Electronic Supplementary Material (ESI) for RSC Advances.

f-orbital covalency in the actinocenes (An=Th-Cm): multiconfigurational studies and topological analysis

Electronic Supplementary Information

Complex	$a_g \oplus b_{1g}$		$a_u \oplus b_{1u}$	
	S	W	S	W
$ThCOT_2$	1.952, 1.952	0.012, 0.012	1.948, 1.948	0.008, 0.008
$PaCOT_2$	1.954, 1.950	0.018, 0.018	1.942, 1.942	0.018, 0.016
$UCOT_2$	1.976, 1.976	0.022, 0.014	1.948, 1.956	0.040, 0.020
$NpCOT_2$	1.965, 1.964	0.020, 0.014	1.928, 1.935	0.090, 0.026
$PuCOT_2$	1.978, 1.978	0.026, 0.014	1.870, 1.910	0.210, 0.046
$AmCOT_2$	1.978, 1.980	0.022, 0.012	1.772, 1.880	0.296, 0.044
$CmCOT_2$	1.981, 1.983	0.018, 0.010	1.959, 1.873	1.105, 0.044

Table S1: Natural orbital occupations of the strongly (S) and weakly (W) occupied orbitals of a_g/b_{1g} symmetry and a_u/b_{1u} symmetry. Occupations are summed since in the full (D_{8h}) symmetry of the complexes considered here $a_{g/u} \oplus b_{1g/1u}$ spans $e_{2g/2u}$. Pairs of values correspond to α- and β-occupations.

Complex	An-C: ρ_{BCP} (a.u.)	An-C: $\nabla^2\rho_{BCP}$ (a.u.)
$ThCOT_2$	0.0432	0.117
$PaCOT_2$	0.0472	0.124
$UCOT_2$	0.0476	0.135
$NpCOT_2$	0.0475	0.140
$PuCOT_2$	0.0471	0.145
$AmCOT_2$	0.0455	0.149
$CmCOT_2$	0.0426	0.147

Table S2: Values of the electron density (ρ) and its Laplacian ($\nabla^2\rho$) evaluated at the metal-carbon bond critical point in $AnCOT_2$.

Complex	N(An) (a.u.)	q(An) (a.u.)
$ThCOT_2$	87.47	2.53
$PaCOT_2$	88.60	2.40
$UCOT_2$	89.78	2.22
$NpCOT_2$	90.86	2.14
$PuCOT_2$	92.03	1.97
$AmCOT_2$	93.18	1.82
$CmCOT_2$	94.12	1.88

Table S3: QTAIM calculated atomic populations and atomic charges of the An centres in $AnCOT_2$.

Complex	λ (a.u.)	Z-λ (a.u.)
$ThCOT_2$	85.89	4.11
$PaCOT_2$	86.86	4.14
$UCOT_2$	88.02	3.98
$NpCOT_2$	89.11	3.89
$PuCOT_2$	90.34	3.66
$AmCOT_2$	91.59	3.41
$CmCOT_2$	92.73	3.27

Table S4: QTAIM calculated localisation indices and differences between atomic number and λ(An) of the An centres in $AnCOT_2$.

Complex	λ^{π} (a.u.)	$\lambda^{5f_{\delta}}$ (a.u.)	$\lambda^{6d_{\delta}}$ (a.u.)
$ThCOT_2$	0.235	0.048	0.147
$PaCOT_2$	0.319	0.111	0.169
$UCOT_2$	0.412	0.185	0.190
$NpCOT_2$	0.521	0.304	0.182
$PuCOT_2$	0.805	0.595	0.179
$AmCOT_2$	1.000	0.817	0.156
$CmCOT_2$	2.058	1.890	0.141

Table S5: Orbitally resolved localisation indices for $AnCOT_2$.

Complex	δ^{π} (a.u.)	δ^{π} (a.u.)	$\delta^{5f_{\delta}}$ (a.u.)	$\delta^{6d_{\delta}}$ (a.u.)
$ThCOT_2$	0.198	0.163	0.0288	0.0558
$PaCOT_2$	0.218	0.168	0.0355	0.0551
$UCOT_2$	0.220	0.172	0.0403	0.0565
$NpCOT_2$	0.218	0.169	0.0427	0.0577
$PuCOT_2$	0.212	0.161	0.0396	0.0517
$AmCOT_2$	0.198	0.150	0.0337	0.0496
$CmCOT_2$	0.174	0.128	0.0160	0.0487

Table S6: Orbitally resolved delocalisation indices for $AnCOT_2$.