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How Amidoximate Binds the Uranyl Cation

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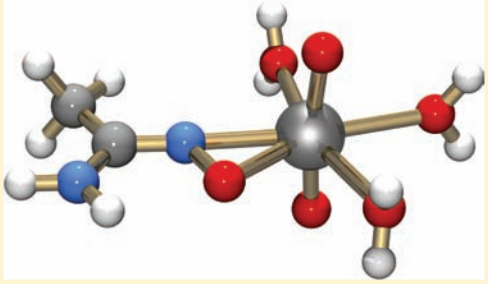
Ⓢ *Supporting Information*

ABSTRACT: This study identifies how the amidoximate anion, AO, interacts with the uranyl cation, UO_2^{2+}. Density functional theory calculations have been used to evaluate possible binding motifs in a series of $[UO_2(AO)_x(OH_2)_y]^{2-x}$ ($x = 1-3$) complexes. These motifs include monodentate binding to either the oxygen or the nitrogen atom of the oxime group, bidentate chelation involving the oxime oxygen atom and the amide nitrogen atom, and η^2 binding with the N−O bond. The theoretical results establish the η^2 motif to be the most stable form. This prediction is confirmed by single-crystal X-ray diffraction of UO_2^{2+} complexes with acetamidoxime and benzamidoxime anions.



■ INTRODUCTION

It is estimated that there is an astonishing 4 billion metric tons of uranium dissolved in the Earth's oceans,[1] believed to be present primarily as $[UO_2(CO_3)_3]^{4-}$ species at ppb concentrations.[2] This has led to efforts to extract uranium from the ocean by using adsorbent materials that are capable of sequestering very low concentrations of uranium from seawater in the presence of much higher concentrations of competing metal ions. This challenge has motivated extensive experimental research on adsorbent development.[1,3,4] It was observed that ion-exchange resins meet the requirements of high physical and chemical stability in seawater, rapid uptake of uranium, and sufficient loading capacity.[4b] Systematic screening tests of 200 organic polymers functionalized with a wide variety of chelating groups revealed that only poly(acrylamidoximes) were able to sequester the uranyl ion, UO_2^{2+}, at the slightly alkaline pH of seawater (8.0−8.3).[4a]

Although amidoxime-based adsorbents have been studied extensively,[4−8] it remains unclear why this functional group exhibits a superior uranium sequestering ability. It is known by potentiometric titrations with prototype ligands, acetamidoxime[9a] and benzamidoxime,[9b] that amidoximes deprotonate to form charge-neutral bis-amidoximato uranyl complexes. Consistent with these solution studies, amidoxime-based polymers are observed to release 2 equiv of H^+ per uranyl adsorbed, leading researchers to propose the two possible binding motifs shown in Figure 1.[6−8] In the first motif, uranium is bound to the oxygen atoms of two amidoxime and two amidoximate ligands.[7] In the second motif, uranium forms five-membered chelate rings by coordinating an oxygen atom and an NH_2 nitrogen atom of two amidoximate ligands.[6,8] Such structures have never been experimentally confirmed, and the exact nature of the binding motif of uranium species in amidoxime-based polymers remains obscure.

Examination of existing crystal structure data provides some insight, but does not answer the question. The Cambridge Structural Database (CSD)[10] contains structures for two amidoxime−uranyl complexes, both of which involve charge-neutral ligands.[11] In these structures (see Figure 2 for an example), the amidoxime ligands tautomerize (OH proton transferred to the oxime nitrogen atom) and bind to uranium through the oxygen atom. Although the CSD does not contain any structures containing amidoximate−uranyl complexes, it does contain a number of structures for amidoximate complexes with transition-metal cations. The observed binding motifs, shown in Figure 2, do not support those proposed in Figure 1. First, while there are instances of amidoximate oxygen atoms bridging between two metal ions, there are no clear examples of an isolated oxygen-binding motif (**I**). Second, multiple structures do exhibit five-membered chelate rings with oxygen and nitrogen donor atoms (**II**), but all involve a different tautomer

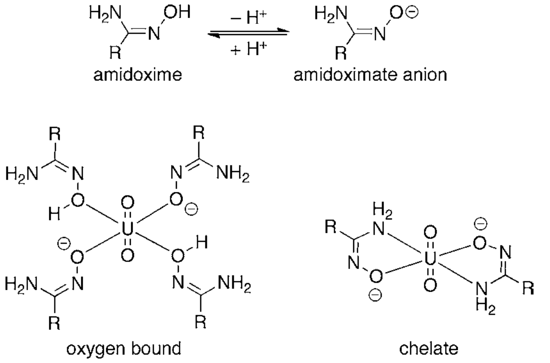


Figure 1. Structure of the amidoxime and amidoximate ligands and UO_2^{2+} binding motifs proposed[6−8] to occur in amidoxime-based polymers. Solvent molecules complementing fifth and/or sixth coordination sites on the uranyl cation are not shown.

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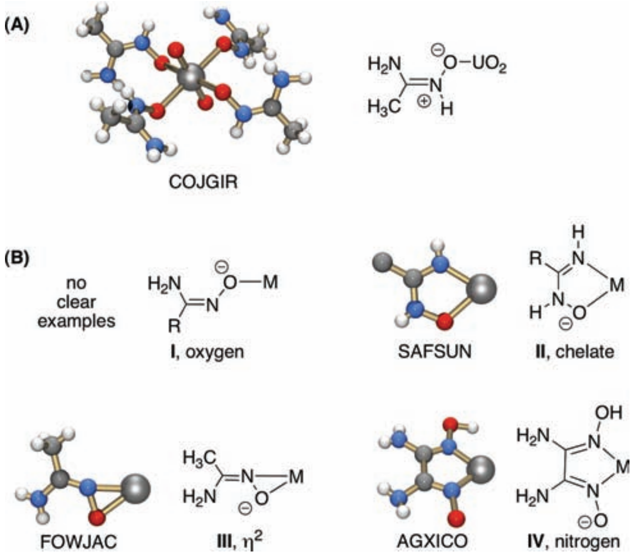

Figure 2. (A) Structure of the $[UO_2(\text{acetamidoxime})_4]^{2+}$ complex (COJGIR).[11] (B) Four possible binding motifs for the amidoximate anion: (**I**) oxygen bound, (**II**) chelate (molybdenum complex, SAFSUN), (**III**) η^2 binding with N−O bond (molybdenum complex FOWJAC), and (**IV**) nitrogen bound (cobalt complex, AGXICO).[12]

than that shown in Figure 1 (NH_2 proton transferred to the oxime nitrogen atom). A third motif (**III**) involves η^2 binding with the N−O bond. Finally, a fourth motif (**IV**), which occurs with bis-amidoximes, involves the deprotonation of either one or both of the OH groups and chelate ring formation through two oxime nitrogen atoms.

To identify which binding motif is preferred when the amidoximate anion binds UO_2^{2+}, we have performed density functional theory (DFT) calculations to evaluate the geometries and relative stabilities of possible binding motifs in a series of complexes containing acetamidoximate (AO) and aqua ligands, $[UO_2(AO)_x(OH_2)_y]^{2-x}$. The theoretical results establish the η^2 motif to be the most stable form. This prediction is confirmed by the first single-crystal X-ray structures of UO_2^{2+} complexes with acetamidoximate and benzamidoximate ligands, both of which exhibit the η^2 motif.

■ METHODOLOGY

Modeling. Calculations were performed with the Gaussian 09 A2 package[13] using density functional theory (DFT) at the B3LYP level of theory.[14] The Stuttgart RSC 1997 effective core potential (ECP) was used for uranium, replacing 60 core electrons to account for scalar relativistic effects.[15] The valence electrons in this basis set are represented by a contracted [8s/7p/6d/4f] basis; 6-31+G(d,p) basis sets were used for carbon, nitrogen, oxygen, chlorine, and hydrogen atoms. The most diffuse function on uranium (having an exponent of 0.005) was removed from the basis in order to improve SCF convergence. Spin−orbit interactions were not considered explicitly, and the SCF procedure was set to: tight, quadratically convergent[16] and without symmetry. This level of theory (B3LYP using a small-core Stuttgart ECP for the metal and a double-ζ basis set for other atoms) is known to yield accurate geometries and energetics for actinyl complexes.[17] Frequency calculations were performed to verify that geometries were minima. Binding enthalpies were calculated as follows: $\Delta H = E(\text{complex}) - E(\text{donor}) - E(\text{acceptor}) + \Delta E_{ZPE} + \Delta E_{\text{thermal}} + \Delta(PV)$, where Δ represents difference between complex and free species and $\Delta(PV) = RT = -0.593$ kcal mol^{-1} at 298.15 K. The influence of aqueous solvation was modeled by performing single-point calculations on previously optimized geometries with the Integral Equation Formalism for Polarized Continuum Model (IEF-PCM).[18] Data for all reported uranyl amidoxime complexes (optimized atomic coordinates and absolute energies) are provided in the Supporting Information.

Table 1. Stabilities of $[UO_2(AO)_x(OH_2)_y]^{2-x}$ Complexes as a Function of AO Binding Motif

stoichiometry	AO motif[a]	ΔH^b (kcal/mol)	$\Delta H_{aq}{}^b$ (kcal/mol)	no. donor atoms in equatorial plane
$[UO_2(AO)(OH_2)_3]^{1+}$				
1	III	0.0	0.00	5
2	II	4.5	3.13	5
3	I	11.6	9.63	4
$[UO_2(AO)_2(OH_2)]$				
4	III/III	0.0	0.00	5
5	III/III	4.5	6.15	5
6	II/II	6.4	3.26	5
7	II/II	7.0	3.59	5
8	I/III	7.4	0.70	4
9	II/II	11.8	5.96	5
$[UO_2(AO)_2(OH_2)_2]$				
10	III/III	0.0	0.00	6
11	III/III	2.4	2.22	6
12	I/III	2.6	6.80	5
13	I/I	5.7	14.93	4
14	II/II	12.0	15.19	6
15	II/II	16.1	11.69	6
16	II/II	16.7	12.01	6
$[UO_2(AO)_2(OH)_3]$				
17	I/III	0.0	0.00	6
18	I/I	1.2	1.97	5
19	I/I	2.0	3.81	5
$[UO_2(AO)_3]^{-1}$				
20	III/III/III	0.0	0.00	6
21	I/III/III	4.1	7.47	5
22	I/II/III	11.2	8.08	5

[a] See Figure 2. [b] ΔH and ΔH_{aq} are enthalpies relative to the lowest energy configuration for each stoichiometry in the gas phase and in aqueous solution, respectively.

Crystallization. Acetamidoxime and benzamidoxime were prepared by treating the corresponding nitriles with NH_2OH according to known procedures.[19] Crystals suitable for X-ray diffraction were grown by slow evaporation over molecular sieves from a MeOH/CH_3NO_2/$ClCH_2CH_2Cl$ solution of $UO_2(NO_3)_2{\cdot}6H_2O$ and acetamidoxime for $[UO_2(CH_3C(NH_2)NO)_2(MeOH)_2]$, and from a MeOH/$CH_3NO_2$ solution of $UO_2(NO_3)_2{\cdot}6H_2O$ and benzamidoxime for $[UO_2(C_6H_5C(NH_2)NO)_2(MeOH)_2]$, in the presence of triethylamine. Single-crystal X-ray data were collected on a Bruker SMART APEX CCD diffractometer with fine-focus Mo Kα radiation operated at 50 kV and 30 mA. The structures were solved by direct methods and refined on F^2 using the SHELXTL software.[20] Absorption corrections were applied using SADABS, part of the SHELXTL package. All non-hydrogen atoms were refined anisotropically. The CH hydrogen atoms were placed in idealized positions and refined with a riding model. The NH and OH hydrogen atoms were located

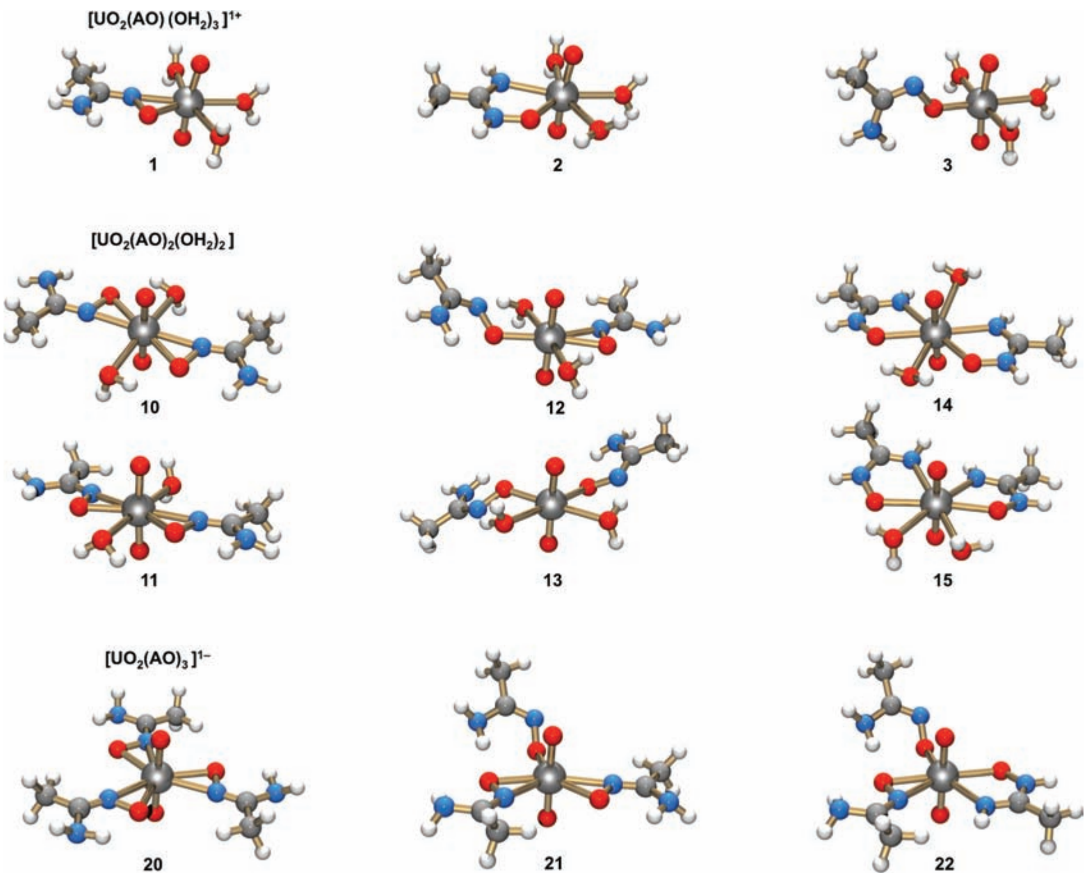

Figure 3. Representative structural isomers for $[UO_2(AO)(OH_2)_3]^{1+}$, $[UO_2(AO)_2(OH_2)_2]$, and $[UO_2(AO)_3]^{-1}$ complexes optimized at the B3LYP level of theory.

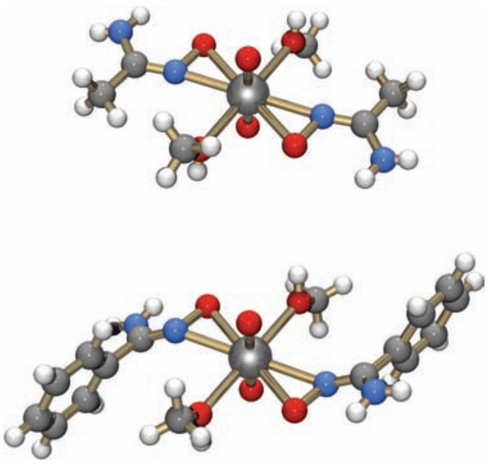

Figure 4. Views of $[UO_2(AO)_2(MeOH)_2]$ and $[UO_2(benzamidoximate)_2(MeOH)_2]$ structures obtained by single-crystal X-ray diffraction.

from the difference Fourier maps and refined isotropically. Details of crystallographic data are listed in the Supporting Information.

Table 2. Geometric Parameters of X-ray Structures for $[UO_2(benzamidoximate)_2(MeOH)_2]$ (A), $[UO_2(AO)_2(MeOH)_2]$ (B), and Calculated Structure, 10

	A	B	10	Δ[a]
distances [Å]				
U═O	1.796	1.789	1.784	0.005
U−N	2.438	2.398	2.424	0.026
U−O	2.352	2.383	2.349	0.034
O−N	1.422	1.409	1.372	0.037
C═N	1.293	1.290	1.291	0.001
U−OH	2.304	2.458	2.624	0.116
angles [deg]				
U−O−N	76.1	73.5	76.3	2.9
U−N−O	69.5	72.3	70.3	1.9
O═U−O	87.9	91.5	90.3	1.2
O═U−N	92.8	89.6	89.0	0.6
O−N═C	114.2	117.2	117.7	0.5
dihedral angles [deg]				
O═U−O−N	98.0	87.0	87.6	0.7
U−O−N═C	142.0	178.4	176.4	2.0
U−O−N−OH	12.2	4.9	5.8	0.9

[a] Absolute value of the differences between X-ray structure **B** and calculated structure **10**.

■ RESULTS AND DISCUSSION

DFT calculations were performed to evaluate the geometries and relative stabilities of different amidoximate binding motifs with the UO_2^{2+} cation. Given its small size, acetamidoximate (Figure 1, R = CH_3), hereafter referred to as AO, was chosen as the representative ligand for these calculations. Initial calculations showed three of four possible binding motifs (see Figure 2), **I** (oxygen), **II** (chelate), and **III** (η^2), to be local minima. Attempts to optimize a geometry containing motif **IV** (nitrogen) proved unsuccessful, leading instead to **III**. In addition, it was not possible to locate a minimum corresponding to the chelated tautomeric form proposed in Figure 1.

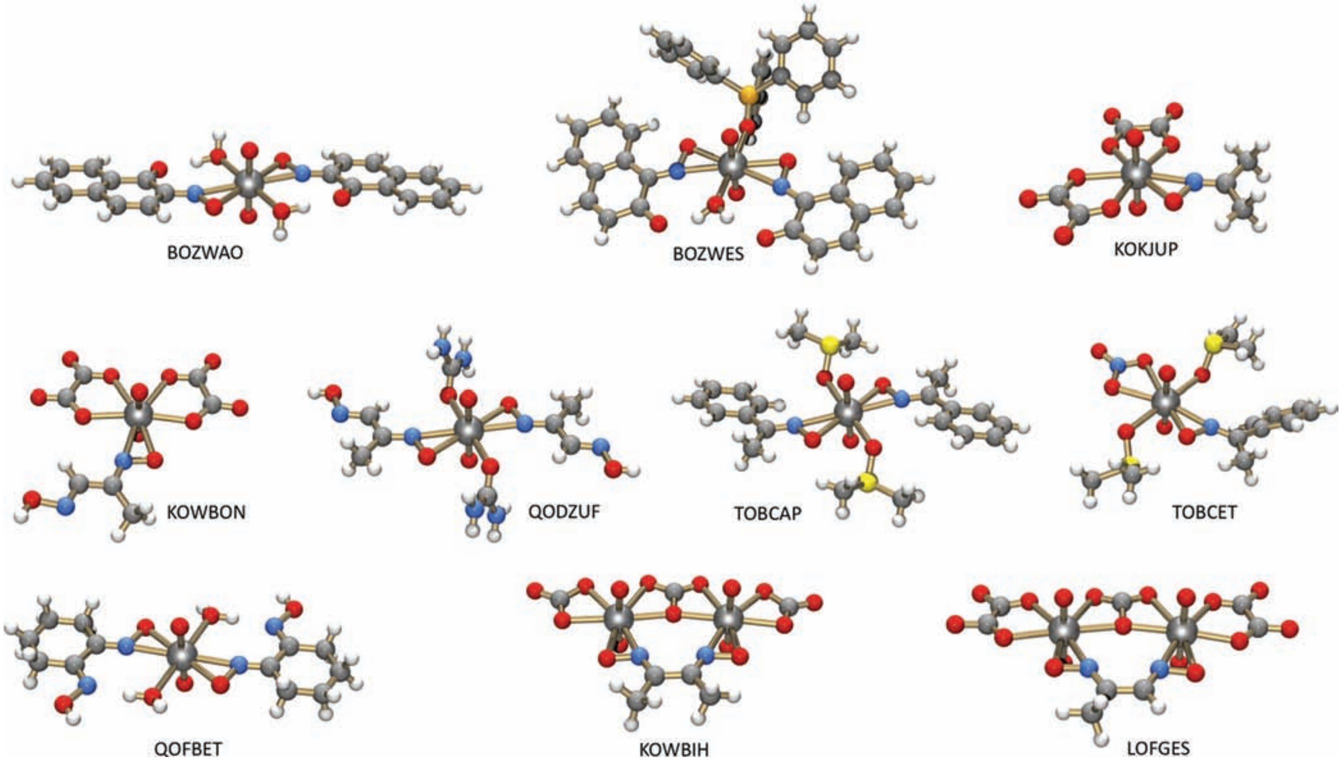

Figure 5. Uranyl−oximate complexes in the CSD (REFCODE given below each structure) all exhibit η^2 binding motifs.[21]

The relative stabilities of motifs **I**, **II**, and **III** were extensively investigated in a series of $[UO_2(AO)_x]^{2-x}$ complexes in which aqua ligands were added to complete the equatorial coordination. This resulted in three categories of complexes: a cationic complex with one AO ligand, $[UO_2[(AO)(OH_2)_3]^{1+}$; neutral complexes with two AO ligands, $[UO_2(AO)_2(OH_2)]$, $[UO_2(AO)_2(OH_2)_2]$, and $[UO_2(AO)_2(OH_2)_3]$; and an anionic complex with three AO ligands, $[UO_2(AO)_3]^{-1}$. For each stoichiometry, Table 1 summarizes the relative stabilities of structural isomers obtained through variation in the AO binding motif. Representative geometries are depicted in Figure 3. Coordinates and absolute energies for all reported complexes are provided in the Supporting Information.

The relative gas-phase enthalpies, ΔH values, in Table 1 demonstrate that complexes with binding motif **III** are energetically more stable than complexes with binding motifs **I** or **II**. This trend is observed for all stoichiometries, indicating that the η^2 motif **III** is the energetically preferred motif for the complexation of uranyl by the amidoximate ligand regardless of the number of AO, the number of aqua ligands, or the charge of the complex. Of the remaining two motifs, the oxygen binding mode, **I**, generally leads to more stable complexes than the chelate mode, **II**. When the IEF-PCM aqueous solvation model is applied to **1**−**22**, the resulting ΔH_{aq} results show that the **III** motif remains the most stable, predicting that η^2 is also the preferred binding motif in the aqueous phase.

To experimentally validate the prediction that the η^2 motif is the preferred uranyl ion binding motif for amidoximate ligands, crystals of $[UO_2(AO)_2(MeOH)_2]$ and $[UO_2(\text{benzamidoximate})_2(MeOH)_2]$ suitable for X-ray diffraction were grown from MeOH/CH_3NO_2 solution after the addition of triethylamine to deprotonate the corresponding amidoxime. The structures of these complexes, shown in Figure 4, confirm that amidoximate ligands bind UO_2^{2+} with the η^2 motif. Selected geometric parameters for these structures are reported in Table 2.

The crystal structure of $[UO_2(AO)_2(MeOH)_2]$ is analogous to structure **10** (Figure 3), which is the calculated lowest-energy form for $[UO_2(AO)_2(OH_2)_2]$. Thus, relative energetics from the B3LYP model, both in the gas phase and in solution, correctly predict the observed experimental configuration. Consistent with prior studies,[17] comparison of the computed versus observed geometric parameters further confirms this level of theory to yield an accurate description of structure in actinyl complexes.

Final experimental corroboration comes from the CSD, which contains a number of examples of uranyl complexes with structurally related oximate ligands.[21] Without exception, these structures (Figure 5) all exhibit an η^2 binding motif.

■ CONCLUSIONS

Theoretical evaluation of structural isomers for $[UO_2(AO)_x(OH_2)_y]^{2-x}$ complexes reveals the existence of three possible binding motifs for the acetamidoximate, AO, ligand: monodentate oxygen coordination, bidentate chelation, and η^2 coordination to the N−O bond. Regardless of the number of AO ligands, the number of aqua ligands, charge of the overall complex, or inclusion of solvation effects, the η^2 binding motif is characterized as the most energetically stable structural configuration. Single-crystal X-ray diffraction revealed the molecular structure of two uranyl−amidoximate complexes that corroborate this theoretical prediction. In addition, all known structures of closely related uranyl−oximate complexes also exhibit the η^2 binding motif. Although the nature of the uranyl complexes formed in amidoxime-based adsorbents remains to be determined, the findings herein are inconsistent with previously proposed binding motifs (Figure 1) and suggest the existence of alternative motifs involving η^2 coordination.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Optimized atomic coordinates and absolute energies for **1**−**22**, full citation for ref 13, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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