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Binuclear Uranium(VI) Complexes with a "Pacman" Expanded Porphyrin: Computational Evidence for Highly Unusual Bis-Actinyl Structures

Qing-Jiang Pan,[a, b] Grigory A. Shamov,[a] and Georg Schreckenbach*[a]

Abstract: On the basis of uranyl complexes reacting with a polypyrrolic ligand (H_4L), we explored structures and reaction energies of a series of new binuclear uranium(VI) complexes using relativistic density functional theory. Full geometry optimizations on $[(UO_2)_2(L)]$, in which two uranyl groups were initially placed into the pacman ligand cavity, led to two minimum-energy structures. These complexes with cation–cation interactions (CCI) exhibit unusual coordination modes of uranyls: one is a T-shaped (**T**) skeleton formed by two linear uranyls $\{O_{exo}{=}U_2{=}O_{endo}{\rightarrow}U_1({=}O_{exo})_2\}$, and another is a butterfly-like (**B**) unit with one linear uranyl coordinating side-by-side to a second *cis*-uranyl. The CCI in **T** was confirmed by the calculated longest distance and lowest stretching vibrational frequency of $U_2{=}O_{endo}$ among the four U=O bonds. Isomer **B** is more stable than **T**, for which experimental tetrameric analogues are known. The formation of **B** and **T** complexes from the mononuclear $[(UO_2)(H_2L)(thf)]$ (**M**) was found to be endothermic. The further protonation and dehydration of **B** and **T** are thermodynamically favorable. As a possible product, we have found a trianglelike binuclear uranium(VI) complex having a O=U=O=U=O unit.

Keywords: cation–cation interactions · density functional calculations · macrocycles · pacman-like complexes · uranium

Introduction

Uranium is the central element in the nuclear fuel cycle as fuel for nuclear reactors and as a major component of the final waste.[1] A greater understanding of its coordination chemistry is essential technologically, for instance, for the safe processing and long-term immobilization of irradiated radionuclides. The early 5f elements such as uranium, neptunium, and plutonium have interesting possibilities that arise from the accessibility of s, p, d, and f orbitals to chemical bonding, thus allowing for exciting coordination chemistry.[2,3] For uranium in the oxidation states of +5 and +6, the most characteristic and stable form is the linear UO_2^{n+} moiety, the uranyl ion.

Since the discovery of cation–cation interactions (CCI) between UO_2^{2+} and NpO_2^{+} in solution,[4] the actinyl oxo group (AnO_2^{n+}) originally considered unreactive has received increased attention in the fields of solution and solid-state chemistry.[5–16] The CCI occurs through coordination of one actinide metal center by the oxo atom of a second actinyl unit. It can lead to the formation of dimers,[4–8] oligomers,[9–11] one-dimensional chains,[12–14] and multi-dimensional networks[15,16] that do not necessarily require the support of ancillary ligands. The CCIs are particularly well recognized for An^{V} (An = U, Np and Pu)[4–6,10,12,17–20] and have recently been identified in U^{VI} chemistry.[11,13–15] It is an extension of this kind of interaction that a number of complexes with the $AnO_2^{n+}{\cdots}M^{m+}$ structure (in which M is an alkali metal or transition metal) were synthesized and structurally characterized.[12,21–25]

The U=O bonding in the uranyl dication involves most of the uranium valence orbitals, making the uranium coordination mainly occur in the equatorial plane.[3,26] Besides the

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[a] Dr. Q.-J. Pan, Dr. G. A. Shamov, Prof. G. Schreckenbach
Department of Chemistry, University of Manitoba
Winnipeg, MB, R3T 2N2 (Canada)
Fax: (+1) 204-474-7608
E-mail: schrecke@cc.umanitoba.ca

[b] Dr. Q.-J. Pan
Key Laboratory of Functional Inorganic Material Chemistry
Ministry of Education and Laboratory of Physical Chemistry
School of Chemistry and Materials Science
Heilongjiang University
Harbin 150080 (PR China)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902014. It contains tables of bond orders and atomic charges for mono- and binuclear complexes; color version of Figure 1; figures of simulated vibrational spectra for the polypyrrolic ligand and uranium complexes; figures of reaction energies for ΔE_0 and ΔG; figure of reaction energies ΔG in the gas phase and solution.

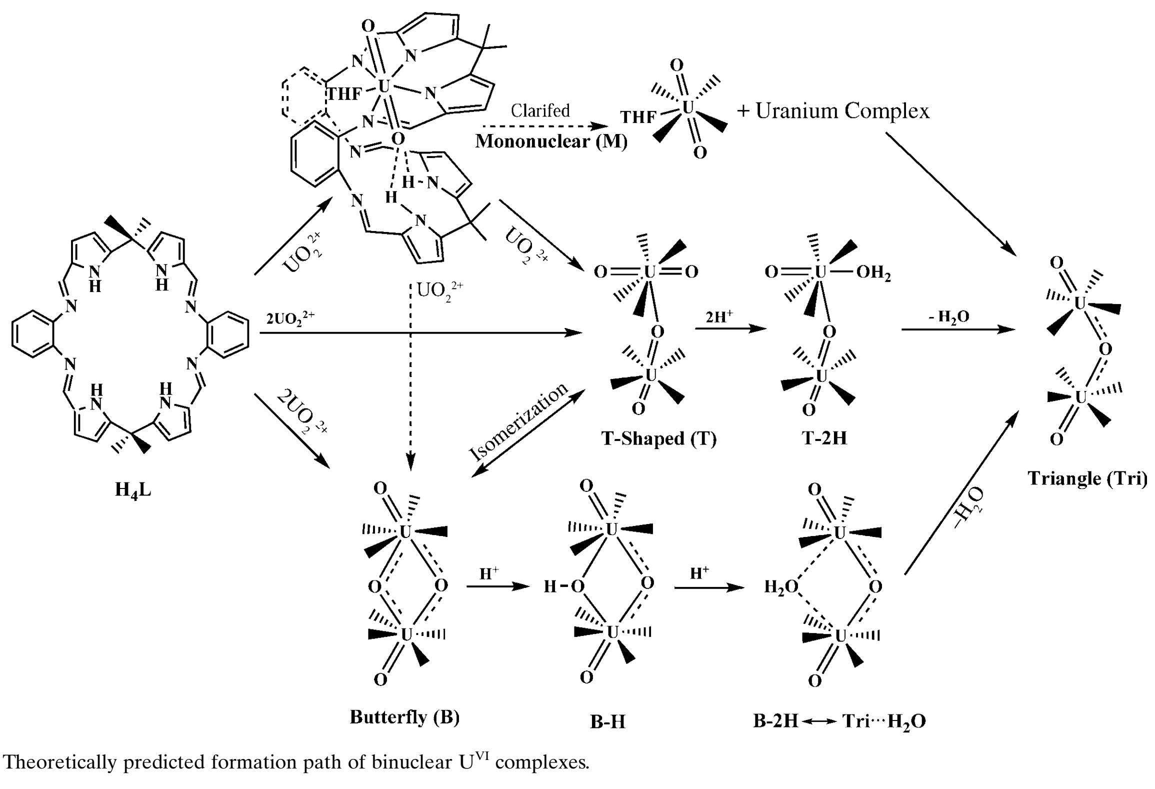
use of multiple ligands,[21,27–35] expanded porpyrins and related macrocycles[36,37] are prospective ligands for actinyl complexation, many of which form stable actinyl complexes.[37–41] The Love[42–48] and Sessler[49,50] groups synthesized a flexible macrocylic ligand H_4L (Scheme 1), in which the cavity is large enough to hold two transition metals. The aryl groups in the macrocycle function as hinges that result in a rigid molecular cleft structure, often called a Pacman structure.[51–53] The studies of Arnold et al. have shown that this pacman-like macrocylic ligand can accommodate one five-coordinate uranyl ion in its equatorial plane.[54] However, the second N4 coordination site of the ligand remains metal-free. Further interaction of the complex with transition metal ions forms a series of heterobinuclear $UO_2^{2+}\cdots M^{2+}$ (M = Mn, Fe, and Co) complexes.[25] These U^{VI} species could be reduced to produce U^{V} complexes.[55,56] Since pacman-like complexes with homobinuclear transition metals (TM)[42–50] and heterobinuclear uranyl–TM structures[25] were synthesized experimentally, it is interesting whether features of the pacman ligand can be exploited to obtain binuclear uranium(VI) complexes.

Herein we present a density functional theory (DFT) study on binuclear U^{VI} complexes of the unique pacman-like ligand, using well-established computational approaches.[57] Two CCI bis-uranyl complexes were predicted with unusual T-shaped and butterfly-like structures. After the protonation and dehydration of these two complexes, we found as a possible product a trianglelike binuclear uranium(VI) complex having a O=U=O=U=O unit. The formation reaction energies were calculated to evaluate the stability of these complexes. The solvent effects on the free energies of the reactions will also be discussed in detail.

Computational Methods

Unless otherwise noted, all the calculations were accomplished by the Priroda code (Version 6).[58–62] Relativistic effects were implemented using a scalar relativistic four-component all-electron approach,[63] which is based on the full Dirac equation but with spin-orbit projected out[64] and neglected. Because the oxidation state of uranium(VI) is kept constant in the present studied reactions, the above approximation and neglect do not create a problem in our calculations.[65] All-electron Gaussian basis sets of triple-ς polarized quality (TZP) for the large component, corresponding kinetically balanced basis sets for the small component, and corresponding Coulomb/exchange optimized fitting basis sets were used.[59]

We performed the calculations using approximate density functional theory (DFT) in the form of the PBE exchange-correlation functional,[66] that is, a generalized gradient approximation (GGA) version of DFT. All structures were optimized in the gas phase without any symmetry constraints. Subsequent analytical frequency calculations were used to confirm the nature of the stationary points on the potential energy surface and also to obtain thermodynamic data. Population-based (Mayer)[67] bond orders and atomic charges as developed by Hirshfeld[68] were calculated based on these PBE calculations. Due to the use of the resolution-of-identity (RI) approximation,[61] the Priroda code has been successfully applied to calculate large molecular systems at the DFT level. It is thus particularly advantageous for calculations on actinide complexes.[65,69–74] Careful comparison with other relativistic methods as implemented in codes such as Gaussian 03 and ADF confirmed that Priroda is entirely reliable for actinide complexes.[65,69–71] Very recently, investigations of binuclear $UO_2^{2+}\cdots M^{2+}$ (An = U, Np and Pu; M = Mn, Fe, Co and Zn) complexes have given reasonable agreement with experimental results.[74]



Scheme 1. Theoretically predicted formation path of binuclear U^{VI} complexes.

To obtain the free energies of solvation, single-point calculations on the basis of the Priroda-optimized geometries were performed using the ADF 2008.01 code.[75–77] An integration parameter of 6.0 was applied. We did not reoptimize structures in the ADF calculations, because not only are the optimizations very expensive but also do not change the geometrical structures and any trends in molecular properties significantly, as stated in our previous studies.[65,73,74] The THF solvent effects were taken into account by the COSMO model as implemented in ADF.[78] Klamt radii were used for the main group atoms (H = 1.30, C = 2.00, N = 1.83, O = 1.72, and Si = 2.40 Å)[79] and for the actinide atom (U = 1.70 Å).[70,74] The scalar relativistic ZORA method[80–82] was applied in the ADF calculations. ZORA-TZP basis sets, similar to those applied in the Priroda calculations, and the same PBE XC functional were used.

Results and Discussion

Geometrical structures and bond orders: Based on possible reactions of uranyl species and the polypyrrolic ligand, we theoretically designed several possible binuclear U^{VI} complexes. These are presented in Scheme 1, along with the experimentally known mononuclear $[(UO_2)(H_2L)(thf)]$ (**M**). For binuclear complexes $[(UO_2)_2(L)]$, two uranyl groups were initially placed into the ligand cavity. Full geometry optimizations led to two minimum-energy structures, confirmed by the frequency calculations. These structures have unusual uranium coordination modes, T-shaped and butterfly-like structures, labeled as **T** and **B**, respectively. We have also studied possible products of their protonation $[(U_2O_4H)(L)]^+$ (**B-H**), $[(U_2O_3)(H_2O)(L)]^{2+}$ (**T-2H** and **B-2H↔Tri···H$_2$O**) and of the subsequent elimination of water—the trianglelike $[(U_2O_3)(L)]^{2+}$ (**Tri**). We named all of the complexes according to the uranium-oxygen skeleton as shown in Scheme 1 and Figure 1 (a color version is provided in Figure S1 of the Supporting Information). Selected geometry parameters are listed in Table 1. More detailed information about bond orders and atomic charges is given in Table S1 of the Supporting Information.

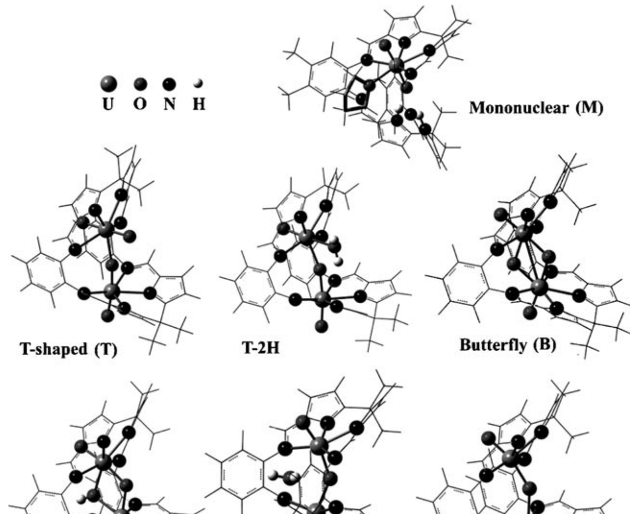


Figure 1. Optimized gas-phase structures of binuclear complexes, T-shaped and butterflylike $(UO_2)_2(L)$ (**T** and **B**), $[(U_2O_4H)(L)]^+$ (**B-H**), $[(U_2O_3)(H_2O)(L)]^{2+}$ (**T-2H** and **B-2H↔Tri···H$_2$O**) and trianglelike $[(U_2O_3)(L)]^{2+}$ (**Tri**), compared with the mononuclear complex $(UO_2)(H_2L)(thf)$ (**M**). See Figure S1 (Supporting Information) for a color version.

As shown in Scheme 1, the reaction of the polypyrrolic ligand with two uranyl ions or the further interaction of **M** with one uranyl ion may form isomers **T** and **B**. These two cation–cation complexes exhibit unusual coordination modes of uranyls. The first one (**T**) is formed through the coordination of one uranyl metal center by the oxo atom of a second uranyl unit with a T-shaped structure. Isomer **B** is a butterfly-shaped unit with one linear uranyl coordinating side-by-side to another *cis*-uranyl. For the complexes reported in the experiments, a parallel structure of two uranyl ions connected by oxygen bridges in polynuclear complexes is the most common.[8,14,15,30,33,83–85] Recently, two T-shaped tetrameric cation–cation complexes with pentavalent[10] and hexavalent[11] uranyls have been reported. Additionally, there are some uranyl metallates with the combined T-shaped and parallel polyuranyl structures found in solid-state chemistry,[13,16] which usually exhibit one- to three-dimensional arrangements. To the best of our knowledge, there are no experimental structural reports on T-shaped and butterfly-like binuclear uranyl cation–cation complexes.

The present studies indicate that the two uranyl ions in the **T** isomer retain their respective basic structures: three shorter U=O distances of about 1.81 Å and one longer one of about 1.85 Å (Table 1); their bond orders were calculated at 2.40 and 2.00, respectively (Table S1 in the Supporting Information). The fourth uranyl bond becomes weaker due to the coordination from the oxygen atom of one uranyl to the uranium atom of the other, implying the presence of a cation–cation interaction. This coordinated O→U distance between the two uranyls was estimated to be 2.39 Å, falling within the range of typical equatorial U−O distances of uranium(VI) complexes.[8,10,11,29–33,83,84] The calculated bond order of 0.37 suggests a bonding strength slightly weaker than the normal single bond, but well within the range of typical equatorial bonds.[69] Such T-shaped structural features reproduce well those known in the tetrameric complexes, $[U^{VI}O_2(OCH(iPr)_2)_2]_4$[11] (*i*Pr = isopropyl) and $[U^{V}O_2(dbm)_2]_4[K_6Py_{10}]\cdot I_2\cdot Py_2$ (dbm = dibenzoylmethanate, Py = pyridine),[10] and in uranyl metallates, $Li_4[(U^{VI}O_2)_{10}(O)_{10}(Mo_2O_8)]$,[13] $Na_2Li_8[(U^{VI}O_2)_{11}O_{12}(WO_5)_2]$[15] and $A[(U^{VI}O_2)_3(HIO_6)_2(OH)(O)(H_2O)]\cdot 1.5H_2O$ (A = Li, Na, K, Rb and Cs).[16]

Isomer **B** is more stable and 12.44 kcal mol^{-1} lower in energy than **T**. The two isomers display dihedral angles between the two N_4 planes of the pacman ligand at about 70° and 90°, respectively. The dihedral angle of **B** is closer to those in the synthesized binuclear U−M (M = Mn, Fe, and Co)[25] and M−M (M = Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Pd, and Cd)[42–50,53] complexes (40–65°). Isomer **B** contains three types of U−O bonds: two short $U{=}O_{exo}$ of 1.82 Å (mean value), two long $U{-}O_{endo}$ of 2.08 Å and two even longer $U{-}O_{endo}$ of 2.13 Å. Regarding U−O bond orders (Table S1 in the Supporting Information), the first group possesses a par-

Table 1. Optimized geometry parameters for mono- and binuclear U^{VI} complexes, $[(UO_2)(H_2L)(thf)]$ (**M**), T-shaped and butterfly-like $[(UO_2)_2(L)]$ (**T** and **B**), $[(U_2O_4H)(L)]^+$ (**B-H**), $[(U_2O_3)(H_2O)(L)]^{2+}$ (**T-2H** and **B-2H**↔**Tri···H$_2$O**) and trianglelike $[(U_2O_3)(L)]^{2+}$ (**Tri**) in the gas phase.

	M[a]	**T**	**T-2H**	**B**	**B-H**	**B-2H** (**Tri···H$_2$O**)	**Tri**	Exptl[b] (UO_2)	Exptl[b] (UO_2···Mn)	Exptl[b] (UO_2···Co)
Bond length [Å]										
U_1–O_{exo}	1.799	1.801	1.813	1.814	1.804	1.801	1.801	1.766	1.768	1.772
		1.805	2.502							
U_1–O_{endo}	1.835	2.387	2.187	2.144	2.313	2.702	2.085	1.790	1.808	1.783
				2.070	2.065	2.067				
U_1–O_{eq}	2.485							2.442	2.458	2.474
U_1–N	2.609	2.638	2.461	2.521	2.499	2.474	2.390	2.586	2.498	2.525
	2.466	2.402	2.351	2.463	2.406	2.327	2.348	2.443	2.426	2.412
U_2–O_{exo}		1.806	1.796	1.818	1.805	1.801	1.803			
U_2–O_{endo}		1.847	1.968	2.111	2.323	2.702	2.048			
				2.093	2.078	2.067				
U_2–N		2.496	2.433	2.489	2.465	2.474	2.416			
		2.412	2.388	2.463	2.410	2.327	2.354			
U_1···U_2		4.214	4.102	3.377	3.512	3.705	3.900		3.804^c	3.726^c
Bond angle [°]										
O_{exo}-U_1-O_{endo}	175.3	179.3	166.0	175.6	168.5	165.7	171.3	177.6	177.4	177.8
		101.5	122.7	102.7	96.8	92.6				
O_{exo}-U_2-O_{endo}		169.9	171.8	176.6	169.4	165.7	161.5			
				104.1	98.2	92.6				
U_1-O_{endo}-U_2		168.9	161.4	106.1	117.5	127.4	141.3			
				108.4	99.6					
O_{endo}-U-O_{endo}				72.6	71.6					
				72.9	71.2					

[a] Mononuclear results were reported in reference [74]. [b] Experimental values of $[(UO_2)(H_2L)(thf)]$ and $[\{(thf)UO_2{\cdots}M(thf)\}(L)]$ (M = Mn and Co) complexes from reference [25,54]. [c] The U···M distances were taken in $[\{(thf)UO_2{\cdots}M(thf)\}(L)]$ (M = Mn and Co) complexes.

tial triple bond, and the other two groups are slightly stronger than a single bond.

In solution, a proton easily reacts with such isomers. Through attacking electron-rich oxygen atoms (Table S1 in the Supporting Information), protonated **T-2H**, **B-H**, and **B-2H** (**Tri···H$_2$O**) complexes were formed. As shown in Table 1 and Figure 1, the protonation changes the structures of **B** and **T** greatly: it lengthens the U_1–O_{exo} distance from 1.81 Å in **T** to 2.50 Å in **T-2H** and, accordingly, the nature of this bond varies from the original strong, multiple bond (bond order 2.38) to a dative bond (0.45); with the increase in the number of protons, the U–O_{endo} of **B** lengthens gradually, by 0.20 Å in **B-H** and by 0.60 Å in **B-2H** (**Tri···H$_2$O**). As shown in Figure 1, the latter exhibits some kind of water-departing structure, in which the water is stabilized by the two weak $H_2O \rightarrow U$ dative bonds (2.70 Å) and the interaction of the hydrogen of water with the phenyl π electrons of the polypyrrolic ligand (1.80 Å). Through a dehydrating reaction of both **T-2H** and **B-2H** (**Tri···H$_2$O**), **Tri** may form. It exhibits two shorter U=O_{exo} distances of 1.80 Å and two longer U–O_{endo} ones of 2.05 and 2.08 Å (calculated bond orders: 2.46, 2.48 and 1.13, 1.20, respectively). The structure of **Tri** resembles those of the experimentally reported binuclear V-O-V[48] and Fe-O-Fe[49] polypyrrolic complexes.

In these binuclear complexes, the *trans*-dioxo uranyl unit stays almost linear (166–179°). The *cis*-dioxo uranyl angle is 104° (mean value) in **B**. The calculated U_1-O_{endo}-U_2 angle is correlated with the bite angle between the two N_4 planes of the pacman ligand. The sum of these two angles roughly equals 180° except for those of **T** and **T-2H**. All of the calculated complexes display two different kinds of equatorial $N \rightarrow U$ dative bonds, longer ones in the range of 2.39–2.64 Å and shorter ones from 2.35–2.47 Å, similar to the experimental values of $[(UO_2)(H_2L)(thf)]$[54] and $[\{(thf)UO_2{\cdots}M(thf)\}(L)]$ (M = Mn and Co).[25] Moreover, relatively short U···U separations, 3.38–4.21 Å, were predicted for these binuclear complexes. The shortest U···U distance of 3.34 Å was found in **B**, with a calculated bond order of 0.33. This may arise from the bridging oxygen atoms that pull the two uranium atoms into close proximity, and the bonding electron density localized on the O=U=O=U four-membered ring could contribute to the short U···U distance.

Vibrational spectra: The vibrational spectrum is one of most effective means to characterize the U=O bonding of the uranyl complexes. The position and intensity of the U=O vibrational bands vary according to different local chemical environments of uranyl ions. In this work, we performed frequency calculations on the macrocycle ligand, mononuclear **M**, and binuclear uranium(VI) complexes. The vibrational frequency spectra in the fingerprint region of 700–1000 cm^{-1} are simulated in Figures 2 and 3 using the Lorentz function. The separated spectra for the various complexes are shown in Figures S2–S9 in the Supporting Information.

The simulated spectrum of **M** shows two strong bands at 775 and 879 cm^{-1}, which were assigned to the symmetric and asymmetric uranyl stretching modes, respectively. They are comparable to the reported infrared spectra at 815 and 909 cm^{-1} for crystalline **M**[25] (especially keeping in mind the known tendency of GGA functionals such as those used

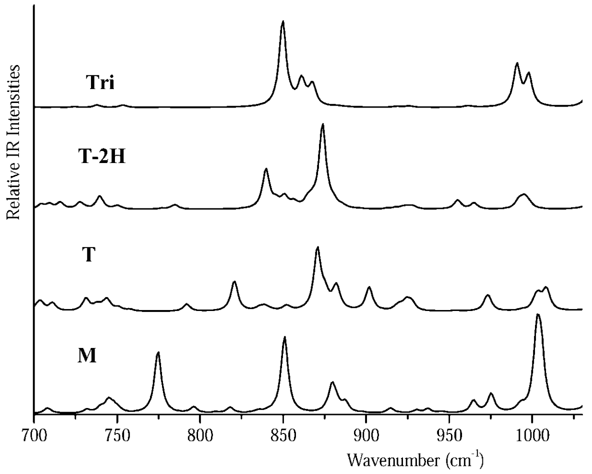


Figure 2. Simulated vibrational spectra of **M**, **T**, **T-2H** and **Tri**, in which the infrared intensities of **Tri** and **M** were divided by 11 and 1.5, respectively.

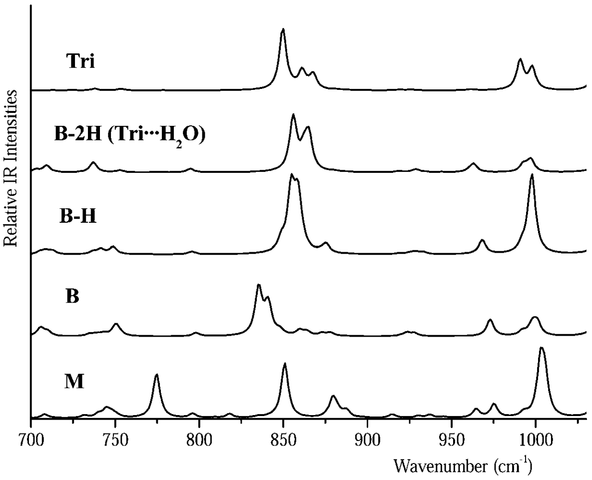


Figure 3. Simulated vibrational spectra of **M**, **B**, **B-H**, **B-2H** and **Tri**, in which the infrared intensities of **Tri** and **M** were divided by 11 and 1.5, respectively.

here to slightly underestimate bond strengths and corresponding stretching frequencies[69–71,86]) and similar to those at 895–907 cm^{-1} for [{(thf)UO$_2$···M(thf)}(L)] (M = Mn, Fe and Co),[25] 830 and 933 cm^{-1} for [UO$_2$(ReO$_4$)$_2$(TPPO)$_3$] (TPPO = triphenylphosphine oxide),[8] 797 cm^{-1} for {[UO$_2$Py$_5$][KI$_2$Py$_2$]}$_n$,[12] 927 cm^{-1} for [UO$_2$I$_2$(Py$_3$)][27] and 921–982 cm^{-1} for [UO$_2$(OTf)$_2$] (OTf = triflate) and its derivatives.[30] In the Raman resonance spectra, the U=O bonding bands were characterized at 823 cm^{-1} for crystalline **M**,[54] 804–811 cm^{-1} for [{(thf)UO$_2$···M(thf)}(L)] (M = Mn, Fe and Co)[25] and 870 and 965 cm^{-1} for [UO$_2$(H$_2$O)$_5$]$^{2+}$.[87]

As a consequence of the introduction of a second uranyl ion and the resulting increase in inequivalence of the chemical environments in the cation–cation complex **T**, the U=O bonding vibrations become more complicated (Figure 2). Other than those found at 821 cm^{-1} (ν(U$_1$=O$_{exo}$+U$_2$=O$_{exo}$)), 871 cm^{-1} (ν(U$_2$=O$_{exo}$)) and 902 cm^{-1} (ν(U$_1$=O$_{exo}$)), a weak band at 758 cm^{-1} was attributed to the U$_2$=O$_{endo}$ stretching vibrational mode. The vibration is shifted to the lower frequency region, which is correlated with the coordination of O$_{exo}$=U$_2$=O$_{endo}$→U$_1$(=O$_{exo}$)$_2$ (cation–cation interaction). We also note that the U$_2$=O$_{endo}$ distance is the longest among the four uranyl U=O bonds of **T**. Experimentally, a lower U=O vibrational frequency of 713 cm^{-1} was found in the T-shaped tetrameric [(U^{VI}O$_2${OCH(*i*Pr)$_2$}$_2$)$_4$].[11] After protonating, this U$_2$=O$_{endo}$ bond in **T-2H** is lengthened to 1.97 Å, and, consequently, its vibration shifts to much lower frequencies of 526, 555, and 577 cm^{-1}. As indicated earlier, the protonation elongates one of the U$_1$−O$_{exo}$ bonds to 2.50 Å in **T-2H** from 1.81 Å in **T** (Table 1), and does change the nature of this bond. The corresponding stretching frequency was calculated at 254 cm^{-1}, comparable to the calculated U−OH$_2$ stretching frequency values of 267, 289, and 322 cm^{-1} in [UO$_2$(H$_2$O)$_5$]$^{2+}$.[69]

Similar structural features regarding the U=O stretching vibrational bands were kept in the course of protonation from **B** to its derivatives (Figure 3). These U=O vibrational peaks were shifted slightly for **B** (835 and 841 cm^{-1}), **B-H** (854 and 859 cm^{-1}) and **B-2H** (855 and 863 cm^{-1}). Significant changes occur mainly in the O=U=O=U ring, which displays lower frequencies in the range of 400–600 cm^{-1}. The dehydration of **B-2H** or **T-2H** will form the triangle-like O=U=O=U=O complex, **Tri**. Both vibrational spectra and structural features of **Tri** are closer to those of **B-2H**, so the latter is also labeled as **Tri···H$_2$O** in the work. The U=O vibrational bands of **Tri** occur at 850, 861, and 868 cm^{-1}.

The vibrational bands related to the pacman-like polypyrrolic ligand are also present in this region (Figure S2), which inevitably perturbs the uranyl bonding and thus result in its shifting. For instance, the two intensive bands at about 850 and 1000 cm^{-1} in **M** are contributed by the ligand. In all binuclear complexes, the bands around 1000 cm^{-1} come from the ligand and U−N vibrations. With respect to the protonated complexes, the O−H vibrations were found in the high frequency region as expected, specifically at 3697 cm^{-1} (**B-H**), 3408 and 3492 cm^{-1} (**B-2H**), and 3598 and 3717 cm^{-1} (**T-2H**).

Energies of formation reaction: To study the thermodynamics of forming the mono- and binuclear complexes indicated in Scheme 1, we chose three different reagents, UO$_2$$^{2+}$, [UO$_2$(H$_2$O)$_5$]$^{2+}$, and [UO$_2(thf)_2${N(SiH$_3$)$_2$}$_2$], to react with the polypyrrolic ligand. The corresponding reactions (1)–(3) are listed in Table 2. We present the calculated total energies (ΔE), energies including zero-point vibration energy (ΔE_0) and free energies (ΔG) of these reactions in Table 3 and plot them in Figure 4 and Figures S10 and S11 in the Supporting Information, respectively.

Since the mononuclear complex **M** was experimentally synthesized, its reaction can be a reference point for evaluating the stability of the binuclear complexes. Comparing the total energies (ΔE) for reactions (1)–(3) in Figure 4, re-

Table 2. Formation reactions of mono- and binuclear U^{VI} complexes on the basis of the polypyrrolic ligand H_4L and different uranyl complexes.

Reagents	Reactions	Products	
reaction (1)			
UO_2^{2+}	$H_4L + UO_2^{2+} + THF + 2H_2O \rightarrow [(UO_2)(H_2L)(thf)] + 2H_3O^+$	**M**	
	$H_4L + 2UO_2^{2+} + 4H_2O \rightarrow [(UO_2)_2(L)] + 4H_3O^+$	**T**	**B**
	$H_4L + 2UO_2^{2+} + 2H_2O \rightarrow [(U_2O_3)(H_2O)(L)]^{2+} + 2H_3O^+$	**T-2H**	**B-2H (Tri⋯H$_2$O)**
	$H_4L + 2UO_2^{2+} + 3H_2O \rightarrow [(U_2O_4H)(L)]^+ + 3H_3O^+$	**B-H**	
	$H_4L + 2UO_2^{2+} + H_2O \rightarrow [(U_2O_3)(L)]^{2+} + 2H_3O^+$	**Tri**	
reaction (2)			
$[UO_2(H_2O)_5]^{2+}$	$H_4L + [UO_2(H_2O)_5]^{2+} + THF \rightarrow [(UO_2)(H_2L)(thf)] + 2H_3O^+ + 3H_2O$	**M**	
	$H_4L + 2[UO_2(H_2O)_5]^{2+} \rightarrow [(UO_2)_2(L)] + 4H_3O^+ + 6H_2O$	**T**	**B**
	$H_4L + 2[UO_2(H_2O)_5]^{2+} \rightarrow [(U_2O_3)(H_2O)(L)]^{2+} + 2H_3O^+ + 8H_2O$	**T-2H**	**B-2H (Tri⋯H$_2$O)**
	$H_4L + 2[UO_2(H_2O)_5]^{2+} \rightarrow [(U_2O_4H)(L)]^+ + 3H_3O^+ + 7H_2O$	**B-H**	
	$H_4L + 2[UO_2(H_2O)_5]^{2+} \rightarrow [(U_2O_3)(L)]^{2+} + 2H_3O^+ + 9H_2O$	**Tri**	
reaction (3)			
$[UO_2(thf)_2\{N(SiH_3)_2\}_2]$	$H_4L + [UO_2(thf)_2\{N(SiH_3)_2\}_2] \rightarrow [(UO_2)(H_2L)(thf)] + 2NH(SiH_3)_2 + THF$	**M**	
	$H_4L + 2[UO_2(thf)_2\{N(SiH_3)_2\}_2] \rightarrow [(UO_2)_2(L)] + 4THF + 4NH(SiH_3)_2$	**T**	**B**
	$H_4L + 2[UO_2(thf)_2\{N(SiH_3)_2\}_2] + 2H_3O^+ \rightarrow [(U_2O_3)(H_2O)(L)]^{2+} + 4THF + 4NH(SiH_3)_2 + 2H_2O$	**T-2H**	**B-2H (Tri⋯H$_2$O)**
	$H_4L + 2[UO_2(thf)_2\{N(SiH_3)_2\}_2] + H_3O^+ \rightarrow [(U_2O_4H)(L)]^+ + 4THF + 4NH(SiH_3)_2 + H_2O$	**B-H**	
	$H_4L + 2[UO_2(thf)_2\{N(SiH_3)_2\}_2] + 2H_3O^+ \rightarrow [(U_2O_3)(L)]^{2+} + 4THF + 4NH(SiH_3)_2 + 3H_2O$	**Tri**	

action (1) is quite different. According to reaction (1), once **M** is formed, other binuclear complexes should be easily obtained. However, this is not the case experimentally.[54] Apparently, the naked UO_2^{2+} ion involved in reaction (1) gave unreasonable results, in accordance with our proposal[69] that the first water coordination sphere of the uranyl ion should be included to describe its related reaction energies, that is, the $[UO_2(H_2O)_5]^{2+}$ model. Thus, reaction (2) seems more reasonable, since the formations of **T** and **B** are endothermic. In the reaction, 108.88 and 96.44 kcal mol^{-1} total energies were provided to form **T** and **B** from **M**, respectively. Slightly less energy was needed in reaction (3), in which the $[UO_2(thf)_2\{N(SiH_3)_2\}_2]$ complex provides the uranyl ion. In addition, both reactions (2) and (3) indicate that once **T** and **B** are formed, protonation is relatively easy and the dehydration from **T-2H** and **B-2H** needs total energies of 15.64 and 33.71 kcal mol^{-1}, respectively. For each reaction, we found the trends in ΔE_0 (Figure S10) and ΔG (Figure S11) similar to those in ΔE (Figure 4) with the only exception that the free energies of reaction (3) would imply a slightly exothermic path to form binuclear complexes from the mononuclear one.

The thermodynamic calculations reported so far were performed in the gas phase, which is different from the solution environment involved in the real experimental reaction. To test the reasonability of the gas-phase results, we employed the COSMO solvent model in the ADF code to account for the behavior of uranium complexes in solution (THF solution). We calculated solvation free energies of −18.68, −19.50, and −19.38 kcal mol^{-1} for the neutral complexes **M**, **T**, and **B**, respectively, and −147.22 kcal mol^{-1} for the positively charged complex **T-2H**. Thus, the introduction of continuum solvation stabilizes the complexes, especially for the charged complexes. In contrast, the inclusion of solvation does not change significantly the free energies of the formation reaction for each complex (in Table 3) and, in particular, the trend of the relative energies (in Figure S12 in the Supporting Information), with the notable exception of reaction (1). As mentioned above, the naked UO_2^{2+} ion in the gas phase cannot give results comparable to those in solution, whereas the $[UO_2(H_2O)_5]^{2+}$ model does. Overall, the agreement of the reaction free energies of complexes between the gas phase and solution shows that the present gas-phase calculations based on reactions (2) and (3) are reliable.

Table 3. Energies (kcal mol^{-1}) of the formation reactions of mono- and binuclear U^{VI} complexes in the gas phase, together with the calculated free energies in solution reactions in parentheses.

		M	**T**	**T-2H**	**B**	**B-H**	**B-2H (Tri⋯H$_2$O)**	**Tri**
reaction (1)	ΔE	−234.76	−407.29	−454.79	−419.73	−483.50	−472.86	−439.15
	ΔE_0	−230.81	−403.62	−454.10	−416.25	−481.37	−471.89	−440.78
	ΔG	−201.86 (41.33)	−376.00 (106.91)	−427.18 (74.89)	−389.46 (93.57)	−453.78	−443.87	−424.20
reaction (2)	ΔE	46.64	155.52	108.02	143.08	79.31	89.95	123.66
	ΔE_0	40.53	139.07	88.59	126.44	61.31	70.79	101.90
	ΔG	24.29 (20.60)	76.31 (65.46)	25.12 (33.43)	62.85 (52.12)	−1.47	8.44	28.11
reaction (3)	ΔE	−18.38	25.48	−22.02	13.04	−50.73	−40.09	−6.38
	ΔE_0	−20.02	17.97	−32.51	5.34	−59.79	−50.31	−19.19
	ΔG	−32.65 (−30.85)	−37.58 (−37.45)	-88.77 (−69.48)	−51.04 (−50.79)	−115.37	−105.46	−85.79

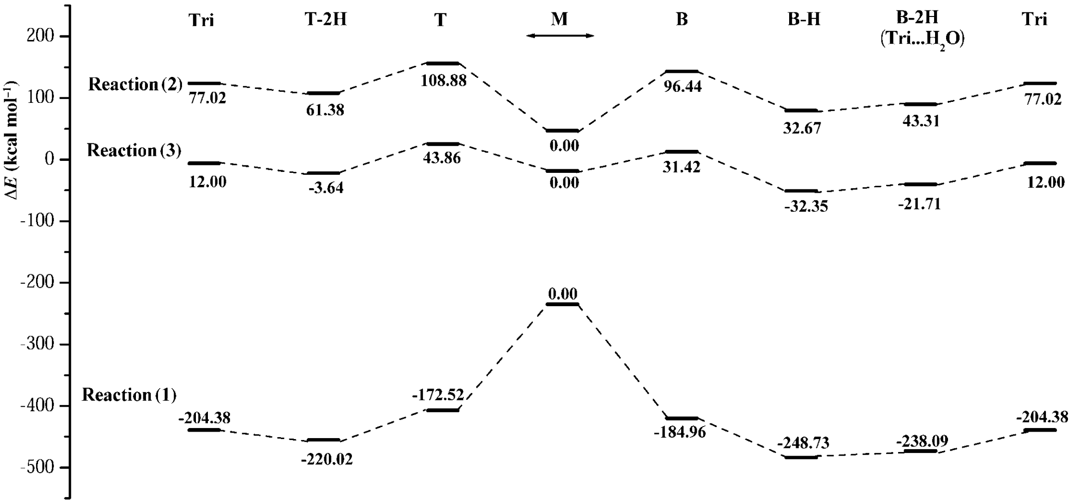


Figure 4. Total energies of formation reactions of mono- and binuclear U^{VI} complexes on the basis of polypyrrolic ligand and uranyl complexes, together with values of reaction energies relative to that of mononuclear complex.

Conclusions

Mono- and binuclear U^{VI} complexes, including several unusual structural isomers, were explored using density functional calculations. The geometry parameters of binuclear complexes are comparable to experimental values of binuclear $UO_2^{2+}\cdots M^{2+}$ complexes (M = Mn and Co).[25] Two cation–cation complexes, **B** and **T**, were found with unusual coordination modes of uranyls: the former is a butterflylike unit with one linear uranyl coordinating side-by-side to another *cis*-uranyl, and the latter is a T-shaped moiety formed by the two linear uranyls. Experimental reports on any structure similar to isomer **B** do not exist; however, experimental tetrameric uranyl analogues of **T** are known.[10,11] As a possible product of both **B** and **T**, we have found a trianglelike binuclear uranium(VI) complex **Tri** having a O=U=O=U=O unit with a shared oxygen.

Frequency calculations confirmed the stationary points for the uranium(VI) complexes and provided detailed information about the characteristic bands of the U=O stretching vibrations. For example, besides those found at 821, 871, and 902 cm^{-1} for $\nu(U{=}O_{exo})$, a weak band at 758 cm^{-1} of **T** was attributed to the $U_2{=}O_{endo}$ stretching vibrational mode. The shift to the lower frequency region was related to the presence of cation–cation interactions $\{O_{exo}{=}U_2{=}O_{endo}\rightarrow U_1({=}O_{exo})_2\}$ in the T-shaped complex.

Amongst the binuclear uranyl complexes, the butterfly-type complex **B** was found to be more stable than the T-shaped complex **T**. Formation of the binuclear **T** and **B** species from the mononuclear **M** was found to be endothermic if realistic uranyl complexes were used as reagents. The further protonation of **T** and **B** is relatively easy; subsequent loss of water costs about 16 and 34 kcal mol^{-1} in energy, respectively. The comparison between the gas phase and solution in the reaction free energies revealed that the gas phase calculations based on reactions (2) and (3) are reliable enough to give reasonable results for the formation of the uranium complexes. We hope that these studies can provide theoretical support for the synthesis of novel binuclear uranium complexes.

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