

Supporting Information:
Insights from quantum chemical calculations
into inner and outer-sphere complexation of
plutonium(IV) by monoamide and carbamide
extractants

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Large-core and small-core pseudopotential results

Table S1: Calculated complexation energies for ligand exchange reactions (3) and (4). ΔE values are in kJ mol^{-1} and were calculated in the gas phase using PBE0 with large-core (LC) and small-core (SC) RECPs.

	inner-sphere		outer sphere	
	LC	SC	LC	SC
MEE \rightarrow EEE	4	2	0	0
EEE \rightarrow PEE	-4	-6	-6	-7
PEE \rightarrow IEE	12	16	38	36

Intrinsic properties of the ligands

Intrinsic properties of the ligands, such as basicity and electronic properties are important parameters for understanding their ability to bind a metal ion. We hereafter report atomic charges, molecular polarizabilities and proton affinities of the ligands, computed as the the enthalpy change associated with the following gas-phase reaction:



The computed atomic charges and molecular polarizabilities for the different ligands are reported in Table S2. Atomic charges were determined from a Natural Population Analysis (NPA).^{S1} The charges of the complexing oxygen atom are slightly affected by the lengthening of the alkyl chains, they vary from -0.61 to -0.63 for monoamides and from -0.63 to -0.65 for carbamides. Carbon and nitrogen electronic charges vary between monoamides and carbamides but do not vary significantly when changing the alkyl groups. The molecular polarizability shows a notable increase, from 8.9 \AA^3 for MMM to 15.9 \AA^3 for PEE. This rise was expected, since the increase in polarizability is equal to expected addition of polarizability for $-\text{CH}_2-$ groups ($\simeq 1.8 \text{ \AA}^3$ per group). As polarizability increases, the dispersion forces are expected to become stronger.

Table S2: Electronic atomic charges (NPA charges q_O , q_N and q_C), molecular polarizabilities (α in \AA^3) and proton affinity (PA) for the different amide ligands in kJ mol^{-1} , relative to that of the MMM ligand.

Charges	q_O	q_N	q_C	α	PA
MMM	-0.613	-0.409	0.653	8.9	0
MME	-0.614	-0.410	0.658	10.6	8
EMM	-0.617	-0.411	0.652	10.6	10
EEM	-0.618	-0.413	0.657	12.3	16
MEE	-0.621	-0.415	0.657	12.3	14
EEE	-0.625	-0.414	0.659	14.1	22
PEE	-0.623	-0.413	0.662	15.9	27
IEE	-0.628	-0.415	0.665	15.8	28
C4M	-0.631	-0.441	0.761	11.8	23
C4E	-0.652	-0.445	0.778	18.9	40

The proton affinities (PA) of the ligands relative to that of the MMM ligand are reported in Table S2. For monoamides, the protonation energy increases when substituting a methyl by an ethyl group, by 10 kJ mol^{-1} in R_1 position and by 8 kJ mol^{-1} in R_2 or R_3 positions. As expected, the proton affinities tend to increase with the oxygen electronic charge and with the size of the alkyl chain. A similar observation can be made for carbamides, the protonation affinity increased from 23 up to 40 kJ mol^{-1} by substituting methyl groups into ethyl. As reported in literature, for organic molecules the proton affinities tend to increase with the size and polarizability of the alkyl substituent.^{S2}

The structural parameters for geometry I

Table S3: Selected interatomic distances (average values d in Å)^a and hydrogen bond angle ($\alpha_{\text{O-H-O}}$) in ° calculated in the $[\text{Pu}(\text{NO}_3)_6](\text{HL}_2)$ complex in geometry I optimized the gas phase. ^a $O_{\text{nit}1}$ denotes oxygen from nitrate ions which are not involve in hydrogen bond. O_{nit} denotes oxygen from nitrate ions which are involved in hydrogen bond.

Ligand	$d_{\text{O}_{\text{nit}}-\text{O}_L}$	$d_{\text{Pu}-\text{O}_{\text{nit}1}}$	$d_{\text{Pu}-\text{N}_{\text{nit}2}}$	$d_{\text{Pu}-\text{N}_L}$	$d_{\text{Pu}-\text{C}_{\text{R}1}}$	α_{HOH}
MMM	2.568	2.544	2.976	5.605	4.910	169.8
MME	2.598	2.541	2.972	5.536	4.905	169.4
EMM	2.603	2.526	2.992	5.411	5.176	165.3
EEM	2.595	2.514	2.959	5.386	5.129	163.0
MEE	2.566	2.544	2.978	5.720	4.897	170.1
EEE	2.589	2.537	2.968	5.703	5.167	163.4
PEE	2.594	2.537	2.974	5.839	5.122	163.4
IEE	2.551	2.537	2.969	5.682	5.996	158.4
C4M	2.592	2.529	2.957	5.427	5.793	171.8
C4E	2.573	2.540	2.972	5.584	5.947	168.2

References

- (S1) Foster, J. P.; Weinhold, F. Natural hybrid orbitals. *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218, DOI: 10.1021/ja00544a007.
- (S2) Meot-Ner (Mautner), M. The proton affinity scale, and effects of ion structure and solvation. *Int. J. Mass Spectrom.* **2003**, *227*, 525 – 554, DOI: 10.1016/S1387-3806(03)00100-3.