Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

UV-vis-NIR spectrophotometry:

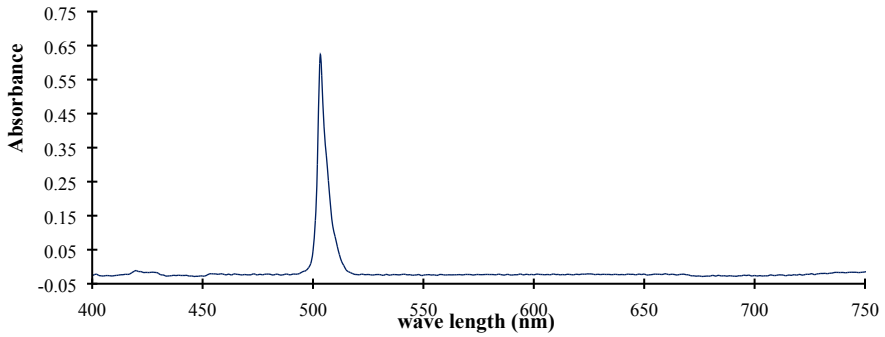

Figure ESI 1: UV-vis-NIR spectrum of Am(III) solution ($C_{Am(III)}$ = 1.6·10^{-3}M) in 1M perchloric medium (sample 1-1).

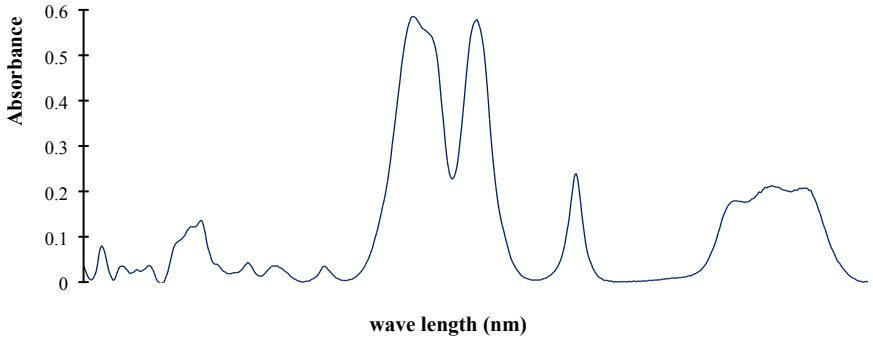

Figure ESI 2: UV-vis-NIR spectrum of Pu(III) solution ($C_{Pu(III)}$ = 1.57·10^{-2}M) in 1M perchloric medium (sample 2).

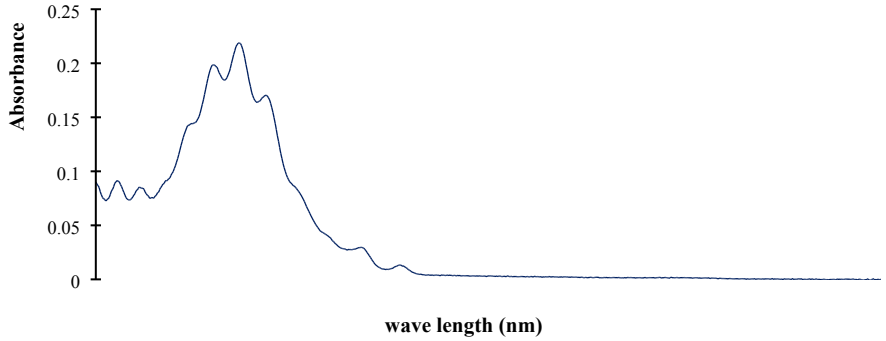

Figure ESI 3: UV-vis-NIR spectrum of U(VI) solution ($C_{U(IV)}$ = 2.835·10^{-2}M) in 1M perchloric medium (sample 3).

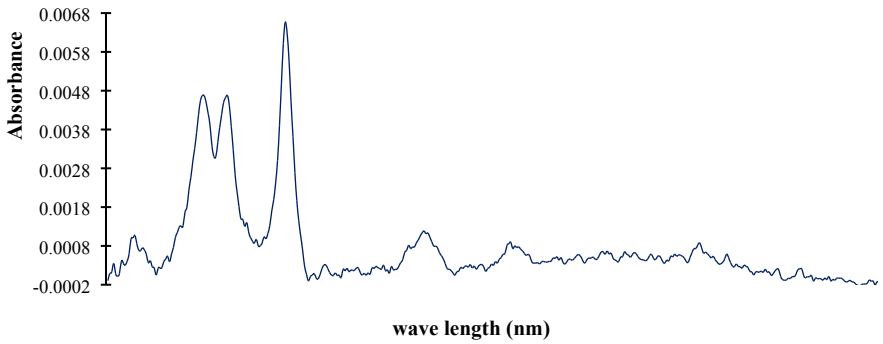

Figure ESI 4 : UV-vis-NIR spectrum of Cm(III) solution ($C_{Cm(III)}$ = 1.64·10^{-4}M) in 1M perchloric medium (sample 5).

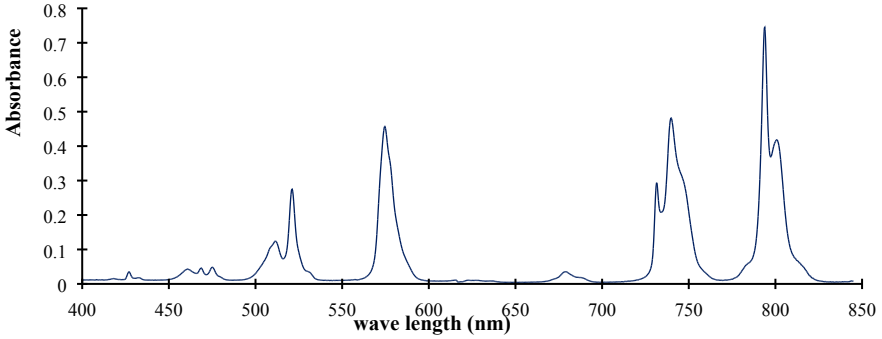

Figure ESI 5: UV-vis-NIR spectrum of Nd(III) solution ($C_{Nd(III)}$ = 6.27·10^{-2}M) in 1M perchloric medium (sample 6-9).

Temperature variation of magnetic susceptibility:

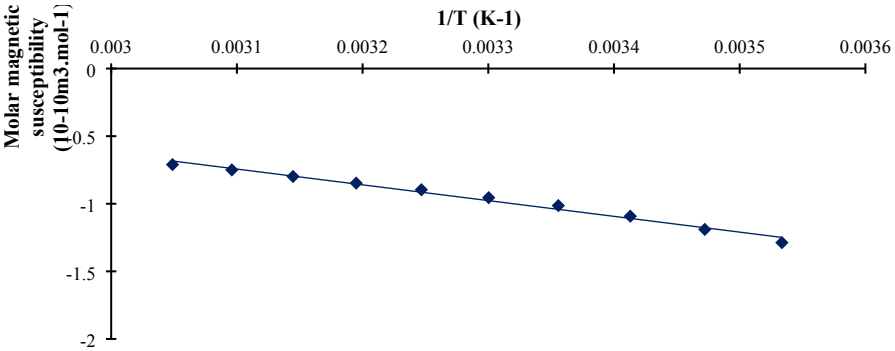

Figure ESI 6: Molar magnetic susceptibility variation vs. 1/T for $HClO_4$ solution.

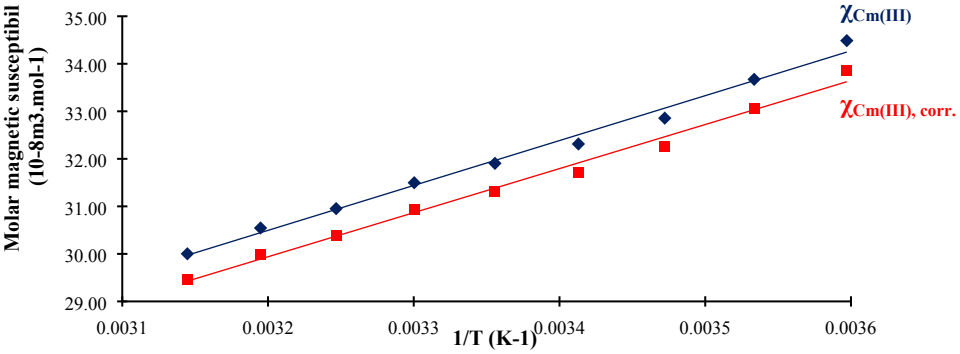

Figure ESI 7: Molar magnetic susceptibility variation vs. 1/T for sample 5 before ($\chi_{Cm(III)}$) and after ($\chi_{Cm(III),\ corr.}$) correction of the α emission effect in 1M perchloric medium.

Computation results:

Table ESI 1: Energy (cm^{-1}) of the free ion levels of Pu^{3+} calculated with GRASP, SO-CASSCF and SO-CASPT2. 21 sextets, 188 quartets and 143 doublets are considered in the SO step for SO-CASSCF and SO-CASPT2.

J	GRASP	SO-CASSCF	SO-CASPT2
5/2	0	0	0
7/2	2737	3130	3464
9/2	5513	6271	6809
3/2	8044	8418	7179
1/2	8071	8586	7474
11/2	8167	9086	9632
5/2	8432	8758	7368

Table ESI 2: Curie constants C (10^{-8} $m^3.K.mol^{-1}$) and temperature-independent susceptibilities χ_{TI} ($10^{-8}m^3.mol^{-1}$) from SO-CASPT2 calculations for Pu^{3+}. LS space: states included in the SO calculation; J space: states included in the calculation of χ.

LS space	J space	ΔE	C	χ_{TI}
^{6}H	5/2		111	0.00
^{6}H	5/2;7/2	1762	106	0.55
^{6}H;^{4}G	5/2		141	0.00
^{6}H;^{4}G	5/2;7/2	2676	141	0.33

Table ESI 3: Energy gaps ΔE_I in cm^{-1}, magnetic moments M_I^u in μ_B, Boltzmann weights P_I, truncated magnetization $M_u^{0\to k}$ in μ_B and magnetic susceptibility χ_M in $m^3.mol^{-1}$ for $[Pu(H_2O)_9]^{3+}$ in a magnetic field of 9.4 Tesla and at T=298 K. Diagonalization of Hamiltonian of Eq. (1) is performed with 6 electronic states.

	ΔE_I	M_I^u	P_I	$M_u^{0\to k}$	χ_M
Direction z	0	0.346	1.00	0.346	
	3	-0.333	0.98	0.009	$0.64\cdot10^{-8}$
	138	0.435	0.51	0.096	
	142	-0.436	0.50	0.007	$0.51\cdot10^{-8}$
	230	0.449	0.33	0.051	
	233	-0.461	0.32	0.005	**$0.40\cdot10^{-8}$**
Direction x	0	0.275	1.00	0.275	
	2.3	-0.250	0.99	0.014	$1.06\cdot10^{-8}$
	139	0.095	0.51	0.030	
	140	-0.093	0.51	0.009	$0.20\cdot10^{-8}$
	230	0.130	0.33	0.021	
	232	-0.157	0.33	0.007	**$0.52\cdot10^{-8}$**
Direction y	0	0.288	1.00	0.288	
	2.4	-0.271	0.99	0.010	$0.76\cdot10^{-8}$
	139	0.257	0.51	0.061	
	141	-0.260	0.51	0.006	$0.50\cdot10^{-8}$
	229	0.528	0.33	0.058	
	233	-0.543	0.32	0.005	**$0.40\cdot10^{-8}$**

Table ESI 4: Curie constants C (10^{-8} $m^3.K.mol^{-1}$), temperature-independent susceptibilities χ_{TI} ($10^{-8}m^3.mol^{-1}$) and susceptibility at 298 K from SO-CASPT2 calculations and experiment for $[Pu(H_2O)_n]^{3+}$ complexes. d_{Pu-OH_2} is the Pu-O distance (Å).

	d_{Pu-OH_2}	C	χ_{TI}	$\chi(298)$
$[Pu(H_2O)_9]^{3+}$	2.49	111.6	0.37	0.74
$[Pu(H_2O)_9]^{3+}$	2.39	99.9	0.39	0.77
$[Pu(H_2O)_9]^{3+}$	2.59	124.8	0.36	0.78
$[Pu(H_2O)_8]^{3+}$	2.39	79.5	0.44	0.70
$[Pu(H_2O)_{10}]^{3+}$	2.39	104.4	0.39	0.75
Exp.		231.9	-0.01	0.77
Exp. corrected		175.9	-0.13	0.46

Table ESI 5: Energy (cm^{-1}) of the free ion levels of Am^{3+} calculated with GRASP, SO-CASSCF and SO-CASPT2. 7 septets, 119 quintets and 91 triplets are considered in the SO step for SO-CASSCF and SO-CASPT2.

J	GRASP	SO-CASSCF	SO-CASPT2
0	0	0	0
1	1883	2011	2569
2	4098	4643	5775
3	6282	7060	8436
4	8339	9212	10601
5	10214	11171	12454
6	11792	12592	13530
0	14118	16213	15235

Table ESI 6: Temperature-independent susceptibilities χ_{TI} ($10^{-8}m^3$. mol^{-1}) from SO-CASPT2 calculations for Am^{3+}. LS space: states included in the SO calculation; J space: states included in the calculation of χ.

LS space	J space	ΔE	χ_{TI}
^7F	0;1	473	4.80
$^7F;^5D$	0;1	1402	1.58
$^7F;^5D;^3P$	0;1	2630	0.70

Table ESI 7 : Energy gaps ΔE_I in cm^{-1}, magnetic moments M_I^u in μ_B, Boltzmann weights P_I, truncated magnetization $M_u^{0\to k}$ in μ_B and magnetic susceptibility χ_M in m^3.mol^{-1} for $[Am(H_2O)_9]^{3+}$ in a magnetic field of 9.4 Tesla and at T=298 K. Diagonalization of Hamiltonian of Eq. (1) is performed with 4 electronic states.

	ΔE_I	M_I^u	P_I	$M_u^{0\to k}$	χ_M
Direction z	0	0.01192	1.00	0.01192	$0.890\cdot10^{-8}$
	2309	-0.0071	0.00002	0.01192	
	2313	0.15792	0.00002	0.01192	
	2430	-0.16274	0.00001	0.01192	**$0.890\cdot10^{-8}$**
Direction x	0	0.01188	1.00	0.01188	$0.887\cdot10^{-8}$
	2308	0.15422	0.00002	0.01188	
	2313	-0.00886	0.00002	0.01188	
	2430	-0.15724	0.00001	0.01188	**$0.887\cdot10^{-8}$**
Direction y	0	0.01076	1.00	0.01076	$0.803\cdot10^{-8}$
	2304	1.42244	0.00002	0.01079	
	2318	-1.42242	0.00001	0.01077	
	2430	-0.01076	0.00001	0.01077	**$0.804\cdot10^{-8}$**

Table ESI 8 : Energy (cm^{-1}) of the free ion levels of Cm^{3+} calculated with GRASP, SO-CASSCF and SO-CASPT2. 1 octuplet, 48 sextets and 76 quartets are considered in the SO step for SO-CASSCF and SO-CASPT2.

J	GRASP	SO-CASSCF	SO-CASPT2
5/2	0	0	0
7/2	25028	28011	23546
5/2	27459	28818	23896
7/2	28810	31302	28331
3/2	29348	32367	27641
9/2	30412	32568	29623

Table ESI 9 : Energy gaps ΔE_I in cm^{-1}, magnetic moments M_I^u in μ_B, Boltzmann weights P_I, truncated magnetization $M_u^{0\to k}$ in μ_B and magnetic susceptibility χ_M in m^3.mol^{-1} for Cm^{3+} in a magnetic field of 9.4 Tesla and at T=298 K. Diagonalization of Hamiltonian of Eq. (1) is performed with 8 electronic states.

	ΔE_I	M_I^u	P_I	$M_u^{0\to k}$	χ_M
Directions x, y, z	0	6.17	1.00	6.17	$4.604\cdot10^{-6}$
	7	2.61	0.97	4.42	$3.298\cdot10^{-6}$
	10	4.07	0.95	4.31	$3.216\cdot10^{-6}$
	18	0.48	0.92	3.39	$2.530\cdot10^{-6}$
	36	-0.52	0.84	2.69	$2.007\cdot10^{-6}$
	42	2.29	0.81	1.95	$1.455\cdot10^{-6}$
	55	4.49	0.77	1.16	$8.657\cdot10^{-7}$
	66	6.03	0.73	0.41	**$3.060\cdot10^{-7}$**

Table ESI 10 : Energy gaps ΔE_I in cm^{-1}, magnetic moments M_I^u in μ_B, Boltzmann weights P_I, truncated magnetization $M_u^{0\to k}$ in μ_B and magnetic susceptibility χ_M in $m^3.mol^{-1}$ for $[Cm(H_2O)_9]^{3+}$ in a magnetic field of 9.4 Tesla and at T=298 K. Diagonalization of Hamiltonian of Eq. (1) is performed with 8 electronic states.

	ΔE_I	M_I^u	P_I	$M_u^{0\to k}$	χ_M
Direction z	0	6.69	1.00	6.69	$4.992\cdot10^{-6}$
	26	4.37	0.88	5.60	$4.179\cdot10^{-6}$
	34	1.61	0.85	4.37	$3.261\cdot10^{-6}$
	42	1.13	0.82	3.62	$2.701\cdot10^{-6}$
	45	-.35	0.80	2.89	$2.157\cdot10^{-6}$
	60	-5.96	0.75	1.59	$1.187\cdot10^{-6}$
	65	-3.32	0.73	0.97	$7.239\cdot10^{-7}$
	75	-4.17	0.69	0.43	$\mathbf{3.209\cdot10^{-7}}$
Direction x	0	6.27	1.00	6.27	$4.679\cdot10^{-6}$
	6	3.30	0.97	4.80	$3.582\cdot10^{-6}$
	13	2.44	0.94	4.04	$3.015\cdot10^{-6}$
	19	1.10	0.91	3.34	$2.492\cdot10^{-6}$
	35	0.35	0.84	2.80	$2.090\cdot10^{-6}$
	43	-2.91	0.81	1.95	$1.455\cdot10^{-6}$
	55	-4.67	0.77	1.16	$8.657\cdot10^{-7}$
	67	-5.89	0.72	0.41	$\mathbf{3.060\cdot10^{-7}}$
Direction y	0	5.71	1.00	6.71	$5.007\cdot10^{-6}$
	5	4.13	0.97	4.93	$3.679\cdot10^{-6}$
	12	2.39	0.94	4.11	$3.067\cdot10^{-6}$
	23	0.99	0.89	3.37	$2.515\cdot10^{-6}$
	36	-0.06	0.84	2.75	$2.052\cdot10^{-6}$
	53	-2.39	0.82	1.98	$1.478\cdot10^{-6}$
	68	-4.79	0.77	1.14	$8.507\cdot10^{-7}$
	66	-5.98	0.71	0.41	$\mathbf{3.060\cdot10^{-7}}$

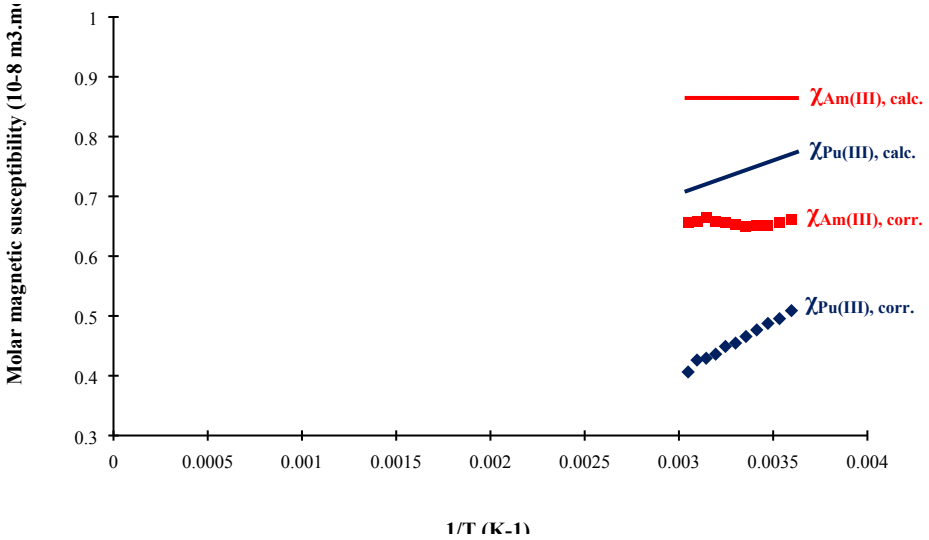

Figure ESI 8 : Experimental molar magnetic susceptibility variation vs. 1/T for sample 1-1 and 2 after correction of their α and β^- radioactivity in 1M perchloric medium ($\chi_{Am(III),\,corr.}$ and $\chi_{Pu(III),\,corr.}$) and calculated for $[Am(H_2O)_9]^{3+}$ and $[Pu(H_2O)_9]^{3+}$ ($\chi_{Am(III),\,calc.}$ and $\chi_{Pu(III),\,calc.}$).