Electronic Supplementary Material (ESI) for Dalton Transactions

The mechanism of the reduction of $[AnO_2]^{2+}$ (An=U, Np, Pu) in aqueous solution and by Fe(II) containing proteins and mineral surfaces, probed by DFT calculations.

Mahesh Sundararajan[1, a], Rajeev S Assary[1, b], Ian H Hillier* [1] and David J Vaughan[2]

[1] School of Chemistry, University of Manchester, Manchester,M13 9PL, UK,

[2] School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester M13 9PL, UK

[a]Theoretical Chemistry Section, Chemistry Group, Bhabha Atomic Research Centre, Mumbai – 400 085, INDIA

[b] Materials Science Division Argonne National Laboratory, Argonne, IL, USA

Supplementary Information

Table S1. Bond lengths (Å) and spin densities of species (**II**) in *D. acetoxidans*, hydroxide and aqua complexes of U, Np and Pu di-nuclear models.

	U			Np			Pu		
	Dac	Hydroxide	Aqua	Dac	Hydroxide	Aqua	Dac	Hydroxide	Aqua
Bond Lengths, Å									
A	1.79	1.78	1.81	1.78	1.79	1.77	1.76	1.77	1.76
B	1.84	1.82	1.86	1.82	1.83	1.80	1.80	1.81	1.76
C	2.42	2.44	2.41	2.44	2.46	2.52	2.50	2.46	2.65
D	4.00	4.16	4.08	4.01	4.07	4.22	4.02	4.06	4.47
E	1.89	1.90	1.90	1.87	1.87	1.86	1.84	1.85	1.82
F	1.81	1.78	1.81	1.80	1.80	1.77	1.79	1.79	1.76
Spin densities, e^-									
M^{VI}	0.16	0.46	0.15	1.42	1.27	1.66	2.66	2.48	2.61
M^{V}	0.96	0.67	0.90	1.99	2.16	1.73	3.07	3.29	3.07

Table S2. Bond lengths (Å) and spin densities of species (**III**) in *D. acetoxidans*, hydroxide and aqua complexes of U, Np and Pu di-nuclear models.

	U			Np			Pu		
	Dac	Hydroxide	Aqua	Dac	Hydroxide	Aqua	Dac	Hydroxide	Aqua
Bond Lengths, Å									
A	1.82	1.82	1.85	1.81	1.81	1.80	1.80	1.81	1.79
B	1.89	1.87	2.05	1.87	1.90	1.85	1.85	1.88	1.82
C	2.40	2.40	2.36	2.49	2.42	2.44	2.50	2.51	2.46
D	3.97	4.11	4.08	4.03	3.96	4.15	3.99	4.06	4.12
E	1.93	1.93	1.94	1.86	1.87	1.88	1.84	1.85	1.86
F	1.85	1.81	1.84	1.82	1.83	1.80	1.80	1.81	1.79
Spin densities, e^-									
M^V	0.81	1.07	1.12	2.21	2.21	2.19	3.35	3.36	3.33
M^V	1.40	1.14	1.13	2.33	2.24	2.24	3.39	3.41	3.39

Table S3. Bond lengths (Å) and spin densities of species (**IV**) in *D. acetoxidans*, hydroxide and aqua complexes of U, Np and Pu di-nuclear models.

	U			Np			Pu		
	Dac	Hydroxide	Aqua	Dac	Hydroxide	Aqua	Dac	Hydroxide	Aqua
Bond Lengths, Å									
A	1.80	1.79	1.81	1.78	1.80	1.78	1.77	1.78	1.76
B	1.85	1.83	1.87	1.83	1.85	1.81	1.81	1.82	1.80
C	2.34	2.37	2.35	2.42	2.39	2.52	2.40	2.37	2.48
D	3.99	4.17	4.08	4.02	4.08	4.24	3.98	3.96	4.21
E	1.94	1.95	1.96	1.89	1.92	1.88	1.88	1.89	1.88
F	2.07	2.02	2.08	2.06	2.08	1.99	2.06	2.06	2.00
Spin densities, e^-									
M^{VI}	0.25	0.62	0.43	2.05	1.67	1.93	2.88	2.98	3.04
M^{IV}	1.94	1.59	1.78	2.42	2.82	2.54	3.88	3.82	3.72

Table S4. Bond lengths (Å) and spin densities of species (**V**) in *D. acetoxidans*, hydroxide and aqua complexes of U, Np and Pu di-nuclear models.

	U			Np			Pu		
	Dac	Hydroxide	Aqua	Dac	Hydroxide	Aqua[b]	Dac	Hydroxide	Aqua
Bond Lengths, Å									
A	1.79	1.77	1.80	1.77	1.79	1.76	1.77	1.77	1.74
B	1.84	1.80	1.84	1.87[a]	1.82	1.76	1.79	1.80	1.76
C	2.54	2.54	2.58	2.40	2.57	27.30	2.42	2.58	2.66
D	4.13	4.59	4.43	3.72	4.44	29.15	4.34	4.41	4.74
E	2.19	2.28	2.22	2.22	2.21	2.01	2.24	2.18	2.24
F	2.04	1.99	2.05	2.05	2.04	2.01	2.05	2.06	2.00
Spin densities, e^-									
M^{VI}	0.01	0.27	0.14	1.30	1.29	2.14	2.46	2.43	2.47
M^{IV}	2.21	1.91	2.02	3.08	3.13	2.29	4.24	4.28	4.19

[a] Forms double bridged structure
[b] Spontaneously cleaves