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ARTICLE TYPE

Density Functional Theory Investigations on the Binding Modes of Amidoximes with Uranyl Ions

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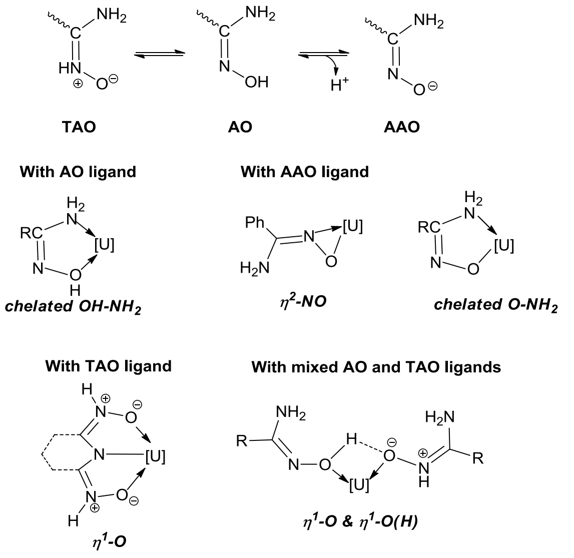
Density functional theory (DFT) calculations have been carried out to examine the relative facilities of different coordination modes of aromatic amidoximes (**AO**s) with $UO_2(NO_3)_2$. Various η^1-, η^2- and chelated κ^2- coordination modes of the possible neutral **AO**, tautomerized neutral (**TAO**, with the hydroxylic hydrogen transferring to the oxmic nitrogen atom) and anionic amidoxime (**AAO**, formed by the deprotonation of **AO**) were examined. The results indicate that η^1-O of the **TAO** and η^1-O/η^2-NO of **AAO** are the most plausible coordination modes. Three types of uranyl complexes, i.e. $UO_2(NO_3)_2$(**TAO**)(**AAO**), $UO_2(NO_3)_2$(**AAO**)$_2$ and $UO_2(EtOH)_2$(**AAO**)$_2$ are predominant binding structures. The good consistency between the calculation results and the experimental observations verifies the proposed conclusions.

1. Introduction

In the past decades, various sorbent materials and complexes (such as functionalized polymers,[1] proteins,[2] and biomass[3]) have been explored for the sorption of uranyl, due to the high importance of uranyl in devloping nuclear energy and treating nuclear waste.[4,5] Among the different materials, amidoxime (**AO** for short) represents one of the most extensively studied categories.[6-11] For example, Güven and co-workers recently developed novel polymers with **AO**s, and established their high adsorbent ability with uranyl ions via batch and flow technique.[6] Rogers and co-workers accomplished the highly selective extraction of uranyl ions (UO_2^{2+}>Th^{4+}>Eu^{3+}) with **AO** functionalized ionic liquids,[7a,b] and successfully identified the x-ray crystal structure of the 4,5-di(AO)-functionalized imidazole ligated uranyl complex.[7c] Rao and co-workers investigated both the binding strength and modes of uranyl ions with glutarimidedioxime via the combined theoretical and experimental strategies.[8] Similarly, our group also made effort in the one-pot preparation of a series of **AO**s with Pd catalyst, and examined their binding abilities to uranyl ions with fluorescence titration experiments.[9]

Associate with the extensive studies on sorption of uranyl ions with **AO**s, various binding structures have been proposed/ characterized (Scheme 1). For example, with sorption behavior and XPS (X-ray photoelectron spectroscopy) analysis,[10] Liu et al recently proposed that the **AO**-grafted multiwalled carbon nanotubes tend to ligate with the uranyl ion via both -O(H) and -NH_2 groups (Scheme 1). Meanwhile, the coordination of the oximic N atom with the uranyl ions has been reported by Mehta et al with the aid of IR spectra.[12] On the other hand, the tautomerized neutral **AO** (with the hydroxylic hydrogen atom transfers to the oximic nitrogen atom, **TAO** in Scheme 1) ligated uranyl complex (with imidedioxime ligands) has been identified with x-ray crystal structure by Witte et al.[13] Similarly, the uranyl complexes with η^2-N-O coordinated **AAO** (short for anionic **AO**, generated via the deprotonation of **AO**) have been recently supported by both x-ray crystal structures[7c,14] and DFT calculations[15,16]. To this end, either **AO**[10,17,18], **TAO**[13,19] or **AAO**[7,14-16,20,21] might be responsible for the binding structure of uranyl complexes. In addition, different coordination modes (i.e. η^1-, η^2- or chelated κ^2-) might be possible for each of these forms. What is more important, the possibility of some other coordination modes (such as the mixed coordination with **AO**,



Scheme 1. The lewis structure and the proposed coordination modes of **AO/TAO/AAOs** in previous studies.

TAO and **AAO**)[16] cannot be excluded yet. In other words, the complexity of the possible coordination modes results in the difficulty in figuring out the most feasible binding structure(s) of **AO**s with uranyl ions.

To systematically evaluate the relative facility of different coordination modes of **AO**s and identify the most feasible ones, we sought to carry out systematic theoretical calculations on the possible **U-AO/TAO/AAO** complexes. With the modeling systems of (Z)-N'-hydroxybenzimidamide (**AO1**) with $UO_2(NO_3)_2$ in EtOH/H_2O solvent in our recent study,[9a] the following issues are mainly concerned: 1) What is the most feasible coordination mode(s) for **AO**, **TAO** and **AAO**, respectively? 2) Among **AO**, **TAO** and **AAO**, whose coordination ability is stronger? And why? 3) What's the most feasible ligation structure starting from $UO_2(NO_3)_2$ and **AO1**? With the answer to these questions, we further carried out detailed investigations on the influence of solvent and **AO** structure on the binding abilities (i.e. the binding structure and the relative sorption ability). The good consistency between the calculation results and the experimental observations verifies the generated conclusions. We hope the current study will benefit the deep understandings on the coordination features of **AO**s with uranyl ions.

2 Computational methods

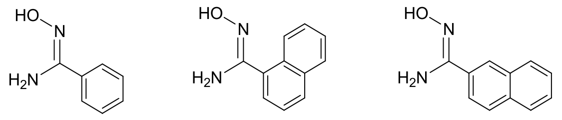
All DFT calculations in this study were performed with Gaussian09 package.[22] Following the recent theoretical studies on the kinetic/thermodynamic discussions on uranyl complexes (with H_2O,[23] AOs,[15] or the other ligands[24]), the geometry optimizations of all species in this study were performed with B3LYP method.[25] The Stuttgart/Dresden's small core (SC)[26] relativistic effective core pseudo potentials (RECPs) utilizing the Wood-Boring quasi-relativistic was used for U, and the total electron 6-311G(d,p) basis set was used for all other atoms. Frequency analysis was performed at the same level of geometry optimization for each species, to ensure that the stationary points to be minima (with zero imaginary frequency) or saddle points (with only one imaginary frequency). The thermodynamic correction of enthalpy and Gibbs free energy was also obtained from the frequency calculations. Different configurations of each species were taken into account, and the most stable one is used for the following discussions.

To take the solvent effect into account, we carried out solution phase single point calculations with SMD model on the gas-phase optimized structures.[27] Throughout this study, the solution phase total electronic energy added with the gas-phase enthalpy corrections was used to describe the solution phase enthalpies for all species.[28]

3. Results and Discussions

3.1 Model reaction

In accordance with our recent experimental measurements on the relative binding affinity of the aromatic **AO**s with $UO_2(NO_3)_2$ (using the fluorescence responses experiments in EtOH solvent, pH 7.4 and 25°C),[9a] the reaction of (Z)-N'-hydroxybenzimidamide (**AO1**, Scheme 2) with $UO_2(NO_3)_2$ was first taken as the modeling system. With the most stable **U-AO1** structures, effort was then put in examining the similar structures and binding abilities with the structurally more complicated (Z)-N'-hydroxy-1-naphthimidamide (**AO2**, Scheme 2) and (Z)-N'-hydroxy-2-naphthimidamide (**AO3**, Scheme 2). In this context, the comparison between the experimental and calculation results on their relative binding abilities enables the evaluation on the reliability of calculation methods, as well as the detailed analysis on the substituent effect of aromatic **AO**s.



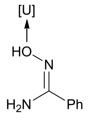
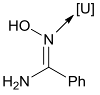
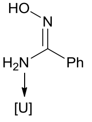
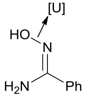
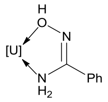
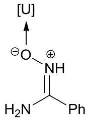
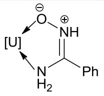
Scheme 2. The examined aromatic AOs in this study.

In EtOH solvent, the formation of trans-$UO_2(NO_3)_2(EtOH)_2$ (**U-EtOH-EtOH**) from EtOH and $UO_2(NO_3)_2$ is highly exothermic by 20.3 kcal/mol (please see Figure S1 in ESI for more details), and thus **U-EtOH-EtOH** was taken as the energetic reference point. In the following, the possible coordination modes of **AO1**, **TAO1** (tautomerized **AO1**) and **AAO1** (anionic **AO1**) from **U-EtOH-EtOH** are discussed, respectively.

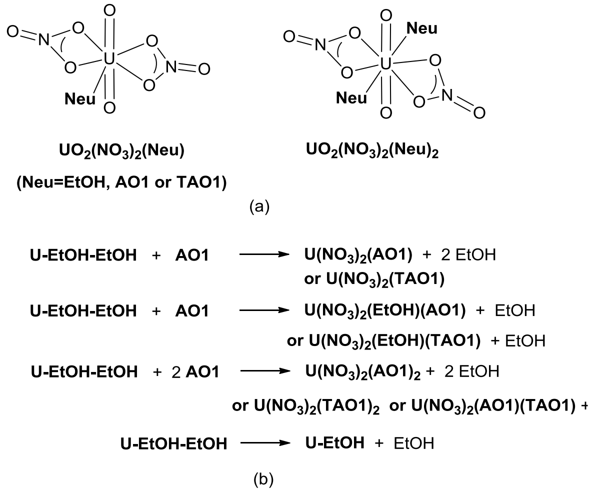
3.2 Comparison between different coordination modes of AO1 and TAO1.

According to the calculation results, the relative enthalpy of **TAO1** is slightly higher than that of **AO1** by 1.3 kcal/mol. The low energy gap indicates that both of them might participate in the ligations with the uranyl ion. Meanwhile, different coordination modes of **AO1** (i.e. η^1-OH, η^1-N, or η^1-NH_2; η^2-OH-N; and chelated κ^2-OH-NH_2) were examined, and these modes are named as **M1-M5** in the nomenclatures of the binding structures (Table 1, and M is short for mode). Similarly, both the η^1-O and the chelated η^2-O-NH_2 coordination modes were taken into account for **TAO1**, and they were named as **M6** and **M7** in the nomenclatures of complexes (Table 1). In this context, both the single or double neutral ligand (**Neu**) ligated structures were examined, and both the cis- and trans-configurations have been taken into account in the latter case (Scheme 3a). The relative enthalpies of all these complexes are calculated from the ligand exchange reactions in Scheme 3b. For clarity reasons, the optimized structures and the relative enthalpies (in kcal/mol) of the selective **U-Neu** complexes (the most stable structure for each coordination mode) are given in Figure 1.

Table 1. The possible coordination modes of **AO1** and **TAO1**, and the symbol for each of them in the nomenclature of the formed U-**AO1**/**TAO1** complexes.

Binding modes for AO1	 η^1-OH	 η^1-N	 η^1-NH_2	 η^2-OH-N	 chelated κ^2-OH-NH_2
Symbol	**M1**	**M2**	**M3**	**M4**	**M5**
Binding modes for TAO1	 η^1-O	 chelated κ^2-O-NH_2			
Symbol	**M6**	**M7**			

According to the calculation results, the relative enthalpies of uranyl complexes with one **Neu** ligand (i.e. EtOH, **AO1** or **TAO1**) follow the order of **U-M6** < **U-M4** ~ **U-M2** < **U-EtOH** < **U-M5** (Note that U-**M1**/**M3** are not stable structures, and they rearrange automatically to **U-M5**/**U-M4** during geometry optimization). The relatively high enthalpy of **U-M5** might be attributed to both the weak U-O and U-N(H)$_2$ bonds (please see Table S1 for more details) and the large chelating angle therein. Similar reason also explains the high instability of the **M7** coordination mode of **TAO1** (Figure S11 in ESI). The relative enthalpy of $UO_2(NO_3)_2$(**Neu**) suggest the relative coordination ability of **TAO1** > **AO1** > EtOH. This sequence is futher evidenced by the relative enthalpies of the double **Neu** coordinated complexes, i.e. **U-M6-EtOH** < **U-M2-EtOH**/**U-M1-EtOH** < **U-EtOH-EtOH** and **U-M6-M6** < **U-M2-M2** < **U-M2-EtOH**/**U-M1-EtOH**. The relatively higher stability of the **TAO1** coordinated complexes via the **M6** type are mainly attributed to the significantly stronger, covalent U-O(**TAO1**) bond therein (relative to the dative U-O(**AO1**) bonds in other complexes in Figure 1). This proposal is supported by both the shorter U-O(**Neu**) bond lengths and the larger Wiberg bond order in **M6**-ligated complexes. For clarity reasons, an example has been given in Table 2, and the full details are provided in Table S1 in ESI.



Scheme 3. (a) The two types of uranyl complexes with one or two **Neu** ligands (**Neu**=EtOH, **AO1** or **TAO1**). (b) The equations used to evaluate the relative enthalpies of the formed uranyl complexes.

Table 2. The structural parameters of **U-M6** vs **U-EtOH**, **U-M5** and **U-M4**.

U-O(AO1/TAO1)	U-EtOH	U-M5	U-M4	U-M6
Bond distance (Å)	**2.448**	**2.619**	**2.648**	**2.316**
Wiberg bond order	**0.4022**	**0.3129**	**0.2687**	**0.6402**

Some other interesting observations were also noted. First, the double neutral ligand coordinated complexes are relatively more stable than the related single coordinated ones (such as **U-EtOH-EtOH** vs **U-EtOH**, Figure 1). Second, the trans-configuration of the double **Neu** coordinated complexes are generally slightly more stable than the related cis-configurations (Figures S1-S10). Third, the hydrogen bonding interactions widely exist between the **AO1**/**TAO1** and the uranyl ion or NO_3^- ligands, and thus provide extra-stability to the concerned molecule.

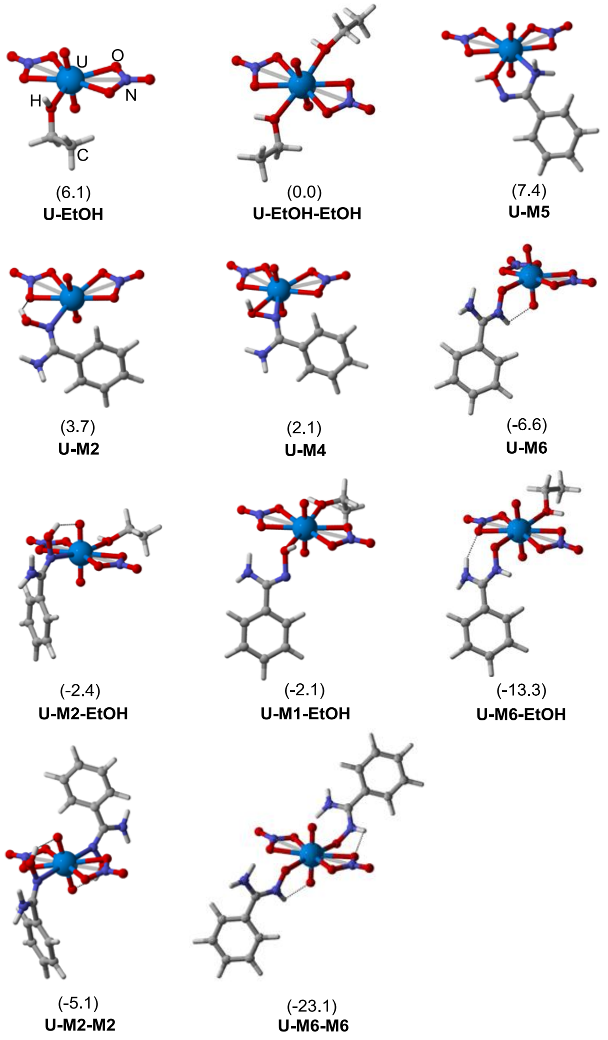
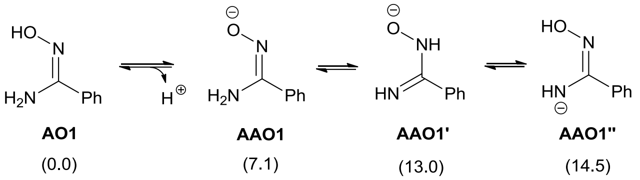


Figure 1. The optimized structures and the relative enthalpies (in kcal/mol) of the selected uranyl complexes.

Due to the significantly stronger coordination ability of the **M6** mode of **TAO1** (relative to other coordination modes of **AO1/TAO1**), **U-M6-M6** (Figure 1) represents the most stable complex in this section.[29]

3.3 Comparison between different coordination modes of AAO1.

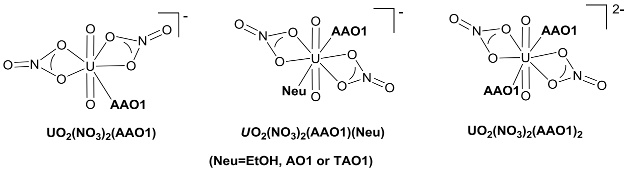
From **AO1**, three anionic **AO1** ligands (i.e. **AAO1**, **AAO1'** and **AAO1''**, Scheme 4) might be possibly formed via the deprotonation process. Due to the difficulty in obtaining the accurate solvation energy of H^+, the isodesmic reaction between **AO1** and EtO^- are used to evaluate the acidities of **AAO1** and the related energetics for formation of **AAO1** (please see ESI for more details).[30-31] The same method is also used for **AAO1'** and **AAO1''**. According to this strategy, the formation of **AAO1**, **AAO1'** and **AAO1''** from **AO1** is endothermic by 7.1, 13.0 and 14.5 kcal/mol, respectively. The low energy gaps (< 15 kcal/mol) between **AO1** and **AAO1**/**AAO1'**/**AAO1''** enables the formation of the anionic species under the experimental conditions (room temperature).[9e] Nonetheless, either **AAO1** or **AAO1** ligated structures are relatively more stable than the related structures with **AAO1'**/**AAO1''**,[32] and thus the following discussions mainly focus on the binding structures of **AAO1**. The detailed calculation results and discussions on **AAO1'**/**AAO1''** ligated structures are provided in the ESI (Figures S25-S29).



Scheme 4. The deprotonation of **AO1** in generation of **AAO1**, **AAO1'**, or **AAO1''** (the relative enthalpies are given in kcal/mol).

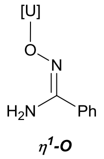
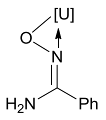
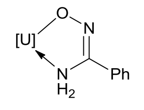
3.3.1 The relative enthalpies of uranyl complexes with $UO_2(NO_3)_2$ and one/two AAO1 groups.

From **U-EtOH-EtOH** or the other **AO1/TAO1** ligated structures (Section 3.2), three types of **AAO1** ligated structures might be possibly formed via the ligand exchange of the neutral ligand (i.e. **EtOH/AO1/TAO1**) with **AAO1**. They are $UO_2(NO_3)_2$(**AAO1**), $UO_2(NO_3)_2$(**AAO1**)(**Neu**), and $UO_2(NO_3)_2$(**AAO1**)$_2$ (Scheme 5). Meanwhile, the different coordination modes of **AAO1** (i.e. η^1-O, η^2-N-O; and chelated η^2-O-NH_2) were taken into account, and they are named as **M8**, **M9** and **M10**, respectively (Table 3). For $UO_2(NO_3)_2$(**AAO1**), all the three coordination modes (**M8**-**M10**) were examined. For $UO_2(NO_3)_2$(**AAO1**)(**Neu**) and $UO_2(NO_3)_2$(**AAO1**)$_2$, the cis-/trans- isomers were both examined and only the **M8** mode of **AAO1** is plausible (**M9** and **M10** modes result in crowded equatorial plane of the uranium center and the U-N bond automatically dissociates during the geometry optimization). The detailed results on the 11 possible structures are given in Figures S13-S15, while the optimized structures and the relative enthalpies for the selected 7 complexes are shown in Figure 2.



Scheme 5. Possible uranyl complexes with $UO_2(NO_3)_2$ and one/two **AAO1** ligand(s) generated from the replacement the neutral ligand(s) with **AAO1**.

Table 3. The possible coordination modes of **AAO1**, and the symbol for each of them in the nomenclature of the formed U-**AAO1** complexes.

Binding modes of AAO1	 η^1-O	 η^2-N-O	 chelate κ^2-O-NH2
Symbol	**M8**	**M9**	**M10**

In Figure 2, the relative enthalpies of $UO_2(NO_3)_2$(**AAO1**) follow the sequence of **U-M9** < **U-M8** < **U-M10**.[33] The relatively stronger coordination ability of **M9** mode is originated by the strong π donation of **AAO1** to the U(f) orbital. Meanwhile, the coordination ability of **AAO1** is relatively stronger than that of all the neutral forms (EtOH/**AO1**/**TAO1**), reflecting from the significantly lower enthalpy of **U-M9** than all the $UO_2(NO_3)_2$(**Neu**) complexes in Figure 1 (i.e. **U-M6**, **U-M4**, **U-M2**, **U-EtOH**, and **U-M5**). The relative enthalpy of different $UO_2(NO_3)_2$(**AAO1**)(**Neu**) complexes follows the order of **U-M8-M6** < **U-M8-EtOH**. The relatively lower enthalpy of **U-M8-M6** is mainly attributed to the stronger coordination ability of **TAO1** (relative to **AO1**/EtOH). Herein, it is interesting to note that the relative enthalpy of **U-M8-EtOH** is comparable to **U-M9**. This observation is in sharp contrast to the significantly exothermic ligation of EtOH to **U-EtOH, U-M2** and **U-M6** in Figure 1 (generating **U-EtOH-EtOH, U-M2-EtOH**, and **U-M6-EtOH**, respectively). The reason for these results might be attributed to the stronger coordination ability **AAO1** ligand, which is reflected from the shorter U-O(**AAO1**) bond distances (e.g. 2.307 Å in **U-M9** vs 2.648 Å in **U-M4**/2.316 Å in **U-M6**).

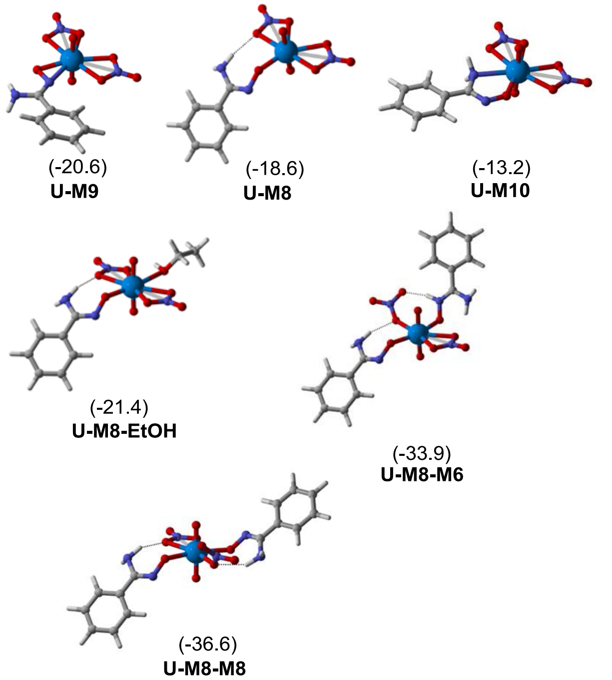
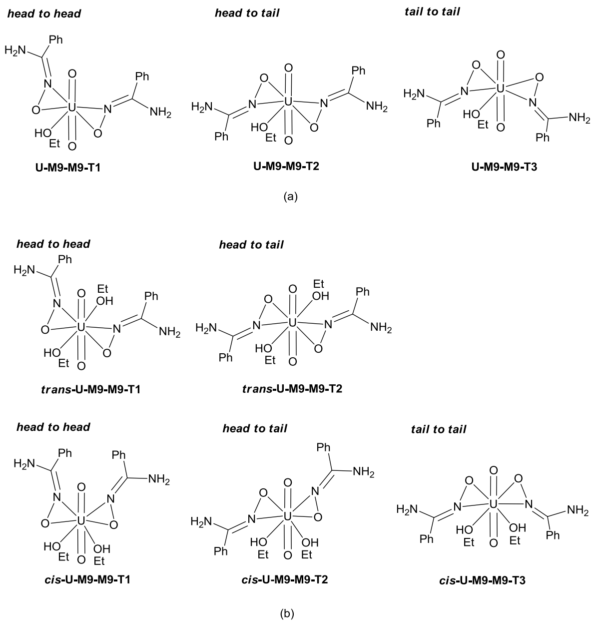


Figure 2. The optimized structures and the relative enthalpies of the selected uranyl complexes with $U(NO_3)_2$ and one or two **AAO1** groups.

3.3.2 The relative enthalpies of uranyl complexes with UO_2(AAO1)$_2$ and one/two EtOH groups.

In addition to the aforementioned replacement of the neutral ligands with **AAO1**, the anionic NO_3^- groups in the uranyl complexes might also be replaced by **AAO1**. To this end, the relative enthalpies of different **UO_2(AAO1)$_2$(EtOH)$_n$** (n=1,2) complexes were examined.[34] For these complexes, the different coordination modes of **AAO1** (Table 3) were taken into account. In addition, the isomeric configurations, i.e. head to head (named as **T1** in the nomenclature, short for type 1); head to tail (named as **T2** in the nomenclature, short for type 2) and tail to tail (named as **T3** in the nomenclature, short for type 2) were all examined. Meanwhile, for the uranyl complexes with double **AAO1** and double EtOH groups, both cis- and trans- conformers were calculated and compared (with ***cis-*** and ***trans-*** symbols, respectively). For clarity reasons, the structures and the nomenclatures with double **M9** ligated complexes has been shown in Scheme 6 as an example.



Scheme 6. An illustrative scheme for the structure and nomenclature of the uranyl complexes with double **AAO1** (via **M9** mode) and one(a) or two (b) EtOH ligands.

After examining the 18 possible structures, the head-tail configurations (**T1-T3**) were found to make little influence on the relative enthalpies of the uranyl conformers (the differences in enthalpy are within 3.0 kcal/mol for each series of complexes, Figures S16-S21 for more details). Therefore, only the 5 thermodynamically most stable complexes for each of these series are given below (Figure 3).

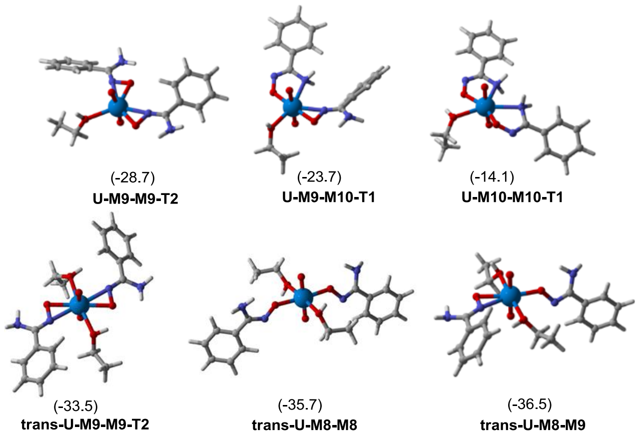


Figure 3. The optimized structures and relative enthalpies of selected uranyl complexes with two **AAO1s** and one/two EtOH.

According to Figure 3, the binding ability of **M9** is significantly stronger than that of **M10**, reflecting from the relative enthalpies of **U-M9-M9-T2** < **U-M9-M10-T1** < **U-M10-M10-T1**. This observation is caused by both the weaker coordination abilities of the $-NH_2$ group and the lack of the π(**AAO1**)-f(U) donations in the **M10** coordination mode. For this reason, the possibility for formation of U(**AAO1**)$_2$(EtOH)$_2$ with one or two **M10** mode ligated **AAO1**s are all omitted.

On the other hand, the close enthalpies of **trans-U-M9-M9-T2**, **trans-U-M8-M9** and **trans-U-M8-M8** indicate the comparable coordination abilities of the **M8** (η^1-O) and **M9** (η^2-N-O) modes in these cases. This result is distinct from Hay's recent study,[14] which indicates that the double η^1-O coordinated UO_2(**AAO4**)$_2$(H_2O)$_2$ (**AAO4**=(Z)-N'-hydroxyacetimidamide) is relatively more stable than the double η^2-N-O coordinated configurations. These results can be understood from the higher replusion between the different ligands on the equatorial plane of uranium center in our systems, introduced by both the bulkier phenyl substituted **AAO1** and the EtOH groups (compared to the methyl substituted **AAO4** and H_2O in Hay's study).

Herein, it's noteworthy that the **M8** (η^1-O) and **M9** (η^2-N-O) modes of **AAO1** can easily transforms to each other kinetically. According to the calculation results, the energy barrier for transformation of **trans-U-M8-M9** and **trans-U-M8-M8** is as low as 2.9 kcal/mol (Figure S32). In other words, the transformation of η^1-O and η^2-N-O coordination modes of amidoximes can be easily achieved kinetically.

In the aforementioned structures, both the NO_3^- groups are replaced by **AAO1** ligands. Note that the possibility that only one NO_3^- was replaced by **AAO1** has also been examined in our study. However, the relative enthalpy of the related complexes are all high (~ 19 kcal/mol), and the details are given in the SI (Figure S22).

3.4 The most feasible U-AO1/TAO1/AAO1 complexes

According to the aforementioned discussions, five modes (**M1-M5**) are plausible for the ligation with **AO1** ligand, two modes (**M6-M7**) are plausible for the ligation with **TAO1**, and three modes (**M8-M10**) are possible for the ligation with **AAO1**. In Section 3.2, the **M6** (η^1-O) mode of the **TAO1** represents the most feasible neutral coordination mode, and **U-M6-M6** (Figure 1, -23.1 kcal/mol) is the most stable one among the different **U-AO1/TAO1** complexes. Interestingly, for the uranyl complexes with **AAO1** ligand, the relative enthalpy of five complexes are comparable and significantly lower than the other ones. They are **U-M8-M6** (-33.9 kcal/mol, Figure 2), **U-M8-M8** (-36.6 kcal/mol, Figure 2), **trans-U-M9-M9-T2** (-33.5 kcal/mol, Figure 3), **trans-U-M8-M8** (-35.7 kcal/mol, Figure 3) and **trans-U-M8-M9** (-36.5 kcal/mol, Figure 3). The significantly higher enthalpy of **U-M6-M6** than those of **U-M8-M6/U-M8-M8/trans-U-M9-M9-T2/trans-U-M8-M8/trans-U-M8-M9** ruled out the possibility of the former case. On the other hand, despite the enthalpy of **trans-U-M9-M9-T2** is relatively lower than those of **U-M8-M6/U-M8-M8/trans-U-M8-M8/trans-U-M8-M9**, the low energy gap (< 3.5 kcal/mol) indicate that all these complexes might be possibly formed and exist in equilibrium.[35] The proportion of them might be affected by solvent and the substituent effect of the **AO** ligand. In this context, effort was then put in analyzing the effect of these factors in detail.

3.4.1 The solvent effect.

Experimentally, water and alcohol (EtOH, and MeOH etc) are frequently used as solvent in the reactions of uranyl ions with **AO**s.[6-13] As EtOH is used for the aforementioned calculations, we wonder whether the most stable complex(s) will change or not in the H_2O solvent. To reduce computational cost, only the reference point and the aforementioned most stable complexes are calculated. For clarity reasons, the calculation results in both of these solvents (H_2O and EtOH) are given in Table 4.

In Table 4, the relative enthalpy of **U-M8-M6** changes from -33.9 kcal/mol in EtOH to -33.4 kcal/mol in H_2O (entry 1). The reason is related to the comparable coordination ability of EtOH and

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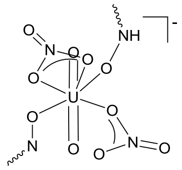
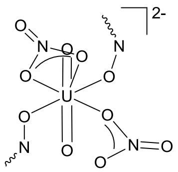
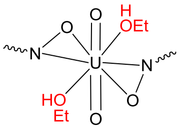
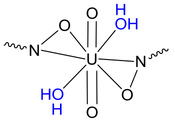
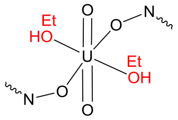
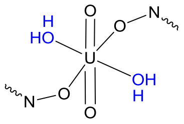
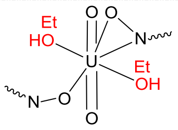
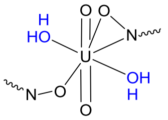
Table 4. The structures, methods to calculate the relative enthalpies and the relative enthalpies of the thermodynamically most stable U-complexes in EtOH and H_2O.

Entries	Solvent	Structure of U-complex[a]	Equations in calculating enthalpy of U-complex[b]	ΔH of U-complex[c]
1	**EtOH**	 **U-M8-M6**	**U-EtOH-EtOH + 2 AO1 → U-M8-M6 + 2 EtOH**	-33.9
	H_2O		**U-H_2O-H_2O + 2 AO1 → U-M8-M6 + 2 H_2O**	-33.4
2	**EtOH**	 **U-M8-M8**	**U-EtOH-EtOH + 2 AO1 → U-M8-M8 + 2 EtOH**	-36.6
	H_2O		**U-H_2O-H_2O + 2 AO1 → U-M8-M8 + 2 H_2O**	-36.1
3	**EtOH**	 **trans-U-M9-M9-T2**	**U-EtOH-EtOH + 2 AO1 → trans-U-M9-M9-T2 + 2 NO_3^-**	-33.5
	H_2O	 **trans-U-M9-M9-T2 (H_2O)**	**U-H_2O-H_2O + 2 AO1 → trans-U-M9-M9-T2 (H_2O) + 2 NO_3^-**	-36.4
4	**EtOH**	 **trans-U-M8-M8**	**U-EtOH-EtOH + 2 AO1 → trans-U-M8-M8 + 2 NO_3^-**	-35.7
	H_2O	 **trans-U-M8-M8 (H_2O)**	**U-H_2O-H_2O + 2 AO1 → trans-U-M8-M8 (H_2O) + 2 NO_3^-**	-33.0
5	**EtOH**	 **trans-U-M8-M9**	**U-EtOH-EtOH + 2 AO1 → trans-U-M8-M9 + 2 NO_3^-**	-36.5
	H_2O	 **trans-U-M8-M9 (H_2O)**	**U-H_2O-H_2O + 2 AO1 → trans-U-M8-M9 (H_2O) + 2 NO_3^-**	-35.1

[a] For clarity reasons, only the oximic O and N atoms are shown here, whereas all other atoms in **TAO1**/**AAO1** are omitted. [b] **U-EtOH-EtOH** and **U-H_2O-H_2O** are taken as the reference point in the two systems, respectively. The reaction enthalpy are used to evaluate the relative enthalpy of the concerned U-complex on column 3. [C] in kcal/mol.

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H_2O on the $UO_2(NO_3)_2$ complexes (please see Figure S33 for details). For the same reason, the relative enthalpies of **U-M8-M8** are also comparable in the two systems (-36.6 in EtOH and -36.1 in H_2O, entry 2). Interestingly, the relative enthalpies of the double **AAO1** ligated structures (entries 3-5) change significantly. The sequence is -33.5 (entry 3) > -35.7 (entry 4) > -36.5 (entry 5) in EtOH, whereas -33.0 (entry 4) > -35.1 (entry 5) > -36.4 (entry 3) in H_2O. In other words, the trend for the relative stability of different UO_2(**AAO1**)$_2$(EtOH)$_2$ complexes is distinct in these two solvents, presumably caused by the higher repulsion between EtOH (relative to H_2O) and **AAO1** ligands on the equatorial plane of the uranium center. The ligation of H_2O (instead of EtOH) lessens the repulsions between different ligands, and thus the double **M9** mode (entry 3) becomes more favored due to the π(**AAO1**)-f(U) donations therein.

3.4.2 The substituent effect of AOs

We finally endeavor to understand the relationships between the structures of **AO**s and their coordination abilities with the uranyl ions. As mentioned in Section 3.1 (Scheme 2), three types of **AO**s were chosen for these discussions.[9a] The relative enthalpies of the most stable, five complexes (**U-M8-M6/U-M8-M8/trans-U-M9-M9-T2/trans-U-M8-M8/trans-U-M8-M9**) were examined for each of these **AO**s. For clarity reasons, the nomenclature of the U-complexes with **AO2** and **AO3** ligand(s) are ended with (**AO2**) and (**AO3**), respectively.

Table 5. The relative enthalpies (in kcal/mol) of U-complexes with different ligands (i.e. **AO1**, **AO2** or **AO3** in Scheme 2).

U-Complex	ΔH(AO1)	ΔH(AO2)	ΔH(AO3)
U-M8-M6	-33.9	-25.2	-40.9
U-M8-M8	-36.6	-26.0	-37.4
trans-U-M9-M9-T2	-33.5	-25.9	-33.9
trans-U-M8-M8	-35.7	-28.8	-40.0
trans-U-M8-M9	-36.5	-30.6	-40.2

From the calculation results in Table 5, it can be seen that the relative enthalpies of different U-complexes vary a lot with the alternation of **AO** ligands. The calculation results indicate that most stable uranyl complex with **AO1**, **AO2** and **AO3** are **U-M8-M8**, **trans-U-M8-M9(AO2)**, and **U-M8-M6(AO3)**, respectively. The formation of these complexes are exothermic by 36.6, 30.6 and 40.9 kcal/mol, respectively. The theoretically predicted sorption ability of **AO2**<**AO1**<**AO3** well reproduces our recent experimental measurements.[9a]

4. Conclusion

Amidoximes (**AO**s) have recently shown great potential in sorption of uranyl ions, whereas the detailed binding modes and the structure-binding ability relationships are remains unclear so far. In the present study, DFT calculations have been performed to systematically investigate the relative facility of different coordination modes of aromatic **AO**s with $UO_2(NO_3)_2$, and the following conclusions are generated:

1) The tautomerized neutral AO (**TAO**, with the hydroxylic H atom transfering to the oximic N atom) represents the most feasible neutral ligand, and it tends to connect with the uranium center via the η^1-O mode. By contrast, both the η^1-O and η^2-N-O coordination modes are plausible for the anionic AOs (**AAO**). The transformations between these two types of coordination modes are kinetically highly feasible.

2) The relative coordination ability of different types of aromatic **AO**s follows the order of **AAO** > **TAO** >> **AO**. Both the covalent U-O(**AAO**) bond character and the strong π(**AAO**)-f(U) donation contribute to the stronger coordination ability of **AAO**.

3) Starting from $UO_2(NO_3)_2$ and aromatic **AO**s, three main types of uranyl complexes, i.e. $UO_2(NO_3)_2$(**TAO**)(**AAO**), $UO_2(NO_3)_2$(**AAO**)$_2$, $UO_2(EtOH)_2$(**AAO**)$_2$ might be predominant for the binding structures. For the first two types, η^1-O mode is feasible for **TAO** and **AAO**. For the third type, **AAO** might ligate with the uranyl center via either η^1-O or η^2-N-O mode. Therefore, the third type actually includes three isomeric structures with double η^2-N-O, double η^1-O or one η^2-N-O&one η^1-O **AAO**s, respectively.

The calculation results show good agreement with the available experimental measurements. Nonetheless, considering that some of the predicted uranyl structures have not been verified by experimental methods (such as x-ray crystal structure) yet, we suggest that more effort should be put in the future.

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28 In the present study, the entropic effect has been examined. It was found that the entropic effect make little influence on the relative energies of complexes with the same number of ligands, while significantly affects the relative energies for complexes with different number of ligands. That is, the ligand addition reactions might become less favorable in Gibbs free energy than that predicted by enthalpies. For exmaple, the formation of **U-EtOH-EtOH** from **U-EtOH** is exothermic in enthalpy, whereas endergonic in Gibbs free energy. Nonetheless, the addition of strong-binding ligands are favored irrespective the enthalpy or Gibbs free energy are used for discussions (i.e. **U-EtOH** vs **U-M6-EtOH**; **U-M6** vs **U-M6-M6**).

For this reason, the concluded three types of complexes (i.e. $UO_2(NO_3)_2$(**TAO**)(**AAO**), $UO_2(NO_3)_2$(**AAO**)$_2$, $UO_2(EtOH)_2$(**AAO**)$_2$) remain significantly more stable than the other ones after including the entropic effect. In addition, another type of complex (i.e. $UO_2(EtOH)$(**AAO**)$_2$) becomes plausible in Gibbs free energy, because the release of one weakly coordinated EtOH from $UO_2(EtOH)_2$(**AAO**)$_2$ is favored by the entropic effect (Please see S18-S20 in ESI for more details).

29. Note that the possibility for the ligand exchange between **AO1/TAO1** and NO_3^- were also examined. As expected, these processes are generally highly disfavored (please see Figure S11 in ESI for more details).

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32 The relative enthalpies of **AAO1'** and **AAO1''** ligated uranyl complexes are also relatively higher than the related **AAO1** ligated complexes (29 structures in Figures S25-S31). Therefore, the possibility for **AAO1'** and **AAO1''** ligated uranyl complexes was excluded.

33 The relative enthalpy of all these **AAO1** ligated uranyl complexes are calculated from the ligand exchange reaction starting from $UO_2(NO_3)_2(EtOH)_2$ and **AO1**. For example, the relative enthalpies of the double **AAO1** ligated complexes are calculated from the reaction: **U-EtOH-EtOH** + **2 AO1** -> **U-AAO1-AAO1**$^{2-}$ + $2H^+$ + 2EtOH.

34 The possibility of the other types of $\mathbf{UO_2(AAO1)_2(Neu)_n}$, n=1 or 2 were omitted due to the high repulsion between different ligands on the equatorial plane of the uranyl center.

35 B3LYP-D3 calculations have been carried out on the most stable structures. It was found that the key structural parameters for the optimized structures with B3LYP and B3LYP-D3 are highly close to each other. Meanwhile, the relative enthalpies of all these five complexes (i.e. **U-M8-M6**, **U-M8-M8**, **Trans-U-M9-M9-T2**, **Trans-U-M8-M8** and **Trans-U-M8-M9**) remain comparable with the inclusion of the dispersion effects. Interestingly, the η^2-coordination modes of UO_2 $(EtOH)_2$(**AAO1**)$_2$ (i.e. **Trans-U-M9-M9-T2**) is slightly more stable than those with the η^1-coordination modes (i.e. **Trans-U-M8-M8** and **Trans-U-M8-M9**) after including the dispersion effect. Please see ESI for more details.

Entry for the Table of Contents

Computational Chemistry

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Density Functional Theory Investigations on the Binding Modes of Amidoximes with Uranyl Ions

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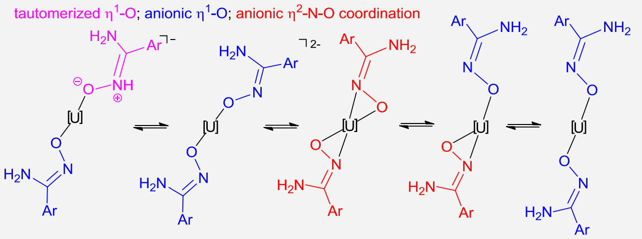

η^1-O of tautomerized amidoximes and η^1-O/η^2-N-O of anionic amidoximes are all plausible coordination modes for amidoximes in ligating uranyl ions.