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Supporting information for article:

Tris-amidoximate Uranyl Complexes *via* η^2 Binding Mode Coordinated in Aqueous Solution showed by X-ray Absorption Spectroscopy and Density Functional Theory Methods

Linjuan Zhang, Meiying Qie, Jing Su, Shuo Zhang, Jing Zhou, Jiong Li, Yu Wang, Shitong Yang, Shuao Wang, Jingye Li, Guozhong Wu and Jian-Qiang Wang

S1. Comparisons of U L_3-edge EXAFS data before and after subtracting the double-electron excitation.

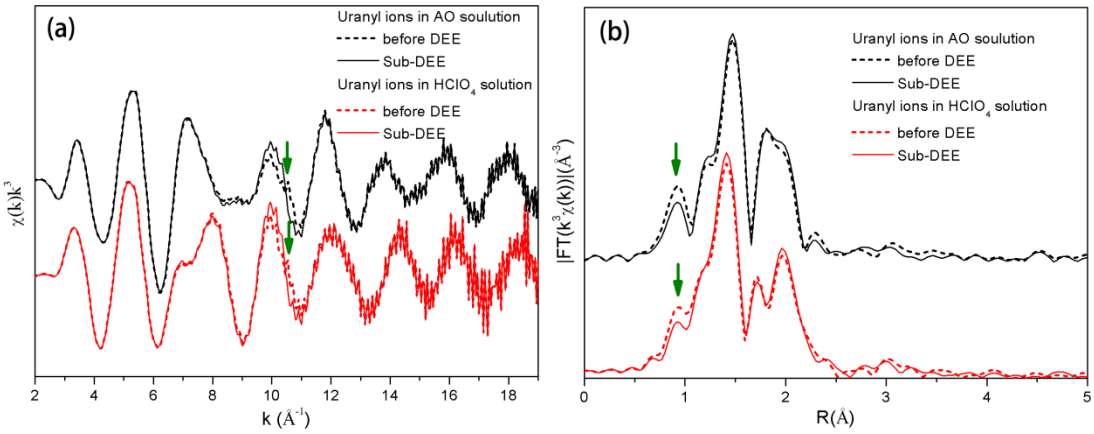

Figure S1 Comparison of experimental uranium L_3-edge k^3-weighted EXAFS oscillation data (a) and Fourier Transform data (b) before and after subtracting the double-electron excitation.

S2. Comparisons of di-AO-uranyl species with η^2/η^2 motifs but with different geometry configurations from CPCM DFT/B3LYP calculations: Optimized structures and EXAFS spectra.

In the same binding motifs, when more than one amidoxime ligand coordinated to the uranyl ions, due to the different relative position of AO/H_2O ligands the number of possible coordination combination configurations increase. For example, when two amidoxime ions combine into the uranyl ion with the same η^2/η^2 motifs, there are three possible geometries as shown in Figure S2. Although in previous theoretical research these possible ligand geometries display different relative stabilities, their corresponding EXAFS pattern are also indistinguishable as shown in Figure S3.

Table S1 Optimized bond lengths of di-AO-uranyl species with η^2/η^2 motifs from CPCM DFT/B3LYP calculations.

Complexes	No	R(U-O_{ax})/ Å	R(U-L_{eq})/ Å	Average R(U-L_{eq})
di-AO	4	1.798, 1.798	2.292,2.298,2.417,2.418,2.538	2.392
species	4-1	1.801, 1.801	2.272,2.273,2.397,2.399,2.465	2.361
	4-2	1.799, 1.799	2.290,2.291,2.408,2.411,2.524	2.385

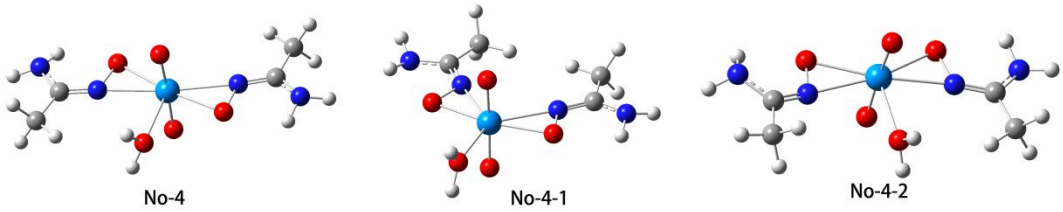

Figure S2 Possible coordination geometries of the $UO_2(AO)_2(H_2O)$ complexes with η^2/η^2 binding motifs.

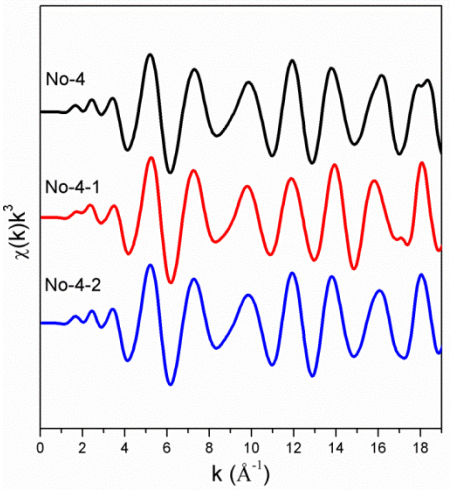

Figure S3 k^3-weighted calculated EXAFS oscillations of uranyl-AO species at the U L_3-edge.

S3. Comparisons of optimized bond lengths in the di-AO-uranyl species affected by coordination number (CN) from CPCM DFT/B3LYP calculations.

In the equatorial plane 5 or 6 ligand atoms may combine into the uranyl ions compensated by water molecule. According to Vukovic's report (Vukovic *et al.*, 2012), the average U-Ligand

distance with coordination number of 6 in the equatorial plane is longer by 0.06 Å than that with coordination number of 5. In Table S2, we also list the distance difference of possible binding geometry in the di-AO species induced by the change of coordination number in the equatorial plane. In the model with coordination number of 6, the longer bond lengths of U-L_{eq} are beyond the experimental value and thus these geometry models are out of our consideration in this work.

Table S2 Comparison of optimized bond lengths in the di-AO-uranyl species affected by coordination number (CN) from CPCM DFT/B3LYP calculations.

Complexes	No	Binding Motifs	R(U=O_{ax})/ Å	R(U-L_{eq})/ Å	Average R(U-L_{eq})	CN
di-AO species	4	c/c	1.802, 1.801	2.273, 2.272, 2.395, 2.400, 2.473	2.363	5
	4-0	c/c	1.805,1.805	2.307,2.404,2.307,2.405,2.569,2.569	2.427	6
	5	b/b	1.799, 1.801	2.305, 2.326, 2.496, 2.525, 2.530	2.436	5
	5-0	b/b	1.795, 1.794	2.420,2.525,2.425,2.520,2.652,2.656	2.533	6
	8	c/a	1.801, 1.803	2.242, 2.295, 2.382, 2.484, 2.522	2.385	5
	8-0	c/a	1.799,1.799	2.302,2.400,2.384,2.531,2.574,2.609	2.467	6

S4. Comparisons of optimized bond lengths and total energies in the tris-AO-uranyl species with different binding motifs from CPCM DFT/B3LYP calculations(Zhang, Su*, et al.*, 2016).

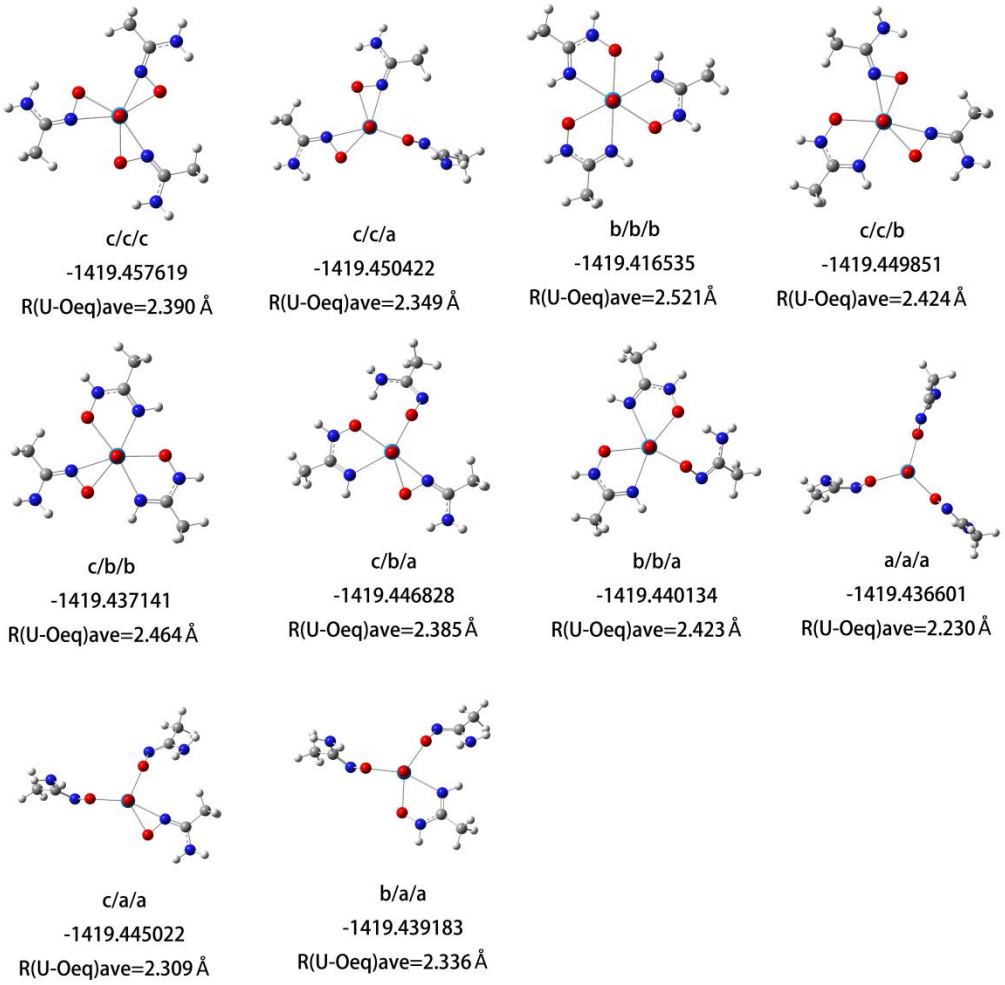

Figure S4 Optimized geometries and total energies after zero-point energy correction (in hartrees) $[UO_2(AO)_3]^-$ complexes.

S5. Comparisons of experimental and simulated XANES spectra.

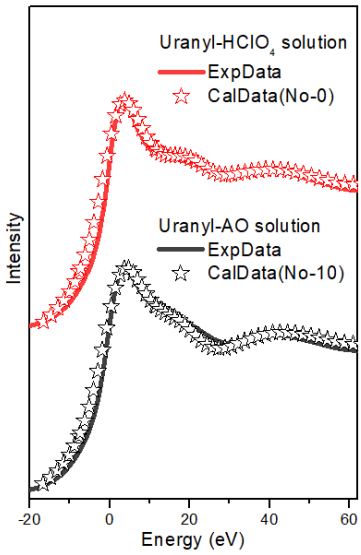

Figure S5 Comparison to experimental and simulated XANES spectra of uranyl-AO and uranyl-HClO4 solutions.

Table S3 Optimized DFT structures of the $[UO_2(AO)_x]^{2-x}$ complexes in Figure 4.

No-1

U	-0.55787900	0.00791500	-0.00059200
O	-0.64401100	0.05475000	1.78078500
O	-0.65848300	0.05646000	-1.78098300
O	-1.66102400	-2.19570300	0.00984200
H	-1.58200100	-2.78937800	-0.77218800
H	-1.57404300	-2.78919100	0.79120200
O	-2.91767800	0.71575800	0.00706700
H	-3.50252000	0.79292100	0.79431300
H	-3.50644100	0.79292200	-0.77708300
O	-0.11436900	2.42165100	-0.00313800
H	0.02921600	2.99433100	-0.79020600
H	0.03507600	2.99505000	0.78230900
O	1.19009500	-1.40416200	-0.01609500

N	1.76851500	-0.14715700	-0.00799900
C	3.07197100	-0.06496500	0.00122800
N	3.85950000	-1.15373500	0.00249300
H	3.43834300	-2.08232600	-0.00526600
H	4.87501600	-1.06978800	0.00403800
C	3.69286000	1.30043100	0.00806500
H	4.34051000	1.43052300	-0.87494400
H	4.31964400	1.43002100	0.90613000
H	2.91071000	2.07018000	-0.00084400

No-4

U	0.03598400	0.02777500	-0.00159500
O	0.01486500	-0.02840400	-1.79876400
N	2.45178000	0.14117500	0.00373700
O	2.00217400	-1.16107200	0.00186400
C	3.73497000	0.32899200	0.00685300
C	4.27615500	1.72647600	-0.00102700
H	4.87867600	1.90289100	-0.90795400
H	3.45509500	2.45415200	0.02704300
H	4.93330000	1.88970000	0.86872300
N	4.61120700	-0.72249000	0.07315700
H	4.20413700	-1.62032800	-0.17735600
H	5.54838900	-0.56113500	-0.28025900
O	0.00838900	-0.02472200	1.79557200
O	-0.66974600	-2.40968800	0.00284700
H	-1.14001800	-2.77188400	-0.76466300
H	-1.13422400	-2.76856300	0.77544800
N	-2.36824400	0.27840600	-0.00564200
O	-1.72349000	1.49649300	-0.00582100
C	-3.66486100	0.29294200	0.00468500

N	-4.36863300	1.46577700	0.07808100
H	-3.83174600	2.29299300	-0.17021100
H	-5.32335300	1.45230600	-0.26473900
C	-4.41376800	-1.00543900	-0.00275100
H	-5.04342200	-1.08424100	-0.90482200
H	-5.07988900	-1.07117500	0.87288000
H	-3.71278800	-1.84874300	0.01518400

No-8

U	-0.16701900	-0.41950800	0.07721800
O	0.11432900	-0.10165600	-1.67288300
O	-0.41593700	-0.79583900	1.82324900
O	0.33092900	2.02159700	0.47009500
H	0.22110000	2.34413700	1.39010800
H	1.33035800	1.96142000	0.33278700
O	0.09600600	-2.85333300	-0.34312900
H	-0.21440500	-3.54700200	0.28044400
H	0.02855600	-3.26067700	-1.23534700
O	2.02617500	-0.20303500	0.48711000
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C	3.95593700	0.78606600	-0.15791600
N	4.55751300	-0.44270300	-0.17474500
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H	5.57074300	-0.46660000	-0.05319500
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H	4.14863600	2.88739700	-0.53864800
H	5.23500800	1.85198200	-1.52001500
H	5.59668600	2.13302800	0.19817900
O	-2.37484500	-0.89029800	-0.33417500
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H	-4.14062700	2.81780600	0.96636200
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N	-4.65581800	0.49344800	-0.54953600
H	-4.66159200	-0.52629000	-0.49773900
H	-5.53755800	0.95173000	-0.31688900

No-10

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H	4.14737000	0.64128900	0.03703400
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C	-0.52693300	3.69784900	-0.00205000
N	0.45893600	4.65764400	0.05691600
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H	0.22427100	5.56663700	-0.34613500
C	-1.96054700	4.13834800	0.00132700
H	-2.18787500	4.73617100	-0.89863900
H	-2.16904000	4.77496900	0.87799100
H	-2.62414800	3.26414600	0.02489800

No-11

U	0.16506600	0.03647100	0.17845600
O	-0.09445300	-0.36943300	-1.56859800
O	0.45638900	0.41645500	1.93199600
O	2.18862700	1.06097000	-0.37204100
N	2.55970800	-0.24884500	-0.12591100
C	3.81754100	-0.54164600	-0.24527700
N	4.74290100	0.38133800	-0.66277700
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No-15

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H	-4.01930600	2.08237900	-0.30935900
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