Supplementary Information

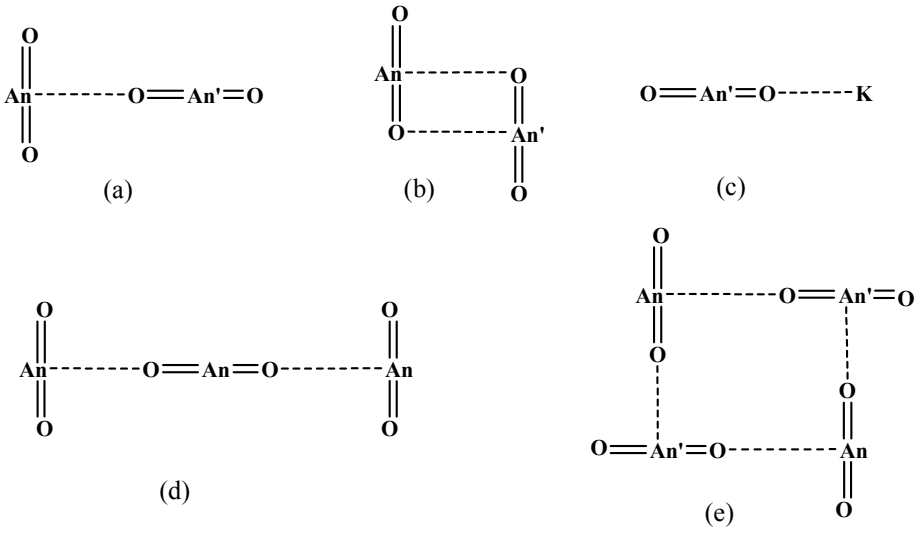

Chart S1. Diagrams of the cation-cation interaction (CCI) between actinyl ions.

The following is a representative selection of some representative papers from the literature, covering experimental CCI complexes (1 to 5) and one theoretical study (6).

1. NpO_2^+·····UO_2^{2+}: *the discovery of CCI*: J. C. Sullivan, A. J. Zielen, J. C. Hindman, *J. Am. Chem. Soc.* **1961**, *83*, 3373-3378.

2. UO_2^+·····UO_2^+: *T-shaped Model (a)*: T. A. Sullens, R. A. Jensen, T. Y. Shvareva, T. E. Albrecht-Schmitt, *J. Am. Chem. Soc.* **2004**, *126*, 2676-2677.

3. NpO_2^+·····NpO_2^+: *Parallel Model (b)*: M. S. Grigoriev, N. N. Krot, A. A. Bessonov, K. Y. Suponitsky, *Acta Crystallogr. Sect. E.-Struct Rep. Online* **2007**, *63*, M561-M562.

4. UO_2^+·····K: *Model (c)*: L. Natrajan, F. Burdet, J. Pecaut, M. Mazzanti, *J. Am. Chem. Soc.* **2006**, *128*, 7152-7153.

5. {UO_2^+···UO_2^+···UO_2^+···UO_2^+}: *Model (e)*: G. Nocton, P. Horeglad, J. Pecaut, M. Mazzanti, *J. Am. Chem. Soc.* **2008**, *130*, 16633-16645.

6. NpO_2^+·····UO_2^{2+}: *theoretical study*: M. L. McKee, M. Swart, *Inorg. Chem.* **2005**, *44*, 6975-6982.

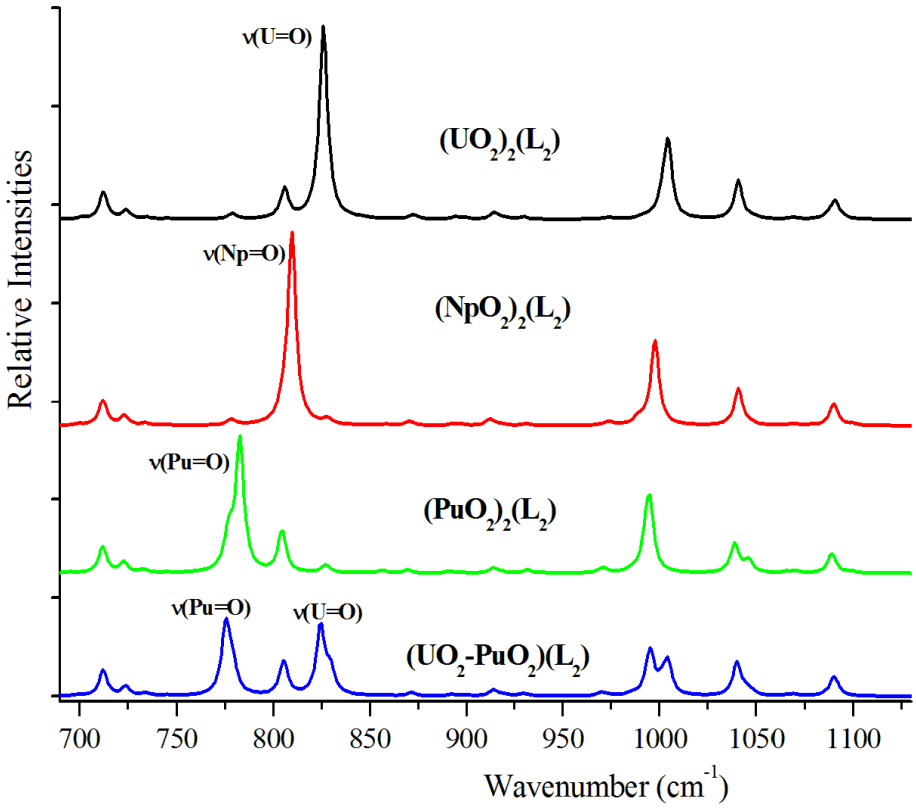

Fig. S1 Simulated vibrational spectra of homobinuclear $[(AnO_2)_2(L^2)]$ (An = U, Np and Pu) and heterobinuclear $[(UO_2)(PuO_2)(L^2)]$ complexes.

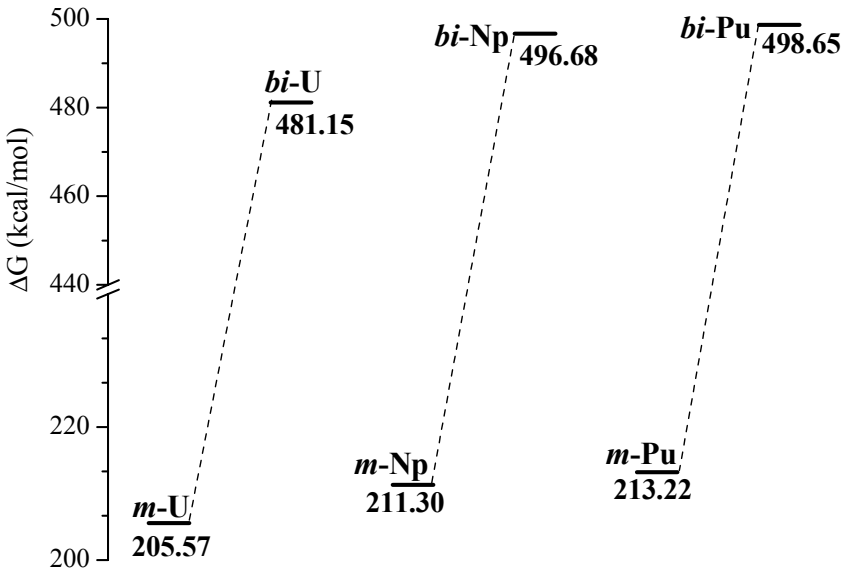

Fig. S2 Free energies of formation reactions for mononuclear $[(AnO_2)(H_2L^2)]^-$ and binuclear $[(AnO_2)_2(L^2)]^{2-}$ (An = U, Np and Pu) complexes in the gas phase.

Table S1. Optimized geometry parameters and bond orders (in parentheses) for binuclear $[(AnO_2)_2(L^2)]^{2n-4}$ (An = U, Np, Pu; n = 2, 1) in the gas phase. (Distance in Å and angles in degree)

	n = 2 (An^{VI})			n = 1 (An^{V})		
	U	Np	Pu	U	Np	Pu
An-O_{exo}	1.802	1.797	1.783	1.827	1.821	1.816
	(2.39)	(2.36)	(2.35)	(2.38)	(2.36)	(2.34)
An-O_{endo}	1.798	1.792	1.778	1.817	1.811	1.800
	(2.38)	(2.35)	(2.34)	(2.37)	(2.35)	(2.34)
$O_{endo}\cdots O_{endo}$	2.940	2.906	2.935	3.116	3.035	3.011
An$\cdots O_{endo}$	3.931	3.943	3.973	4.043	4.001	4.060
O=An=O	175.6	176.5	178.3	176.1	176.3	177.3

Table S2. Optimized geometry parameters and bond orders (in parentheses) for mononuclear $[(AnO_2)(H_2L^2)]^{n-2}$ (An = U, Np, Pu; n = 2, 1) in the gas phase.

	n = 2 (An^{VI})			n = 1 (An^{V})			Expt. [a.]
	U	Np	Pu	U	Np	Pu	U^{VI}
Bond length (Å)							
An-O_{exo}	1.801 (2.40)	1.787 (2.38)	1.785 (2.35)	1.830 (2.39)	1.817 (2.38)	1.809 (2.36)	1.766
An-O_{endo}	1.817 (2.30)	1.802 (2.29)	1.801 (2.26)	1.853 (2.24)	1.851 (2.20)	1.837 (2.19)	1.790
$O_{endo}\cdots H$	2.034 (0.05)	2.041 (0.05)	2.093	1.946 (0.08)	1.862 (0.10)	1.882 (0.10)	
Bond angle (°)							
O=An=O	176.3	178.9	179.6	173.6	176.5	177.8	177.6

[a.] Experimental values for $[(THF)(UO_2)(H_2L^1)]$ from ref. 14.

Table S3. Formation reactions of mononuclear $[(AnO_2)(H_2L^2)]^{n-2}$ and binuclear $[(AnO_2)_2(L^2)]^{2n-4}$ (An = U, Np, Pu; n = 2, 1) on the basis of the polypyrrolic ligand H_4L^2 and uranyl complexes.

$H_4L^2 + [AnO_2(H_2O)_5]^{n+} \rightleftharpoons [(AnO_2)(H_2L^2)]^{n-2} + 2H_3O^+ + 3H_2O$
$H_4L^2 + 2[AnO_2(H_2O)_5]^{n+} \rightleftharpoons [(AnO_2)_2(L^2)]^{2n-4} + 4H_3O^+ + 6H_2O$

Table S4. Optimized geometry parameters and bond orders (in parentheses) for homobinuclear $[(AnO_2)_2(L^2)]$ (An = U and Pu) and heterobinuclear $[(UO_2)(PuO_2)(L^2)]$ in the gas phase. (Distance in Å, angles in degree, and energy in kcal/mol)

	$[(UO_2)_2(L^2)]$	$[(PuO_2)_2(L^2)]$	$(UO_2)(PuO_2)(L^2)$
$U\text{-}O_{exo}$	1.802 (2.39)		1.802 (2.39)
$U\text{-}O_{endo}$	1.798 (2.38)		1.797 (2.38)
$Pu\text{-}O_{exo}$		1.783 (2.35)	1.783 (2.35)
$Pu\text{-}O_{endo}$		1.778 (2.34)	1.779 (2.33)
$O_{endo}\cdots O_{endo}$	2.940	2.935	2.936
$U\cdots O_{endo}$	3.931		3.944
$Pu\cdots O_{endo}$		3.973	3.950
O=U=O	175.6		175.7
O=Pu=O		178.3	178.1
ΔG_r	79.14	70.70	75.16

Table S5. Optimized geometry parameters and bond orders (in parentheses) for heterobinuclear $[(S)(AnO_2)(Mn)(S')(L^2)]$ (S = vacant, S' = THF, An = U; S = S' = THF, An = U; S = S' = Py, An = U, Np, Pu) in the gas phase.

	$[(UO_2)(Mn)(THF)(L^2)]$	$[(THF)(UO_2)(Mn)(THF)(L^2)]$	$[(Py)(UO_2)(Mn)(Py)(L^2)]$	$[(Py)(NpO_2)(Mn)(Py)(L^2)]$	$[(Py)(PuO_2)(Mn)(Py)(L^2)]$	$[(THF)(UO_2)(Mn)(THF)(L^1)]^a$
Bond length (Å)						
$An\text{-}O_{exo}$	1.807 (2.41)	1.805 (2.40)	1.807 (2.39)	1.797 (2.38)	1.792 (2.36)	1.768
$An\text{-}O_{endo}$	1.817 (2.34)	1.813 (2.34)	1.814 (2.35)	1.811 (2.31)	1.810 (2.26)	1.808
An-X		2.550 (0.37)	2.631 (0.36)	2.658 (0.33)	2.689 (0.30)	2.458
Mn-Y	2.234 (0.31)	2.237 (0.31)	2.227 (0.36)	2.244 (0.36)	2.254 (0.36)	2.217
$Mn\cdots O_{endo}$	3.616	3.709	3.714	3.587	3.499	3.804
Bond angle (°)						
$O_{exo}\text{-}An\text{-}O_{endo}$	172.9	175.2	173.6	176.7	177.8	177.4
$An\text{-}O_{endo}\text{-}Mn$	167.1	176.7	179.6	178.4	178.5	

[a.] Experimental values of $[(THF)(UO_2)(Mn)(THF)(L^1)]$ from ref. 15.