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ARTICLE TYPE

# Promising Density Functional Theory Methods for Predicting the Structures of Uranyl Complexes

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The structural parameters of uranyl complexes may provide important hints for understanding the electronic structures of the U-X (ligand) bond. The present study aims to find out a reliable theoretical method to simulate the structures of different uranyl complexes. Examining the performance of different relativistic effective core pseudopotentials (RECPs) and different density functional theory (DFT) methods, we found that the overall performance of BB1K/(SDD-MWB60:6-311G(d,p)) (**M2-B1**) and LC-BLYP/(SDD-MWB60:6-311G(d,p)) (**M7-B1**) methods is relatively better than all the other examined ones (including the popular B3LYP method). Good linear correlations has been gained between the calculation results with **M2-B1** or **M7-B1** and the experimental ones (x-ray crystal structure). The  $R^2$  of both these methods are about 0.985, and the SD are both about 0.05 Å for 68 U-X bond distances. On this basis, the preliminary ligand structure-binding ability analysis of U-O bonds and the elucidation of the binding mode of the azide group in concerned U-N(azide) compound have been provided.

## 1. Introduction

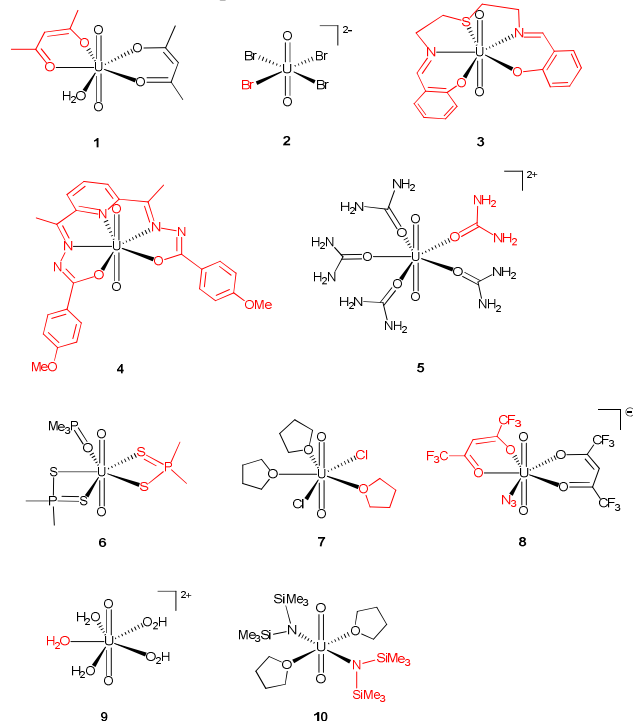
The extraction of uranyl dication ( $\text{UO}_2^{2+}$ ) is fundamentally important for the development of nuclear energy, fuel and materials.<sup>1</sup> Generally,  $\text{UO}_2^{2+}$  exist in natural environment as the ligand coordinated complexes, and the tolerated ligands includes water, carbonate, and nitrite etc.<sup>2</sup> Therefore, the design of novel ligands with stronger binding ability with  $\text{UO}_2^{2+}$  (relative to the aforementioned ones) are promising for the extraction of uranium and the migration of nuclear wastes. In the past decades, various ligands (such as amidoximate,<sup>3</sup> glutarimidedioxime,<sup>4</sup> and glycine<sup>5</sup>) have been designed from both experimental and theoretical aspects.<sup>6,7</sup> In addition, the x-ray crystal structure characterization, the electronic structure analysis, the spectroscopic probes on the uranyl complexes and the kinetic measurements on the ligand exchange reactions have all been frequently used for better understanding of the binding modes between  $\text{UO}_2^{2+}$  and the concerned ligands.<sup>8-15</sup> For example, the charge distribution and the molecular structure of  $[\text{UO}_2(\text{OH})_x(\text{H}_2\text{O})_y]^{n+/-}$  have been widely studied with different methods (such as Raman Frequency<sup>9a</sup> and theoretical calculations<sup>9b,c</sup>), and the pKa value of the solvent was found to be determinant for the predominant structure of the uranyl species. Similarly, the oxo exchange reactions between uranyl complexes and water have also been extensively studied by spectroscopy and density functional theory (DFT) calculations.<sup>10</sup>

Systematic understandings on the ligand structure-binding ability relationships might provide important hints for future development of novel and efficient uranyl extraction materials.<sup>8</sup> Due to the experimental difficulties (such as the high cost and

complicated handling procedures), theoretical calculations have recently become an increasingly attractive method for studying the uranyl complexes. Nonetheless, the currently used theoretical methods are under debate in some cases. For example, the relative accuracy of the small core (SC)<sup>16</sup> relativistic effective core pseudopotentials (RECPs) and the large core (LC) RECPs<sup>17</sup> remains unknown. Despite SC-RECP has been proposed to be more accurate than LC-ECP in many previous studies,<sup>18,19</sup> we wonder whether this conclusions generally applicable for various uranyl systems or not? Meanwhile, both the Hartree-Fock (HF) and the Wood-Boring (WB) quasi-relativistic ECPs correspond to the SC-RECPs (in Gaussian software)<sup>20</sup> and are able to treat U atom, while the relative accuracy of these two SC-ECPs remains unclear. What's more important, the popular B3LYP functional has been frequently used in previous theoretical studies,<sup>21,22</sup> while its reliability has been found to be inferior in several cases.<sup>9f,23</sup> With the increasing awareness of the failure of the traditional hybride functionals (e.g. in treating seperated molecules<sup>24</sup> and intramolecular structures,<sup>25</sup> and interactions<sup>26</sup>) and the recent development of the functionals (such as the long-range correction (LC) DFT methods introduced by Iikura *et al.*,<sup>27</sup> the Coulomb-attenuating model (CAM-B3LYP) of Yanai *et al.*<sup>28</sup> and the M06 functionals developed by Truhlar *et al.*<sup>29</sup>), the overall performance of the DFT calculations in treating organic, metal-organic systems and the weak interactions (such as hydrogen bond) has been greatly improved.<sup>30-33</sup> Therefore, these developed functionals might show great potential in imporving the current theoretical calculations on uranyl complexes.

In the present study, systematic examination has been performed to assess the performance of different theoretical

methods (including both the RECPs and the DFT functionals) in modeling the structures of uranyl complexes. After a survey of the single x-ray crystal structures on the reported mononuclear uranyl complexes, 10 structurally typical uranyl complexes (bearing different types of ligands such as H<sub>2</sub>O, 1,3-diketone, halide, amide etc, Figure 1) were chosen as the samples, and the linear correlations between the calculated U-X (X=O, N, S etc) bond distances and experimental ones are used to evaluate the



**Figure 1.** The selected uranyl complexes for evaluation of different theoretical methods.

performance of different methods. The calculation results indicate that Stuttgart's SC-ECP with WB quasi-relativistic (SDD-MWB60) gives better performance relative to all the concerned LC-ECPs (including Stuttgart RLC ECP, the Lan12dz ECP, and the CRENL ECP), while the overall performance of Stuttgart's SC-ECP with HF relativistic (SDD-MHF60) is the worst among different ones. What's more important, both BBIK and LC-BLYP are proficient in predicting the U-X bond distances

**Table 1.** Comparison between the bond distances (BD) calculated by B3LYP/(ECP:6-311G(d,p)) and the experimental results for the uranyl C-S compounds in Figure 1.<sup>a-f</sup>

Compound	U-X	BD <sup>exp</sup>	BD <sup>M1-B1</sup>	BD <sup>M1-B2</sup>	BD <sup>M1-B3</sup>	BD <sup>M1-B4</sup>	BD <sup>M1-B5</sup>
	U-O <sup>1</sup>	1.733	1.775	1.716	1.753	1.779	1.756
	U-O <sup>2</sup>	1.753	1.779	1.719	1.756	1.782	1.759
	U-O <sup>3</sup>	2.338	2.339	2.492	2.350	2.364	2.355
	U-O <sup>4</sup>	2.385	2.394	2.551	2.404	2.502	2.410
	U-O <sup>5</sup>	2.488	2.587	2.822	2.615	2.614	2.617
	U-O <sup>6</sup>	2.382	2.474	2.709	2.497	2.423	2.504
	U-O <sup>7</sup>	2.349	2.341	2.474	2.351	2.363	2.356

(relative to the other examined DFT methods including B3LYP, CAM-B3LYP, PBE1W, M06, and MPW3LYP), reflecting from the significantly lower systematic error (i.e. the intercept of the linear fit) between the calculation results and the experimental characterized ones. In addition to the accurate modeling of structural parameters of uranyl complexes, the preliminary ligand structure-binding strength analysis of different O-ligated ligands and the detailed analysis on the binding modes of one U-N(azide) bond has been carried out. We wish the clarified method could benefit the future systematic studies on the ligand structure-binding ability relationships and the design of more plausible uranyl extraction ligands.

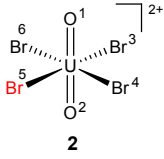
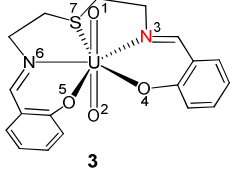
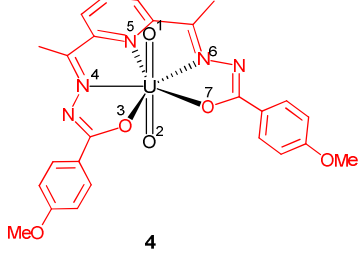
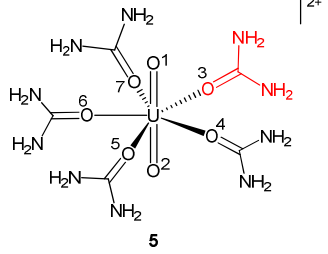
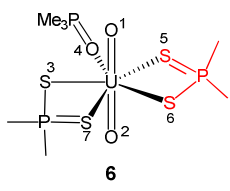
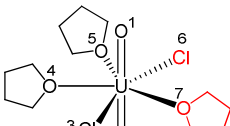
## 2. Results and Discussion

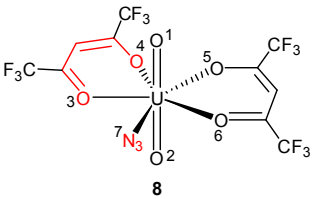
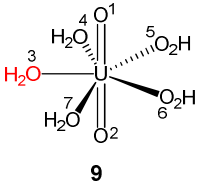
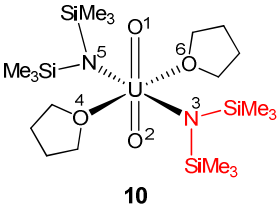
### 2.1 Comparison between different calculation methods

In the present study, 10 structurally representative mononuclear uranyl complexes were chosen as the samples, according to the following concerns: (a) the ligand bearing different elements, including C, H, O, N, S, P, Si, F, Cl, Br were taken into account. (b) different types of ligands, such as the dative ligands of H<sub>2</sub>O, tetrahydrofuran (THF), amide and the covalent ligands such as halide, 1,3-diketone, amine ligands, were included. (c) both the monodentate and the multidentate chelated ligands were selected.

#### 2.1.1 The performance of different effective core potentials (ECPs) with B3LYP method.

In the present study, the general performance of different RECPs on uranium atom were first examined. The examined RECPs include: the Stuttgart RSC 1997 ECP (with either MWB60 or MHF60 relativistics), the Stuttgart RLC ECP, the Lan12dz ECP, and the CRENL ECP. The former two RECPs correspond to SC-RECPs, and are designated as SDD-MWB60 and SDD-MHF60, respectively. The latter three RECPs correspond to LC-RECPs. All these RECPs (except SDD-MHF60) are cited from the EMSL basis set library,<sup>34</sup> and SDD-MHF60 RECPs are used directly from the Gaussian software. The traditional B3LYP method is used for the calculations in this section, and 6-311G(d,p) basis set<sup>35</sup> are used for all other atoms except U. The related calculation results are given in Table 1.

 <p style="text-align: center;"><b>2</b></p>	<b>U-O<sup>1</sup></b>	1.766	1.771	1.717	1.748	1.775	1.751
	<b>U-O<sup>2</sup></b>	1.766	1.771	1.718	1.748	1.775	1.751
	<b>U-Br<sup>3</sup></b>	2.814	2.929	3.087	2.949	2.969	2.950
	<b>U-Br<sup>4</sup></b>	2.816	2.929	3.088	2.949	2.969	2.950
	<b>U-Br<sup>5</sup></b>	2.814	2.929	3.090	2.949	2.969	2.950
	<b>U-Br<sup>6</sup></b>	2.816	2.930	3.095	2.949	2.969	2.950
 <p style="text-align: center;"><b>3</b></p>	<b>U-O<sup>1</sup></b>	1.650	1.783	1.721	1.759	1.784	1.762
	<b>U-O<sup>2</sup></b>	1.662	1.791	1.727	1.766	1.793	1.769
	<b>U-N<sup>3</sup></b>	2.595	2.709	2.926	2.739	2.730	2.734
	<b>U-O<sup>4</sup></b>	2.299	2.229	2.379	2.238	2.259	2.246
	<b>U-O<sup>5</sup></b>	2.215	2.235	2.379	2.243	2.263	2.250
	<b>U-N<sup>6</sup></b>	2.601	2.691	2.915	2.718	2.721	2.717
	<b>U-S<sup>7</sup></b>	2.964	3.039	3.250	3.084	3.084	3.075
 <p style="text-align: center;"><b>4</b></p>	<b>U-O<sup>1</sup></b>	1.769	1.777	1.719	1.755	1.781	1.758
	<b>U-O<sup>2</sup></b>	1.768	1.777	1.720	1.755	1.781	1.758
	<b>U-O<sup>3</sup></b>	2.303	2.323	2.459	2.380	2.399	2.388
	<b>U-N<sup>4</sup></b>	2.493	2.615	2.822	2.657	2.665	2.657
	<b>U-N<sup>5</sup></b>	2.521	2.456	2.642	2.484	2.494	2.483
	<b>U-N<sup>6</sup></b>	2.470	2.632	2.836	2.641	2.651	2.641
	<b>U-O<sup>7</sup></b>	2.321	2.369	2.541	2.332	2.351	2.340
 <p style="text-align: center;"><b>5</b></p>	<b>U-O<sup>1</sup></b>	1.777	1.779	1.710	1.752	1.778	1.754
	<b>U-O<sup>2</sup></b>	1.778	1.791	1.718	1.763	1.792	1.766
	<b>U-O<sup>3</sup></b>	2.337	2.371	2.508	2.383	2.392	2.387
	<b>U-O<sup>4</sup></b>	2.337	2.371	2.508	2.383	2.392	2.387
	<b>U-O<sup>5</sup></b>	2.442	2.457	2.675	2.480	2.485	2.488
	<b>U-O<sup>6</sup></b>	2.366	2.400	2.567	2.421	2.433	2.430
	<b>U-O<sup>7</sup></b>	2.442	2.457	2.675	2.480	2.485	2.488
 <p style="text-align: center;"><b>6</b></p>	<b>U-O<sup>1</sup></b>	1.741	1.766	1.715	1.743	1.769	1.755
	<b>U-O<sup>2</sup></b>	1.743	1.776	1.717	1.752	1.779	1.756
	<b>U-S<sup>3</sup></b>	2.867	2.952	3.142	2.976	2.979	2.964
	<b>U-O<sup>4</sup></b>	2.317	2.382	2.605	2.393	2.411	2.405
	<b>U-S<sup>5</sup></b>	2.867	2.946	3.084	2.966	2.987	2.974
	<b>U-S<sup>6</sup></b>	2.881	2.936	3.131	2.960	2.984	2.964
	<b>U-S<sup>7</sup></b>	2.881	2.940	3.146	2.966	2.978	2.958
 <p style="text-align: center;"><b>7</b></p>	<b>U-O<sup>1</sup></b>	1.765	1.774	1.714	1.750	1.775	1.753
	<b>U-O<sup>2</sup></b>	1.766	1.774	1.715	1.750	1.775	1.753
	<b>U-Cl<sup>3</sup></b>	2.697	2.715	2.791	2.726	2.742	2.723

	<b>U-O<sup>4</sup></b>	2.466	2.566	2.806	2.593	2.595	2.599
	<b>U-O<sup>5</sup></b>	2.464	2.560	2.814	2.593	2.597	2.599
	<b>U-Cl<sup>6</sup></b>	2.687	2.712	2.791	2.724	2.744	2.725
	<b>U-O<sup>7</sup></b>	2.444	2.474	2.701	2.493	2.502	2.501
 <p style="text-align: center;"><b>8</b></p>	<b>U-O<sup>1</sup></b>	1.688	1.776	1.712	1.754	1.756	1.756
	<b>U-O<sup>2</sup></b>	1.725	1.778	1.715	1.756	1.758	1.759
	<b>U-O<sup>3</sup></b>	2.417	2.485	2.666	2.497	2.502	2.502
	<b>U-O<sup>4</sup></b>	2.424	2.509	2.679	2.524	2.532	2.532
	<b>U-O<sup>5</sup></b>	2.412	2.509	2.679	2.524	2.532	2.532
	<b>U-O<sup>6</sup></b>	2.401	2.485	2.666	2.497	2.502	2.502
	<b>U-N<sup>7</sup></b>	2.382	2.301	2.459	2.316	2.320	2.320
 <p style="text-align: center;"><b>9</b></p>	<b>U-O<sup>1</sup></b>	1.751	1.749	1.689	1.728	1.753	1.730
	<b>U-O<sup>2</sup></b>	1.751	1.749	1.690	1.728	1.753	1.730
	<b>U-O<sup>3</sup></b>	2.402	2.486	2.630	2.501	2.510	2.508
	<b>U-O<sup>4</sup></b>	2.384	2.485	2.628	2.500	2.503	2.507
	<b>U-O<sup>5</sup></b>	2.384	2.492	2.633	2.512	2.510	2.517
	<b>U-O<sup>6</sup></b>	2.402	2.494	2.635	2.514	2.527	2.522
	<b>U-N<sup>7</sup></b>	2.455	2.500	2.639	2.523	2.527	2.527
 <p style="text-align: center;"><b>10</b></p>	<b>U-O<sup>1</sup></b>	1.789	1.797	1.738	1.770	1.798	1.774
	<b>U-O<sup>2</sup></b>	1.789	1.797	1.739	1.770	1.798	1.775
	<b>U-N<sup>3</sup></b>	2.316	2.343	2.441	2.363	2.376	2.360
	<b>U-O<sup>4</sup></b>	2.432	2.516	2.870	2.543	2.559	2.548
	<b>U-N<sup>5</sup></b>	2.317	2.343	2.412	2.363	2.376	2.364
	<b>U-O<sup>6</sup></b>	2.445	2.518	2.876	2.545	2.562	2.550
<b>Intercept (k)</b>		-0.050	-0.158	-0.056	-0.071	-0.060	
<b>R<sup>2</sup></b>		0.9830	0.8590	0.9751	0.9787	0.9755	
<b>SD</b>		0.050	0.144	0.061	0.056	0.060	
<b>RMSD</b>		0.070	0.213	0.083	0.090	0.085	

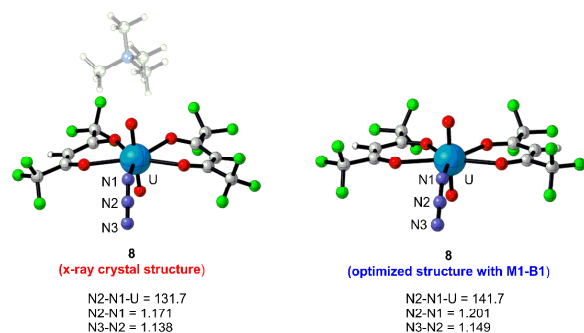
<sup>a</sup>The regression slopes for all correlations between calculation and experimental results are fixed at 1.00, and the linear correlation used is  $BD^{exp} = BD^{calc} + k$  (BD represents the U-X bond distances). <sup>b</sup>The linear correlation coefficient  $R^2$  correspond to the adjacent R square, SD (standard deviation) =  $[\sum(x_i - \bar{x})^2 / (N-1)]^{1/2}$  (N=62,  $i=1-62$ ,  $x_i$  represents the calculated data for each species,  $\bar{x}$  is the fitted value of the 74 calculated data); RMSD (root-mean-square deviation) =  $[\sum(x_i - y_i)^2 / N]^{1/2}$  (N=68,  $x_i$  represents the calculated data for each data, and  $y_i$  represents the related experimental data). <sup>c</sup>All the bond distances are given in angstrom. <sup>d</sup>M1, B1, B2, B3, B4 and B5 denote to B3LYP, SC-SDD(MWB)/6-311G(d,p), SC-SDD(MHF)/6-311G(d,p), LC-SDD/6-311G(d,p), LC-LanL2DZ/6-311G(d,p), and LC-CRENBL/6-311G(d,p), respectively. <sup>e</sup>The x-ray crystal structure for **1-10** are cited from ref. 36-45.

Some conclusions can be generated from the calculation results in Table 1. First, the overall performance of the SDD-10 MHF60 (**B2**) in modeling the uranyl structures are relatively worse than all the other RECPs, reflecting from significant deviations (e.g. U-O<sup>5</sup> bond distance in **1** and the U-N<sup>3</sup> bond distance in **3**) and the bad correlation factors (k, R<sup>2</sup>, SD and

RMSD) shown in Table 1. Second, the calculated bond distances 15 with all the other examined RECPs (the SC-RECP of **B1**, and the LC-RECPs of **B3-B5**) are close to the related ones of the x-ray crystal structure: the R<sup>2</sup> of linear correlation relationships are all beyond 0.97, and the SD values are lower than 0.07 Å. Third, despite of the good correlations (with **B1** or **B3-B5**), all these

calculation methods tend to slightly overestimate the U-X bond distances systematically, reflecting from all the negative intercepts (k) of the linear correlation relationships ( $BD^{exp}=BD^{calc}+k$ ). Fourth, the overall performance of the SDD-MWB60 (**B1**) in simulating the U-X bond distances is slightly better than those with the LC-RECPs (**B3-B5**), while the overall accuracy of all the examined LC-RECPs are all comparable (Table 1).

An interesting observation has been noted from the calculation results in Table 1. The experimentally measured U-X bond distances are generally close to or slightly overestimated by the theoretical calculations (except for SDD-MHF60), whereas the U-N<sup>7</sup> bond distance in **8** is significantly underestimated for all these methods (by 0.05 ~ 0.1 Å). To elucidate the reason for such observations, we compared the structural parameters of the azide group in **8** with those in the related x-ray crystal structure reported by Prasad et al.<sup>43</sup> In Figure 2, the key bond distances and the bond angles have been slightly overestimated by calculations, indicating the slightly overestimated double bond character of the



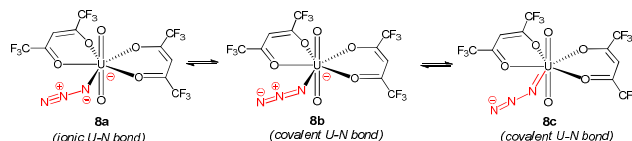
**Figure 2.** The comparison between the x-ray crystal structure (with  $[N(CH_3)_4]^+$ ) and the optimized structure of **8** calculated with **M1-B1** method. The bond distance and angles are given in angstrom and degree, respectively.

**Table 2.** Comparison between the bond distances (BD) calculated by *DFT/B1* and the experimental results for the complex **1**.<sup>a-c</sup>

Compound	U-X	BD <sup>exp</sup>	BD <sup>M1-B1</sup>	BD <sup>M2-B1</sup>	BD <sup>M3-B1</sup>	BD <sup>M4-B1</sup>	BD <sup>M5-B1</sup>	BD <sup>M6-B1</sup>	BD <sup>M7-B1</sup>
<p><b>1</b></p>	U-O <sup>1</sup>	1.733	1.775	1.735	1.801	1.774	1.773	1.757	1.738
	U-O <sup>2</sup>	1.753	1.779	1.738	1.805	1.776	1.776	1.761	1.741
	U-O <sup>3</sup>	2.338	2.339	2.319	2.347	2.352	2.335	2.329	2.318
	U-O <sup>4</sup>	2.385	2.394	2.411	2.382	2.402	2.397	2.438	2.410
	U-O <sup>5</sup>	2.488	2.587	2.531	2.629	2.607	2.571	2.537	2.496
	U-O <sup>6</sup>	2.382	2.474	2.404	2.499	2.477	2.465	2.407	2.410
	U-O <sup>7</sup>	2.349	2.341	2.319	2.345	2.352	2.337	2.327	2.318
Intercept (k)			-0.045	-0.004	-0.054	-0.044	-0.032	-0.018	0.000
R <sup>2</sup>			0.9814	0.9933	0.9666	0.9803	0.9854	0.9925	0.9952
SD			0.053	0.027	0.058	0.045	0.039	0.028	0.022
RMSD			0.050	0.025	0.077	0.061	0.048	0.032	0.021

<sup>a</sup> The regression slopes for all correlations of calculation and experimental results are fixed at 1.00, and the linear correlation used is  $BD^{exp}=BD^{calc}+k$  (BD represents the U-X bond distances in Å). <sup>b</sup>M2, M3, M4, M5, M6 and M7 denote to BB1K, PBE1W, M06, MPW3LYP, CAM-B3LYP, and LC-BLYP, respectively.

U-N bond (the proportion of the resonance structure of **8c**, Scheme 1) (More details about this structure is given in Section 2.3, *vide supra*). The origin of such observation might be related to that the calculated geometry are more idealized/symmetric, and thus facilitating better orbital conjunctions between the uranium center and the azide ligand. For the same reason, the 1,3-diketone ligands in **8** accept a better planar structure relative to the experimental characterized ones (Figure 2).



**Scheme 1.** The main resonance structures of the azide group in complex **8**.

### 2.1.2 The performance of different DFT methods with SDD-MWB60 RECPs (**B1**)

The calculation results and the discussions in Section 2.1.1 indicate that the overall performance of the SDD-MWB60 (**B1**) is relatively better than all the other examined ones, and therefore this RECP is used for the comparison between different DFT methods. Several typical DFT methods, including the traditional hybrid B3LYP functional (M1),<sup>22</sup> the Global-hybrid meta-GGA (Generalized gradient approximations) BB1K functional,<sup>24</sup> the GGA PBE1W<sup>25</sup> and M06 functionals<sup>26</sup>, the hybrid GGA functional MPW3LYP<sup>27</sup> and the range-separated functionals LC-BLYP or CAM-B3LYP were taken into account.

Considering that the overall performance of calculation method in treating the complexes **1-10** are generally in consistency, we use the calculations on complex **1** as an sample to reduce the computational cost in this section. The related calculation results are given in Table 2.



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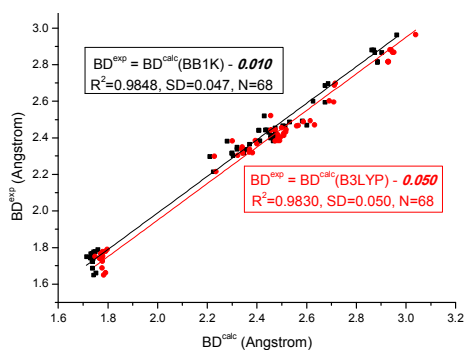
From the calculation results in Table 2, it can be seen that the overall performances of BB1K (M2) and LC-BLYP (M7) are relatively better than all the other examined DFT methods, reflecting from the significantly better correlation coefficients ( $k$ ,  $R^2$ , and SD) and the lower deviations value (RMSD). Meanwhile, the performance of CAM-B3LYP (M6) is slightly worse than the aforementioned two methods, and relatively better than the other ones. The PBE1W (M3) represents the worst one among all these methods.

On the basis of the calculation results in Table 2, we further used BB1K, LC-BLYP and CAM-B3LYP methods to optimize all the structures in Figure 1 to make sure these methods are generally reliable in simulating different types of uranyl complexes. For clarity reasons, the detailed calculation results

have been given in the supporting information. From the correlation and the deviation coefficients with B3LYP, BB1K, CAM-B3LYP and LC-BLYP methods (Table 3), we found that despite the  $R^2$  and SD values are comparable for all these methods, the RMSD value and especially the intercept values generated with BB1K, CAM-B3LYP, and LC-BLYP methods are significantly better than the related ones with B3LYP method. This conclusion is also supported by the comparisons between the linear correlation plots of the BB1K (as an example) and the B3LYP methods (Figure 3). In addition, the overall performance of BB1K and LC-BLYP is comparable and relatively better than CAM-B3LYP, indicating that these two methods could be better choices in predicting/modeling the structures of uranyl complexes.

**Table 3.** Comparison between the linear correlations between experiments and different theoretical methods for the complexes 1-10.

		B3LYP	BB1K	CAM-B3LYP	LC-BLYP
U-X in 1-10 (X=O, N, Cl ...)	Intercept (k)	-0.050	-0.010	-0.032	-0.012
	$R^2$	0.9830	0.9848	0.9861	0.9871
	SD	0.050	0.047	0.047	0.045
	RMSD	0.070	0.048	0.057	0.047



**Figure 3.** The linear correlation between the experimentally reported U-X bond distances of 1-10 and the calculated ones with M2-B1(BB1K, in black) and M1-B1 (B3LYP, in red) methods.

**Table 4.** Comparison between the linear correlations between experiments and different theoretical methods (M1, M2, and M7-B1) for U-O and U-X bonds in 1-10.

		M1-B1	M2-B1	M7-B1
U-O (48 data)	Intercept (k)	-0.044	-0.008	-0.005
	$R^2$	0.9833	0.9847	0.9862
	SD	0.044	0.042	0.039
	RMSD	0.062	0.042	0.0393
U-X (X=N, Br, Cl...) (20 data)	Intercept (k)	-0.065	-0.018	-0.028
	$R^2$	0.9333	0.9325	0.9409
	SD	0.0614	0.059	0.055
	RMSD	0.088	0.060	0.061

From the results in Table 4, it can be seen that the overall performance of the calculation method in modeling the U-O bond distances are generally better than those of the other bonds. The intercept of the correlations related to the U-X bonds are always larger than that related to the U-O bonds, and the other linear correlation coefficients ( $R^2$  and SD) are also relatively worse for the U-X bonds. In addition to these observations, the overall performance of BB1K and LC-BLYP remains relatively better

## 2.2 The theoretical simulations on the categorized U-O and U-X (X=N, Cl, Br, S etc) bonds

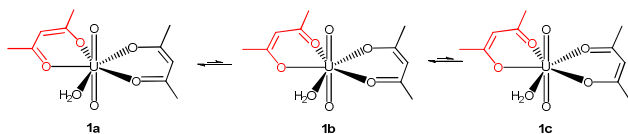
The calculation results in Section 2.1 indicate that both BB1K/(SDD-MWB60:6-311G(d,p)) (M2-B1) and LC-BLYP/(SDD-MWB60:6-311G(d,p)) (M7-B1) methods are proficient in predicting the U-X bond distances. In this section, the concerned U-X bonds in Figure 1 was categorized, and the performance of B3LYP (M1-B1), BB1K (M2-B1) and LC-BLYP (M7-B1) were examined in detail.

than that of B3LYP for both U-O and U-X bond distance categories. This conclusion is consistent with the aforementioned conclusions on the priority of BB1K and LC-BLYP. Both of them are proposed to be more promising in modeling the uranyl complexes relative to the popular B3LYP method.

### 2.3 The ligand structure-binding ability relationships of O-ligated ligand

With the aid of BB1K and LC-BLYP methods, some preliminary analysis on the binding ability of different types of O-ligated ligands have been provided in this section.

The selected uranyl complexes in Figure 1 consists of different types of O-ligand (on the equatorial plane), including water, tetrahydrofuran (THF), urea, 1,3-diketone (with  $-\text{Me}$  or  $-\text{CF}_3$  substituents), trimethylphosphine oxide and the multidentate O-ligands (in **3** and **4**). From the calculation results shown in Table 3, it can be seen that the equatorial U-O bond distances in **1-10** generally follow the sequence of: U-O ( $\text{H}_2\text{O}$ ,  $\sim 2.55$  Å) > U-O (THF,  $\sim 2.50$  Å) > U-O (1,3-diketone,  $\sim 2.40$  Å) > U-O (urea/trimethylphosphine oxide,  $\sim 2.35$  Å) > U-O (multidentate,  $\sim 2.25$  Å). The results imply that the covalent U-O bond distances are relatively shorter than the dative ones, and this proposal is also supported by the relatively shorter U-O bond distances in  $\text{UO}_2(\text{OH})_5$  than the related ones in  $\text{UO}_2(\text{OH}_2)_5$  ( $2.34$  Å<sup>10e</sup> vs  $2.46$  Å). Meanwhile, among different U-O dative bonds, the U-O( $\text{sp}^3$ ) bond distances are relatively longer than U-O( $\text{sp}^2$ ) bonds, presumably due to the  $\pi$  back-donation from the f orbital of U center and  $\pi^*$  orbitals of the related unsaturated chemical bonds (such as C=O and P=O). According to the aforementioned discussions, the slightly shorter U-O bond distances distinct from  $\text{H}_2\text{O}$  in **1** relative to the nearby ones seem to suggest that the former ones are formally more similar to the U-O( $\text{sp}^3$ ) while the latter ones are more likely the U-O( $\text{sp}^2$ ) bonds. In other words, the two C-O bonds in the 1,3-diketone ligands are not symmetric, and the Lewis structure of **1a** in Figure 4 can better describe its electronic structure than all the other ones. Similar observation and conclusion is also applicable to the Lewis structure of **8**. In addition, the slightly longer U-O bond distances of the 1,3-diketone ligand in **8** relative to the related ones in **1** indicate that the electron-withdrawing group ( $-\text{CF}_3$ ) slightly weakens the binding strength of the 1,3-diketone ligand.

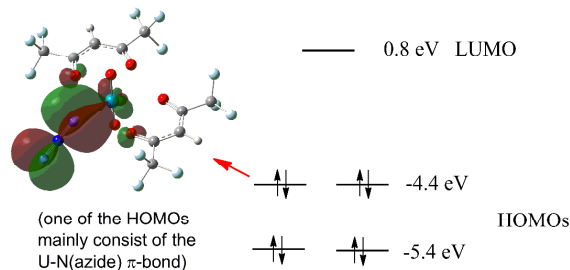


**Figure 4.** The main resonance structures (on the 1,3-diketone ligands) of complex **1**.

### 2.4 The elucidation of the electronic structure of the U-N(azide) bond in **8**

As mentioned in Section 2.1.1, three resonance structures (**8a-c** in Scheme 1) are mainly responsible for the structure of **8**, and the theoretical calculations tend to slightly overestimated the double bond character of the U-N(azide) bond. Nonetheless, the

detailed bond character of **8**, i.e. whether the ionic/covalent bond or single/double bond character is predominant remains unknown. From the optimized structures with **M2-B1** method (Table 3), it can be seen that the U-N<sup>7</sup> bond distance in **8** is significantly shorter than the U-O<sup>5</sup> bond distance in the structurally similar complex **1**. Meanwhile, the U-N<sup>7</sup> bond distance in **8** is also shorter than the ionic U-N<sup>3/5</sup> bond distances in **10**. Based on these observations, we suggest that the U-N<sup>7</sup> bond in **8** is unlikely a single bond. On the other hand, the Mulliken charge on the azide group of **8** (with **M2-B1** method) is  $-0.542$ , while the Mulliken charge on the neutral  $\text{H}_2\text{O}$  ligand of the similar structure of **1** is  $+0.110$ . The calculation result indicates that  $[\text{UO}_2(\text{CF}_3\text{CO})_2\text{CH}_2]^-$  group formally donates electron to the amide group, contributing to the covalent bond character of the U-N bond. The NBO analysis on **8** also support this conclusion, because the Wiberg bond order of the U-N bond is about double that of the dative/covalent U-O single bonds in the 1,3-diketone ligand ( $0.82$  vs  $0.36$ , please see supporting information for more details). Finally, one of the frontier orbitals of **8** clearly shows the  $\pi$ -bond character between the U center and the azide group (Figure 5). Therefore, all of the aforementioned observations support that the U-N(azide) bond is a covalent double bond. In other words, the resonance structure of **8c** is predominant among different ones.



**Figure 5.** The frontier orbitals of **8**.

## 3. Conclusions

The uranyl complexes have been recently extensively studied due to their great potential in nuclear fuel and materials. The past decades have witnessed the great progress of theoretical calculations in treating the uranyl complexes. Nonetheless, the reliability of the various used theoretical methods have been frequently under debate. In the present study, we chose 10 typical uranyl complexes (with different types of ligands) as the samples to identify a general reliable method in simulating the different types of uranyl complexes. The following conclusions have been generated:

- (1) Comparing the performance of different small-core (SC) and large-core (LC) relativistic effective core potentials (RECPs), we noted that the relative accuracy of the Stuttgart's SC-ECP (SDD-MWB60) is the best, while all the examined LC-ECP (including the Stuttgart RLC ECP, the Lan12dz ECP, and the CRENBL ECP) are slightly worse. Interestingly, the overall performance of Stuttgart's MHF60 relativistic (SDD-MHF60) is the worst, and the deviations of most of the U-X bond distances are fairly large. Therefore, SDD-MWB60 is the recommended ECP for treating U atom, while the LC-ECPs could be used alternatively when the concerned complexes are relatively bulky to reduce the



computational cost. SDD-MHF60 RECP should be avoided in treating the structural parameters of uranyl complexes.

(2) With the SC-ECP of SDD-MWB60 for U and 6-311G(d,p) for all the other atoms, the comparison between different DFT methods (including B3LYP, BB1K, PBE1W, M06, MPW3LYP, CAM-B3LYP and LC-BLYP) implies that the overall performance of BB1K and LC-BLYP are relatively better than all the other ones (including the popular B3LYP methods), reflecting from the significantly smaller absolute deviations between the calculated U-X bond distances and the experimentally measured ones.

(3) With BB1K/(SDD-MWB60:6-311G(d,p)) (**M2-B1**) or LC-BLYP/(SDD-MWB60:6-311G(d,p)) (**M7-B1**) method, the linear correlation between the calculation results and the experimental ones is fairly good, with the systematic error (intercept) close to 0.01 Å,  $R^2$  close to 0.985 for the examined 68 U-X (X=O, N, Br, S, Cl etc) bond distances. On this basis, the structure-binding ability relationships of different O-ligated ligands and the binding modes of the concerned U-N(azide) bond has been performed. It's expected that the bond distance of more uranyl complexes can be predicted with these methods.

We hope the present study will benefit future theoretical studies on the uranyl complexes. The examination on the reliability of the proposed methods in treating the energetics/spectroscopies as well as the systematic study on the ligand structure-binding ability relationships are currently underway.

### Calculation methods

All calculations in this study were carried out on Gaussian 09 platform.<sup>46</sup> The gas-phase geometry optimization and frequency calculations are all performed at the same level. The examination on the RECPs are carried out with the B3LYP method, and the 6-311G(d,p) basis set is used for all other atoms except U. The performance of different DFT methods were carried out with the clarified Stuttgart RSC 1997 ECP with MWB relativistic (SDD-MWB) for U and 6-311G(d,p) basis set for the other atoms. Finally, BB1K/(SDD-MWB60:6-311G(d,p)) is used for the structural analysis of **8** and **11**. All species in the present study are calculated at 298.15 K under 1 atm atmosphere. The 3D-structures in Figures 2 and 5 are prepared with Cylview software.<sup>47</sup>

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### Notes and references

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- Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x/
- <sup>65</sup> 1. L. R. Morss, N. M. Edelstein, J. Fuger, J. J. Katz, The Chemistry of the Actinide and Transactinide Elements, 3rd ed.; Springer: Berlin, NY, 2006.
2. (a) W. A. de Jong, E. Aprà, T. L. Windus, J. A. Nichols, R. J. Harrison, K. E. Gutowski, D. A. Dixon *J. Phys. Chem. A* **2005**, *109*, 11568. (b) Y. Lu *Nat. Chem.* **2014**, *6*, 175.
3. (a) C. W. Abney, S. Liu, W. Lin *J. Phys. Chem. A* **2013**, *117*, 11558. (b) P. S. Barber, S. P. Kelley, R. D. Rogers *RSC Adv.* **2012**, *2*, 8526.
4. G. Tian, S. J. Teat, Z. Zhang, L. Rao, *Dalton Trans.* **2012**, *41*, 11579.
5. J. Su, K. Zhang, W. H. E. Schwarz, J. Li *Inorg. Chem.* **2011**, *50*, 2082.
- <sup>75</sup> 6. (a) A. E. V. Gorden, J. Xu, K. N. Raymond, P. Durbin, *Chem. Rev.* **2003**, *103*, 4207. (b) Q.-J. Pan, S. O. Odoh, G. Schreckenbach, P. L. Arnold, J. B. Love *Dalton Trans.* **2012**, *41*, 8878.
7. (a) P. L. Arnold, A. J. Blake *Inorg. Chem.* **2004**, *43*, 8206. (b) Q.-J. Pan, G. A. Shamov, G. Schreckenbach *Chem. Eur. J.* **2010**, *16*, 2282. (c) G. Szigethy, K. N. Raymond *J. Am. Chem. Soc.* **2011**, *133*, 7942. (d) L. Zhou, M. Bosscher, C. Zhang, S. Özçubukçu, L. Zhang, W. Zhang, C. J. Li, J. Liu, M. P. Jensen, L. Lai, C. He *Nat. Chem.* **2014**, *6*, 236. (e) G. Nocton, P. Horeglad, V. Vetere, J. Pécaut, L. Dubois, P. Maldivi, N. M. Edelstein, M. Mazzanti *J. Am. Chem. Soc.* **2010**, *132*, 495.
- <sup>85</sup> 8. (a) C. D. Auwer, E. Simoni, S. Conradson, C. Madic *Eur. J. Inorg. Chem.* **2003**, 3843. (b) N. Kaltsoyannis *Chem. Soc. Rev.* **2003**, *32*, 9. (c) R. G. Denning, *Struct. Bonding Berl.* **1992**, *79*, 215. (d) D. Wang, W. F. van Gunsteren, Z. Chai *Chem. Soc. Rev.* **2012**, *41*, 5836. (e) M. Bühl, G. Wipff *ChemPhysChem* **2011**, *12*, 3095. (f) S. Fortier, T. W. Hayton
- <sup>90</sup> *Coord. Chem. Rev.* **2010**, *254*, 197.
9. (a) Y. Oda, A. Aoshima *J. Nucl. Sci. Technol.* **2002**, *39*, 647. (b) S. Tsushima, T. Reich *Chem. Phys. Lett.* **2001**, *347*, 127. (c) I. Infante, B. V. Stralen, L. Visscher *J. Comput. Chem.* **2006**, *27*, 1156. (d) G. Schreckenbach, P. J. Hay, R. L. Martin *Inorg. Chem.* **1998**, *37*, 4442. (e)
- <sup>95</sup> B. Siboulet, C. J. Marsden, P. Vitorge *Chem. Phys.* **2006**, *326*, 289. (f) J. P. Austin, M. Sundararajan, M. A. Vincent, I. H. Hillier *Dalton Trans.* **2009**, 5902. (g) K. I. M. Ingram, L. J. L. Haller and N. Kaltsoyannis, *Dalton Trans.*, **2006**, 2403. (h) Z. Cao, K. Balasubramanian *J. Chem. Phys.* **2009**, *131*, 164504.
- <sup>100</sup> 10. (a) Z. Szabó, I. Grenthe *Inorg. Chem.* **2007**, *46*, 9372-9378. (b) D. L. Clark, S. D. Conradson, R. J. Donohoe, D. W. Keogh, D. E. Morris, P. D. Palmer, R. D. Rogers, C. D. Tait *Inorg. Chem.* **1999**, *38*, 1456. (c) G. Gordon, H. Taube *J. Inorg. Nucl. Chem.* **1961**, *19*, 189. (d) H. P. Hratchian, J. L. Sonnenberg, P. J. Hay, R. L. Martin, B. E. Bursten, H. B.
- <sup>105</sup> Schlegel *J. Phys. Chem. A* **2005**, *109*, 8579. (e) H. Moll, A. Rossberg, R. Steudtner, B. Drobot, K. Müller, S. Tsushima, *Inorg. Chem.* **2014**, *53*, 1585. (f) Z. Szabó, I. Grenthe, *Inorg. Chem.* **2010**, *49*, 4928. (g) S. Tsushima *Inorg. Chem.* **2012**, *51*, 1434. (h) D. Rios, M. del C. Michelini, A. F. Lucena, J. Marçalo, J. K. Gibson *J. Am. Chem. Soc.* **2012**, *134*,
- <sup>110</sup> 15488. (i) S. J. Harley, C. A. Ohlin, R. L. Johnson, A. F. Panasci, W. H. Casey *Angew. Chem. Int. Ed.* **2011**, *50*, 4467.
11. (a) Q.-J. Pan, Georg. Schreckenbach *Inorg. Chem.* **2010**, *49*, 6509. (b) F. Quilès, C. Nguyen-Trung, C. Carteret, B. Humbert *Inorg. Chem.* **2011**, *50*, 2811. (c) P. L. Arnold, E. Hollis, G. S. Nichol, J. B. Love, J.-
- <sup>115</sup> C. Griveau, R. Caciuffo, N. Magnani, L. Maron, L. Castro, A. Yahia, S. O. Odoh, G. Schreckenbach *J. Am. Chem. Soc.* **2013**, *135*, 3841.
12. (a) H.-Y. Wu, R.-X. Wang, W. Yang, J. Chen, Z.-M. Sun, J. Li, H. Zhang *Inorg. Chem.* **2012**, *51*, 3103. (b) Y. Dai, C. H. Lu, Q. B. Ren, L. Lu, J. H. Li, B. X. Liu, *J. Nucl. Mat.* **2012**, *427*, 239. (c) T. Z. Forbes, J.
- <sup>120</sup> G. McAlpin, R. Murphy, P. C. Burns, *Angew. Chem., Int. Ed.*, **2008**, *47*, 2824. (d) G. E. Sigmon, P. C. Burns, *J. Am. Chem. Soc.*, **2011**, *133*, 9137. (e) C.-S. Lee, C.-H. Lin, S.-L. Wang, K.-H. Lii *Angew. Chem. Int. Ed.* **2010**, *49*, 4254. (f) A. S. P. Gomes, C. R. Jacob, F. Réal, L. Visscher, V. Vallet *Phys. Chem. Chem. Phys.* **2013**, *15*, 15153. (g) D. K. Unruh, K.
- <sup>125</sup> Gojdas, A. Libo, T. Z. Forbes *J. Am. Chem. Soc.* **2013**, *135*, 7398. (h) C.

- Volkringer, N. Henry, S. Grandjean, T. Loiseau *J. Am. Chem. Soc.* **2012**, *134*, 1275. (i) Y. Yue, R. T. Mayes, J. Kim, P. F. Fulvio, X.-G. Sun, C. Tsouris, J. Chen, S. Brown, S. Dai *Angew. Chem. Int. Ed.* **2013**, *52*, 13458. (j) A. Kremleva, B. Martorell, S. Krüger, N. Rösch *Phys. Chem. Chem. Phys.* **2012**, *14*, 5815. (k) H. Wu, O. Chen, J. Zhuang, J. Lynch, D. LaMontagne, Y. Nagaoka, Y. C. Cao *J. Am. Chem. Soc.* **2011**, *133*, 14327.
13. (a) K. E. Gutowski, D. A. Dixon, *J. Phys. Chem. A* **2006**, *110*, 8840. (b) G. A. Shamov, G. Schreckenbach, *J. Am. Chem. Soc.* **2008**, *130*, 13735. (c) M. del C. Michelini, N. Russo, E. Sicilia *J. Am. Chem. Soc.* **2007**, *129*, 4229.
14. (a) E. R. Batista, R. L. Martin, P. J. Hay *J. Chem. Phys.* **2004**, *121*, 11104. (b) Q.-J. Pan, Y.-M. Wang, R.-X. Wang, H.-Y. Wu, W. Yang, Z.-M. Sun, H.-X. Zhang *RSC Adv.* **2013**, *3*, 1572. (c) P. Tecmer, N. Govind, K. Kowalski, W. A. de Jong, L. Visscher *J. Chem. Phys.* **2013**, *139*, 034301. (d) M. Bühl, G. Schreckenbach, N. Sieffert, G. Wipff *Inorg. Chem.* **2009**, *48*, 9977. (e) L. P. Spencer, P. Yang, S. G. Minasian, R. E. Jilek, E. R. Batista, K. S. Boland, J. M. Boncella, S. D. Conradson, D. L. Clark, T. W. Hayton, S. A. Kozimor, R. L. Martin, M. M. Macinnes, A. C. Olson, B. L. Scott, D. K. Shuh, M. P. Wilkerson *J. Am. Chem. Soc.* **2013**, *135*, 2279. (f) P. Tecmer, R. Bast, K. Ruud, L. Visscher *J. Phys. Chem. A* **2012**, *116*, 7397. (g) M. Bühl, N. Sieffert, G. Wipff *Chem. Phys. Lett.* **2009**, *467*, 287. (h) G. S. Groenewold, M. J. van Stipdonk, J. Oomens, W. A. de Jong, M. E. McIlwain *Int. J. Mass Spectro.* **2011**, *308*, 175. (i) J. Su, P. D. Dau, Y.-H. Qiu, H.-T. Liu, C.-F. Xu, D.-L. Huang, L.-S. Wang, J. Li *Inorg. Chem.* **2013**, *52*, 6617. (j) E. van Besien, K. Pierloot, C. Görrler-Walrand *Phys. Chem. Chem. Phys.* **2006**, *8*, 4311. (k) J. Su, Y.-L. Wang, F. Wei, W. H. E. Schwarz, J. Li *J. Chem. Theory Comput.* **2011**, *7*, 3293.
15. (a) P. L. Arnold, G. M. Jones, S. O. Odoh, G. Schreckenbach, N. Magnani, J. B. Love *Nat. Chem.* **2012**, *4*, 221. (b) P. L. Arnold, A.-F. Pécharman, J. B. Love *Angew. Chem. Int. Ed.* **2011**, *50*, 9456. (c) S. Tsushima *Inorg. Chem.* **2009**, *48*, 4856-4862. (d) S. Kannan, A. E. Vaughn, E. M. Weis, C. L. Barnes, P. B. Duval, *J. Am. Chem. Soc.* **2006**, *128*, 14024. (e) L. A. Seaman, P. Hrobárik, M. F. Schettini, S. Fortier, M. Kaupp, T. W. Hayton *Angew. Chem. Int. Ed.* **2013**, *52*, 3259. (g) G. A. Shamov *J. Am. Chem. Soc.* **2011**, *133*, 4316. (h) J.-C. Tourneau, J.-C. Berthet, T. Cantat, P. Thuéry, N. Mézailles, M. Ephritikhine *J. Am. Chem. Soc.* **2011**, *133*, 6162. (i) C. Fillaux, D. Guillaumont, J.-C. Berthet, R. Copping, D. K. Shuh, T. Tylliszczak, C. D. Auwer *Phys. Chem. Chem. Phys.* **2010**, *12*, 14253. (j) Y. Gong, J. K. Gibson *J. Phys. Chem. A* **2013**, *117*, 783. (k) K. E. Gutowski, V. A. Cocalia, S. T. Griffin, N. J. Bridges, D. A. Dixon, R. D. Rogers *J. Am. Chem. Soc.* **2007**, *129*, 526. (l) G. S. Groenewold, A. K. Gianotto, K. C. Cossel, M. J. Van Stipdonk, D. T. Moore, N. Polfer, J. Oomens, W. A. de Jong, L. Visscher *J. Am. Chem. Soc.* **2006**, *128*, 4802. (m) W. A. Zordok, W. H. El-Shwiniy, M. S. El-Attar, S. A. Sadek *J. Mol. Struct.* **2013**, *1047*, 267. (n) X. Wang, L. Andrews, C. J. Marden *Inorg. Chem.* **2009**, *48*, 6888. (o) Y. Gong, H.-S. Hu, L. Rao, J. Li, J. K. Gibson *J. Phys. Chem. A* **2013**, *117*, 10544. (p) H. Xiao, H.-S. Hu, W. H. E. Schwarz, J. Li *J. Phys. Chem. A* **2010**, *114*, 8837. (q) G. Liu, L. Rao, G. Tian *Phys. Chem. Chem. Phys.* **2013**, *15*, 17487. (r) G. A. Shamov, G. Schreckenbach *J. Am. Chem. Soc.* **2008**, *130*, 13735.
16. W. Kuchle, M. Dolg, H. Stoll, H. Preuss *J. Chem. Phys.* **1994**, *100*, 7535.
17. P. J. Hay, R. L. Martin *J. Chem. Phys.* **1998**, *109*, 3875.
18. G. Schreckenbach, G. A. Shamov *Acc. Chem. Res.* **2010**, *43*, 19.
19. (a) Y.-K. Han, K. Hirao *J. Chem. Phys.* **2000**, *113*, 7345. (b) Y. K. Han *J. Comput. Chem.* **2001**, *22*, 2010.
20. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al. Gaussian, Inc., Wallingford CT, **2009**, Gaussian 09, Revision B.01.
21. G. Schreckenbach, P. J. Hay, R. L. Martin *J. Comput. Chem.* **1999**, *20*, 70.
22. (a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
23. (a) G. A. Shamov, G. Schreckenbach *J. Phys. Chem. A* **2005**, *109*, 10961. (b) M. Bühl, G. Schreckenbach *Inorg. Chem.* **2010**, *49*, 3821.
24. A. Dreuw, M. Head-Gordon *J. Am. Chem. Soc.* **2004**, *126*, 4007.
25. M. E. Foster, B. M. Wong *J. Chem. Theory Comput.* **2012**, *8*, 2682.
26. (a) B. M. Wong, M. Piacenza, F. D. Sala *Phys. Chem. Chem. Phys.* **2009**, *11*, 4498. (b) D. Jacquemin, E. A. Perpète, G. Scalmani, M. J. Frisch, R. Kobayashi, C. Adamo *J. Chem. Phys.* **2007**, *126*, 144105.
27. H. Iikura, T. Tsuneda, T. Yanai, K. Hirao *J. Chem. Phys.* **2001**, *115*, 3540.
28. T. Yanai, D. P. Tew, N. C. Handy *Chem. Phys. Lett.* **2004**, *393*, 51.
29. (a) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215. (b) Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157.
30. E. E. Dahlke, D. G. Truhlar, *J. Phys. Chem. B* **2005**, *109*, 15677.
31. Y. Zhao, B. J. Lynch, D. G. Truhlar, *J. Phys. Chem. A* **2004**, *108*, 2715.
32. Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2004**, *108*, 6908.
33. For recent examples with the newly developed DFT methods, please see (a) H. Cao, M. He, D. Han, J. Li, M. Li, W. Wang, S. Yao *Environ. Sci. Technol.* **2013**, *47*, 8238. (b) M. E. Tucceri, M. P. Badenes, C. J. Cobos *J. Phys. Chem. A* **2013**, *117*, 10218. (c) S. Qu, Y. Dang, C. Song, M. Wen, K.-W. Huang, Z.-X. Wang *J. Am. Chem. Soc.* **2014**, *136*, 4974. (d) A. Demeter, K. Horváth, K. Böör, L. Molnár, T. Soós, G. Lendvay *J. Phys. Chem. A* **2013**, *117*, 10196. (e) A. Sierraalta, R. Añez, P. Alejos *J. Phys. Chem. A* **2013**, *117*, 2619. (f) X.-J. Qi, Z. Li, Y. Fu, Q.-X. Guo, L. Liu *Organometallics* **2008**, *27*, 2688. (g) E. E. Dahlke, D. G. Truhlar *J. Phys. Chem. B* **2005**, *109*, 15677. (h) W.-R. Zhang, Y. Fu, H.-J. Wang, Q.-X. Guo *Chin. J. Org. Chem.* **2008**, *28*, 459. (i) M. Walker, A. J. A. Harvey, A. Sen, C. E. H. Dessent *J. Phys. Chem. A* **2013**, *117*, 12590. (j) S. Luo, D. G. Truhlar *J. Chem. Theory Comput.* **2012**, *8*, 4112. (k) H.-Z. Yu, Y.-M. Yang, L. Zhang, Z.-M. Dang, G.-H. Hu *J. Phys. Chem. A* **2014**, *118*, 606. (l) A. D. Kulkarni, D. G. Truhlar *J. Chem. Theory Comput.* **2011**, *7*, 2325. (m) E. E. Dahlke, D. G. Truhlar *J. Phys. Chem. B* **2006**, *110*, 10595. (n) R. Shang, Z.-W. Yang, Y. Wang, S.-L. Zhang, L. Liu *J. Am. Chem. Soc.* **2010**, *132*, 14391. (p) D. Jacquemin, E. A. Perpète, I. Ciofini, C. Adamo, R. Valero, Y. Zhao, D. G. Truhlar *J. Chem. Theory Comput.* **2010**, *6*, 2071. (q) L. Xu, M. J. Hilton, X. Zhang, P.-O. Norrby, Y.-D. Wu, M. S. Sigman, O. Wiest *J. Am. Chem. Soc.* **2014**, *136*, 1960. (r) E. E. Dahlke, M. A. Orthmeyer, D. G. Truhlar *J. Phys. Chem. B* **2008**, *112*, 2372. (s) P.-J. Cai, F.-Q. Shi, Y. Wang, X. Li, Z.-X. Yu *Tetrahedron* **2013**, *69*, 7854.
34. (a) D. Feller *J. Comp. Chem.*, **1996**, *17*, 1571. (b) K.L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorathi, J. Chase, J. Li, T. L. Windus, *J. Chem. Inf. Model.*, **2007**, *47*, 1045.
35. Note that the effect of different total electron basis set (i.e. 6-311G\*\* and 6-311++G\*\*) were also tested. The detailed calculation results and the discussions are given in the supporting information.
36. N. W. Alcock, D. J. Flanders *Acta Crystallogr., Sect. C* **1987**, *43*, 1480-1483.
37. Note that several x-ray crystal structures have been reported for the [UO<sub>2</sub>Br<sub>4</sub>]<sup>2-</sup>R<sup>2+</sup>, depending on the different counterion. For simplicity, the structural parameters of bis(4,6-dimethyl-3-thioxo-3H-1,2,-dithiolo(4,3-c)pyrindinium)tetrabromo-dioxo-uranium (ref. 24a) are selected for discussions, because the no significant interaction between the uranyl moiety and the counterion moiety was observed in this complexes. (a) E. Conradi, R. Bohrer, U. Müller *Chem. Ber.* **1986**, *119*, 2582. (b) A. Marzotto, R. Graziani, G. Bombieri, E. Forsellini *J. Cryst. Mol. Struct.* **1974**, *4*, 253. (c) L. H. Jensen, D. Dickerson, Q. Johnson *Acta Crystallogr., Sect. B* **1974**, *30*, 840. (d) M.-O. Sormein, M. Mendès, C. Cannes, C. LeNaour, P. Nockemann, K. Van Hecke, L. Van Meervell, J.-C. Berthet, C. Hennig *Polyhedron* **2009**, *28*, 1281. (e) K. Gossens, K. Lava, P. Nockemann, K. Van Hecke, L. Van Meervelt, P. Pattison, K. Binnemans, T. Cardinaels *Langmuir* **2009**, *25*, 5881. (f) K. Gossens, K. Lava, P. Nockemann, K. Van Hecke, L. Van Meervelt, K. Driesen, C. Görrler-Walrand, K. Binnemans, T. Cardinaels *Chem. Eur. J.* **2009**, *15*, 656. (g) P. Nockemann, K. Servaes, R. Van Deun, K. Van Hecke, L. Van Meervelt, K. Binnemans, C. Görrler-Walrand *Inorg. Chem.* **2007**, *46*, 11335.
38. D. E. Fenton, P. A. Vigato, U. Casellato, R. Graziani, M. Vidali *Inorg. Chim. Acta.* **1981**, *51*, 195.
39. G. Paolucci, G. Marangoni, G. Bandoli, D. A. Clemente *J. Chem. Soc., Dalton Trans.* **1980**, 1304.
40. The structural parameters of ref. 27a is used. (a) Y. N. Mikhailov, A. S. Kanishcheva, L. A. Zemskova, V. E. Mistryukov, N. T. Kuznetsov, K. A. Solntsev *Zh. Neorg. Khim.* **1982**, *27*, 2343. (b) A. Zalkin, H. Ruben, D. H. Templeton *Inorg. Chem.* **1979**, *18*, 519.

- 
41. A. E. Storey, F. Zonnevillage, A. A. Pinkerton, D. Schwarzenbach  
*Inorg. Chim. Acta.* **1983**, *75*, 103.
42. M. P. Wikerson, C. J. Burns, R. T. Paine, B. L. Scott *Inorg. Chem.*  
**1999**, *38*, 4156.
- 5 43. L. Prasad, E. J. Gabe, B. Glavincevski, S. Brownstein *Acta  
Crystallogr. Sect. C Cryst. Struct. Commun.* **1983**, *39*, 181.
44. The structural parameters of ref. 31a is used for discussion due to the  
slightly weaker interactions between the uranyl group and the  
environment. (a) P. Thuéry. *Cryst. Eng. Comm.* **2009**, *11*, 1081. (b) R. D.
- 10 Rogers, L. K. Kurihara, M. M. Benning J. *Inclusion Phenom.  
Macrocyclic Chem.* **1987**, *5*, 645. (c) L. Deshayes, N. Keller, M. Lance,  
M. Nierlich, J.-D. Vigner. *Acta Crystallogr., Sect. C* **1994**, *50*, 1541.
45. A. E. Vaughn, C. L. Barnes, P. B. Duval *J. Chem. Cryst.* **2007**, *37*,  
779.
- 15 46. A. Navaza, C. de Rango *Acta Cryst.* **1983**, C39, 1625-1628.
47. CYLview, 1.0b; C. Y. Legault, Université de Sherbrooke, 2009.