Electronic Supplementary Material (ESI) for Dalton Transactions.

Covalency in $AnCl_2$ (An=Th-No)

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Supplementary Information

Table SI1: The PBE0 $<S^2>$ values following the ECP geometry optimisations and subsequent single point all electron calculations on $AnCl_2$ (An=Th-No). Data are reported as the difference between the formal and actual values. Accompanied by the 5f electron count and calculated electronic states and point group for both calculations.

An	5f electrons α,β	Small core ECP	Electronic state (point group)	All electron	Electronic State (point group)
Th	2,0	0.0046	$^3B_2(C_{2v})$	0.0044	$^3A_2(C_{2v})$
Pa	3,0	0.0072	$^4B_1(C_{2v})$	0.0061	$^4B_1(C_{2v})$
U	4,0	0.0097	$^5B_2(C_{2v})$	0.0069	$^5A_2(C_{2v})$
Np	5,0	0.0115	$^6B_2(C_{2v})$	0.0098	$^6A_1(C_{2v})$
Pu	6,0	0.0147	$^7B_1(C_{2v})$	0.0132	$^7B_1(C_{2v})$
Am	7,0	0.0137	$^8A_2(C_{2v})$	0.0138	$^8A_2(C_{2v})$
Cm	7,0	0.0135	$^9A_2(C_{2v})$	0.0133	$^9A_2(C_{2v})$
Bk	7,1	0.0100	$^8B_2(C_{2v})$	0.0104	$^8A_2(C_{2v})$
Cf	7,3	0.0079	$^5A_1(C_{2v})$	0.0399	$^5B_2(C_{2v})$
Es	7,4	0.0081	$^4A_1(C_{2v})$	0.0091	$^4B_1(C_{2v})$
Fm	7,5	0.0028	$^3B_1(C_{2v})$	0.0031	$^3A_1(C_{2v})$
Md	7,6	0.0007	$^2B_2(C_{2v})$	0.0006	$^2B_2(C_{2v})$
No	7,7	0.0000	$^1A_1(C_{2v})$	0.0000	$^1A_1(C_{2v})$

Table SI2: Average bond lengths (Å), Bond Angles (°) and Dihedral Angles (°) for $AnCl_2$ (where An=Th-No) with small core ECP for the PBE0 functional. Note that the geometries where the lower multiplicity (of 6 and 7) are used for $CmCl_2$ and $BkCl_2$ is represented by *(low m)*.

An	Th	Pa	U	Np	Pu	Am	Cm	Cm *(low m)*	Bk	Bk *(low m)*	Cf	Es	Fm	Md	No
Average bond length $AnCl_2$	2.556	2.535	2.524	2.512	2.558	2.557	2.492	2.481	2.476	2.543	2.531	2.511	2.502	2.511	2.503
Bond Angle $AnCl_2$	158.6	110.4	116.7	117.0	116.3	112.5	121.5	115.6	122.5	114.5	116.5	118.6	119.4	129.7	120.8

Table SI3: An Natural populations in $AnCl_2$ (PBE0/all electron). (Note that (low m) represents where the lower multiplicity (of 6 and 7) are used for both the ECP geometry optimisation and single-point all electron calculation for $CmCl_2$ and $BkCl_2$).

An	5f	6d	7s	7p
Th	0.36	1.80	0.83	0.03
Pa	2.07	0.94	0.82	0.03
U	3.13	0.84	0.83	0.04
Np	4.59	0.59	0.58	0.03
Pu	5.90	0.47	0.26	0.02
Am	6.96	0.42	0.20	0.02
Cm	7.07	0.80	0.85	0.01
Bk	8.05	0.82	0.87	0.01
Cf	9.93	0.38	0.26	0.02
Es	10.98	0.37	0.21	0.02
Fm	12.00	0.35	0.19	0.02
Md	13.01	0.32	0.17	0.02
No	13.99	0.32	0.21	0.02
Cm (low m)	7.13	0.68	0.91	0.06
Bk (low m)	8.63	0.45	0.55	0.03

Table SI4: The Wiberg Bond Index (WBI), QTAIM metrics (delocalisation Index δ(An,Cl), $(-G/V)_{BCP}$ and bond critical point electron density (ρ_{BCP}), all in au) for the An-Cl bond and NPA/QTAIM partial charge on the metal atom in $AnCl_2$, where An=Th–No. (Note that (low m) represents where the lower multiplicity (of 6 and 7) are used for both the ECP geometry optimisation and single-point all electron calculation for $CmCl_2$ and $BkCl_2$).

An	WBI	NBO charge	δ(An,Cl)	$(-G/V)_{BCP}$	ρ_{BCP}	QTAIM charge
Th	0.86	1.05	1.02	0.73	0.082	1.34
Pa	0.83	1.09	0.97	0.74	0.082	1.35
U	0.80	1.13	0.98	0.76	0.082	1.35
Np	0.75	1.18	0.99	0.76	0.084	1.33
Pu	0.64	1.32	0.85	0.80	0.073	1.42
Am	0.59	1.37	0.80	0.83	0.070	1.43
Cm	0.73	1.20	0.94	0.79	0.082	1.34
Bk	0.75	1.18	0.97	0.79	0.085	1.32
Cf	0.58	1.38	0.79	0.83	0.072	1.43
Es	0.57	1.40	0.77	0.84	0.072	1.43
Fm	0.55	1.41	0.75	0.85	0.072	1.43
Md	0.52	1.44	0.72	0.86	0.069	1.45
No	0.53	1.43	0.72	0.87	0.068	1.45
Cm (lower m)	0.75	1.18	0.97	0.78	0.083	1.32
Bk (lower m)	0.64	1.31	0.86	0.82	0.072	1.40

Table SI5: The Enthalpy of Reaction/ kJ mol^{-1} (all electron calculations for all bar PBE0 ECP) Note that for Cm and Bk the parenthesised values are the enthalpy values when the dichloride frequency calculation was performed with the lower multiplicity (of 6 and 7 respectively) .

Functional	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
PBE0	429.74	393.85	326.39	401.67	328.32	225.28	348.03 *(390.01)*	379.12 *(362.37)*	280.48	220.00	151.34	62.24	13.82
PBE	425.85	389.77	373.62	346.95	292.27	216.50	322.34 *(360.80)*	341.81 *(305.98)*	239.27	199.82	161.16	107.87	60.94
B3Pw91		396.06	363.93	395.34			341.77	369.32 *(333.48)*					
BLYP		382.15	362.86	337.68			333.02	332.63 *(296.74)*					
B3LYP		389.91	361.48	361.26			341.77	376.33 *(345.08)*					
PBE0 ECP							344.15	345.90					

The origin of the peak at Bk for the enthalpy of reaction in Figure 3

In Figure 3 (which shows the enthalpy data of the following reaction - $AnCl_3 \rightarrow AnCl_2 + ½\ Cl_2$ (An=Th-No)) there is a peak at Bk with the PBE0 functional, and a plateau with the PBE functional. This trend does not match previous experimental and theoretical work, which has the peak located at Cm - and moreover, cannot be explained chemically. As highlighted in the computational details, both $CmCl_2$ and $BkCl_2$ were calculated with higher multiplicities, (due to high spin contamination with the lower multiplicities) which forced population of their 6d and 7s orbitals. For the ECP geometry optimisation calculations both $CmCl_2$ and $BkCl_2$ produced a lower energy geometry with this higher multiplicity. However, for the single point all electron calculation, $BkCl_2$ the higher multiplicity was in fact higher in energy (by 17 kJ mol^{-1}). Thus, the higher enthalpy value shown in Figure SI1 below for a range of functions, may have arisen due to the higher energy calculated using all-electron approach for $BkCl_2$ – suggesting that the correct ground state is not described with this higher multiplicity for the all-electron calculation, unlike $CmCl_2$. However, as shown below in Figure SI1 with PBE0, even though (unlike the all-electron calculation) there isn't a peak at Bk when the enthalpy values calculated using ECPs, there is still not a significant peak in enthalpy at Cm.

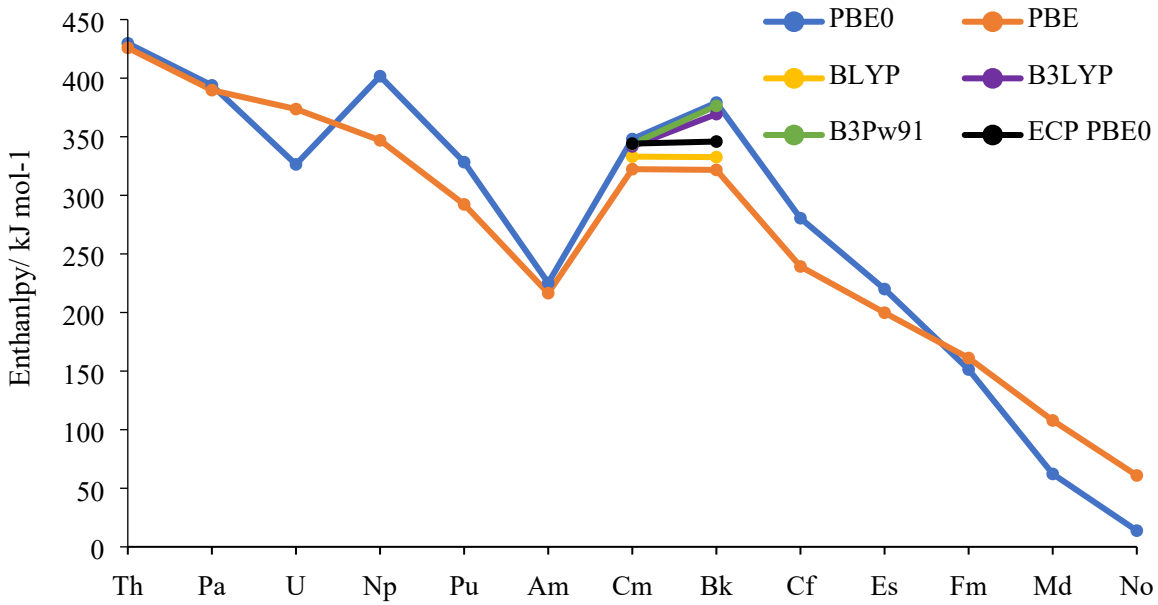


Figure SI1: The enthalpy of reaction of the following reaction: $AnCl_3 \rightarrow AnCl_2 + ½\ Cl_2$ (An=Th-No) for a range of functionals (blue/purple/green for the hybrid functionals, yellow/orange for the GGA functionals and black for the PBE0 ECP data). Each geometry was optimised with the corresponding functional and then single point all electron calculation performed (except PBE0 ECP).

Therefore, to further investigate the effect of multiplicity, we re-ran the frequency calculation for $BkCl_2$ (for the same range of functionals and ECP geometries as above) but with the original lower multiplicity, of 6 instead of 8, for the single point calculation - which note produced highly spin contaminated systems with all functionals. As shown in Figure SI2, this change lowered the enthalpy of reaction value for Bk for each functional; with the GGA's now in good agreement with the previous studies.

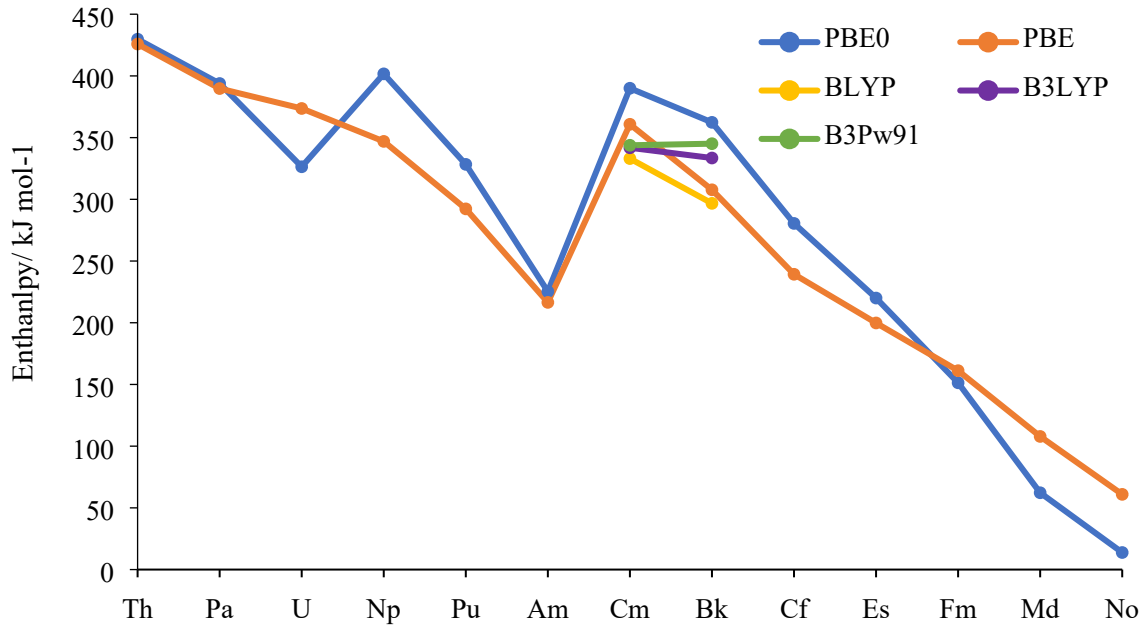


Figure SI2: The enthalpy of the following reaction: $AnCl_3 \rightarrow AnCl_2 + ½\ Cl_2$ (An=Th-No) for a range of functionals (blue/purple/green for the hybrid functionals and yellow/orange for the GGA functionals), with $BkCl_2$ possessing a multiplicity of 6 instead of 8 in the main paper in the all-electron calculation. The geometry is the same as above in Figure 1.

Note that when a multiplicity of 6 is used for both the ECP geometry optimisation and all electron single-point calculation, Bk no longer has: population of the 6d orbital (see Table SI3), a bond length (see Table SI1 and Figure SI3 below) and An-Cl covalency (see Table SI4 and the Delocalisation Index in Figure SI4 below) which is in line with the earlier actinides. This supports the suggestion in the main paper, that the longer bond lengths and increased covalency of elements Th-Np, Cm and Bk are caused by the increase population of the 6d orbital.

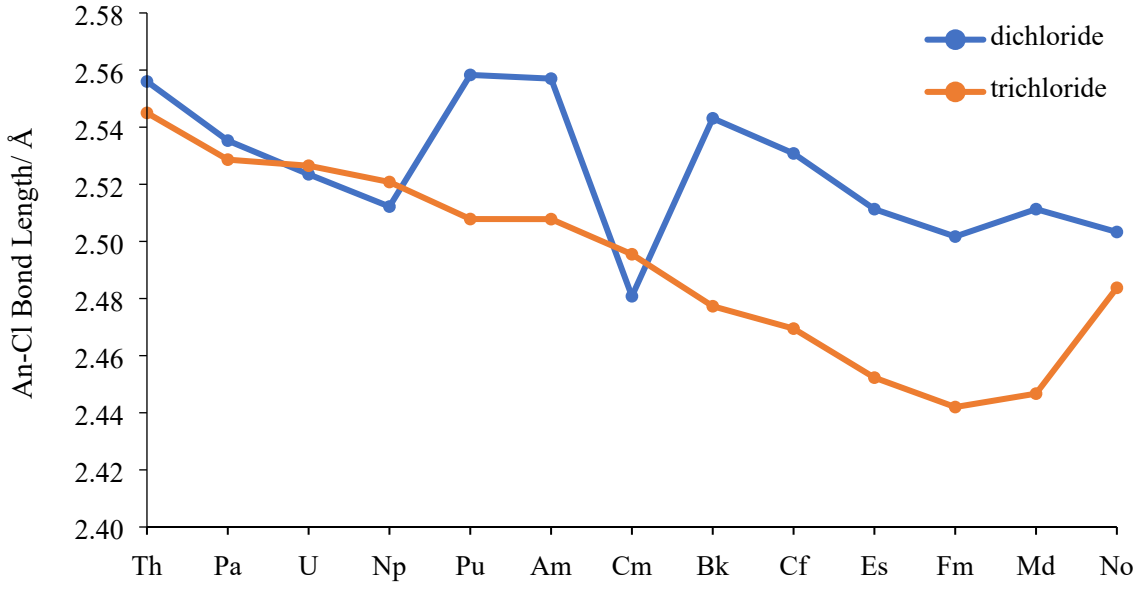


Figure SI3 - An-Cl bond lengths in $AnCl_2$ (compared to $AnCl_3$ from our previous work[27]) where $CmCl_2$ and $BkCl_2$ has a multiplicity of 7 and 6 respectively.

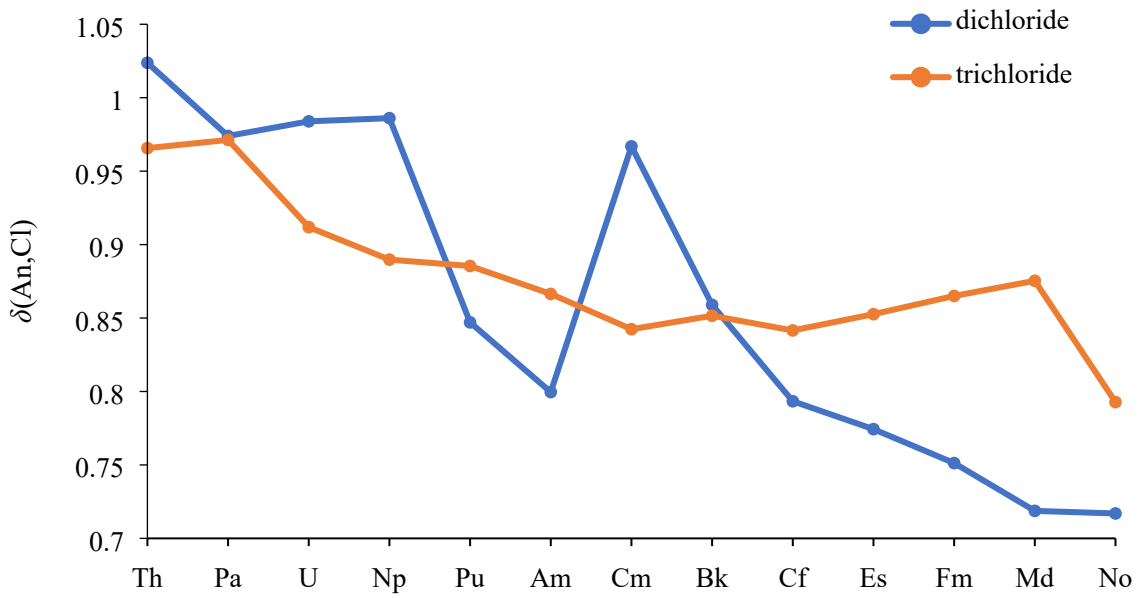


Figure SI4: The An-Cl Delocalisation Index δ(An,Cl) for $AnCl_2$ (compared to $AnCl_3$ from our previous work[27]) when $CmCl_2$ and $BkCl_2$ has a multiplicity of 7 and 6 respectively in both the ECP geometry optimisation and all electron calculation.

Table SI6: NRT analysis; average α and β spin covalent, ionic and ionic/covalent An-Cl Natural bond orders in $AnCl_2$ (An=Th–Md)

An	α covalent	α ionic	α ionic/covalent	β covalent	β ionic	β ionic/covalent
Th	0.21	1.20	5.85	0.19	1.27	6.70
Pa	0.22	1.23	5.56	0.19	1.21	6.40
U	0.21	1.24	5.95	0.14	0.86	6.08
Np	0.21	1.24	5.84	0.12	0.88	7.04
Pu	0.13	0.87	6.66	0.10	0.90	9.09
Am	0.12	0.88	7.16	0.10	0.90	9.36
Cm	0.16	1.06	6.60	0.14	0.86	6.29
Bk	0.16	1.07	6.78	0.19	1.24	6.64
Cf	0.11	0.89	8.30	0.11	0.89	8.30
Es	0.10	0.90	8.77	0.10	0.90	8.64
Fm	0.10	0.90	9.20	0.10	0.90	8.82
Md	0.09	0.91	10.47	0.10	0.90	9.33

Table SI7: Metal contribution (%) to the An–Cl bonding NBOs (as $NoCl_2$ has a full shell, the NBOs are not divided into α and β spin, hence the α σ and π represent the total σ and π m%)

An	Average	$\alpha\ \sigma$	$\alpha\ \pi$	$\beta\ \sigma$	$\beta\ \pi$
Th	7.88	9.73	6.35	9.80	5.62
Pa	8.50	11.69	6.40	10.82	5.10
U	8.27	11.75	5.96	10.51	4.84
Np	7.72	11.76	5.67	9.31	4.14
Pu	6.19	9.33	4.62	7.31	3.48
Am	6.00	9.29	4.18	7.15	3.39
Cm	7.58	10.36	5.22	10.32	4.43
Bk	7.78	9.99	5.23	10.8	5.07
Cf	5.85	8.31	3.51	8.23	3.36
Es	5.64	7.88	3.35	7.73	3.58
Fm	5.47	7.53	3.17	7.52	3.64
Md	4.98	6.65	2.87	6.46	3.94
No	5.21	7.42	2.99	-	-

Table SI8: NAO contribution (%) to the σ α An-Cl bonding NBOs (as $NoCl_2$ has a full shell, the NBOs are not divided into α and β spin, hence the α σ and π represent the total σ and π m%).

An	s	p	d	f
Th	0.81	0.18	4.96	3.71
Pa	1.39	0.03	8.50	1.76
U	1.48	0.03	8.40	1.84
Np	2.87	0.03	7.05	1.80
Pu	3.27	0.03	5.34	0.67
Am	3.50	0.03	5.46	0.28
Cm	1.36	0.06	8.86	0.06
Bk	1.38	0.06	8.49	0.06
Cf	3.40	0.03	4.80	0.06
Es	3.24	0.03	4.53	0.06
Fm	3.07	0.04	4.36	0.04
Md	2.67	0.05	3.87	0.03
No	3.20	0.04	4.10	0.04

Table SI9: NAO contribution (%) to the σ β An-Cl bonding NBOs.

An	s	p	d	f
Th	1.54	0.06	4.05	4.08
Pa	2.77	0.03	6.51	1.50
U	2.72	0.02	6.18	1.57
Np	2.72	0.03	5.28	1.27
Pu	2.14	0.02	4.19	0.95
Am	2.32	0.02	3.90	0.90
Cm	3.01	0.02	5.65	1.62
Bk	3.84	0.02	5.59	1.33
Cf	3.24	0.03	4.15	0.80
Es	3.07	0.03	4.04	0.57
Fm	3.01	0.03	3.85	0.62
Md	2.73	0.06	3.26	0.38

Table SI10: NAO contribution (%) to the $\pi\ \alpha$ An-Cl bonding NBOs (as $NoCl_2$ has a full shell, the NBOs are not divided into α and β spin, hence the α σ and π represent the total σ and π m%).

An	s	p	d	f
Th	0.00	0.41	3.09	2.82
Pa	0.00	0.27	4.37	1.75
U	0.00	0.37	4.62	0.96
Np	0.00	0.30	4.70	0.67
Pu	0.01	0.23	3.69	0.68
Am	0.00	0.39	3.73	0.05
Cm	0.00	0.46	4.68	0.07
Bk	0.00	0.51	4.63	0.07
Cf	0.00	0.40	3.05	0.05
Es	0.00	0.42	2.87	0.05
Fm	0.00	0.43	2.67	0.06
Md	0.00	0.51	2.28	0.07
No	0.00	0.45	2.47	0.06

Table SI11: NAO contribution (%) to the $\pi\ \beta$ An-Cl bonding NBOs.

An	s	p	d	f
Th	0.00	0.25	2.96	2.39
Pa	0.00	0.16	3.46	1.46
U	0.00	0.20	3.30	1.33
Np	0.00	0.17	2.95	1.02
Pu	0.00	0.23	2.51	0.74
Am	0.00	0.25	2.53	0.61
Cm	0.00	0.22	3.02	1.18
Bk	0.00	0.24	3.15	1.67
Cf	0.00	0.38	2.65	0.32
Es	0.02	0.19	2.45	0.91
Fm	0.01	0.19	2.38	1.04
Md	0.04	0.22	2.10	1.58

Table SI12: The average energy difference between the α and β 5f and 3p, and 6d and 3p NAOs and the β An and Cl NHOs (Hartrees) in $AnCl_2$ (An = Pu-Md, PBE0/all electron).

An	Pu	Am	Cm	Bk	Cf	Es	Fm	Md
f NAO α	0.127	0.070	-0.084	-0.116	-0.002	-0.007	-0.016	-0.024
f NAO β	0.380	0.386	0.263	0.204	0.224	0.149	0.092	0.028
d NAO α	0.279	0.279	0.257	0.262	0.300	0.306	0.321	0.331
d NAO β	0.330	0.329	0.322	0.316	0.318	0.323	0.328	0.330
σ NHO β	–	0.471	0.436	0.417	0.414	0.401	0.412	0.400
π NHO β	–	0.338	0.310	0.286	0.324	0.340	0.338	0.321

Table SI13: NHO overlap for $AnCl_2$ (An=Th-Md, PBE0/all electron). (As $NoCl_2$ has a full shell, the NHOs are not divided into α and β spin, hence the α σ and π represent the total σ and π).

An	$\alpha\ \sigma$	$\alpha\ \pi$	$\beta\ \sigma$	$\beta\ \pi$
Th	0.55	0.55	0.57	0.51
Pa	0.56	0.52	0.58	0.52
U	0.54	0.45	0.56	0.47
Np	0.53	0.43	0.55	0.44
Pu	0.54	0.42	0.53	0.43
Am	0.54	0.42	0.53	0.43
Cm	0.54	0.42	0.53	0.42
Bk	0.54	0.42	0.53	0.40
Cf	0.54	0.43	0.52	0.43
Es	0.54	0.44	0.51	0.42
Fm	0.55	0.44	0.54	0.44
Md	0.55	0.45	0.53	0.39
No	0.54	0.42	-	-

Dichlorides

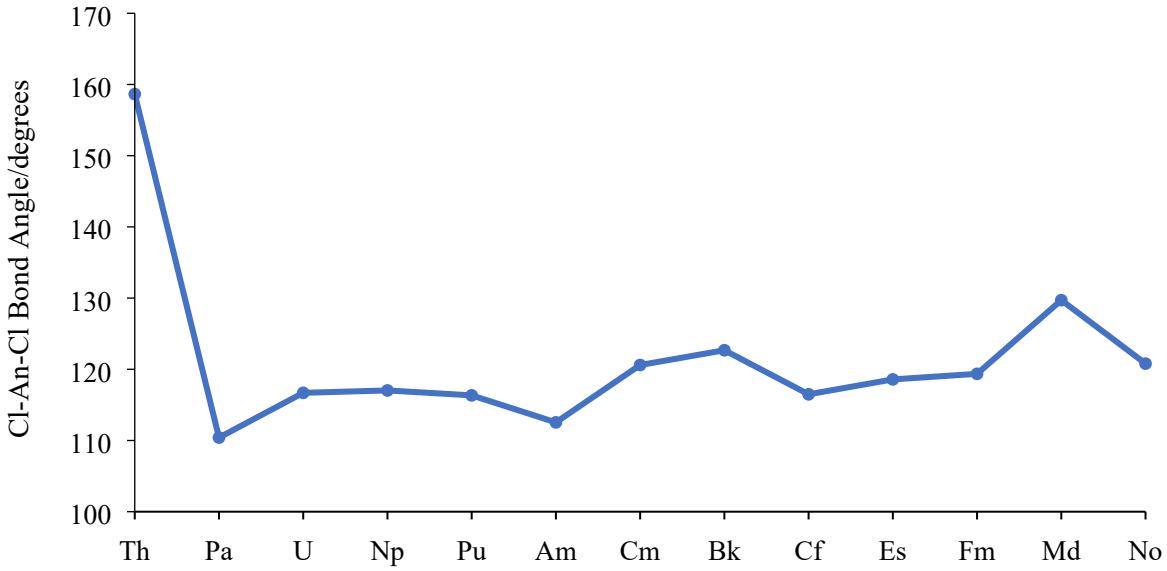


Figure SI5 – The Cl-An-Cl bond angle for $AnCl_2$ (An=Th-No)

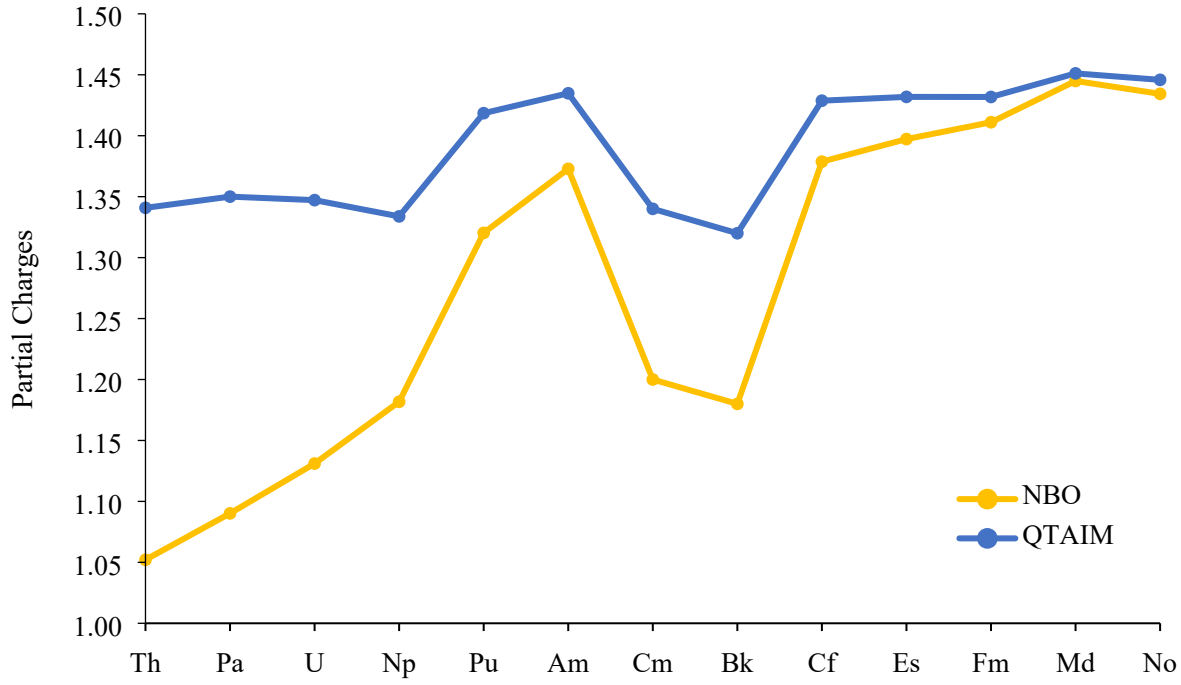


Figure SI6- The NBO and QTAIM partial charges for $AnCl_2$ (An=Th-No)

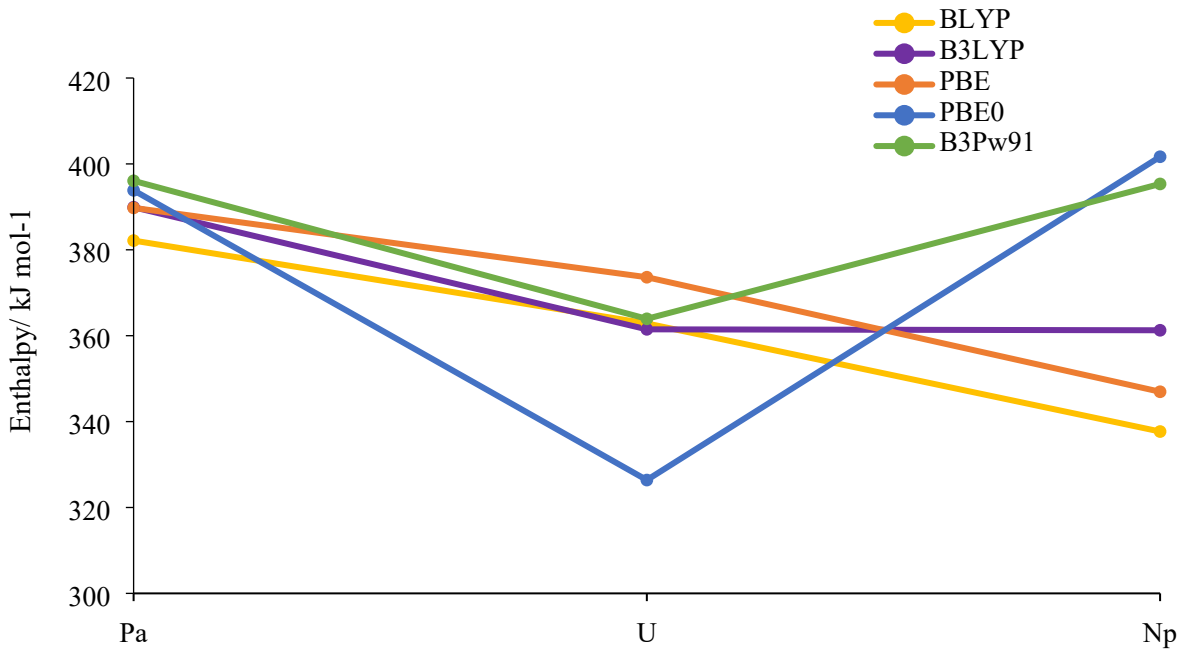


Figure SI7- The enthalpy for $AnCl_2$ An=Pa-Np for a range of functionals - blue/green for the hybrids and yellow/orange for the GGAs. (Note, that both the ECP geometry optimisation and the all-electron frequency calculations were performed with the corresponding functional).

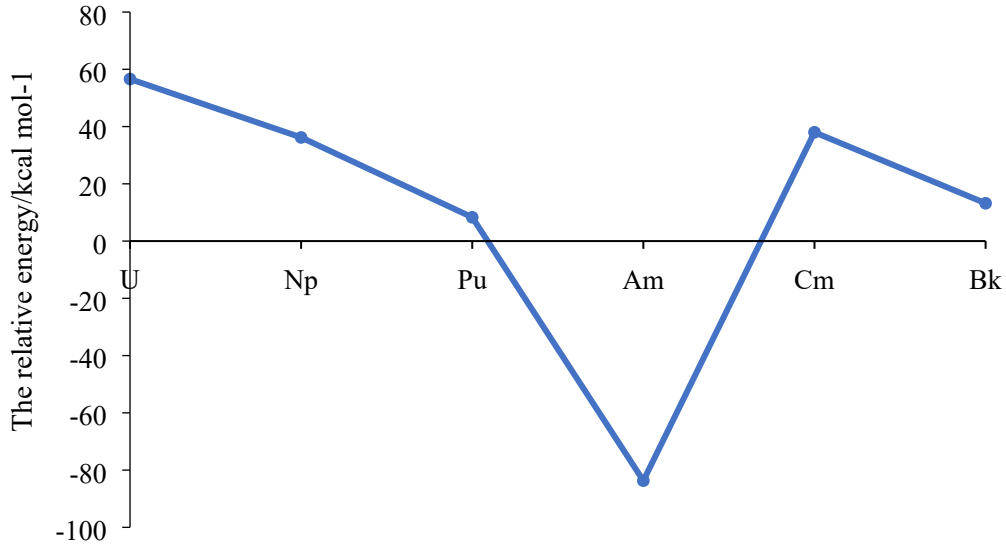


Figure SI8 – The relative ΔH_{0K} AnO_2^{2+} in kcal mol^{-1} (at CCSD(T)/(a)VTZ-DK level) for III and II oxidation states (III-II), created from the data in Vasiliu *et al.*'s work.[31]

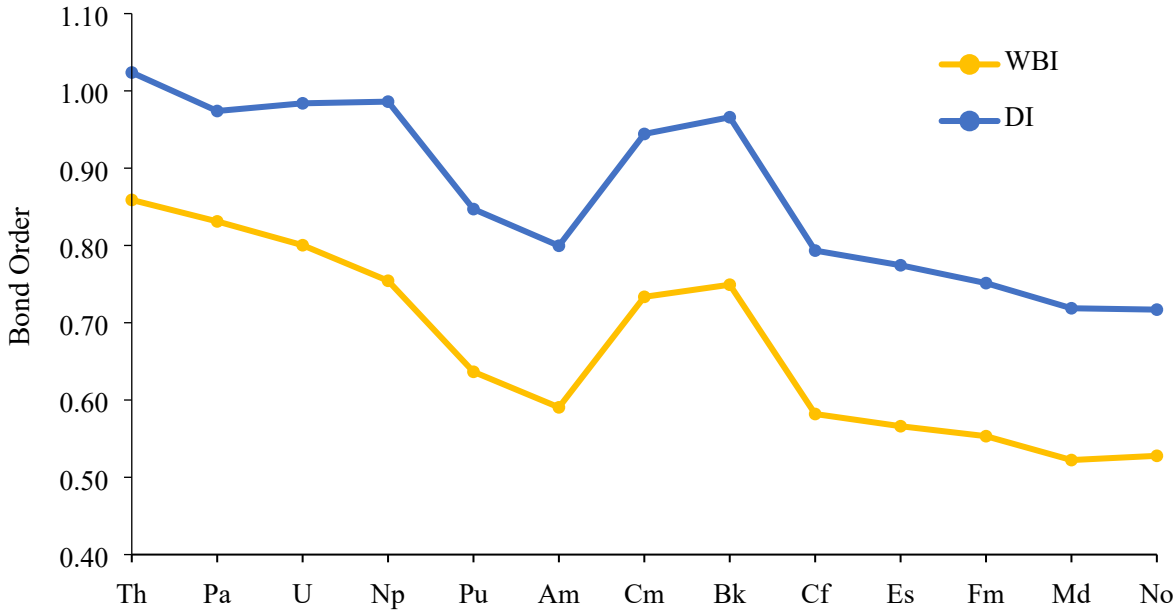


Figure SI9- The An-Cl Wiberg Bond Index (WBI) and Delocalisation Index (DI or δ(An,Cl)) for $AnCl_2$ (An=Th-No).

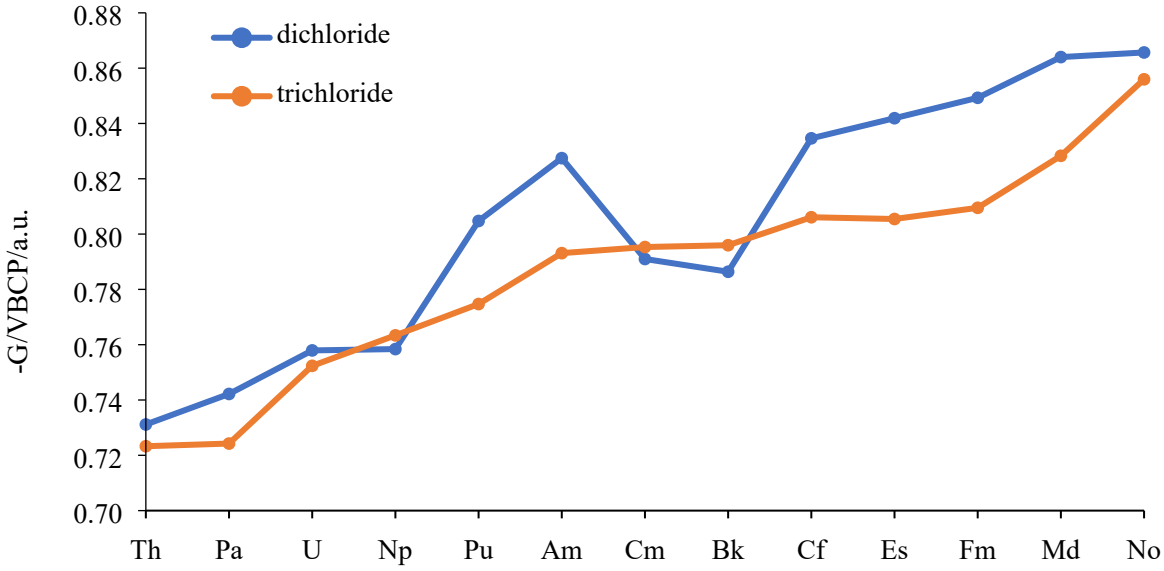


Figure SI10- $(-G/V)_{BCP}$ for $AnCl_2$ and $AnCl_3$[27] (An=Th-No)

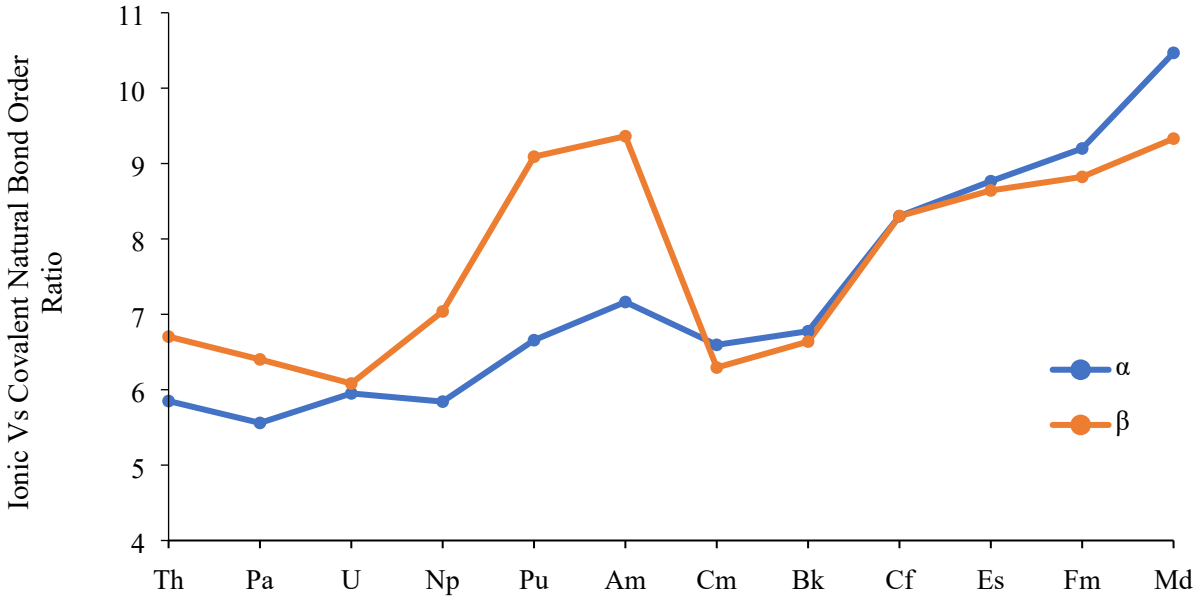


Figure SI11- The ratio of the ionic to covalent contributions to the α and β natural bond order in $AnCl_2$ (An=Th-Md).

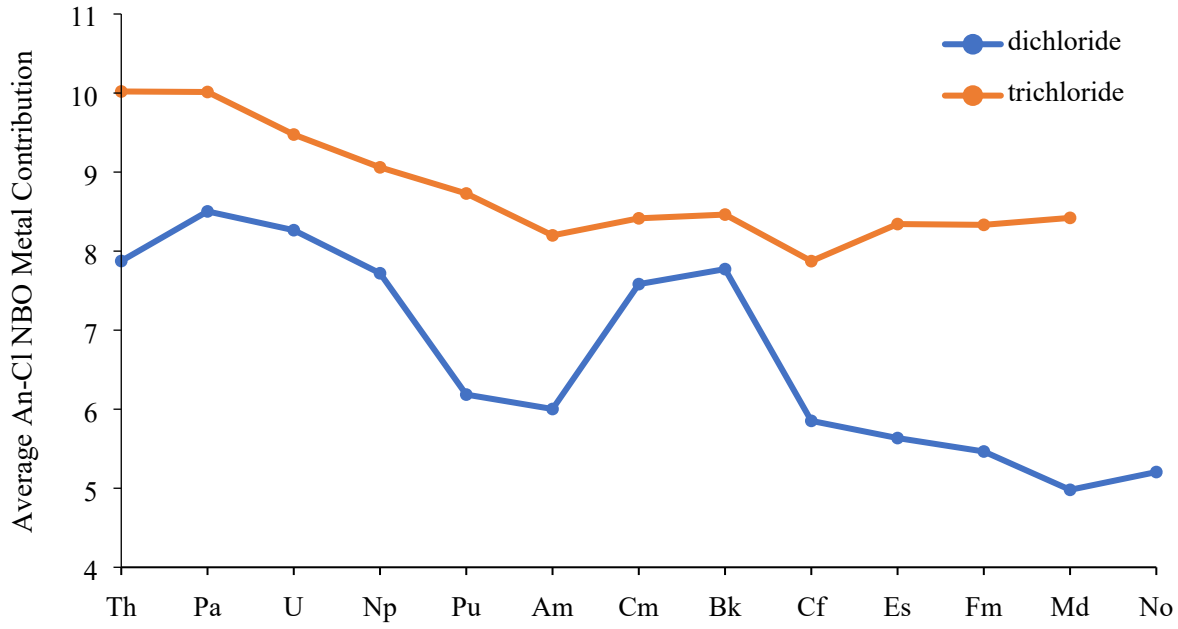
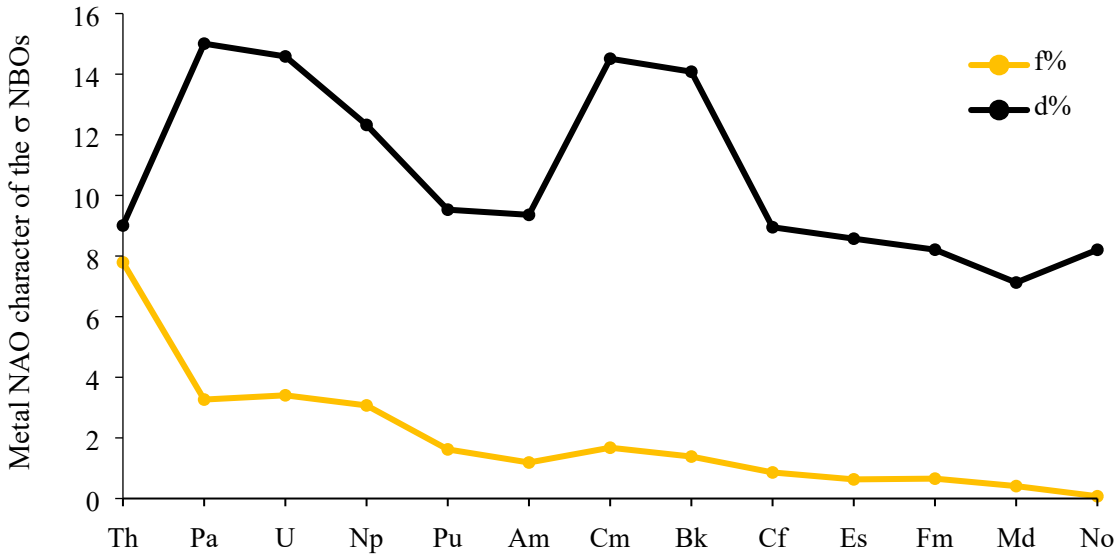
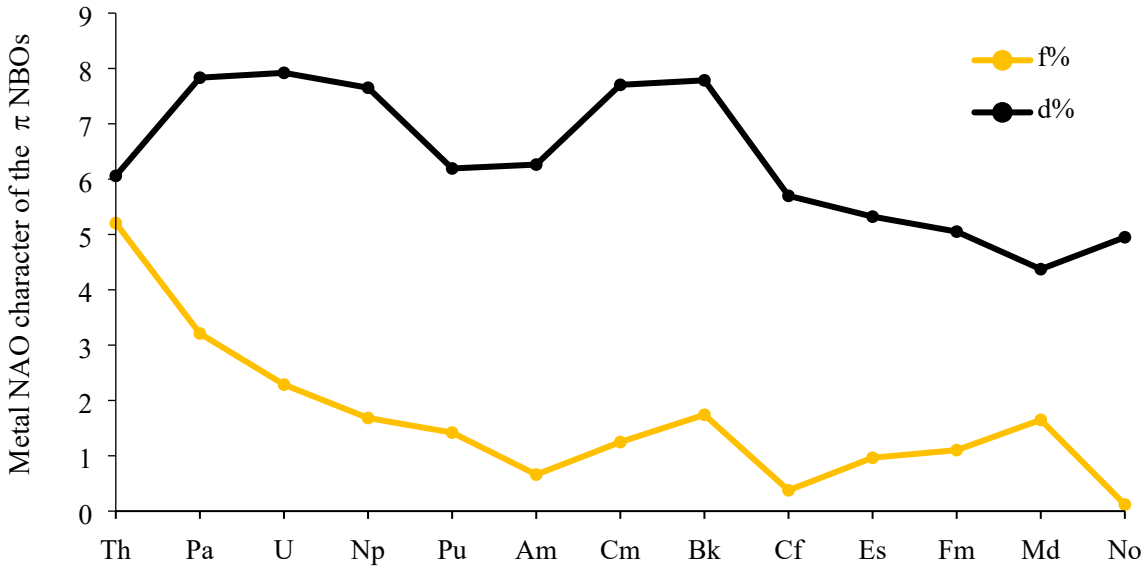


Figure SI12- The Average metal contribution (%) to the metal–chlorine NBOs in $AnCl_2$ and $AnCl_3$. $NoCl_3$ is omitted as it did not converge on σ type + π type NBOs for all three An-Cl bonds.

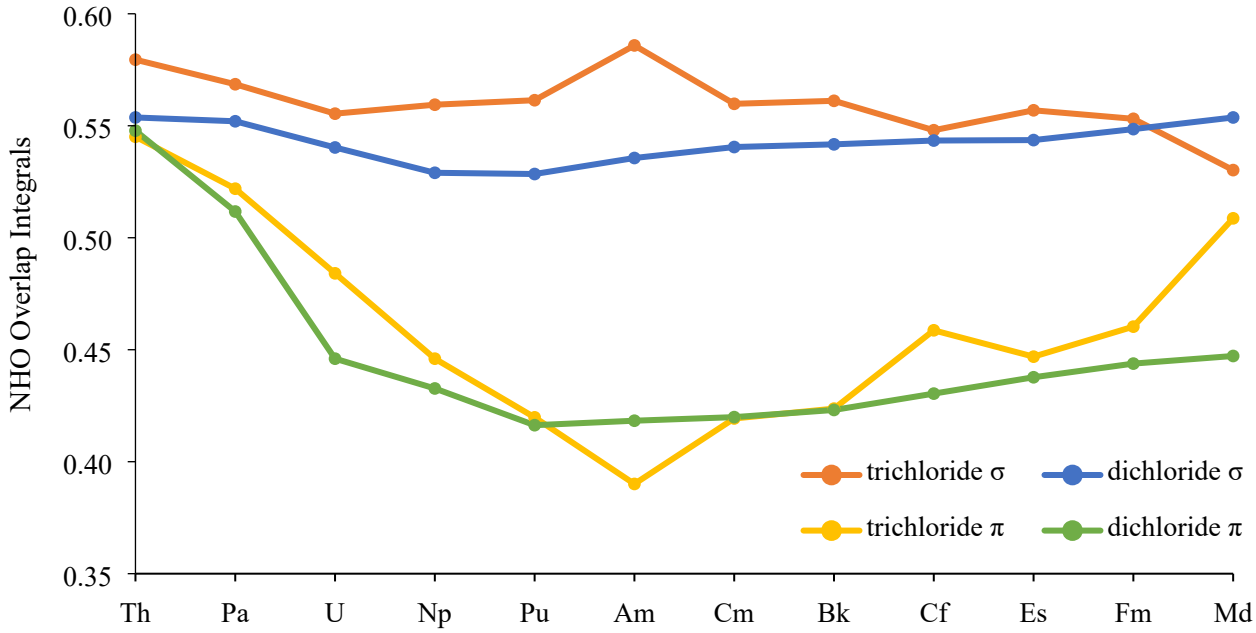


(a) σ-type

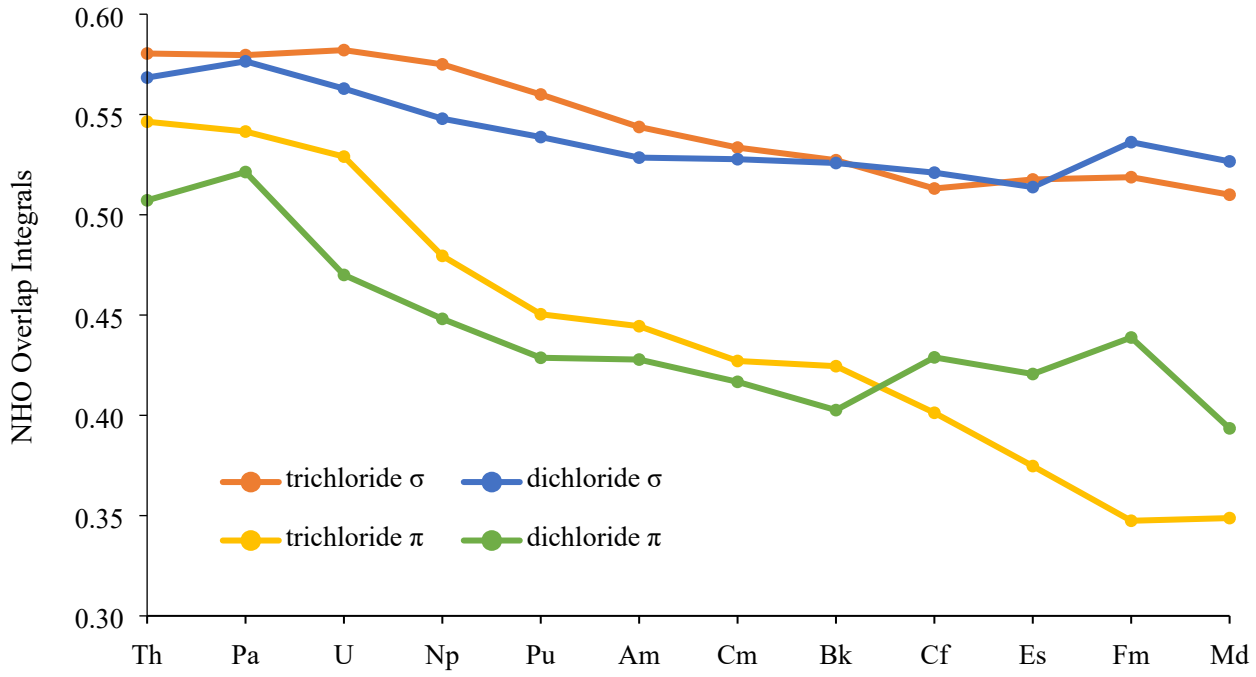


(b) π-type

Figure SI13 - Actinide d and f natural atomic orbital contributions (%) to the (a) σ type and (b) π type NBOs for $AnCl_2$ – the α and β values have been averaged for An = Th-Md.



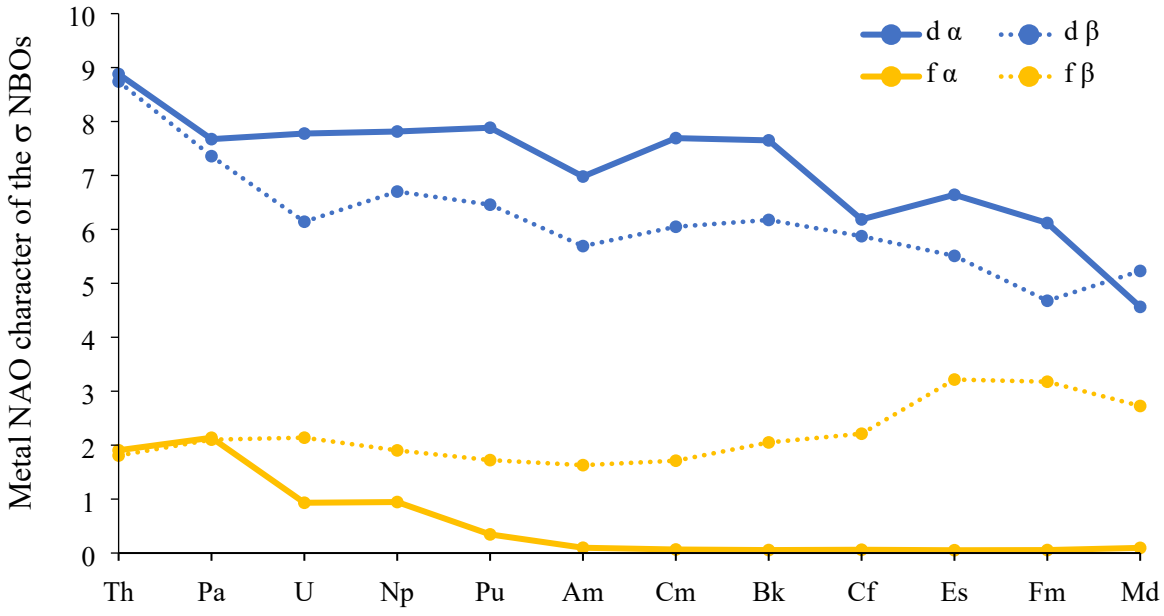
(a) α



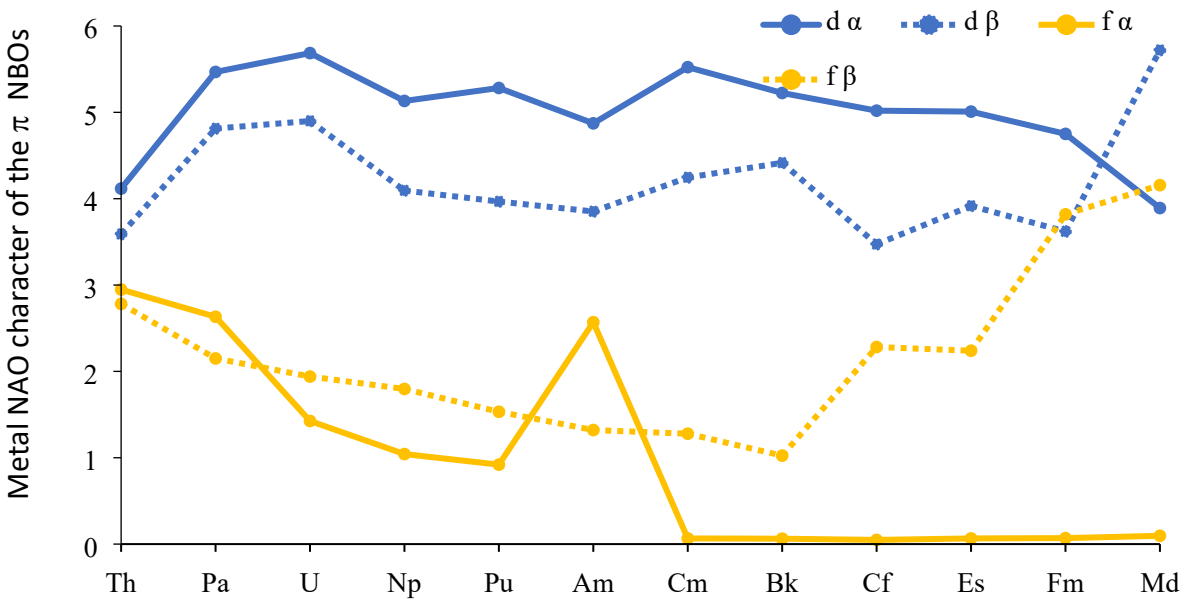
(b) β

Figure SI14- The overlap of the metal and chlorine Natural Hybrid Orbitals in $AnCl_2$ and $AnCl_3$[27] (An = Th–Md) for the α (a) and β spin (b). No is omitted as it did not converge on *σ* type + *π* type NBO for all three An-Cl bonds for $NoCl_3$.

Trichlorides



(a) σ-type



(b) π-type

Figure SI15 - Actinide d and f natural atomic orbital contributions (%) to the (a) σ type and (b) π type NBOs for $AnCl_3$. $NoCl_3$ is omitted as it did not converge on σ type + π type NBO for all three An-Cl bonds. From previous work[27]

XYZ

Th	0.00000000	0.00000000	0.12983900
Cl	0.00000000	2.51176200	-0.34369100
Cl	0.00000000	-2.51176200	-0.34369100
U	0.00000000	0.00000000	0.44021000
Cl	0.00000000	2.14811000	0.88406600
Cl	0.00000000	-2.14811000	0.88406600
Pa	0.00000000	0.00000000	0.39352400
Cl	0.00000000	2.08191700	-1.05325500
Cl	0.00000000	-2.08191700	-1.05325500
Np	0.00000000	0.00000000	0.39381700
Cl	0.00000000	2.04550200	-1.07720500
Cl	0.00000000	-2.04550200	-1.07720500
Pu	0.00000000	0.00000000	0.35839800
Cl	0.00000000	2.17351200	-0.99086600
Cl	0.00000000	-2.17351200	-0.99086600
Am	0.00000000	0.00000000	0.37420100
Cl	0.00000000	2.12662000	-1.04556200
Cl	0.00000000	-2.12662000	-1.04556200
Cm	0.00000000	0.00000000	0.32281000
Cl	0.00000000	2.16477000	-0.91145400
Cl	0.00000000	-2.16477000	-0.91145400
Bk	0.00000000	0.00000000	0.30825000
Cl	0.00000000	2.17272000	-0.87943000
Cl	0.00000000	-2.17272000	-0.87943000
Cf	0.00000000	0.00000000	0.34308000
Cl	0.00000000	2.15189400	-0.98887800
Cl	0.00000000	-2.15189400	-0.98887800
Es	0.00000000	0.00000000	0.32786600
Cl	0.00000000	2.15912300	-0.95466800
Cl	0.00000000	-2.15912300	-0.95466800
Fm	0.00000000	0.00000000	0.32043400
Cl	0.00000000	2.15948600	-0.94245300
Cl	0.00000000	-2.15948600	-0.94245300
Md	0.00000000	0.00000000	0.26874600
Cl	0.00000000	2.27329500	-0.79833400
Cl	0.00000000	-2.27329500	-0.79833400

No	0.00000000	0.00000000	0.30911700
Cl	0.00000000	2.17660200	-0.92735000
Cl	0.00000000	-2.17660200	-0.92735000

Lower Multiplicity Structures

Cm	0.00000000	0.00000000	0.37149500
Cl	0.00000000	2.04791200	-1.04892800
Cl	0.00000000	-2.04791200	-1.04892800

Bk	0.00000000	0.00000000	0.35722300
Cl	0.00000000	2.13841200	-1.01913700
Cl	0.00000000	-2.13841200	-1.01913700