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Theoretical predictions of cofacial bis(actinyl) complexes of a stretched Schiff-base calixpyrrole ligand**

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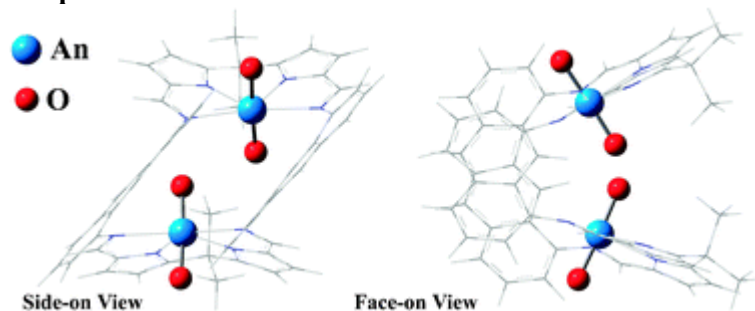
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Supporting information:

^[†]Electronic supplementary information (ESI) available: Chart and the literature on CCI, tables of geometry parameters and bond orders of mono- and binuclear complexes, table of formation reactions, and figures of the free energies of formation reactions for actinyl(V) complexes and simulated vibrational spectra. See <http://dx.doi.org/10.1039/C1CC10979K>

Graphical abstract:



Abstract

Actinyl and actinyl-transition metal complexation by a polypyrrolic macrocycle with anthracenyl linkers between the N₄-donor compartments was evaluated using relativistic density functional theory which predicts that a highly unusual cofacial bis-actinyl structure complex is stable.

Introduction

In aqueous nuclear fuel processing and under environmental conditions, the most characteristic and stable form of uranium is the linear UO₂²⁺ ion, which, due to its high solubility and mobility makes it important in the long-term environmental risks associated with the disposal of radioactive waste.¹ In the uranyl ion, the U=O bonding involves most of the uranium valence orbitals, making the uranium coordination mainly occur in the equatorial plane.² In contrast, pentavalent actinyl(V) chemistry is known to exhibit cation–cation interactions (CCI) due to the increased Lewis basicity of the yl oxygens.³ The CCI, the coordination of the oxo atom of one actinyl unit to the actinyl metal center of another (as seen in Chart S1, ESI†), can lead to the formation of dimers, oligomers, one-dimensional chains and multi-dimensional networks^{4–8} that do not necessarily require the support of ancillary ligands. Therefore, a greater understanding of actinyl coordination chemistry is essential, technologically, for the safe processing and long-term immobilization of irradiated radionuclides.

A number of Schiff-base macrocycles have been used for the complexation of actinyl and transition metal cations.^{9–12} The flexible Schiff-base pyrrole macrocycle H₄L¹ in Chart 1, for example, has a cavity large enough to coordinate two transition metals^{10–12} and its *ortho*-substituted aryl linkers function as hinges that result in a rigid molecular cleft structure, often called a “Pacman” structure.¹³ The studies of Arnold and Love *et al.* have shown that the reaction of H₄L¹ with uranyl silylamides yields mononuclear [(THF)(UO₂)(H₂L¹)],¹⁴ which can be further functionalized to give heterobinuclear [(THF)(OUO^{•••}M)(THF)(L¹)] (M = Mn, Fe and Co)¹⁵ and one-electron reduced uranium(V) products.^{16,17} Our theoretical studies¹⁸ showed that the H₄L¹ ligand can accommodate two uranyl ions to form bis-uranyl complexes (UO₂)₂(L¹). Of particular interest is the fact that the two UO₂²⁺ moieties exhibit the butterfly-like and T-shaped structures as seen in Chart 2.

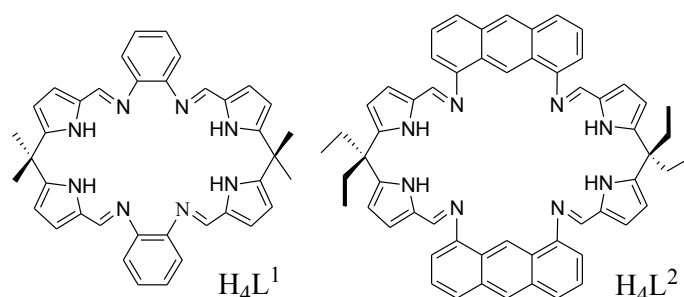


Chart 1. Polypyrrolic macrocycles with aryl (H₄L¹) and anthracenyl (H₄L²) linkers.

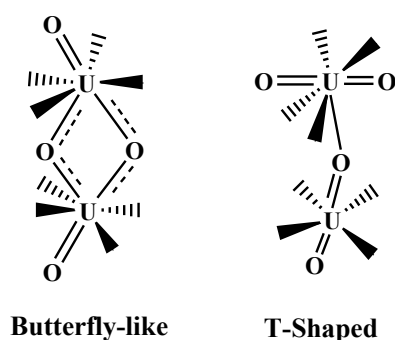


Chart 2. The bis-uranyl skeleton structures of the isomeric $(\text{UO}_2)_2(\text{L}^1)$ complexes. For clarity, the ligand is omitted.

Very recently, a polypyrrolic macrocycle with an anthracenyl spacer between the two N_4 -donor compartments (Chart 1, H_4L^2) has been shown to bind two palladium(II) ions.⁹ The aryl spacer in H_4L^2 (anthracene) is longer than in H_4L^1 (benzene), providing more space and a more cofacial orientation of the donor compartments, which should make H_4L^2 a promising candidate to coordinate more than one actinyl ion. Here we present theoretical work that predicts that this new macrocycle will accommodate two actinyl cations and allows new types of actinyl–actinyl (CCI) interactions and geometries to be isolated and studied.

Relativistic density functional theory with the PBE functional was applied to calculate possible structures of the actinyl complexes. The ethyl groups in H_4L^2 (Chart 1) were replaced with methyl in the calculations to reduce the computational cost. All optimizations were accomplished by the Priroda code,^{19,20} where a scalar relativistic four-component all-electron approach and all-electron correlation-consistent triple- ζ polarized quality basis sets were used.¹⁹ Subsequent analytical frequency calculations confirmed the nature of the stationary points on the potential energy surface. We simulated vibrational spectra of some complexes as shown in Fig. S1 of the ESI. † Population-based Mayer²¹ bond orders were calculated based on these PBE calculations. Our previous investigation¹⁸ demonstrated that the free energies of solvation were calculated to be very close on the basis of two models: (1) Priroda optimized geometry in the gas phase, followed by (single-point) ADF/COSMO solvation;^{22,23} (2) ADF/COSMO optimized geometry in solution. In this communication, we used the first model to calculate the solvation energy.

From the theoretical point of view, the macrocyclic H_4L^2 has the ability to accommodate two actinyl ions. Full geometry optimizations on $[(\text{UO}_2)_2(\text{L}^2)]$, where two uranyl groups were initially placed into the calixpyrrole ligand cavity, led to a minimum-energy structure as shown in Fig. 1a. The complex exhibits an approximately cofacial bis-uranyl structure in which a lateral twist of the macrocycle combined with vertical expansion away from coplanarity decreases the repulsion between the *endo*-oxo atoms. The nature of the macrocyclic linker strongly affects the configuration of the bis-actinyl complex. Indeed, our previous theoretical study¹⁸ found that $(\text{UO}_2)_2(\text{L}^1)$ forms isomeric butterfly-like and T-shaped bis-uranyl configurations (Chart 2).

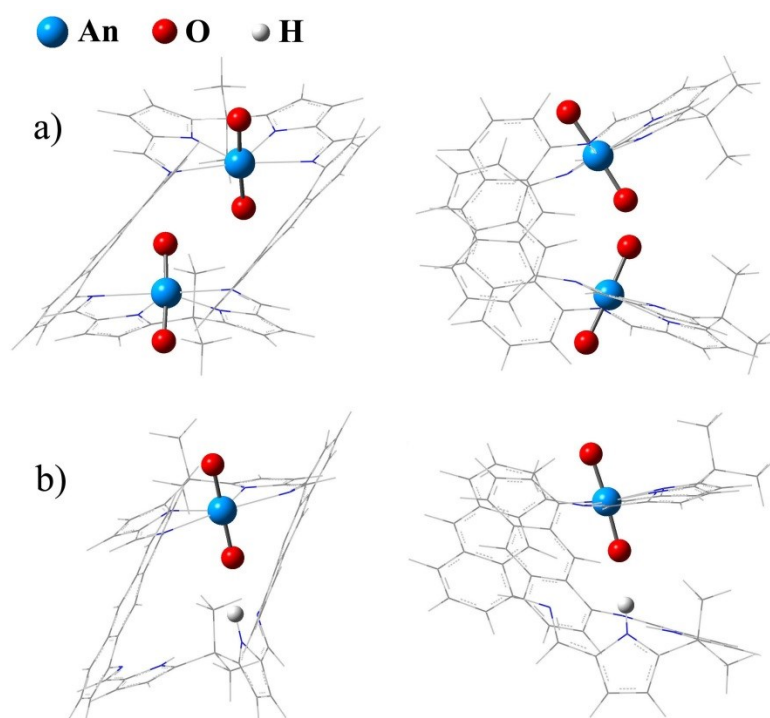


Figure 1. Structures of (a) binuclear $[(\text{AnO}_2)_2(\text{L}^2)]^{2n-4}$ and (b) mononuclear $[(\text{AnO}_2)(\text{H}_2\text{L}^2)]^{n-2}$, where An = U, Np, Pu and $n = 2, 1$ (left: face-on view; right: side-on view).

The calculated results (Table S1, ESI†) indicate that the two uranyl ions in binuclear $[(\text{UO}_2)_2(\text{L}^2)]$ retain their respective basic structures. The $\text{U}=\text{O}_{exo}$ (1.802 Å) and $\text{U}=\text{O}_{endo}$ (1.798 Å) bond lengths are very similar and correspond to bond orders of 2.39 and 2.38, respectively. A slightly shorter $\text{U}=\text{O}_{endo}$ bond originates from the repulsion of the *endo*-oxo atoms. We did not find the apparent CCI interaction between two uranyl ions as the $\text{U}^{\cdots}\text{O}_{endo}$ separation was calculated to be 3.931 Å. The *trans*-dioxo uranyl unit stays almost linear with an angle of 176° . Optimizations on analogous $[(\text{AnO}_2)_2(\text{L}^2)]^{2n-4}$ (An = U, Np, Pu; $n = 2, 1$) reveal that these bis-actinyl complexes exhibit similar structural features, Fig. 1a. One can note that the calculated An=O bond lengths gradually decrease in going from U, Np to Pu in oxidation states of VI or V. This agrees with the concept of the actinide contraction. Upon reduction from VI to V, the An=O distances are lengthened. Similar trends have been found in previous calculations on $[\text{U}^{\text{VI}}\text{O}_2(\text{H}_2\text{O})_5]^{2+}$ and $[\text{U}^{\text{V}}\text{O}_2(\text{H}_2\text{O})_5]^+$.²⁴

Six mononuclear complexes, $[(\text{AnO}_2)(\text{H}_2\text{L}^2)]^{n-2}$ (An=U, Np, Pu; $n = 2, 1$), were also designed and optimized and the structure of the U complex is shown in Fig. 1b. The laterally-twisted ligand (L^2) geometry is quite different from that in the mononuclear L^1 complexes.¹⁴ The actinyl in the mononuclear L^2 complex has shorter An= O_{exo} bond length compared to the respective An= O_{endo} , and their bond orders were calculated to cover the range of 2.19–2.40, with the highest and lowest values corresponding to U^{VI} and Pu^{V} , respectively (Table S2, ESI†). Apparently, the $\text{O}_{endo}^{\cdots}\text{H}$ bonding slightly weakens the An= O_{endo} interaction. It is interesting that only one hydrogen bonding was found, even though the system has two available H atoms within the cavity. This

contrasts with $[(\text{AnO}_2)(\text{H}_2\text{L}^1)]$ ($\text{An}=\text{U}, \text{Np}, \text{Pu}$) which possess two $O_{\text{endo}}\cdots\text{H}$ bonds. Both aryl linkers and geometrical features of the L^1 and L^2 ligands lead to different hydrogen bondings in these mononuclear complexes.

In mononuclear complexes of L^2 , the actinide contraction of $\text{An}=\text{O}$ distances was well reproduced along U, Np to Pu, whereas the corresponding bond orders suggest a gradual reduction of these bonds along the series. The agreement between experimental values for $[(\text{UO}_2)(\text{THF})(\text{H}_2\text{L}^1)]^{14}$ and our calculated results of $[(\text{UO}_2)(\text{H}_2\text{L}^2)]$ (Table S2, ESI†) confirms the reliability of our calculations for structural predictions.

To study the thermodynamics of forming the mono- and binuclear complexes, we designed reactions of $[\text{AnO}_2(\text{H}_2\text{O})_5]^{n-2}$ ($n = 2, 1$) with the polypyrrrolic ligand. The corresponding reactions are listed in Table S3 (ESI†). The calculated free energies (ΔG) of these reactions are plotted in Fig. 2 (for the An^{VI} complexes) and Fig. S2 (ESI†) (for An^{V}). One can see that the energies of reaction leading to binuclear complexes are 44–50 kcal mol^{-1} higher than those of the corresponding mononuclear ones in the gas phase, denoting an endothermic process. Our results indicate that the energies decrease in going from U, Np to Pu for mononuclear complexes; however, the trend is different for binuclear complexes where $[(\text{NpO}_2)_2(\text{L}^2)]$ has the highest energy of 80 kcal mol^{-1} . The energy of the mixed $[(\text{UO}_2)(\text{PuO}_2)(\text{L}^2)]$ complex is intermediate between those of the binuclear U and Pu complexes, Table S4 (ESI†). In the ADF/COSMO calculations, solvation free energies of -27 and -34 kcal mol^{-1} for $[(\text{UO}_2)(\text{H}_2\text{L}^2)]$ and $[(\text{UO}_2)_2(\text{L}^2)]$, respectively, were determined. Furthermore, the solvation stabilizes the formation energy of the binuclear complex by about 11 kcal mol^{-1} , and raises it by about 2 kcal mol^{-1} for the mononuclear complex, thus making the reaction process from $[(\text{UO}_2)(\text{H}_2\text{L}^2)]$ to $[(\text{UO}_2)_2(\text{L}^2)]$ easier (Fig. 2).

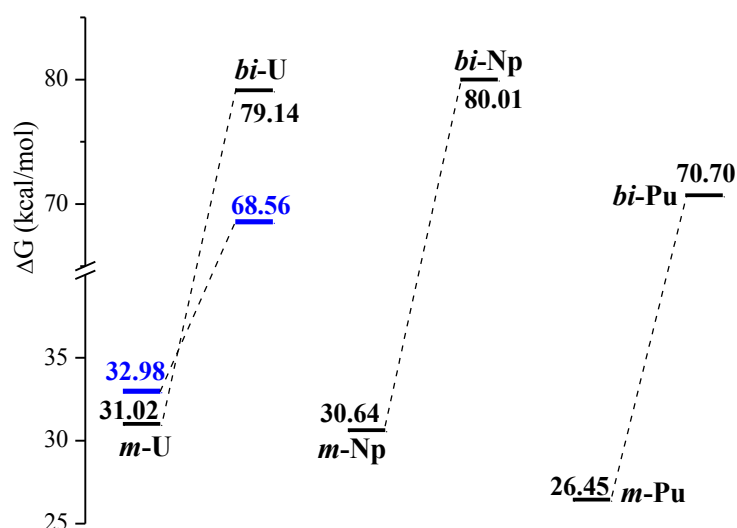


Figure 2. Free energies of formation reactions for mononuclear $[(\text{AnO}_2)(\text{H}_2\text{L}^2)]$ and binuclear $[(\text{AnO}_2)_2(\text{L}^2)]$ ($\text{An} = \text{U}, \text{Np}$ and Pu) complexes in the gas phase, compared with those of uranyl complexes in aqueous solution (blue lines and numbers).

In light of the experimentally-observed reactions of $[(\text{UO}_2)(\text{THF})(\text{H}_2\text{L}^1)]$ with transition metal ions, we designed a series of heterobinuclear $\text{AnO}_2^{2+}\cdots\text{Mn}^{2+}$ complexes (Table S5, ESI†). In $[(\text{S})(\text{UO}_2)(\text{Mn})(\text{S}')(\text{L}^2)]$ (S = vacant, S' = THF; S = S' = Py, THF), the equatorial coordination of the uranyl ion varies between 4–5-coordinate (Fig. 3), consistent with other reported uranyl complexes.^{25–27}

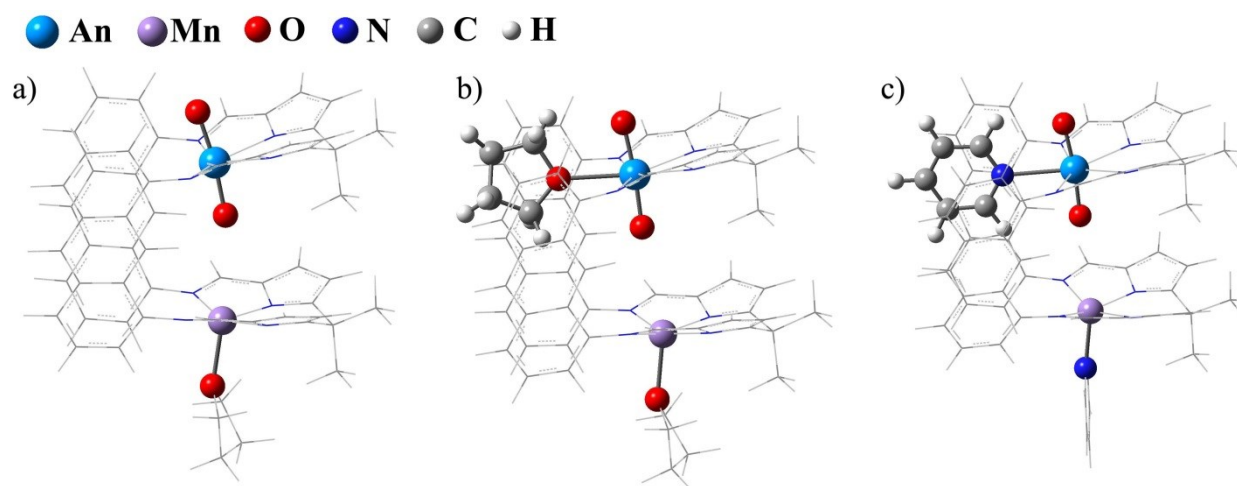


Figure 3. Structures of (a) $[(\text{UO}_2)(\text{Mn})(\text{THF})(\text{L}^2)]$, (b) $[(\text{THF})(\text{UO}_2)(\text{Mn})(\text{THF})(\text{L}^2)]$ and (c) $[(\text{Py})(\text{AnO}_2)(\text{Mn})(\text{Py})(\text{L}^2)]$ (An = U, Np, and Pu).

The three $\text{UO}_2^{2+}\cdots\text{Mn}^{2+}$ complexes with and without the fifth equatorial coordination to uranyl display similar calculated geometry parameters. Moreover, our calculated results are comparable to experimental values of $[(\text{THF})(\text{UO}_2)(\text{Mn})(\text{THF})(\text{L}^1)]$ ¹⁵ as seen in Table S5 (ESI†). Differences of less than 0.04 Å in distances and 4° in angles were found between the calculated and experimental values except for the $\text{Mn}^{2+}\cdots\text{O}_{\text{endo}}$ distance which is elongated by 0.18 Å in the complexes of L^2 due to the longer aryl linker between the two metal compartments. The adoption of fourfold equatorial coordination for the actinyl ion in these calculations is reasonable, not only because of similar results with and without the fifth equatorial ligand, but also because of saving computational cost.

In summary, the polypyrrolic macrocycle with the anthracenyl linker provides an environment suited to the coordination of two actinyl ions, forming highly unusual cofacial bis-actinyl complexes, $[(\text{AnO}_2)_2(\text{L}^2)]^{2n-4}$ (An = U, Np, Pu; $n = 2, 1$). In contrast, the aryl-linked macrocycle (H_4L^1) shows energetic preference for a butterfly-like and a T-shaped bis-uranyl complex.¹⁸

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