sites and the resulting dynamic exchange are unlikely to occur in this case.

Charges and Bond Orders. The Hirshfeld charges in the uranyl complexes (Table 1) show that there is significant charge transfer from the ligand anions to the uranyl cations, which makes the total charge on the UO_2 fragment only weakly positive. Interestingly, the total UO_2 charge for the complexes substituted with ligand **2** is lower than that for **1**. This means that the charge transfer is larger for the former, especially for the uranyl(VI) case. As will be discussed in more detail below, these charge effects can be related to the shorter bond distances in the complexes of the substituted system **2**. At the same time, the nitrogen atoms in complexes of **2** bear higher negative charges than those for complexes of **1**. The calculated uranium-to-nitrogen population bond orders (Table 1) for **2** are also higher than those for **1**.

Bonding Analysis. Estimating the relative stability of different complexes is not a simple task. The straightforward calculation of the free energy corresponding to the real ligand-exchange process is usually not possible, and a suitable model has to be chosen. Earlier,[32] we proposed the use of the following two reactions:

$$AnO_2^{n+} + L^{2-} \rightarrow AnO_2L^{(n-2)} \quad n = 1, 2 \qquad (1)$$

$$LH_2 + UO_2Cl_2^{m-} \rightarrow LUO_2^{m-} + 2HCl \quad m = 0, 1 \qquad (2)$$

The former reaction allows for energy decomposition (fragment analysis). It is most straightforward in modeling the complex formation but might lead to problems with describing ligand dianions. Equation 2 contains the neutral ring system LH_2 and allows for a comparison of ligand affinities between U^V and U^{VI}. Calculated gas-phase electronic energies corresponding to eqs 1 and 2 and also enthalpies and free energies of eq 2 are provided in Table 1.

Both eqs 1 and 2 predict that the UO_2**1** complex is less stable by about four kcal/mol (ΔH) than its substituted analogue UO_2**2**. However, the substituted complex UO_2**2**$^-$ is now less stable by just under 2 kcal/mol than UO_2**1**$^-$. The trend in the free energies is very similar.

To determine the reasons for the better "fit" of the uranyl(VI) cation into **2**, we performed an ETS decomposition[33] of the energies of eq 1. The results are provided in Table 3. We note that the TBEs and, in particular, their trends are very similar between the ADF-ZORA and Priroda-all-electron calculations, again giving confidence in our computational procedure for the analysis. Let us now turn to the results of the ETS analysis proper.

One can see from Table 3 that for both complexes of the dodeca-substituted isoamethyrin ligand **2**, the deformation

Table 3. ETS Decomposition of the Energy According to Eq 1 (see Computational Details Section for Description). All Energies in kcal/mol. In Parentheses Are Differences of the Energy Components between Complexes of **1** and **2** for Uranyl(VI) and Uranyl(V)

	$\Delta E(1)$ (Priroda)	E_{def}	TBE (Priroda)	TBE (ADF)	E_{Pauli}	E_{Elstat}	E_{Orb}
UO_2**1**	−638.85	14.06	−652.91	−649.83	106.63	−517.05	−239.40
UO_2**2**	−643.21	28.55	−671.77	−674.13	134.09	−528.83	−279.39
	(−4.4)	(14.5)	(−18.9)	(−24.3)	(27.5)	(−11.8)	(−40.0)
UO_2**1**$^-$	−350.38	8.80	−359.18	−354.95	99.39	−319.40	−135.48
UO_2**2**$^-$	−348.78	21.13	−369.91	−366.06	126.96	−331.06	−161.97
	(1.6)	(12.3)	(−10.7)	(−11.1)	(27.6)	(−11.7)	(−26.5)

energy is higher than that for the ligand **1**. However, for the uranium(VI) complex the unfavorable E_{def} value is compensated by a more negative TBE value. Combining E_{Pauli} and E_{Elstat} into a "steric" term, we can see that this term gets higher for **2** than for **1**. This corresponds to a somewhat stronger steric repulsion between uranyl and the ligand. However, for the uranium(VI) case, the E_{Orb} term, which is responsible for covalent bonding and polarizational effects, becomes much more negative for **2** than for **1**.

Thus, shorter cation-to-ligand distances caused by sterically enforced bending of the ligand **2** provide for stronger covalent interactions and/or stronger polarization of the ligand anion by the uranyl dication, and this is the reason for the higher stability of its uranyl(VI) complex. This picture correlates well with the calculated bond orders, already discussed above (Table 1). In contrast, the UO_2^{2+} cation is far too small for the cavity of the unsubstituted, planar ligand **1**.

The UO_2^+ cation is larger than the UO_2^{2+} cation. Thus, one might speculate that the reason for the calculated differences in relative stabilities of their complexes with **1** and **2** is the higher sterical repulsion between the ligand and the cation for the latter. However, the ETS decomposition of the energy of eq 1 does not support this hypothesis: Indeed, Table 3 shows that the differences between all the terms of the energy (except E_{Orb}) for ligands **1** and **2** are almost the same for complexes of uranium(V) and uranium(VI). This includes the steric term, i.e., the sum of E_{Pauli} and E_{Elstat}. Differences in this steric term between complexes of ligand **1** and those of ligand **2** are almost exactly the same for both cations. Thus, the term that is solely responsible for the difference is E_{Orb}. This can be understood from the generally weaker bonds in complexes of uranyl(V). Energies of complexation based on eq 2 support the observation that the U^{VI} complexes are more stable than their U^{V} counterparts.

4. Summary and Conclusion

In summary, we have studied the four complexes formed between $UO_2^{+/2+}$ and the ring systems **1** and **2** using modern density functional theory and a scalar relativistic all-electron method. The calculations on the substituted complexes UO_2**2**$^{m-}$, $m = 0$, 1, employing 1587 basis functions for 103 atoms, amount to some of the largest ab initio/DFT calculations performed on actinide species to date. (The number of basis functions cited refers to the large component. The basis set for the small component is much more extensive than that, due to the requirements of kinetic balance.[24])

In performing quantum-chemical calculations on heavy-element compounds, a number of approximations have to be made, concerning the relativistic model, the model chemistry (in this case, the choice of approximate DFT XC functional and the choice of basis set), and the modeling or neglect of condensed-phase effects. From experience and extensive previous testing,[13,16,18,28,32,43] we are confident regarding the relativistic approximation as well as the choice of basis sets that are essentially converged. Regarding the choice of XC functional, we have found that hybrid DFT gives, in general, better results for energetics.[28,44] However, in this work, we are mostly interested in trends among closely related compounds, and such trends are reproduced just as well by GGA functionals as by the computationally much more demanding hybrid functionals. Finally, we have also discussed condensed-phase (solvation) effects, particularly with respect to their influence on the bond lengths. These effects are neglected in the current study.

We have addressed the questions raised at the beginning of this Article. The following conclusions emerge. (i) Accurate calculations on complexes of this size are possible even on a modest Beowulf cluster, provided efficient codes such as Priroda[20,25] are used. Comparison to experiment is possible for the UO_2**2** complex, and the good level of agreement is similar to that of earlier studies where we have found that equatorial bond lengths are systematically overestimated by gas-phase calculations.[16,28] Note that the current gas-phase calculations do not account for condensed-phase effects such as crystal packing or solvation. Condensed-phase effects generally lead to shorter bonds, particularly for the equatorial ligands.[16] (ii) We have shown clearly that the external alkyl susbstituents must not be neglected, although approximations of this sort are often attempted in quantum-chemical simulations. These alkyl ligands are responsible for the experimentally observed bent conformation of UO_2**2**. By analogy with UO_2**2**$^-$, one can reasonably assume that they are also responsible for the bending in the corresponding neptunyl complex. The free ligands **1** and **2** show the same planar and bent conformations, correspondingly. While both uranyl(VI) and uranyl(V) ions are too small for the planar ligand cavity, they still form planar complexes with the unsubstituted ligand **1**. Bending of the ligand results in a much better fit for the uranium (VI) complex, allowing for stronger covalent/polarization interactions. This is evident from the shorter U−N distances in the complex with the bent ligand, as compared to the planar one. (The existence of two short and four longer U−N distances in the complexes is an indication that the uranyl cation is still slightly smaller than the optimal size for the given cavity, though, i.e., the fit is still not perfect for this cation (Table 1).) Overall, the bending and the accompanying increase in covalent and polarization interactions result in the substituted complex

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being some 4 kcal/mol more stable than the unsubsitituted one. However, the trend is reversed for the uranyl(V) cation. One might conclude that the substituted ligand **2** is not as favorable for actinyls(V) as it is for actinyls(VI) as compared with the unsubstituted planar form **1**. This is a result of the lesser strength of covalent bonding and polarization effects for the actinyl(V) cations, as was shown by the ETS analysis procedure. However, steric effects were found to be unimportant for the differences between uranyl(V) and uranyl(VI). Further studies on the Np and Pu analogues as well as on related ring systems with six and five donor atoms are underway.

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