Electronic Supplementary Material (ESI) for Chemical Science

Exploring the Solution Behavior of *f*-Element Coordination Compounds: A Case Study on some Trivalent Rare Earth and Plutonium Complexes

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TOC:

XAFS (X-Ray Absorption Fine Structure)

Pu L3 XAFS measurements were performed at the INE-Beamline for actinide research[S1] at the Ångströmquelle Karlsruhe, ANKA. The ANKA storage ring is operated at 2.5 GeV electron energy with a mean electron current of 120 mA. A pair of Ge(422) crystals ($2d$ = 2.310 Å) is used in the double crystal monochromator (DCM). Higher harmonic radiation in the incident beam was suppressed by the two mirrors in the optics of the INE-Beamline and by detuning the parallel alignment of the DCM crystals to 70% of maximum photon flux intensity at the beginning of each scan. The incident intensity is measured by an Ar-filled ionization chamber at ambient pressure and held constant by a digital MOSTAB feedback unit. Spectra were recorded in standard fluorescence detection mode at room temperature using a 5-pixel low-E solid-state Ge detector and recording windowed Pu Lα fluorescence intensity as a function of incident energy.

For the XAFS measurements in solution, 0.4 ml of the blue-green THF solution of **6** were filled into 0.4 ml capped polyethylene vials and mounted in a special air tight sample holder. The holder was loaded and sealed in an inert gas glove box, transported under Ar to the INE-Beamline and connected to an Ar supply line to guarantee constant inert gas flow during data acquisition. For the solid sample, 5 to 10 mg of the green-blue precipitate of **6** were re-crystallized from acetonitrile/diethylether. The resulting green-blue crystals were crushed to a fine powder, then filled into a 0.4 capped polyethylene vial and mounted into the same holder.

Pu L3 spectra photon energies were calibrated by assigning the first inflection point of the Zr *K*-XANES for a Zr metal foil simultaneously measured with the samples to 17998 eV. Three to four scans were recorded in transmission and fluorescence mode using a five-element Ge solid-state detector (Canberra LEGe type) and then averaged for subsequent analysis.

EXAFS oscillations were extracted and Fourier transformed (FT) using the Athena routine of the IFEFFIT software package (version 1.2.11).[S2] Metric parameters describing the first coordination shell surrounding the Pu cation were obtained: coordination numbers (C.N.), interatomic distances (R), mean square radial displacements or EXAFS Debye-Waller factors (σ^2), and relative shifts in ionization energy (ΔE_0). All fitting operations to data were performed in R space after Fourier transformation (k ranges: 1.84 - 12.08 $Å^{-1}$ (solid-state) and 1.93 - 10.16 $Å^{-1}$ (solution); R range: 1.27 - 2.51 Å (solid state), 1.22 - 2.73 Å (solution)) using k weightings of 1, 2, and 3 and using symmetric square windows with dk = 0.2 $Å^{-1}$ "Hanning sills". The amplitude reduction factor S_0^2 was held constant at 1 during fits; E_0 and Debye-Waller factors were varied. Theoretically calculated scattering phase-shifts and backscattering amplitude functions were used in the fits. These were calculated with the *ab initio* multiple-scattering code feff8.[S3] A cluster composed of 81 atoms (*e.g.*, the Pu cation, the ligand and all three triflate counter anions) with cartesian coordinates of the molecular structure of **6** (see main article) were used for the calculation. The EXCHANGE 3 2 1 control card in feff8 was specified (defines a Dirac-Hara local-density approximation for the real part of the photoelectron self-energy, a 2 eV real and 1 eV imaginary shift of the electron-gas estimated Fermi level), and muffin tins were automatically overlapped by default. The FT data was initially fit to the EXAFS equation using a model of one coordination shell containing N and O. Because these are $Z + 1$ elements, EXAFS cannot differentiate between them as backscattering nearest neighbors. Fits using N and those using O yielded essentially the same results. For all performed fits, the obtained r factor (overall goodness of fit) was 0.03 or smaller, which means that data and fit agree within 3% or better.

Table S1. Selected bond lengths [pm] and angles [°] of the compounds **1**,[a] **2**,[a] **3**, **4**, and **6**.

	1 (ligand)[a]	**2** (Y)[a]	**3** (La)	**4** (Sm)	**6** (Pu)
M–N_{Py}	n.a.	2.544(4)	2.664(5)	2.582(6)	2.611(2)
M–N_{Py}	n.a.	2.548(4)	2.695(5)	2.592(7)	2.622(2)
M–N_{Py}	n.a.	2.549(4)	2.693(5)	2.592(6)	2.628(3)
Av. M–N_{Py}[b]	n.a.	2.547(2)	2.68(1)	2.590(7)	2.620(7)
M–N_{Im}	n.a.	2.539(4)	2.688(5)	2.585(6)	2.639(2)
M–N_{Im}	n.a.	2.608(4)	2.707(5)	2.614(6)	2.646(2)
M–N_{Im}	n.a.	2.672(4)	2.787(5)	2.706(6)	2.754(2)
Av. M–N_{Im}[b]	n.a.	2.61(5)	2.76(5)	2.64(5)	2.68(6)
M–O	n.a.	2.311(3)	2.437(4)	2.368(5)	2.411(2)
M–O	n.a.	2.320(4)	2.461(4)	2.382(5)	2.429(2)
M–O	n.a.	232(4)/237(2)*	2.48(1)/2.52(2)*	2.43(5)/2.45(3)*	2.541(2)
P–N_{Me}	1.668(3)	1.650(4)	1.658(5)	1.653(6)	1.673(2)
P–N_{Me}	1.674(3)	1.681(4)	1.693(5)	1.676(7)	1.678(3)
P–N_{Me}	1.676(4)	1.690(4)	1.695(5)	1.684(7)	1.679(3)
P–S	1.912(2)	1.909(2)	1.906(2)	1.909(3)	1.917(1)
N_{Py}–M–N_{Py}	n.a.	73.8(1)	73.8(2)	73.6(2)	72.82(7)
N_{Py}–M–N_{Py}	n.a.	125.3(1)	129.0(2)	127.0(2)	131.93(7)
N_{Py}–M–N_{Py}	n.a.	139.7(1)	143.9(2)	140.5(2)	138.07(8)

[a] M. W. Löble, M. Casimiro, D. T. Thielemann, P. Oña-Burgos, I. Fernández, P. W. Roesky and F. Breher, *Chem. Eur. J.*, 2012, **18**, 5325.

[b] The error in the average bond lengths is equal to the standard deviation in the three experimental values.

* Disordered OTf positions.

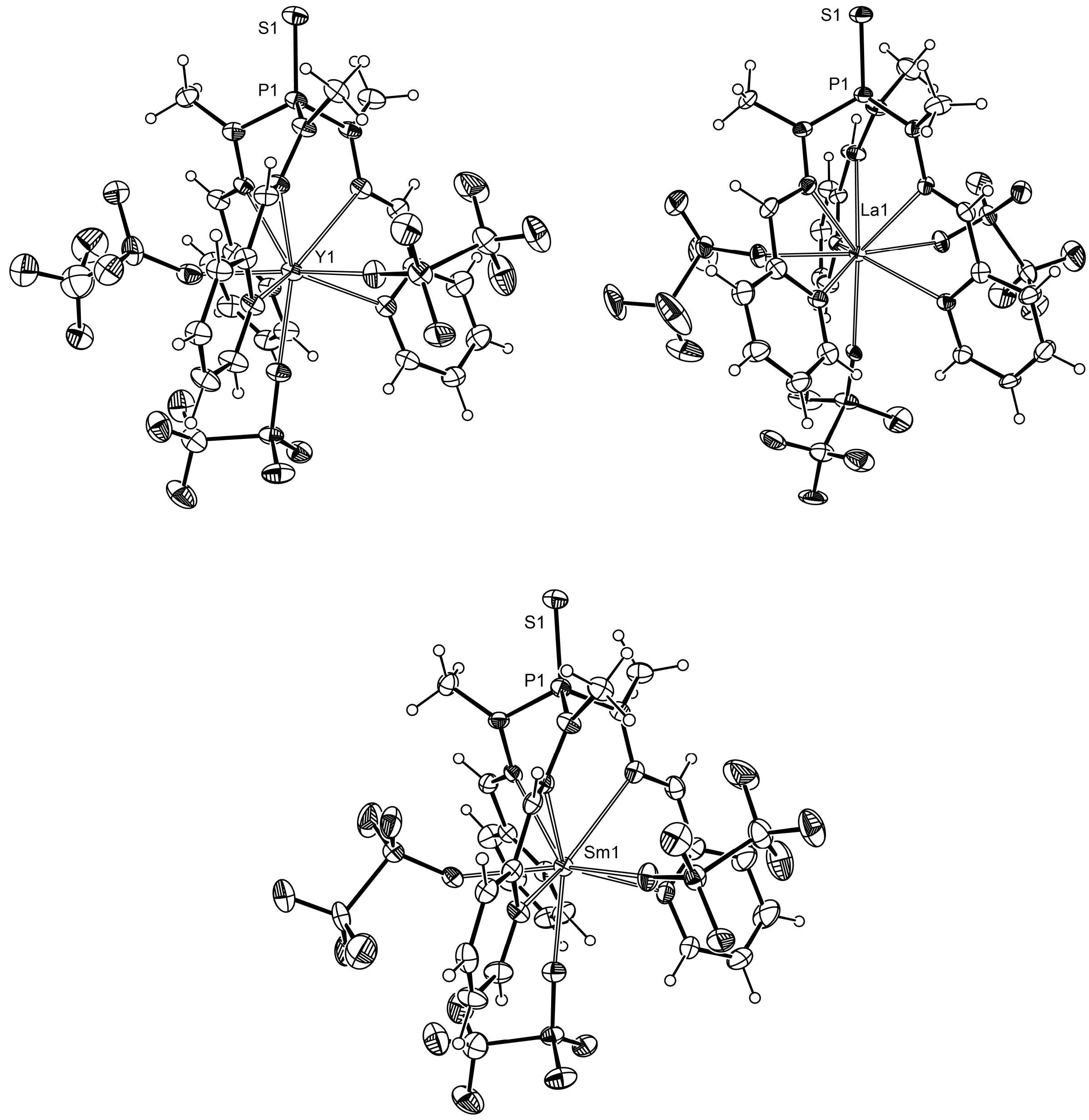

Figure S2. Molecular structures of compounds **2**-**4**; Anisotropic displacement parameters at the 30% probability level. Solvent molecules and disordered anion positions have been omitted for clarity. For selected bond lengths and angles see Table S1.

Table S2. Crystallographic data for **3** (La), **4** (Sm) and **6** (Pu).

Compound	**3**	**4**	**6**[a]
Empirical formula	$C_{24}H_{24}F_9N_9O_9PS_4La\cdot thf$	$2(C_{24}H_{24}F_9N_9O_9PS_4Sm)\cdot CH_3CN, Et_2O$	$C_{30}H_{33}F_9N_{12}O_9PPuS_4\cdot 3\ CH_3CN$
M	1123.75	2241.44	1277.89
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P{-1}$
a /pm	11.106(2)	9.764(2)	13.2866(4)
b /pm	16.930(3)	19.857(4)	13.3751(5)
c /pm	22.000(4)	22.899(5)	13.8490(5)
α /°			83.93
β /°	91.61(3)	97.37(3)	70.156(1)
γ /°			80.123(1)
V /$\cdot 10^6$ pm^3	4135(1)	4403(2)	2277.6(1)
μ /mm^{-1}	1.378	1.656	1.765
ρ_{calcd} /g cm^{-3}	1.805	1.691	1.863
Crystal dimensions /mm	0.20 × 0.20 × 0.10	0.30 × 0.30 × 0.20	0.09 x 0.08 x 0.05

Z	4	2	2
T /K	200(2)	200(2)	173(2)
$2\theta_{\max}$ /°	50.00	49.46	54.00
Refls. Measured	19618	29512	7875
Refls. Unique	7235	7495	7093
Parameters/restraints	625/238	665/304	607 / 0
R_1 [$I \geq 2\sigma(I)$]	0.0555	0.0601	0.0193
wR_2 (all data)	0.1109	0.1644	0.0493
max./min. res. elec. dens. /e $\cdot 10^{-6}$ pm^{-3}	0.640/–0.782	2.104/–0.969	1.025/–0.725

[a] Note that due to security reasons, measurements with radioactive samples are not performed over night and therefore a lower coverage of data was obtained (71.5% up to 54° 2θ). However, the data/parameter ration is >10 and , thus, sufficient.

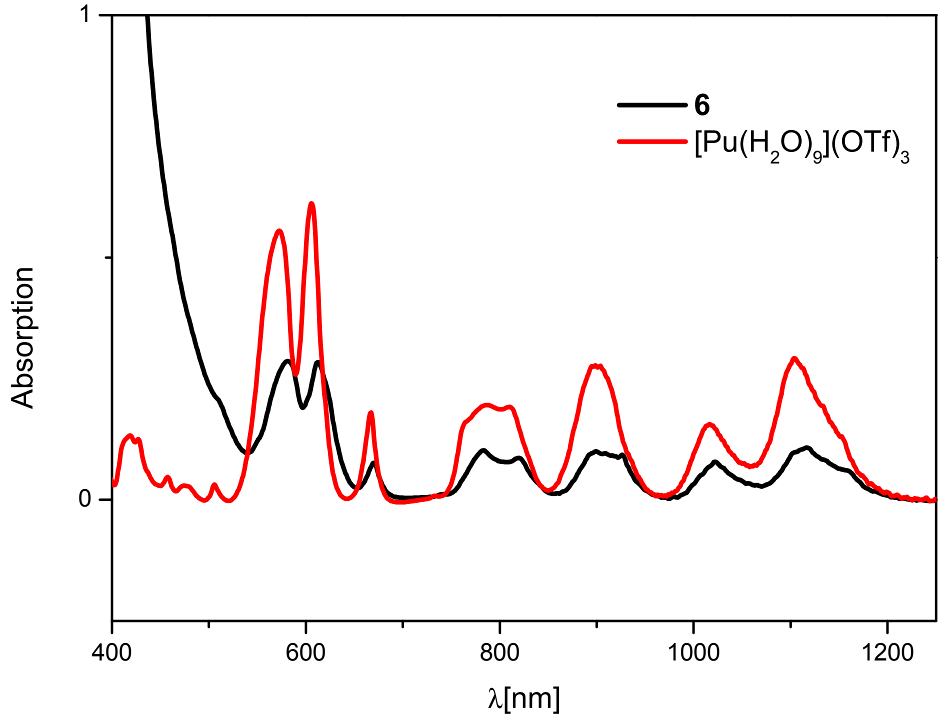

Figure S3. UV/Vis spectrum of **6** (black) and $[Pu(H_2O)_9](OTf)_3$ (red, for comparison) in acetonitrile solution.

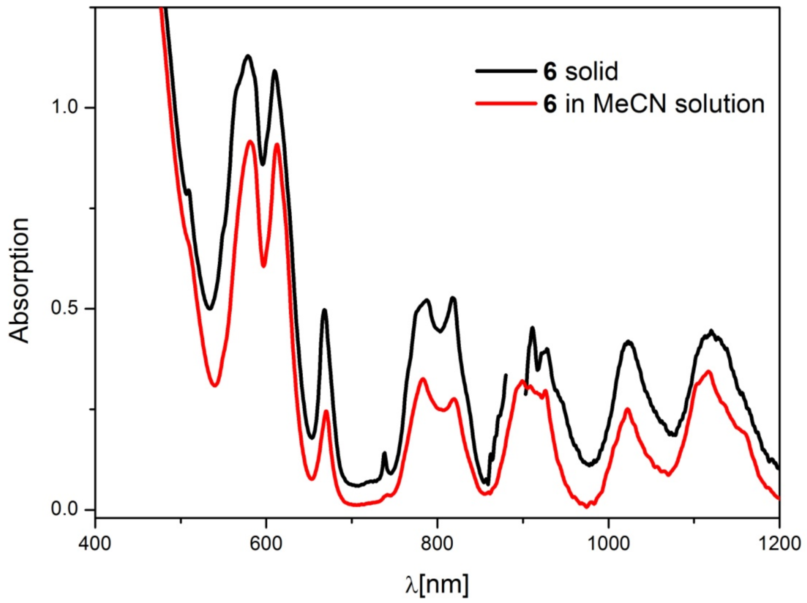

Figure S4. UV/Vis spectrum of **6** in solid state (black) and in acetonitrile solution (red).

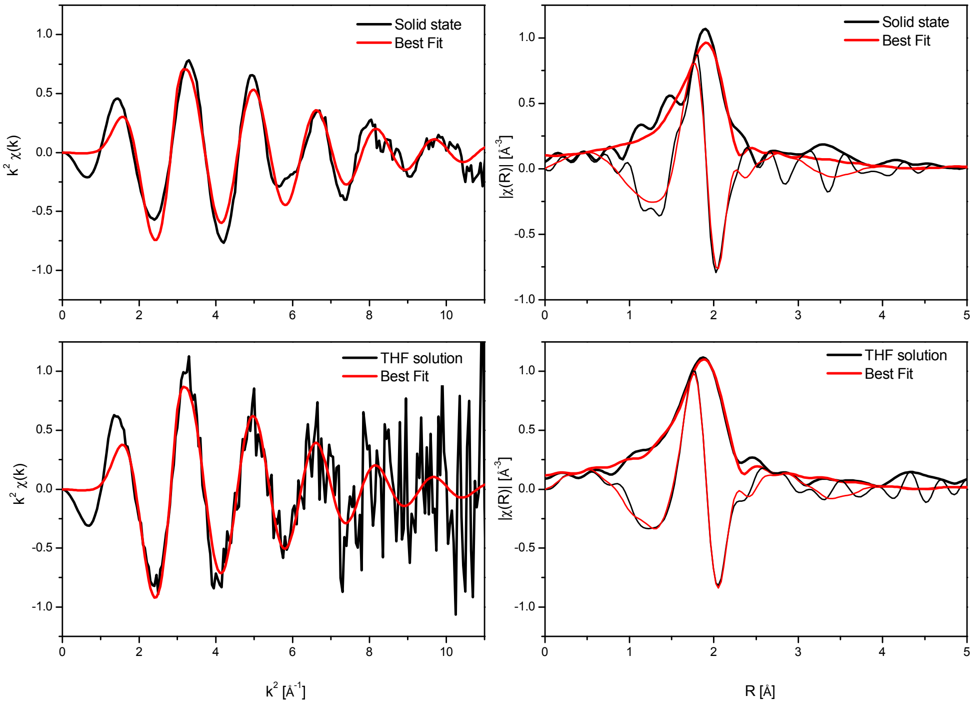

Figure S5. k^2-weighted $\chi(k)$-function (left panel, black data, red: back-transformed fit) and Fourier-transform (FT) (right panel, solid line: FT magnitude, thin solid line: FT imaginary part, black: data, re: R-space fit) for the Pu(III) compound [Pu(**1**)(OTf)$_3$] (**6**) in the solid state (top) and in THF solution (bottom).

Table S3. Diffusion coefficients (*D*) and hydrodynamic radii (r_H) for **2–6** at room temperature in d$_3$-acetonitrile.

Compound	*c* [Mol/L]	Nucleus	*Δ*(ms)	*D* (10^{-10} m^2 s^{-1})[a]	D_C/D_A[b]	r_H (Å)[c]	$r_{X\text{-ray}}$
3 (La)[d]	0.061	^{1}H	68-118	9.324	0.877	6.3	6.9
		^{19}F	68.5-118.5	10.637		5.6	
2 (Y)[e]	0.061	^{1}H	68-118	9.022	0.788	6.6	6.4
		^{19}F	68-118	11.455		5.2	
3 (La)[d]	0.030	^{1}H	68-117.5	10.015	0.852	6.2	6.9
		^{19}F	67.5-117	11.748		5.3	
4 (Sm)	0.030	^{1}H	68-93	9.987	0.789	6.2	6.4
		^{19}F	67.5-92.5	12.655		4.9	
5 (Lu)	0.030	^{1}H	68-93	9.704	0.725	6.4	n.a.
		^{19}F	67.5-67.75	13.376		4.6	
6 (Pu)	~0.030	^{1}H	67.5-117.75	9.334	0.655	6.3	6.5
		^{19}F	67.5-117.75	14.245		4.2	

[a] Error in experimental *D* value: ± 2 %.

[b] For "perfect" ion pairing one would expect a D_C/D_A value of 1. For the Pu complex **6**, a r_H value for the cationic part of the complex of 6.3 Å was detected, which is very similar to the ones observed for the rare earth complexes (6.2 – 6.6 Å). However, the smallest r_H value for the anionic part (4.2 Å) was observed for **6** furnishing a D_C/D_A value of 0.66 and, thus, the strongest tendency to form solvent-separated ion pairs within this series of complexes. In methanol, a solvent where ion pairing is minimal, the sizes (r_H) of solvated $[PF_6]^-$ and $[BF_4]^-$ anions were estimated to be about 2.5 - 2.8 Å, whereas for the solvated $[OTf]^-$ anion the value is ca. 3.0 - 3.3 Å.[S4] Assuming that the r_H value of the cation remains at *ca.* 6.3 Å (which would imply the coordination of solvent molecules instead of $[OTf]^-$), one can roughly estimate that the D_C/D_A value for "perfectly" separated ion pair approaches *ca.* 0.5.

[c] Viscosity $\eta = 0.363 \times 10^{-3}$ kg m^2 s^{-2} was taken from www.knovel.com.

[d] The first entry for **3** was used for Figure 4 of the main article.

[e] M. W. Löble, M. Casimiro, D. T. Thielemann, P. Oña-Burgos, I. Fernández, P. W. Roesky and F. Breher, *Chem. Eur. J.*, 2012, **18**, 5325.

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