

Crystallographic Structure and Crystal Field Parameters in the $[\text{An}(\text{DPA})_3]^{2-}$ series, An=U , Np , Pu.

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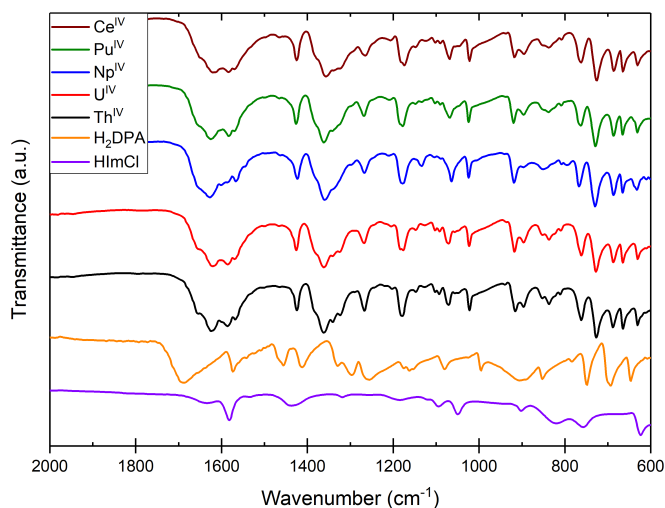


Figure S1: IR spectra of $[\text{An}(\text{DPA})_3] \cdot (\text{C}_3\text{H}_4\text{N}_2)_2 \cdot (\text{H}_2\text{O})_3$ for An=Th, U, Np and Pu, imidazole and H₂DPA

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Table S1: Quantum numbers for the ground state of the free ions. n is the number of $5f$ electrons, L , S , J are orbit, spin and total quantum numbers, g_J the Landé factor.

An	n	L	S	J	g_J
U ^{IV}	2	5	1	4	4/5
Np ^{IV}	3	6	3/2	9/2	8/11
Pu ^{IV}	4	6	2	4	3/5

Table S2: Standard deviation (in cm⁻¹) of the energies of the N_{st} first states calculated with methods meth1 and meth2.

meth1=orca	SF-CASSCF	SF-NEVPT2	SF-NEVPT2	SO-CASSCF	SO-NEVPT2	SO-NEVPT2
meth2=molcas	SF-CASSCF	SF-SSCASPT2	SF-MSCASPT2	SO-CASSCF	SO-SSCASPT2	SO-MSCASPT2
U ^{IV}						
N_{st}	11 27	11 27	11 27	9 63 90	9 63 90	9 63 90
σ	10 56	511 724	236 434	2 4 4	62 28 83	32 27 76
Np ^{IV}						
N_{st}	13 40	13 40	13 40	10 100 200	10 100 200	10 100 200
σ	1 16	117 97	78 110	1 42 38	49 145 194	58 141 192
Pu ^{IV}						
N_{st}	13 40	13 40	13 40	9 100 200	9 100 200	9 100 200
σ	4 70	207 314	193 317	3 88 79	29 161 221	22 158 226

$$\sigma = \sqrt{\sum_{I=1}^{N_{st}} (E_I^{meth1} - E_I^{meth2})^2} / N_{st}$$

Table S3: Bond length, LoProp charges, QTAIM atomic charges and descriptors at the BCPs of the M-O and M-N bonds in the $[\text{Ln}(\text{DPA})_3]^{3-}$ and $[\text{An}(\text{DPA})_3]^{2-}$ series. All values are averaged over the 6 M-O or 3 M-N bonds respectively.

	Xrays		LoProp			Integrated prop.			Descriptors at bond critical points							
	$R(\text{\AA})$		q			q			ρ_b (a.u.)		$\nabla^2\rho_b$ (a.u.)		$ V_b /G_b$ (a.u.)		H_b (a.u.)	
	M-O	M-N	M	O	N	M	O	N	M-O	M-N	M-O	M-N	M-O	M-N	M-O	M-N
Ln^{III}																
Ce	2.511	2.632	2.50	-0.77	-0.32	2.67	-1.38	-1.32	0.046	0.040	0.180	0.134	1.042	1.066	-0.002	-0.0024
Pr	2.454	2.597	2.51	-0.77	-0.32	2.57	-1.38	-1.32	0.044	0.041	0.176	0.143	1.019	1.066	-0.0009	-0.0026
Nd	2.471	2.577	2.52	-0.76	-0.32	2.41	-1.37	-1.33	0.045	0.042	0.185	0.147	1.025	1.063	-0.0011	-0.0025
Sm	2.454	2.552	2.52	-0.77	-0.32	2.49	-1.37	-1.32	0.045	0.042	0.193	0.155	1.009	1.042	-0.0004	-0.0017
Eu	2.443	2.538	2.53	-0.77	-0.32	2.52	-1.37	-1.34	0.045	0.042	0.198	0.159	1.003	1.035	-0.0001	-0.0015
Tb	2.410	2.499	2.52	-0.77	-0.32	2.55	-1.37	-1.34	0.047	0.043	0.210	0.168	0.996	1.028	0.0002	-0.0012
Dy	2.408	2.491	2.52	-0.77	-0.31	2.56	-1.39	-1.32	0.046	0.043	0.210	0.173	0.989	1.024	0.0006	-0.0011
Ho	2.396	2.477	2.52	-0.77	-0.31	2.68	-1.39	-1.32	0.045	0.043	0.209	0.174	0.983	1.019	0.0009	-0.0008
Er	2.395	2.463	2.51	-0.77	-0.31	2.41	-1.37	-1.33	0.051	0.044	0.241	0.179	0.999	1.014	0.0000	-0.0006
Tm	2.376	2.448	2.51	-0.77	-0.31	2.43	-1.36	-1.33	0.046	0.044	0.219	0.181	0.977	1.012	0.0013	-0.0005
Yb	2.372	2.439	2.52	-0.77	-0.31	2.38	-1.36	-1.32	0.046	0.044	0.217	0.181	0.977	1.014	0.0012	-0.0006
An^{IV}																
U	2.380	2.543	3.17	-0.81	-0.35	3.20	-1.38	-1.38	0.067	0.054	0.251	0.168	1.149	1.163	-0.011	-0.0082
Np	2.368	2.513	3.19	-0.81	-0.35	3.10	-1.36	-1.40	0.068	0.056	0.259	0.182	1.143	1.158	-0.0108	-0.0085
Pu	2.354	2.500	3.21	-0.81	-0.35	3.10	-1.37	-1.39	0.069	0.057	0.271	0.187	1.134	1.153	-0.0107	-0.0085
others																
Tm SF ^a	2.376	2.448	2.51	-0.77	-0.31	2.43	-1.36	-1.33	0.046	0.044	0.220	0.181	0.976	1.010	0.0013	-0.0005
U SF ^a	2.380	2.543	3.17	-0.81	-0.35	3.20	-1.37	-1.41	0.067	0.053	0.249	0.174	1.151	1.137	-0.0111	-0.0069
U SF SS ^b	2.380	2.543	3.17	-0.81	-0.35	3.19	-1.37	-1.41	0.067	0.053	0.249	0.174	1.149	1.134	-0.0110	-0.0067

a: Spin-free ground state from a state average procedure. *b*: Spin-free ground state from a state specific procedure.

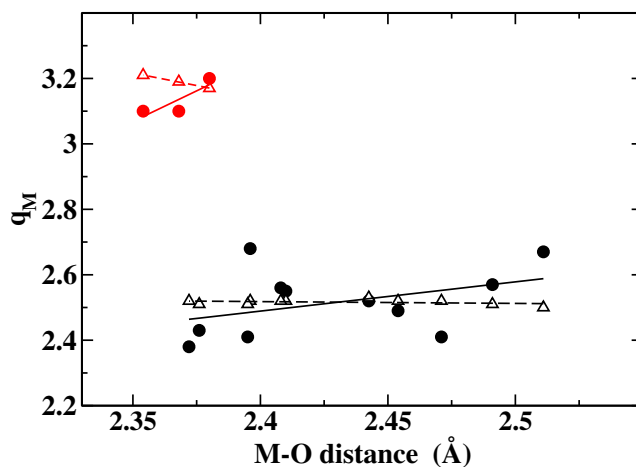


Figure S2: Atomic charge of the metal center determined by QTAIM (circles) and LoProp (triangles) methods as a function of the M-O distance (Å) in the [Ln(DPA)₃]³⁻ (black) and [An(DPA)₃]²⁻ (red) series. Straight lines show linear regressions.

Table S4: Mulliken charges per orbital type and charge (Mulliken and LoProp) of the metal center from CASSCF in the [An(DPA)₃]²⁻ series.

6s	6p	5f	7s	7p	6d	ch-mull	ch-loprop
U ^{IV}							
1.95	5.90	2.55	0.25	0.36	1.10	1.79	3.17
Np ^{IV}							
1.95	5.89	3.49	0.27	0.37	1.12	1.85	3.19
Pu ^{IV}							
1.93	5.86	4.46	0.30	0.38	1.15	1.86	3.21

Table S5: δm_u (μ_B) and δh (cm^{-1}) distances between *ab initio* and model matrices (see Eqs. 7 and 8) for the $[\text{An}(\text{DPA})_3]^{2-}$ series.

	δm_X	δm_Y	δm_Z	δh
U^{IV}				
SF-CASSCF	0.90	0.92	0.89	761
SO-CASSCF	0.51	0.50	0.49	80
SO-SSCASPT2	0.49	0.48	0.42	124
SO-MSCASPT2	0.51	0.50	0.49	199
Np^{IV}				
SF-CASSCF	0.53	0.53	0.56	300
SO-CASSCF	0.70	0.73	0.39	171
SO-SSCASPT2	0.73	0.75	0.40	219
SO-MSCASPT2	0.69	0.77	0.35	142
Pu^{IV}				
SF-CASSCF	0.45	0.45	0.48	214
SO-CASSCF	1.03	0.99	0.39	217
SO-SSCASPT2	1.94	2.12	0.51	488
SO-MSCASPT2	1.13	1.15	0.39	256

Table S6: CFPs (in cm^{-1}) in the $[\text{An}(\text{DPA})_3]^{2-}$ series.

		B_0^2	\bar{B}_1^2	\bar{B}_2^2	B_0^4	\bar{B}_1^4	\bar{B}_2^4	\bar{B}_3^4	\bar{B}_4^4	B_0^6	\bar{B}_1^6	\bar{B}_2^6	\bar{B}_3^6	\bar{B}_4^6	\bar{B}_5^6	\bar{B}_6^6
U^{IV}																
AILFT	SO-CASSCF	647	280	35	-2202	574	135	3034	138	-1681	40	259	2541	279	118	3210
	SO-NEVPT2	553	227	26	-1729	473	92	2495	128	-1488	34	239	2388	259	98	3095
ITO	SF-CASSCF	935	218	38	-1538	397	206	3231	86	-1005	120	67	2439	58	190	3345
	SO-CASSCF	662	217	26	-2324	382	172	3006	80	-1056	64	32	1368	58	132	1780
	SO-SSCASPT2	552	168	50	-1354	349	192	3193	42	-886	41	87	1127	128	75	1447
	SO-MSCASPT2	477	88	32	-1269	56	344	3647	332	-1146	104	490	1054	273	98	1422
Np^{IV}																
AILFT	SO-CASSCF	619	206	6	-1930	469	119	2507	99	-1747	44	193	2326	196	115	3102
	SO-NEVPT2	496	166	5	-1435	355	90	1934	78	-1321	32	141	1713	137	86	2337
ITO	SF-CASSCF	970	193	24	-1373	264	42	1940	56	-1729	176	65	2345	157	287	3099
	SO-CASSCF	329	179	40	-1927	221	58	1732	73	-1127	118	62	1959	125	256	2460
	SO-SSCASPT2	254	163	62	-1788	305	130	2053	66	-1121	175	39	2005	125	242	2316
	SO-MSCASPT2	-181	291	146	-1920	421	272	2533	127	-624	198	161	1897	134	288	2252
Pu^{IV}																
AILFT	SO-CASSCF	622	171	27	-1910	502	168	2356	84	-1689	40	183	2218	156	155	2911
	SO-NEVPT2	482	130	20	-1434	382	128	1792	63	-1394	33	146	1804	127	128	2389
ITO	SF-CASSCF	252	140	24	-1623	469	148	2374	111	-1599	35	195	2385	168	183	2848
	SO-CASSCF	1016	182	201	-174	70	10	292	6	-137	4	16	164	6	12	189
	SO-SSCASPT2	654	425	453	359	180	37	195	236	-167	78	71	95	100	34	99
	SO-MSCASPT2	1624	122	361	-199	65	34	312	27	-129	3	20	186	10	18	196

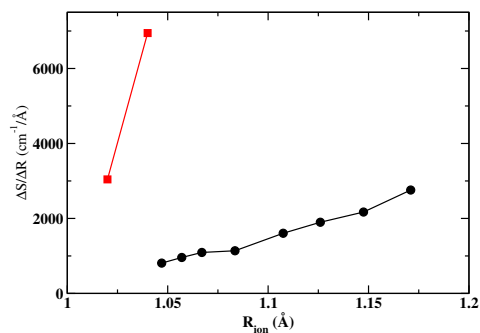


Figure S3: Variation of the crystal field strength with respect to the ionic radius $\Delta S/\Delta R$ ($\text{cm}^{-1} \cdot \text{\AA}^{-1}$) in $[\text{Ln}(\text{DPA})_3]^{3-}$ (black, taken from [1]) and $[\text{An}(\text{DPA})_3]^{2-}$ (red) series.

Table S7: Slater-Condon parameters and SOC parameter in cm^{-1} calculated with AILFT in the $[\text{An}(\text{DPA})_3]^{2-}$ series.

	F^2	F^4	F^6	ζ
U^{IV}				
SO-CASSCF	72007	47087	35539	1992
SO-NEVPT2	51022	43593	30756	
Np^{IV}				
SO-CASSCF	75777	49551	37091	2296
SO-NEVPT2	55146	40573	33777	
Pu^{IV}				
SO-CASSCF	78978	51671	38487	2604
SO-NEVPT2	58191	43283	35492	

References

- [1] Jung, J.; Islam, M. A.; Pecoraro, V. L.; Mallah, T.; Berthon, C.; Bolvin, H. Derivation of lanthanide series crystal field parameters from first principles. *Chem. Eur. J.* **2019**, *25*, 15112–15122.