Theoretical Studies on the AnO_2^{n+} (An=U, Np; n=1, 2) Complexes with Di-(2-ethylhexyl) Phosphoric Acid

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Supporting Information

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Table S3. Changes of the Gibbs free energy (kcal/mol) for the complexes of AnO_2^{n+} (*n*=1, 2) and L (L=DEHP⁻) in aqoeous solution and organic Aolution obtained by the B3LYP method.

Table S4 The bond length and the symmetrical and antisymmetrical stretching frequency (υ_s and υ_{as}, cm⁻¹) of An=O$_{axial}$ for the 2:1-type complexes.

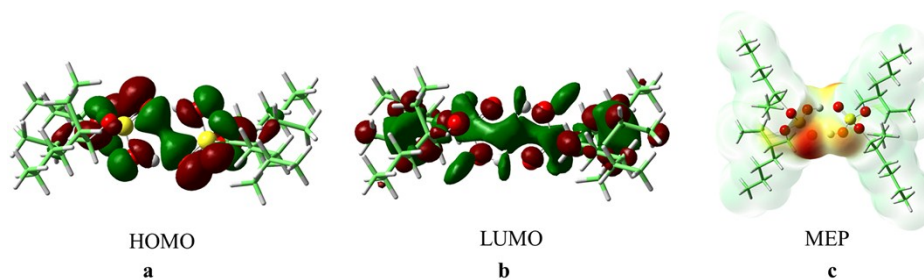**Complete Gaussian 09 reference (Reference 21)**

HOMO
a

LUMO
b

MEP
c

Figure S1. HOMO (a), LUMO (b) of HDEHP dimer, and MEP mapped on the isodensity surface (c) for the dimer; The isosurface value is set as 0.02 for MO and 0.0004 for MEP, the color range is taken from -0.0525 (the most electronegative region, red) to 0.0525 (the most electropositive region, blue).
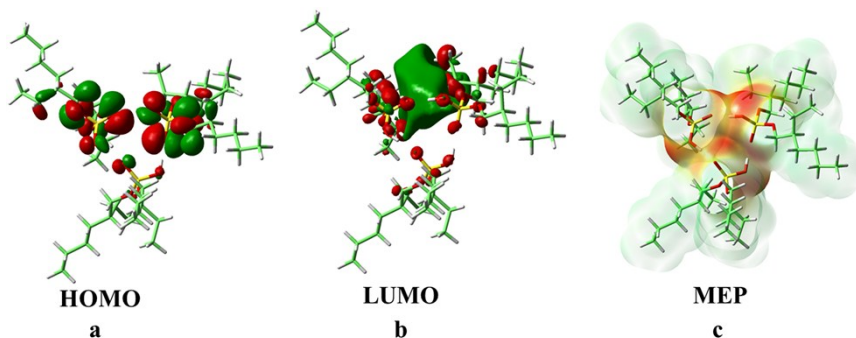

HOMO
a

LUMO
b

MEP
c

Figure S2. HOMO (a), LUMO (b) of HDEHP trimer, and MEP mapped on the isodensity surface (c) for the trimer; The isosurface value is set as 0.02 for MO and 0.0004 for MEP, the color range is taken from -0.0471 (the most electronegative region, red) to 0.0471 (the most electropositive region, blue).
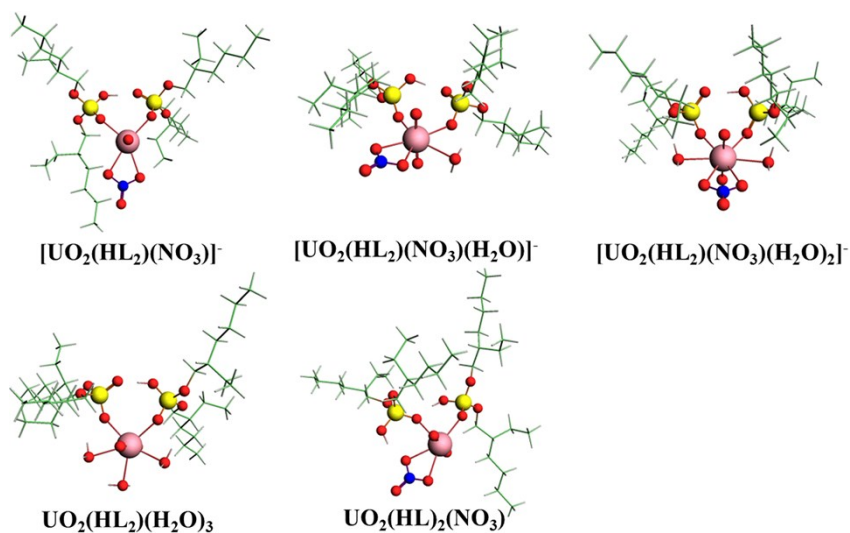
$[UO_2(HL_2)(NO_3)]^-$ $[UO_2(HL_2)(NO_3)(H_2O)]^-$ $[UO_2(HL_2)(NO_3)(H_2O)_2]^-$

$UO_2(HL_2)(H_2O)_3$ $UO_2(HL)_2(NO_3)$

Figure S3. Optimized structures of UO_2^+ complexes by the B3LYP method. Green and white sticks represent C and H, while yellow, red, blue, and pink spheres represent P, O, N, and U, respectively.
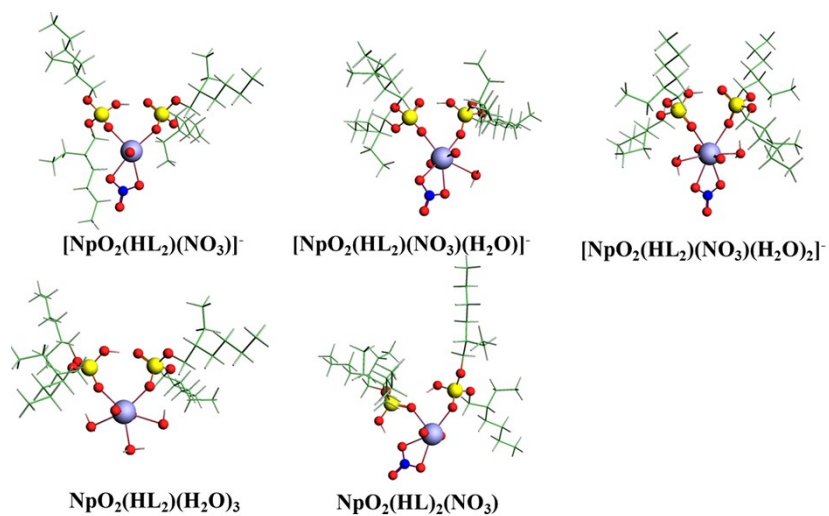

$[NpO_2(HL_2)(NO_3)]^-$ $[NpO_2(HL_2)(NO_3)(H_2O)]^-$ $[NpO_2(HL_2)(NO_3)(H_2O)_2]^-$

$NpO_2(HL_2)(H_2O)_3$ $NpO_2(HL)_2(NO_3)$

Figure S4. Optimized structures of NpO_2^+ complexes by the B3LYP method. Green and white sticks represent C and H, while yellow, red, blue, and purple spheres represent P, O, N, and Np, respectively.
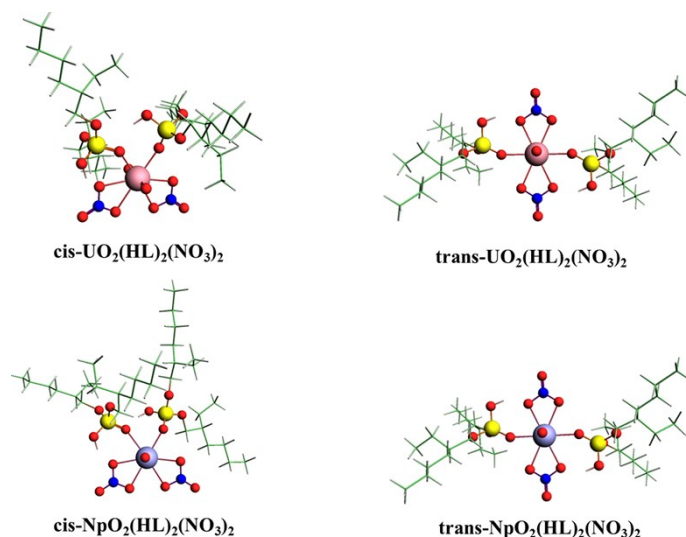
Figure S5. The isomers of the $AnO_2(HL)_2(NO_3)_2$ (An=U, Np) complexes. Green and white sticks represent C and H, while yellow, red, blue, pink, and purple spheres represent P, O, N, U, and Np, respectively.

Table S1. QTAIM analysis of the bonds between ligands and metal for the UO_2^{2+}, NpO_2^{2+} complexes. The average electron density (ρ) and laplacian ($\nabla^2\rho$) values (a.u.) are presented.

Species	Bonds	U(VI)		Np(VI)	
		$\rho\times10^2$	$\nabla^2\rho\times10^2$	$\rho\times10^2$	$\nabla^2\rho\times10^2$
$AnO_2(HL_2)(NO_3)$	$An-O_P$	7.74	31.8	7.87	32.9
	$An-O_{NO_3^-}$	5.99	19.9	6.00	20.4
$AnO_2(HL_2)(NO_3)(H_2O)$	$An-O_P$	7.49	31.3	7.47	31.3
	$An-O_{NO_3^-}$	5.44	18.4	5.42	18.8
	$An-O_{H_2O}$	4.24	16.1	4.25	16.6
$AnO_2(HL_2)(NO_3)(H_2O)_2$	$An-O_P$	6.15	25.0	6.11	24.7
	$An-O_{NO_3^-}$	4.73	15.9	4.55	15.6
	$An-O_{H_2O}$	4.01	14.7	3.85	14.4
$[AnO_2(HL_2)(H_2O)_3]^+$	$An-O_P$	8.15	31.8	8.19	32.1
	$An-O_{H_2O}$	4.28	16.2	4.27	16.3
$AnO_2(HL)_2(NO_3)_2$	$An-O_P$	5.73	23.8	5.67	24.1
	$An-O_{NO_3^-}$	4.64	16.0	4.59	16.2

Table S2. QTAIM analysis of the bonds between ligands and metal for the UO_2^+, NpO_2^+ complexes. The average electron density (ρ) and laplacian ($\nabla^2\rho$) values (a.u.) are presented.

Species	Bonds	U(V)		Np(V)	
		$\rho \times 10^2$	$\nabla^2\rho \times 10^2$	$\rho \times 10^2$	$\nabla^2\rho \times 10^2$
$[AnO_2(HL_2)(NO_3)]^-$	$An\text{-}O_P$	5.47	23.0	5.34	23.6
	$An\text{-}O_{NO_3^-}$	4.37	15.9	4.32	16.2
$[AnO_2(HL_2)(NO_3)(H_2O)]^-$	$An\text{-}O_P$	4.78	20.1	4.98	22.1
	$An\text{-}O_{NO_3^-}$	4.30	15.7	4.16	16.3
	$An\text{-}O_{H_2O}$	3.26	11.8	2.75	10.2
$[AnO_2(HL_2)(NO_3)(H_2O)_2]^-$	$An\text{-}O_P$	4.17	17.1	3.56	15.5
	$An\text{-}O_{NO_3^-}$	3.14	11.3	3.73	14.0
	$An\text{-}O_{H_2O}$	3.01	11.1	3.08	11.7
$[AnO_2(HL_2)(H_2O)_3]$	$An\text{-}O_P$	5.28	22.0	4.98	21.8
	$An\text{-}O_{H_2O}$	3.46	12.8	3.37	12.9
$AnO_2(HL)_2(NO_3)$	$An\text{-}O_P$	4.91	20.3	4.54	20.0
	$An\text{-}O_{NO_3^-}$	4.42	16.4	4.51	17.9

Table S3. Changes of the Gibbs free energy (kcal/mol) for the complexes of AnO_2^{n+} (n=1, 2) and L (L=DEHP⁻) in aqoeous solution and organic Aolution obtained by the B3LYP method[a].

Reaction	ΔG_{aq}	ΔG_{org}
$AnO_2(H_2O)_5^{2+} + (HL)_2 + NO_3^- \rightarrow AnO_2(HL_2)(NO_3) + H^+ + 5H_2O$	-9.8/-12.4	-17.5/-21.1
$AnO_2(H_2O)_5^{2+} + (HL)_2 + NO_3^- \rightarrow AnO_2(HL_2)(NO_3)(H_2O) + H^+ + 4H_2O$	-15.9/-18.5	-23.9/-26.2
$AnO_2(H_2O)_5^{2+} + (HL)_2 + NO_3^- \rightarrow AnO_2(HL_2)(NO_3)(H_2O)_2 + H^+ + 3H_2O$	-7.7/-9.1	-16.8/-17.0
$AnO_2(H_2O)_5^{2+} + (HL)_2 \rightarrow [AnO_2(HL_2)(H_2O)_3]^+ + H^+ + 2H_2O$	-0.3/-2.0	8.9/7.9
$AnO_2(H_2O)_5^{2+} + (HL)_2 + 2NO_3^- \rightarrow AnO_2(HL)_2(NO_3)_2 + 5H_2O$	-26.8/-26.4	-35.1/-35.0
$AnO_2(H_2O)_5^+ + (HL)_2 + NO_3^- \rightarrow [AnO_2(HL_2)(NO_3)]^- + H^+ + 5H_2O$	3.8/6.4	15.9/16.6
$AnO_2(H_2O)_5^+ + (HL)_2 + NO_3^- \rightarrow [AnO_2(HL_2)(NO_3)(H_2O)]^- + H^+ + 4H_2O$	2.8/13.0	14.4/22.3
$AnO_2(H_2O)_5^+ + (HL)_2 + NO_3^- \rightarrow [AnO_2(HL_2)(NO_3)(H_2O)_2]^- + H^+ + 3H_2O$	10.0/19.1	21.8/21.7
$AnO_2(H_2O)_5^+ + (HL)_2 \rightarrow AnO_2(HL_2)(H_2O)_3 + H^+ + 2H_2O$	15.9/22.7	11.2/9.3
$AnO_2(H_2O)_5^+ + (HL)_2 + NO_3^- \rightarrow AnO_2(HL)_2(NO_3) + 5H_2O$	7.0/3.9	-0.6/0.7

[a] .../... represent the results of UO_2^{n+} and NpO_2^{n+} (n=1, 2) complexes, respectively. For H⁺, the experimental value -263.982 kcal/mol was adopted.[1]

Table S4. The bond length and the symmetrical and antisymmetrical stretching frequency (υ_s and υ_{as}, cm^{-1}) of An=O$_{axial}$ (An=U, Np) for the 2:1-type complexes.

Species	U=O$_{axial}$[a]	υ_s[c]	υ_{as}[c]
UO$_2$(HL$_2$)$_2$	1.783(1.767)[b]	820	901
NpO$_2$(HL$_2$)$_2$	1.759	821	919
[UO$_2$(HL$_2$)$_2$]$^-$	1.848	724	763
[NpO$_2$(HL$_2$)$_2$]$^-$	1.813	742	798

[a] The average bond lengths. [b] The value in the parenthesis is the corresponding experimental data.[2] [c] The calculated vibrational frequencies are calibrated with scaling factor 0.968 at the B3LYP/6-311G(d, p) level[3].

Complete Gaussian 09 reference (Reference 21)

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Notes

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