Structural Analysis of the Complexation of Uranyl, Neptunyl, Plutonyl, and Americyl with Cyclic Imide Dioximes

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Table S.1 shows the magnitude of complex frequencies from vibrational frequency calculations for all compounds.

Table S.2 shows the contribution from zero-point energy (ZPE) corrections to the Gibbs free energy (ΔG) of reaction.

Table S.3 shows the contribution from the entropy (S) onto the Gibbs free energy (ΔG) of reaction.

Table S.4 shows the partial charges calculated with NBO for AnO_2^{2+}, backbone, HX^-, NO_3^-, and CH_3OH fragments in $AnO_2(HX)(NO_3)(CH_3OH)$, and $AnO_2(HX)_2$, with An = U, Np, Pu, and Am, and HX = HA, HB, and HC.

Table S.5 shows the bond length differences between calculated and experimental values for U-O1, U-O3, U-O4, U-N2, and N3-O4 (Å).

Table S.6 shows interatomic distance in backbone in H_2X, $AnO_2(HX)(NO_3)(CH_3OH)$, and $AnO_2(HX)_2$.

Table S.7 shows the calculated normalized $\Delta(\Delta G)_{rxn}$ for $AnO_2(HX)(NO_3)(CH_3OH)$, and $AnO_2(HX)_2$, with An = U, Np, Pu, Am, and HX = HA, HB, and HC.

Additionally, structural characteristics, population analysis, and relative Gibbs free energies of reaction for uranyl compounds are studied with the recently developed Strongly Constrained and Appropriately Normed Semilocal (SCAN) density functional revealing that U-O distances are between 0.01 and 0.05Å from those in structures optimized with the B3LYP functional. Differences in partial charges between the uranyl fragment and the backbone of the ligands are less than 0.2 units lower when calculated with SCAN than with B3LYP. Relative Gibbs free energies of reaction calculated with SCAN are between 2 and 28 kcal mol-1 from those calculated with the B3LYP functional.

Table S.8 shows the difference in predicted U-X (with X = O1, O2, O3, O4, N2, OI, OII, and OIII) distances, and O3-U-O4 angle in $UO_2(HX)(NO_3)(CH_3OH)$ and $UO_2(HX)_2$ (with HX = HA, HB, and HC) optimized with the SCAN and B3LYP functionals.

Table S.9 shows difference in calculated partial charge between the uranyl fragment and backbone in $UO_2(HX)(NO_3)(CH_3OH)$ and $UO_2(HX)_2$ (with HX = HA, HB, and HC) structures optimized with the SCAN and B3LYP functionals.

Table S.10 shows the calculated $\Delta(\Delta G)_{rxn}$ with the B3LYP and SCAN functionals (according to Eq. 1, and 2) for $UO_2(HX)(NO_3)(CH_3OH)$, and $UO_2(HX)_2$ (with HX = HA, HB, and HC) with respect to $UO_2(HB)(NO_3)(CH_3OH)$ (as shown in Eq. 3.a and 3.b), and shown in kcal mol^{-1}.

Table S.1-a: Magnitude of complex frequencies from vibrational frequency calculations for all compounds.

Compound	U	Np	Pu	Am
$AnO_2(HA)(NO_3)(CH_3OH)$	11	29	15	-
$AnO_2(HB)(NO_3)(CH_3OH)$	18	30	-	-
$AnO_2(HC)(NO_3)(CH_3OH)$	-	17	24	-
$AnO_2(HA)_2$	73 and 23	53 and 16	41 and 31	40
$AnO_2(HB)_2$	69 and 20	77 and 52	36 and 24	-
$AnO_2(HC)_2$	69	71 and 9	22	-

Table S.1-b: Magnitude of complex frequencies from vibrational frequency calculations for uranyl compounds calculated with the SCAN and B3LYP functionals. [Note that these optimizations are performed with NWChem 6.8 whereas other B3LYP predicted properties in this study are calculated with NWChem 6.5 and 6.6].

Functional	Compound	Magnitude
B3LYP	$UO_2(HA)(NO_3)(CH_3OH)$	10.62
	$UO_2(HB)(NO_3)(CH_3OH)$	19.56
	$UO_2(HC)(NO_3)(CH_3OH)$	-
	$UO_2(HA)_2$	79.33 and 28.26
	$UO_2(HB)_2$	73.01 and 11.44
	$UO_2(HC)_2$	68.60
SCAN	$UO_2(HA)(NO_3)(CH_3OH)$	69.16 and 52.73
	$UO_2(HB)(NO_3)(CH_3OH)$	98.65 and 58.12
	$UO_2(HC)(NO_3)(CH_3OH)$	18.94
	$UO_2(HA)_2$	18.87 and 7.04
	$UO_2(HB)_2$	67.37, 38.25, and 25.30
	$UO_2(HC)_2$	27.19

Table S.2: Contribution from zero-point energy (ZPE) correction onto the Gibbs free energy (ΔG) of the compound. [Calculated as ZPE/ΔG x 100].

Compound	U	Np	Pu	Am
$AnO_2(HA)(NO_3)(CH_3OH)$	0.01%	0.01%	0.01%	0.01%
$AnO_2(HB)(NO_3)(CH_3OH)$	0.01%	0.01%	0.01%	0.01%
$AnO_2(HC)(NO_3)(CH_3OH)$	0.01%	0.01%	0.01%	0.01%
$AnO_2(HA)_2$	0.02%	0.02%	0.02%	0.02%
$AnO_2(HB)_2$	0.02%	0.01%	0.01%	0.01%
$AnO_2(HC)_2$	0.02%	0.02%	0.02%	0.02%

Table S.3: Contribution from the entropy (S) onto the Gibbs free energy (ΔG) of the compound. [Calculated as S/ΔG x 100].

Compound	**U**	**Np**	**Pu**	**Am**
$AnO_2(HA)(NO_3)(CH_3OH)$	0.00001%	0.00001%	0.00001%	0.00001%
$AnO_2(HB)(NO_3)(CH_3OH)$	0.00001%	0.00001%	0.00001%	0.00001%
$AnO_2(HC)(NO_3)(CH_3OH)$	0.00002%	0.00001%	0.00001%	0.00001%
$AnO_2(HA)_2$	0.00001%	0.00001%	0.00001%	0.00001%
$AnO_2(HB)_2$	0.00001%	0.00001%	0.00001%	0.00001%
$AnO_2(HC)_2$	0.00001%	0.00001%	0.00001%	0.00001%

Table S.4: Partial charges calculated with NBO for AnO_2^{2+}, backbone, HX^-, NO_3^-, and CH_3OH fragments in $AnO_2(HX)(NO_3)(CH_3OH)$, and $AnO_2(HX)_2$, with An = U, Np, Pu, and Am, and HX = HA, HB, and HC.

Fragment	**An**	**$AnO_2(HA)(NO_3)(CH_3OH)$**	**$AnO_2(HB)(NO_3)(CH_3OH)$**	**$AnO_2(HC)(NO_3)(CH_3OH)$**	**$AnO_2(HA)_2$**	**$AnO_2(HB)_2$**	**$AnO_2(HC)_2$**
AnO_2^{2+}	**U**	0.75	0.78	0.74	0.72	0.78	0.71
	Np	0.70	0.73	0.70	0.69	0.74	0.66
	Pu	0.67	0.70	0.67	0.63	0.70	0.61
	Am	0.73	0.75	0.72	0.71	0.75	0.69
Backbone (O3-N1-C1-N2-C2-N3-O4)	**U**	-1.13	-1.15	-1.16	-1.09	-1.11	-1.14
	Np	-1.09	-1.13	-1.14	-1.06	-1.08	-1.11
	Pu	-1.07	-1.11	-1.12	-1.02	-1.07	-1.09
	Am	-1.11	-1.13	-1.16	-1.05	-1.08	-1.12
HX^-	**U**	-0.33	-0.38	-0.32	-0.36	-0.39	-0.35
	Np	-0.31	-0.36	-0.31	-0.34	-0.37	-0.33
	Pu	-0.28	-0.34	-0.28	-0.31	-0.35	-0.31
	Am	-0.33	-0.37	-0.33	-0.35	-0.37	-0.34
NO_3^-	**U**	-0.56	-0.55	-0.56	-	-	-
	Np	-0.53	-0.52	-0.54	-	-	-
	Pu	-0.54	-0.52	-0.53	-	-	-
	Am	-0.53	-0.52	-0.53	-	-	-
CH_3OH	**U**	0.14	0.15	0.14	-	-	-
	Np	0.14	0.15	0.14	-	-	-
	Pu	0.14	0.16	0.15	-	-	-
	Am	0.14	0.15	0.14	-	-	-

Table S.5: Bond length differences between calculated and experimental values for U-O1, U-O3, U-O4, U-N2, and N3-O4 (Å). Bond lengths for $UO_2(HA)(NO_3)(CH_3OH)$ are reported by Bernstein, et. al.[1] Bond lengths for $UO_2(HC)_2$ are reported by Tian, et. al.[2]]

	Compound	**Experimental**	**Calculated**	**Difference**
U-O1	$UO_2(HA)(NO_3)(CH_3OH)$	1.781	1.775	-0.006
	$UO_2(HC)_2$	1.785	1.781	-0.004
U-O3	$UO_2(HA)(NO_3)(CH_3OH)$	2.398	2.435	0.037
	$UO_2(HC)_2$	2.535	2.510	-0.025
U-O4	$UO_2(HA)(NO_3)(CH_3OH)$	2.420	2.504	0.084
	$UO_2(HC)_2$	2.430	2.510	0.080
U-N2	$UO_2(HA)(NO_3)(CH_3OH)$	2.514	2.616	0.102
	$UO_2(HC)_2$	2.563	2.657	0.094
N3-O4	$UO_2(HA)(NO_3)(CH_3OH)$	1.371	1.332	-0.039
	$UO_2(HC)_2$	1.362	1.326	-0.036

Table S.6: Interatomic distance in backbone in H_2X, $AnO_2(HX)(NO_3)(CH_3OH)$, and $AnO_2(HX)_2$, with An = U, Np, Pu, and Am, and X = A, B, C.

Values	**An**	**$AnO_2(HA)(NO_3)(CH_3OH)$**	**$AnO_2(HB)(NO_3)(CH_3OH)$**	**$AnO_2(HC)(NO_3)(CH_3OH)$**	**$AnO_2(HA)_2$**	**$AnO_2(HB)_2$**	**$AnO_2(HC)_2$**	**H_2A**	**H_2B**	**H_2C**
O3-N1	U	1.320	1.322	1.326	1.319	1.323	1.326	1.415	1.415	1.424
	Np	1.318	1.319	1.324	1.319	1.325	1.326			
	Pu	1.320	1.319	1.325	1.319	1.322	1.326			
	Am	1.317	1.319	1.324	1.318	1.322	1.324			
N1-C1	U	1.318	1.310	1.309	1.319	1.312	1.311	1.291	1.282	1.284
	Np	1.318	1.310	1.309	1.320	1.312	1.311			
	Pu	1.319	1.311	1.310	1.321	1.312	1.312			
	Am	1.318	1.310	1.309	1.320	1.312	1.312			
C1-N2	U	1.348	1.351	1.347	1.343	1.347	1.341	1.380	1.388	1.383
	Np	1.349	1.352	1.348	1.343	1.347	1.340			
	Pu	1.347	1.352	1.347	1.341	1.349	1.340			
	Am	1.349	1.352	1.349	1.343	1.348	1.341			
N2-C2	U	1.340	1.344	1.338	1.343	1.347	1.341	1.380	1.388	1.383
	Np	1.339	1.344	1.337	1.343	1.348	1.340			
	Pu	1.340	1.344	1.337	1.341	1.349	1.340			
	Am	1.340	1.344	1.338	1.343	1.348	1.341			
C2-N3	U	1.320	1.312	1.313	1.319	1.312	1.311	1.291	1.282	1.284
	Np	1.320	1.312	1.313	1.320	1.312	1.311			
	Pu	1.321	1.313	1.313	1.321	1.312	1.312			
	Am	1.320	1.313	1.313	1.320	1.312	1.312			
N3-O4	U	1.332	1.334	1.336	1.319	1.323	1.326	1.415	1.415	1.424
	Np	1.334	1.335	1.337	1.319	1.321	1.326			
	Pu	1.331	1.334	1.337	1.319	1.322	1.326			
	Am	1.332	1.334	1.335	1.318	1.322	1.324			

Table S.7: Calculated $\Delta(\Delta G)_{rxn}$ according to Eq. 1, and 2 for $AnO_2(HX)(NO_3)(CH_3OH)$, and $AnO_2(HX)_2$, with An = U, Np, Pu, Am, and HX = HA, HB, and HC. Results are normalized to $AmO_2(HB)(NO_3)(CH_3OH)$, and shown in kcal mol^{-1}.

Compound	**$\Delta(\Delta G)_{rxn}$ normalized to $AmO_2(HB)(NO_3)(CH_3OH)$**
$UO_2(HA)(NO_3)(CH_3OH)$	-19.591
$NpO_2(HA)(NO_3)(CH_3OH)$	-19.376
$PuO_2(HA)(NO_3)(CH_3OH)$	-26.248
$AmO_2(HA)(NO_3)(CH_3OH)$	-10.290
$UO_2(HB)(NO_3)(CH_3OH)$	-8.728
$NpO_2(HB)(NO_3)(CH_3OH)$	-8.495
$PuO_2(HB)(NO_3)(CH_3OH)$	-16.797
$AmO_2(HB)(NO_3)(CH_3OH)$	-
$UO_2(HC)(NO_3)(CH_3OH)$	-28.840
$NpO_2(HC)(NO_3)(CH_3OH)$	-27.415
$PuO_2(HC)(NO_3)(CH_3OH)$	-34.568
$AmO_2(HC)(NO_3)(CH_3OH)$	-18.753
$UO_2(HA)_2$	-42.638
$NpO_2(HA)_2$	-40.559
$PuO_2(HA)_2$	-48.479
$AmO_2(HA)_2$	-31.132
$UO_2(HB)_2$	-22.666
$NpO_2(HB)_2$	-21.428
$PuO_2(HB)_2$	-28.351
$AmO_2(HB)_2$	-13.904
$UO_2(HC)_2$	-59.013
$NpO_2(HC)_2$	-56.609
$PuO_2(HC)_2$	-63.616
$AmO_2(HC)_2$	-46.196

Differences in predicted characteristics in structures optimized with the SCAN and B3LYP functionals

The $UO_2(HX)(NO_3)(CH_3OH)$ and $UO_2(HX)_2$ (with HX = HA, HB, and HC) structures optimized with the SCAN and B3LYP functionals show predicted U-O distances to be slightly longer with SCAN with differences of less than 0.0122 Å in the uranyl fragment (O1 and O2), and less than 0.0488 Å with equatorial oxygen atoms (O3 and O4). The U-N2 distance is predicted to be between 0.0363 and 0.0421 Å shorter in the structures optimized with SCAN than with B3LYP. The O3-U-O4 angle is predicted to be between 0.70 and 1.10° wider in structures optimized with SCAN than with those optimized with B3LYP. Differences in U-O1, U-O2, U-O3, U-O4, U-N2, U-OI, U-OII, U-OIII distances, and O3-U-O4 angles for structures optimized with SCAN and B3LYP are included in Table 7. The magnitudes of complex vibrational frequency modes in the SCAN/B3LYP comparison are reported in Table S.1 in the SI.

The difference between partial charges from the uranyl fragment and the backbone is predicted to be approximately 0.2 larger in structures optimized with the B3LYP functional than in those optimized with the SCAN functional, as shown in Table 8.

The associated Gibbs free energies of reaction to the structures optimized with the SCAN and B3LYP functional relative to $UO_2(HB)(NO_3)(CH_3OH)$ show a $|\Delta(\Delta G)_{rxn}|$ between 2 and 28 kcal mol^{-1} between relative Gibbs free energies of reaction calculated with the SCAN and B3LYP functionals, as shown in Table 9. However, the relative Gibbs free energies of reaction predict $UO_2(HB)(NO_3)(CH_3OH)$ to be slightly more stable than $UO_2(HA)(NO_3)(CH_3OH)$ when calculated with the SCAN functional (3.46 kcal mol^{-1} lower), but not with B3LYP (10.65 kcal mol^{-1} higher). $UO_2(HC)(OH_2)_2$ is predicted to be more stable than $UO_2(HB)(NO_3)(CH_3OH)$ when calculated with both B3LYP and SCAN with a lower ΔG_{rxn} of 20.59 and 18.29 kcal mol^{-1}, respectively. $UO_2(HA)_2$, $UO_2(HB)_2$, and $UO_2(HC)_2$ is predicted to be more stable than $UO_2(HB)(NO_3)(CH_3OH)$ [$UO_2(HA)_2$ by 33.09 kcal mol^{-1} when calculated with B3LYP and 5.32 kcal mol^{-1} with SCAN; $UO_2(HB)_2$ by 13.52 kcal mol^{-1} with B3LYP and 1.62 kcal mol^{-1} with SCAN; and $UO_2(HC)_2$ by 50.90 kcal mol^{-1} with B3LYP and 37.44 kcal mol^{-1} with SCAN].

In conclusion, stability trends predicted with structures optimized with B3LYP and SCAN show variations in relative energies [with respect to $UO_2(HB)(NO_3)(CH_3OH)$] between -11 kcal mol^{-1} and -51 kcal mol^{-1} with B3LYP, and between 3 and 37 kcal mol^{-1} with SCAN. This difference in predicted Gibbs free energies of reaction when altering the functional of choice is consistent with predictions in an actinide nitrate study which tested the dependence of predicted thermochemical properties on the level of theory of choice.[36]

Table S.8: Difference in predicted U-X (with X = O1, O2, O3, O4, N2, OI, OII, and OIII) distances, and O3-U-O4 angle in $UO_2(HX)(NO_3)(CH_3OH)$ and $UO_2(HX)_2$ (with HX = HA, HB, and HC) optimized with the SCAN and B3LYP functionals (reported in Å and degrees (°), for interatomic distances and angles, respectively).

	U-O1	U-O2	U-O3	U-O4	U-N2	U-OI	U-OII	U-OIII	O3-U-O4
$UO_2(HA)(NO_3)(CH_3OH)$	-0.0113	-0.0102	0.0288	0.0326	0.0396	0.0438	0.0399	0.0501	-0.9
$UO_2(HB)(NO_3)(CH_3OH)$	-0.0114	-0.0103	0.0343	0.0488	0.0371	0.0441	0.0371	0.0483	-1.1
$UO_2(HC)(NO_3)(CH_3OH)$	-0.0122	-0.0112	0.0315	0.0334	0.0391	0.0430	0.0384	0.0485	-0.9
$UO_2(HA)_2$	-0.0107	-0.0107	0.0335	0.0335	0.0421	-	-	-	-0.7
$UO_2(HB)_2$	-0.0103	-0.0103	0.0452	0.0448	0.0363	-	-	-	-1.0
$UO_2(HC)_2$	-0.0108	-0.0108	0.0351	0.0351	0.0403	-	-	-	-0.7

Table S.9: Difference in calculated partial charge between the uranyl fragment and backbone in $UO_2(HX)(NO_3)(CH_3OH)$ and $UO_2(HX)_2$ (with HX = HA, HB, and HC) structures optimized with the SCAN and B3LYP functionals.

Compound	B3LYP	SCAN
$UO_2(HA)(NO_3)(CH_3OH)$	1.12	0.87
$UO_2(HB)(NO_3)(CH_3OH)$	1.16	0.91
$UO_2(HC)(NO_3)(CH_3OH)$	1.15	0.91
$UO_2(HA)_2$	1.06	0.83
$UO_2(HB)_2$	1.14	0.90
$UO_2(HC)_2$	1.11	0.89

Table S.10: Calculated $\Delta(\Delta G)_{rxn}$ with the B3LYP and SCAN functionals (according to Eq. 1, and 2) for $UO_2(HX)(NO_3)(CH_3OH)$, and $UO_2(HX)_2$ (with HX = HA, HB, and HC) with respect to $UO_2(HB)(NO_3)(CH_3OH)$ (as shown in Eq. 3.a and 3.b), and shown in kcal mol^{-1}.

Compound	B3LYP	SCAN
$UO_2(HA)(NO_3)(CH_3OH)$	-10.65	3.46
$UO_2(HC)(NO_3)(CH_3OH)$	-20.59	-18.29
$UO_2(HA)_2$	-33.09	-5.32
$UO_2(HB)_2$	-13.52	-1.62
$UO_2(HC)_2$	-50.90	-37.44

Stability trends predicted with structures optimized with B3LYP and SCAN show variations in relative energies [with respect to $UO_2(HB)(NO_3)(CH_3OH)$] between -11 kcal mol^{-1} and -51 kcal mol^{-1} with B3LYP, and between 3 and 37 kcal mol^{-1} with SCAN.

References

(1) Bernstein, K. J.; Do-Thanh, C.-L.; Penchoff, D. A.; Alan Cramer, S.; Murdock, C. R.; Lu, Z.; Harrison, R. J.; Camden, J. P.; Jenkins, D. M. The Synthesis and Spectroscopic Characterization of an Aromatic Uranium Amidoxime Complex. *Inorganica Chim. Acta* **2014**, *421*, 374–379.

(2) Tian, G.; Teat, S. J.; Zhang, Z.; Rao, L. Sequestering Uranium from Seawater: Binding Strength and Modes of Uranyl Complexes with Glutarimidedioxime. *Dalton Trans.* **2012**, *41* (38), 11579–11586.