Supporting Information

Periodic Trends in Actinyl Thio-Crown Ether Complexes

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Table S1. Relative energy (ΔE, kcal/mol) of side-on and insertion isomers, and binding energy (BE) for the formation of $AnO_2(12TC4)^{2+}$ and $AnO_2(12TC4)_2^{2+}$ from isolated AnO_2^{2+} and 12TC4 fragments at PBE/TZP/DZP level.

	$AnO_2(12TC4)^{2+}$						$AnO_2(12TC4)_2^{2+}$					
	side-on		insertion		side-on		double-decker		insertion		double-decker	
An	ΔE		ΔE		BE		ΔE		ΔE		BE	
	SR	SO	SR	SO	SR	SO	SR	SO	SR	SO	SR	SO
U	0.0	0.0	17.3	27.4	-198.7	-200.7	0.0	0.0	31.3	34.1	-270.0	-272.1
Np	0.0	0.0	18.4	34.1	-198.6	-198.5	0.0	0.0	34.7	27.5	-267.4	-267.7
Pu	0.0	0.0	21.2	27.5	-195.2	-193.5	0.0	0.0	30.9	29.3	-263.9	-262.7
Am	0.0	0.0	10.6	29.3	-193.8	-192.0	0.0	0.0	28.9	31.0	-266.1	-264.6
Cm	0.0	0.0	7.2	31.0	-182.3	-187.9	0.0	0.0	29.0	27.4	-256.0	-260.0

* ΔE = E[side-on] – E[insertion] for $AnO_2(12TC4)^{2+}$ and ΔE = E[double-decker] – E[insertion] for $AnO_2(12TC4)_2^{2+}$; BE(binding energy) = $E[AnO_2(12TC4)^{2+}] – E[AnO_2^{2+}] – E[12TC4]$.

Table S2. Selected average bond lengths (Å) and O≡An≡O bond angles (°) of the ground state D_2 $AnO_2(12TC4)_2^{2+}$ in vacuum and in water as evaluated by COSMO solvation model (in parentheses) at PBE/TZP/DZP level.[a]

An	Spin State 2S+1	Point group	Elec. Conf.	Bond length		Bond angle
				An≡O	4*An-S[b]	O≡An≡O
U	1	C_2	f^0	1.796 (1.799)	3.075 (3.067)	144.0 (147.8)
Np	2	C_2	f_ϕ^1	1.793 (1.795)	3.024 (2.993)	151.6 (150.3)
Pu	3	C_2	$f_\phi^1 f_\delta^1$	1.777 (1.779)	3.002 (2.991)	163.1 (161.6)
Am	4	C_2	$f_\phi^1 f_\delta^2$	1.780 (1.777)	2.989 (2.958)	180.0 (179.0)
Cm	5	C_2	$f_\phi^2 f_\delta^2$	1.812 (1.806)	3.022 (3.004)	180.0 (179.7)

a. The actinide 5f orbitals are nonliterally labeled using the axial symmetry in actinyls. b. An-S bond distances larger than 3.7 Å are not listed.

Table S3. Geometrical parameters and binding energies of the ground state C_2 $AnO_2(12TC4)^{2+}$ at PBE/TZP/DZP level.

An	Spin State 2S+1	Point group	Bond length (Å)		Bond angle (degree)	BE (kcal/mol)		O≡An≡O Stretch (cm^{-1})	
			An≡O	An-S	O≡An≡O	SR	SO	Asym.	Sym.
U	1	C_2	1.796	2.931,3.069	139.4	-198.7	-200.7	910(142)	861(101)
Np	2	C_2	1.787	2.932,3.085	145.1	-198.6	-198.5	907(130)	841(80)
Pu	3	C_2	1.775	2.926,3.279	159.9	-195.2	-193.5	915(119)	808(68)
Am	4	C_2	1.766	2.934,3.994	177.8	-193.8	-192.0	918(38)	775(62)
Cm	5	C_2	1.794	2.894,3.860	178.2	-182.3	-187.9	831(39)	740(19)

Table S4. Energy comparison (kcal/mol) between two isomers, "insertion" and "side-on" $AnO_2(15TC5)^{2+}$ at PBE/TZP/DZP level

		Insertion			Side-on		
An	Spin State 2S+1	Point group	ΔE		Point group	ΔE	
			SR	SO		SR	SO
U	1	C_1	0.00	0.00	C_1	35.8	36.2
Np	2	C_1	0.00	0.00	C_1	41.7	41.6
Pu	3	C_1	0.00	0.00	C_1	38.1	37.5

Table S5. Selected average bond lengths (Å), O≡An≡O bond angles (°) and calculated vibrational frequencies (cm^{-1}) and infrared intensities (Int., km/mol) of the ground state *insertion* AnO_2^{2+}(15TC5) in vacuum and in water as evaluated by COSMO solvation model (in parentheses) and binding energy (BE, kcal/mol) for AnO_2^{2+} + 15TC5 = $AnO_2(15TC5)^{2+}$ at PBE/TZP/DZP level.

An	Spin State 2S+1	Point group	Bond length		Bond angle	BE		O≡An≡O Stretch			
			An≡O	An-S	O≡An≡O	SR	SO	ν_3	Int.	ν_1	Int.
U	1	C_1	1.778, 1.799 (1.786,1.792)	2.931 (2.931)	180.0 (180.0)	-245.0	-251.1	970	142	858	4
Np	2	C_1	1.762, 1.782 (1.771,1.776)	2.921 (2.921)	180.0 (179.9)	-240.6	-245.6	966	131	847	3
Pu	3	C_1	1.761, 1.774 (1.766,1.768)	2.915 (2.919)	180.0 (179.8)	-245.2	-249.0	957	124	829	1
Am	4	C_1	1.756, 1.774 (1.763,1.767)	2.906 (2.913)	180.0 (178.6)	-242.5	-245.7	936	101	796	1
Cm	5	C_1	1.770, 1.779 (1.772,1.775)	2.902 (2.904)	180.0 (180.0)	-231.8	-239.8	898	60	749	1

Table S6. Selected average bond lengths (Å) and O≡An≡O bond angles (°) and calculated vibrational frequencies (cm^{-1}) and intensities (Int., km/mol) of the ground state *insertion* $AnO_2(18TC6)^{2+}$ in vacuum and in water as evaluated by COSMO solvation model (in parentheses) and binding energy (BE, kcal/mol) for AnO_2^{2+} + 18TC6 = $AnO_2(18TC6)^{2+}$ at PBE/TZP/DZP level.

An	Spin State	Point group	Bond length		Bond angle	BE		O≡An≡O stretch			
			An≡O	An-S	O≡An≡O	SR	SO	ν_3	Int.	ν_1	Int.
U	1	C_1	1.781,1.798 (1.791,1.796)	3.090 (3.070)	180.0 (179.8)	-265.3	-271.6	963	150	861	2
Np	2	C_1	1.765,1.782 (1.774,1.780)	3.088 (3.070)	179.8 (179.6)	-260.8	-265.0	962	139	851	2
Pu	3	C_1	1.761,1.775 (1.766,1.772)	3.080 (3.069)	179.3 (179.7)	-262.4	-266.0	952	118	817	2
Am	4	C_1	1.760,1.775 (1.767,1.773)	3.098 (3.080)	179.8 (179.8)	-266.2	-267.2	929	102	794	2
Cm	5	C_1	1.778,1.798 (1.788,1.797)	3.142 (3.131)	179.8 (179.9)	-243.9	-251.7	872	73	720	0

Table S7. Bond Lengths (Å), Mayer Bond Orders, and Mulliken Charges and Spins of C_2 $AnO_2(12TC4)^{2+}$ (An = U, Np, Pu, Am and Cm) at the SR−PBE/TZ2P level.

	Bond Length		Bond Order		Mulliken Charge			Mulliken Spin		
	O-An	S-An	O-An	S-An	An	O	S	An	O	S
U	1.796	3.069	2.130	0.500	1.58	-0.45	0.26			
		2.931		0.564			0.27			
Np	1.787	3.085	2.102	0.557	1.53	-0.43	0.27	1.38	-0.10	-0.04
		2.932		0.492			0.27			-0.05
Pu	1.775	3.279	2.039	0.404	1.59	-0.45	0.27	2.84	-0.17	-0.13
		2.926		0.541			0.26			-0.12
Am	1.766	3.994	1.992	0.144	1.65	-0.45	0.32	4.39	-0.26	-0.29
		2.934		0.361			0.19			-0.11
Cm	1.794	3.860	1.749	0.210	1.64	-0.48	0.37	5.30	-0.23	-0.38
		2.894		0.400			0.17			-0.01

Table S8. Bond Lengths (Å), Mayer Bond Orders, and Mulliken Charge and NPA charge of $AnO_2(12TC4)_2^{2+}$ (An = U, Np, Pu, Am and Cm) at the SR−PBE/TZ2P level.

Species	Bond Length		Mayer Bond Order		Mulliken Charge		NPA	
	O-An	S-An	O-An	S-An	An	O	An	O
U	1.806	3.074	2.059	0.375	1.59	-0.52	1.16	-0.58
Np	1.799	3.085	2.007	0.348	1.59	-0.51	1.53	-0.31
Pu	1.777	3.055	1.931	0.309	1.79	-0.53	2.35	-0.39
Am	1.780	3.086	1.793	0.249	1.55	-0.43	3.08	-0.45
Cm	1.812	3.0222	1.671	0.236	1.78	-0.53	3.09	-0.45

Table S9. Average Bond Lengths (Å), Mayer Bond Orders, and Mulliken Charges of $AnO_2(15TC5)^{2+}$ (An = U, Np, Pu, Am and Cm) at the SR−PBE/TZ2P level.

	Bond Length, Å		Mayer Bond Order		Mulliken Charge		
	O-An	S-An	O-An	S-An	An	O	S
U	1.788	2.930	2.016	0.444	1.67	-0.55	0.23
Np	1.772	2.921	2.004	0.441	1.63	-0.53	0.23
Pu	1.767	2.915	1.985	0.439	1.62	-0.51	0.22
Am	1.765	2.906	1.979	0.417	1.56	-0.49	0.23
Cm	1.775	2.902	1.814	0.406	1.49	-0.47	0.23

Table S10. Average Bond Lengths (Å), Mayer Bond Orders, and Mulliken Charges of $AnO_2(18TC6)^{2+}$ (An = U, Np, Pu, Am and Cm) at the SR−PBE/TZ2P level.

	Bond Length, Å		Mayer Bond Order		Mulliken Charge		
	O-An	S-An	O-An	S-An	An	O	S
U	1.790	3.090	2.020	0.375	1.58	-0.55	0.20
Np	1.773	3.088	2.008	0.360	1.56	-0.53	0.20
Pu	1.768	3.080	1.992	0.348	1.58	-0.51	0.19
Am	1.768	3.098	1.958	0.313	1.52	-0.49	0.20
Cm	1.788	3.142	1.804	0.289	1.48	-0.50	0.20

Table S11. Average Mulliken Charges of AnO_2^{2+}, $AnO_2(12TC4)_2^{2+}$, $AnO_2(15TC5)^{2+}$ and $AnO_2(18TC6)^{2+}$ (An = U, Np, Pu, Am and Cm) at the SR−PBE/TZ2P level.

Species	AnO_2^{2+}		$AnO_2(12TC4)_2^{2+}$		$AnO_2(15TC5)^{2+}$		$AnO_2(18TC6)^{2+}$	
	An	O	An	O	An	O	An	O
U	2.76	-0.38	1.59	-0.52	1.67	-0.55	1.58	-0.55
Np	2.66	-0.33	1.59	-0.51	1.63	-0.53	1.56	-0.53
Pu	2.57	-0.29	1.79	-0.53	1.62	-0.51	1.58	-0.51
Am	2.62	-0.31	1.55	-0.43	1.56	-0.49	1.52	-0.49
Cm	2.41	-0.21	1.78	-0.53	1.49	-0.47	1.48	-0.50

Table S12. Average Hirshfeld Charges of AnO_2^{2+}, $AnO_2(12TC4)_2^{2+}$, $AnO_2(15TC5)^{2+}$ and $AnO_2(18TC6)^{2+}$ (An = U, Np, Pu, Am and Cm) at the SR−PBE/TZ2P level.

Species	AnO_2^{2+}		$AnO_2(12TC4)_2^{2+}$		$AnO_2(15TC5)^{2+}$		$AnO_2(18TC6)^{2+}$	
	An	O	An	O	An	O	An	O
U	2.18	-0.09	0.52	-0.27	0.58	-0.24	0.52	-0.26
Np	2.09	-0.04	0.46	-0.25	0.51	-0.22	0.44	-0.25
Pu	2.07	-0.04	0.59	-0.27	0.64	-0.23	0.58	-0.25
Am	2.01	-0.01	0.47	-0.26	0.57	-0.21	0.53	-0.24
Cm	1.87	0.06	0.40	-0.23	0.36	-0.15	0.37	-0.20

Table S13. Average MDC_q Charges of AnO_2^{2+}, $AnO_2(12TC4)_2^{2+}$, $AnO_2(15TC5)^{2+}$ and $AnO_2(18TC6)^{2+}$ (An = U, Np, Pu, Am and Cm) at the SR−PBE/TZ2P level.

Species	AnO_2^{2+}		$AnO_2(12TC4)_2^{2+}$		$AnO_2(15TC5)^{2+}$		$AnO_2(18TC6)^{2+}$	
	An	O	An	O	An	O	An	O
U	2.48	-0.24	2.09	-0.80	1.99	-0.61	2.00	-0.66
Np	2.33	-0.16	1.96	-0.78	1.88	-0.58	1.89	-0.64
Pu	2.25	-0.12	1.85	-0.75	1.76	-0.55	1.79	-0.60
Am	2.17	-0.09	1.63	-0.66	1.66	-0.52	1.67	-0.56
Cm	2.40	-0.20	1.66	-0.69	1.56	-0.47	1.60	-0.54

Table S14. The calculated natural localized molecular orbitals (NLMOs) of $AnO_2(12TC4)_2^{2+}$, $AnO_2(15TC5)^{2+}$ and $AnO_2(18TC6)^{2+}$ (An = U, Np, Pu, Am and Cm) complexes.

Species	Type	Occ.	NLMO
$AnO_2(12TC4)_2^{2+}$			
U	$\sigma_{S\text{-}U}$	4*1.91	$89.1\%S(sp^{3.38}) + 10.9\%U(s^{0.4}d^{0.8}f)$
	$\pi_{S\text{-}U}$	4*1.92	$96.1\%S(sp^{1.3}) + 2.4\%U(d^{1.1}f)$
Np	$\sigma_{S\text{-}Np}$	4*1.93	$88.4\%S(sp^{2.37}) + 10.2\%Np(sd^{2.5}f)$
	$\pi_{S\text{-}Np}$	4*1.92	$96.2\%S(sp^{1.9}) + 2.2\%Np(d^{2}f)$
Pu	$\sigma_{S\text{-}Pu}$	4*1.93	$91.0\%S(sp^{2.2}) + 7.6\%Pu(d^{3.8}f)$
	$\pi_{S\text{-}Pu}$	4*1.94	$96.9\%S(sp^{2.0}) + 1.4\%Pu(d^{4}f)$
Am	$\sigma_{S\text{-}Am}$	4*1.93	$91.2\%S(sp^{2.4}) + 6.5\%Am(d^{4.8}f)$
	$\pi_{S\text{-}Am}$	4*1.94	$97.2\%S(sp^{1.8}) + 1.1\%Am(d^{6.8}f)$
Cm	$\sigma_{S\text{-}Cm}$	4*1.94	$90.6\%O(sp^{2.4}) + 8.0\%Cm(sd^{6.8f})$
	$\pi_{S\text{-}Cm}$	4*1.94	$97.0\%O(sp^{1.8}) + 1.3\%Cm(d^{9.0}f)$
$AnO_2(15TC5)^{2+}$			
U	$\sigma_{S\text{-}U}$	5*1.87	$81.3\%S(sp^{4.3}) + 16.6\%U(s^{0.6}d^{2.1}f)$
	$\pi_{S\text{-}U}$	5*1.92	$97.8\%S(sp) + 1.0\%U(d^{0.8}f)$
Np	$\sigma_{S\text{-}Np}$	5*1.93	$88.4\%S(sp^{2.37}) + 10.2\%Np(sd^{2.5}f)$
	$\pi_{S\text{-}Np}$	5*1.92	$96.2\%S(sp^{1.9}) + 2.2\%Np(d^{2}f)$
Pu	$\sigma_{S\text{-}Pu}$	5*1.93	$91.0\%S(sp^{2.2}) + 7.6\%Pu(d^{3.8}f)$
	$\pi_{S\text{-}Pu}$	5*1.94	$96.9\%S(sp^{2.0}) + 1.4\%Pu(d^{4}f)$
Am	$\sigma_{S\text{-}Am}$	5*1.90	$85.1\%S(sp^{4.2}) + 13.1\%Am(s^{1.1}d^{3.0}f)$
	$\pi_{S\text{-}Am}$	5*1.94	$98.0\%S(sp) + 0.7\%Am(d^{2.2}f)$
Cm	$\sigma_{S\text{-}Cm}$	5*1.90	$86.7\%S(sp^{3.7}) + 11.7\%Cm(s^{1.2}d^{3.7}f)$
	$\pi_{S\text{-}Cm}$	5*1.96	$98.0\%S(sp^{1.1}) + 0.7\%Cm(d^{2.6}f)$
$AnO_2(18TC6)^{2+}$			

U	σ_{S-U}	6*1.89	83.2%S($sp^{4.8}$) + 14.3%U($s^{0.3}d^{1.5}f$)
	π_{S-U}	6*1.96	97.8%S(sp) + 0.7%U(df)
Np	σ_{S-Np}	6*1.89	84.6%S($sp^{4.6}$) + 13.0%Np($s^{0.4}d^{1.7}f$)
	π_{S-Np}	6*1.96	97.9%S(sp) + 0.6%Np($d^{1.5}f$)
Pu	σ_{S-Pu}	6*1.93	91.0%S($sp^{2.2}$) + 7.6%Pu($d^{3.8}f$)
	π_{S-Pu}	6*1.94	96.9%S($sp^{2.0}$) + 1.4%Pu($d^{4}f$)
Am	σ_{S-Am}	6*1.98	84.0%S(p) + 15.8%Am($d^{0.7}f$)
	π_{S-Am}	6*1.96	98.1%S(sp) + 0.4%Am($d^{4.6}f$)
Cm	σ_{S-Cm}	6*1.92	89.8%S($sp^{3.3}$) + 8.6%Cm($s^{1.7}d^{5.3}f$)
	π_{S-Cm}	6*1.82	98.6%S($sp^{0.9}$) + 0.2%Cm($d^{7.1}f$)

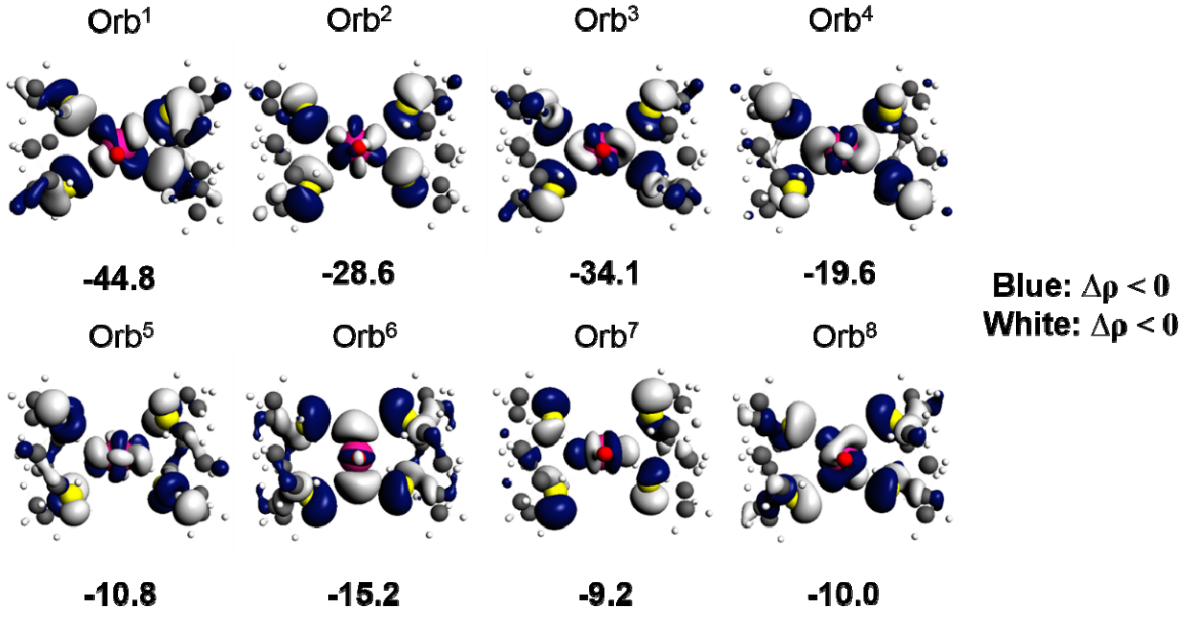

Figure S1. Plot of representative An-S_{12TC4} bonding interactions of $AnO_2(12TC4)_2^{2+}$ from ETS-NOCV method from an open-shell B3LYP calculation (energy unit: kcal/mol, isovalue=0.03).

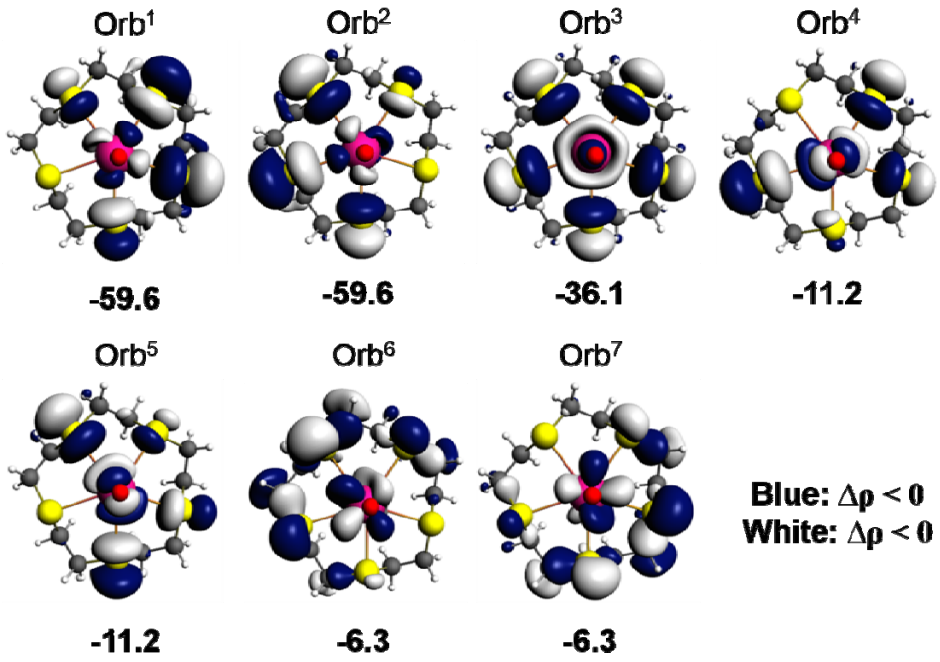

Figure S2. Plot of representative An-S_{15TC5} bonding interactions of $AnO_2(15TC5)^{2+}$ from ETS-NOCV method from an open-shell B3LYP calculation (energy unit: kcal/mol, isovalue=0.03).

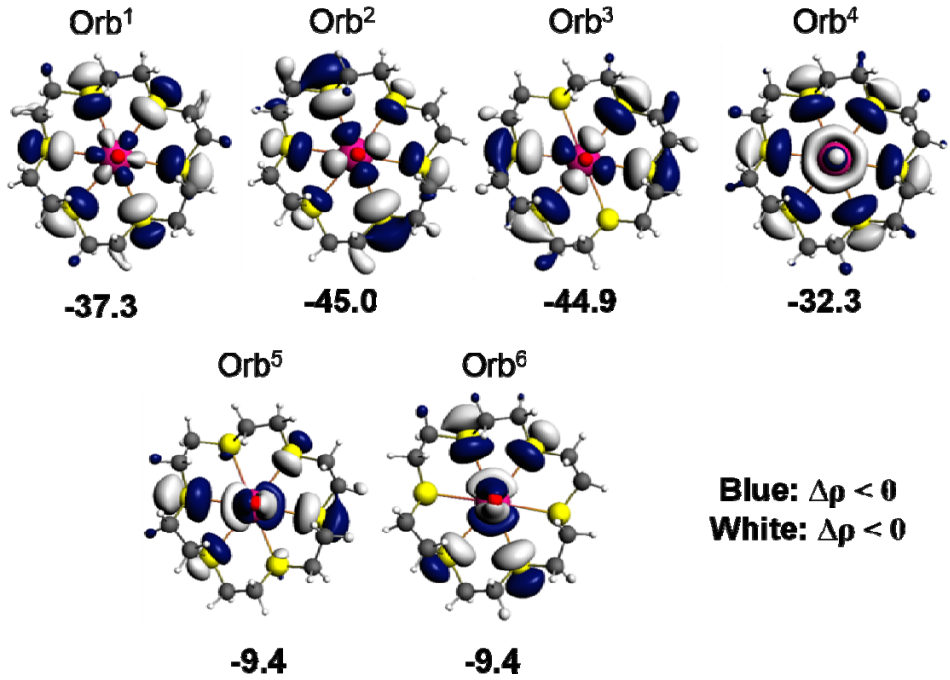

Figure S3. Plot of representative An-S_{18TC6} bonding interactions of $AnO_2(18TC6)^{2+}$ from ETS-NOCV method from an open-shell B3LYP calculation (energy unit: kcal/mol, isovalue=0.03).

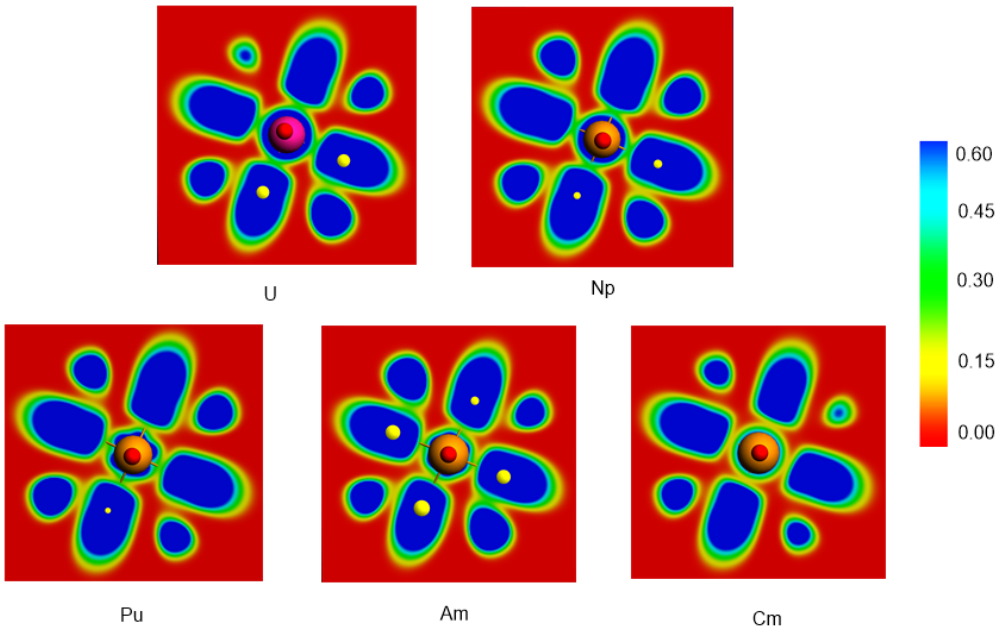

Figure S4. Two-dimensional ELF contours for the planes containing the five An−S_e bonds in AnO_2^{2+}(12TC4). The results are based on the SR-ZORA PBE/TZ2P calculated densities.

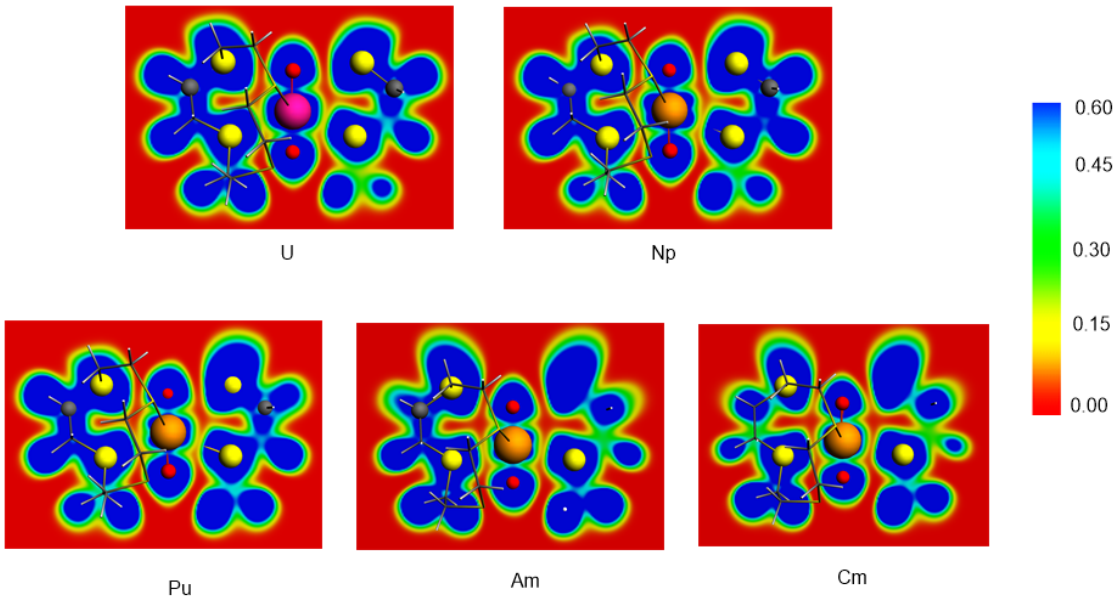

Figure S5. Two-dimensional ELF contours for the planes containing the four An−S_{12TC4} bonds in $AnO_2^{2+}$$(12TC4)_2$. The results are based on the SR-ZORA PBE/T2ZP calculated densities.

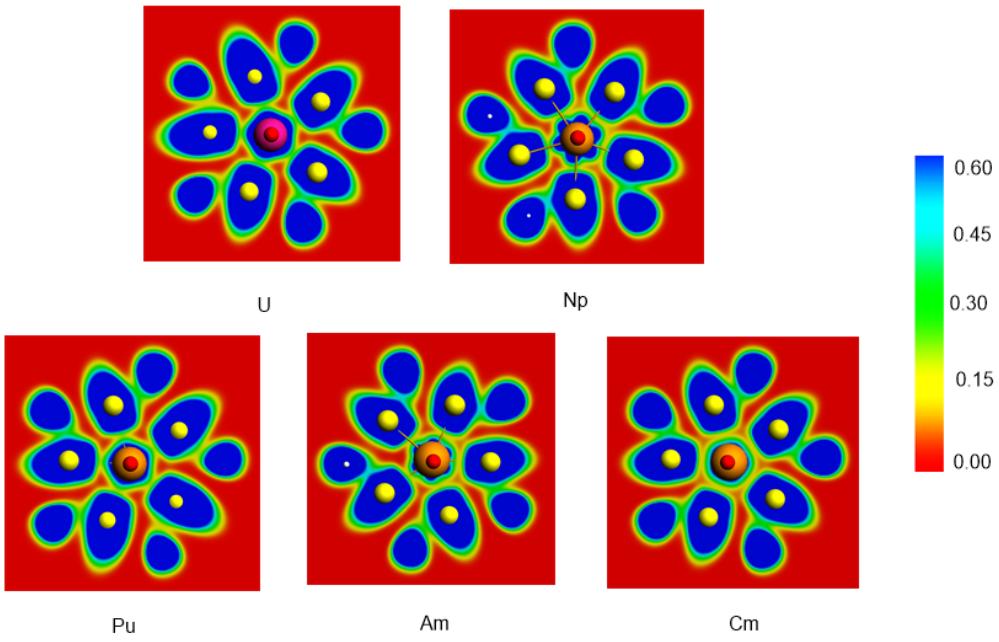

Figure S6. Two-dimensional ELF contours for the planes containing the five An−S_{15TC5} bonds in AnO_2^{2+}(15TC5). The results are based on the SR-ZORA PBE/T2ZP calculated densities.

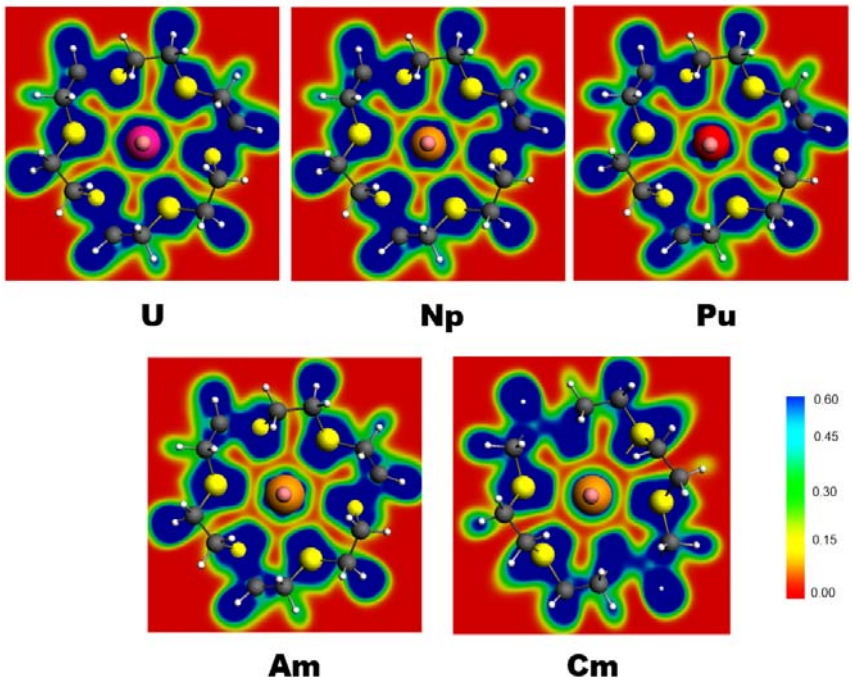

Figure S7. Two-dimensional ELF contours for the planes containing the six An−S_{18TC6} bonds in AnO_2^{2+}(18TC6). The results are based on the SR-ZORA PBE/T2ZP calculated densities.