

Comparative NMR study of partitioning-relevant complexes with trivalent actinides and lanthanides to elucidate the origin of their selectivity

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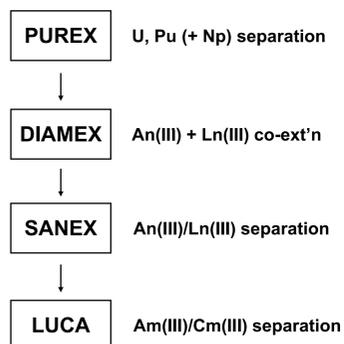
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Objectives

Long-term radiotoxicity of spent nuclear fuels is governed by plutonium and minor actinides (Np, Am, Cm). Separation of An(III) from Ln(III) is a crucial step for P&T and P&C strategies. BTPs are known to have high separation factors for trivalent actinides over lanthanides. Knowledge of the origin of their selectivity allows for a rational design in ligand development.

In current reprocessing strategies, spent nuclear fuel is dissolved in nitric acid. To facilitate a potential SANEX process co-extraction of nitrates is desirable, as otherwise charge compensating lipophilic anions are necessary. Previous studies showed strong dependence on charge compensating ions, but direct correlation to the hardness or size of the anion could not be determined.



NMR theory

Separation of all contributions to the observed chemical shift of certain ligand nuclei.

$$\delta^{obs} = \delta^{para} + \delta^{dia} = (\delta^{FCS} + \delta^{PCS}) + (\delta_{compl}^{dia} + \delta_{lig}^{dia} + \delta^{anion})$$

Paramagnetic contributions can be separated from the overall observed chemical shift by referencing to a isostructural diamagnetic complex. Subsequent splitting into a FERMI contact (δ^{FCS}) and a pseudo contact or dipolar part (δ^{PCS}) can be achieved by application of variable temperature measurements.

$$\delta^{para} \cdot T = \delta^{FCS} + \frac{\delta^{PCS}}{T}$$

BLEANEY methodology separates contact from pseudo contact contributions by extrapolation to infinitely high temperatures. The axis intercept is a measure of the covalency in the ligand metal bond, the slope is a measure for the dipolar interaction between ligand and paramagnetic metal ion.

Anions are essential for the charge compensation of the complexes. They either insert into the complex and compete with the organic ligands or coordinate to its surface. For a complete description of all contributions to the overall chemical shift of a nucleus in a complex, knowledge about solvent and anion effects on the structure is necessary.

Results

Effects of anions

BTP ligands lead to sterical hindrance in direct proximity to the central metal ion. Anions compete against N-donor ligands. **DFT calculations** (TURBOMOLE, BP86, TZVP-quality, Ln: f-in-core PP) of complexes with D_3 geometry slightly overestimate bond lengths [Å]. However, trends for distances of the anion to the metal center develop in opposite directions along the lanthanide series, while ligand-metal distances follow the cation size.

Ln	free complex			Chloride				Nitrate				
	N _{py}	N _{tr}	C _{para}	N _{py}	N _{tr}	C _{para}	Cl ⁻	O _{Nitrate}	N _{py}	N _{tr}	C _{para}	N _{Nitrate}
La	2,74	2,70	5,55	2,69	2,69	5,47	4,36	4,34	2,73	2,70	5,53	5,62
Sm	2,63	2,63	5,44	2,58	2,61	5,38	4,41	4,27	2,63	2,62	5,42	5,56
Eu	2,61	2,62	5,42	2,57	2,60	5,36	4,42	4,26	2,61	2,61	5,41	5,54
Yb	2,53	2,55	5,34	2,49	2,53	5,28	4,43	4,19	2,52	2,54	5,32	5,48
Lu	2,52	2,55	5,33	2,48	2,53	5,28	4,44	4,19	2,52	2,54	5,31	5,48

Table 1: Results from DFT calculations (TURBOMOLE, BP86, TZVP-quality, Ln: f-in-core PP). Along the lanthanide series the ligand distances (N_{py}) follow the trend of the lanthanide contraction. Chloride distances (Cl⁻) in contrast to Nitrate distances (O_{Nitrate}) develop in the opposite direction.

NMR results for Lutetium complexes:

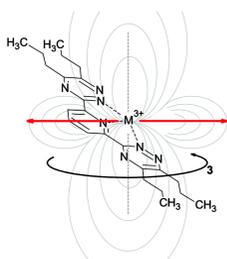
- NO₃⁻** – increase of electron density in the ligand (shift to negative values), nitrate inserts deeply into the pockets while displacing BTP
- Cl⁻** – decrease in electron density (shift to positive values), more efficient complexation of ligands, competition of anion against ligand
- ClO₄⁻** – (soluble) complexes incorporate anion by decreasing complexation efficiency (more shielding) to increase solubility

Lu	NO ₃ ⁻ [Hz]		Cl ⁻ [Hz]		ClO ₄ ⁻ [Hz]	
	¹ H	¹³ C	¹ H	¹³ C	¹ H	¹³ C
Position						
4	-5,8	-4	12,9	25	-23,1	—
3, 5	-7,1	-10	9,9	5	-14,5	—
2, 6	—	—	—	-9	—	—
7	—	-1	—	-5	—	—
10	—	-7	—	8	—	—
11	—	-6	—	14	—	—
13a	10,9	-5	13,6	-5	-15,7	—
13b	-7,7	-5	-1,4	-5	—	—
14	-0,6	-6	1,9	-1	16,7	—
15	-10,9	-4	-7,8	-3	2,4	—
16	-2,2	-0	8,5	1	-12,7	—
17	-5,7	8	-0,3	11	-8,1	—
18	-2,9	-1	1,0	-1	9,8	—

Table 2: Diamagnetic chemical shifts [Hz] of Lutetium complexes with different charge compensating anions. All shifts are referenced on the triflate complex, eliminating all metal dependent contributions.

Other Lanthanides:

Samarium and Europium complexes have approximately the same size. Corresponding to small PCS of Sm/Eu the observed additional paramagnetic effects are very small. In **Ytterbium complexes** these paramagnetic effects are more pronounced. **NO₃⁻** complexes show higher shifts towards positive values than **Cl⁻**. A direct extraction of anionic effects is hampered by the superimposed paramagnetic interactions. However, a change in ligand-metal distances leads to changes of the PCS isosurfaces where the observed nuclei are located.



Separation of paramagnetic contributions

Contributions to paramagnetic shift via temperature dependent measurements following BLEANEY methodology of complexes of the form [Ln(nPrBTP)₃](NO₃)₃. Error bars are smaller than the depicted symbols. Preliminary results with additional methods for the separation of the paramagnetic contributions suggest, that the BLEANEY methodology overestimates the FERMI contact contribution.

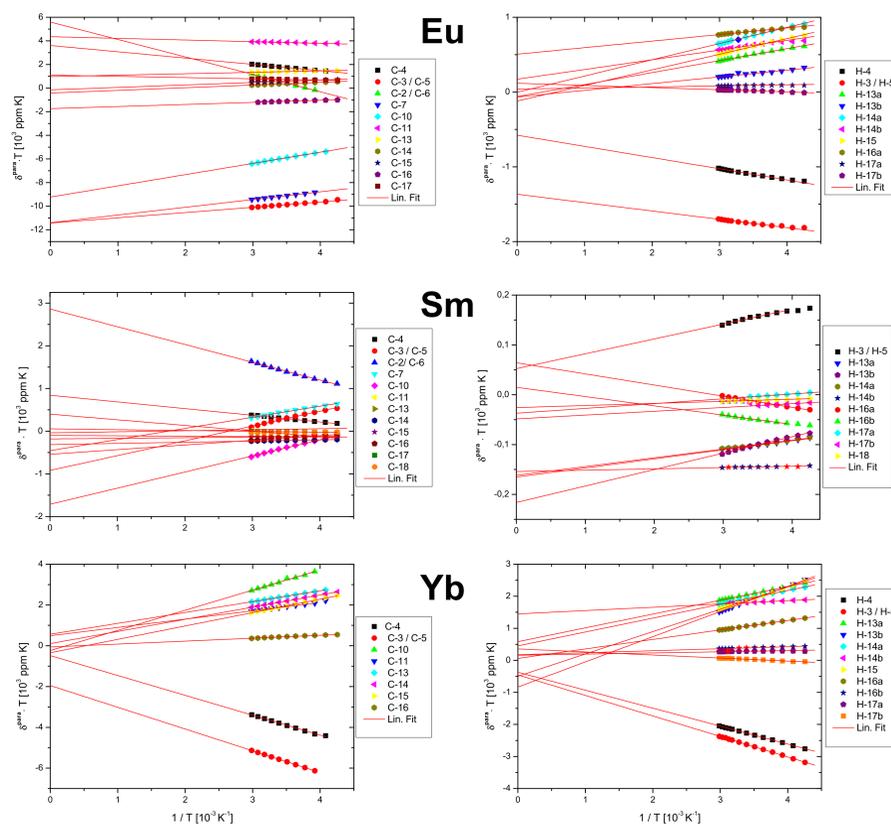


Figure 1: Graphical results of the linear regression according to BLEANEY methodologies, separating the FERMI contact contribution as axes intercept and the dipolar or pseudo contact contribution to the paramagnetic chemical shift as slope. The Pearson R of all linear fits exceeded 0,98.

¹ H	Europium [ppm]		Samarium [ppm]		Ytterbium [ppm]	
	δ ^{FCS}	δ ^{PCS}	δ ^{FCS}	δ ^{PCS}	δ ^{FCS}	δ ^{PCS}
4	-1,92	-1,66	—	—	-1,24	-6,23
3, 5	-4,56	-1,24	0,17	0,33	-1,52	-7,11
13a	-0,20	1,78	-0,55	0,20	1,94	4,78
13b	-0,16	0,93	-0,89	0,37	-2,78	8,73
14a	-0,01	2,41	-0,54	0,20	1,50	4,81
14b	0,57	1,43	-0,51	0,03	4,83	1,15
15	-0,40	2,32	—	—	-1,66	7,75
16a	1,69	0,97	0,21	-0,25	0,20	3,29
16b	—	—	0,05	-0,21	0,58	0,69
17a	0,13	0,16	-0,12	-0,11	0,53	0,40
17b	0,39	-0,33	-0,16	0,08	1,19	-1,06
18	—	—	-0,09	0,05	—	—

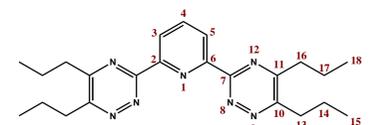


Figure 2: nPrBTP – n-Propyl-2,6-Bis(1,2,4-Triazin-3-yl)pyridin

High symmetry (D_3) leads to overall moderate paramagnetic chemical shifts. Differences in covalent to dipolar contributions to the chemical shift are mainly due to the change of the metal ion.

Europium: FERMI contact shift contributions are higher than pseudo contact part.

Samarium: Overall small contributions, FERMI contact and dipolar contribution are equal.

Ytterbium: Only small FERMI contact but high dipolar contribution detectable, paramagnetic relaxation enhancement (PRE) effects in core structure.

¹³ C	Europium [ppm]		Samarium [ppm]		Ytterbium [ppm]	
	δ ^{FCS}	δ ^{PCS}	δ ^{FCS}	δ ^{PCS}	δ ^{FCS}	δ ^{PCS}
4	12,0	-5,9	2,8	-1,7	-1,6	-10,8
3, 5	-38,1	5,0	3,1	3,8	-6,5	-11,9
2, 6	18,7	-16,4	9,5	-4,6	—	—
7	-38,0	7,3	1,5	2,9	—	—
10	-30,8	10,6	5,7	4,2	-0,8	11,0
11	14,5	-1,7	1,3	-1,5	1,6	4,5
13	3,3	1,4	0,3	-0,1	1,9	5,9
14	-1,4	2,5	1,0	0,3	0,4	6,6
15	-0,5	2,3	0,6	0,2	-1,1	7,3
16	-5,8	2,0	1,8	1,2	-0,2	1,6
17	3,7	-1,2	0,2	-0,2	—	—
18	—	—	0,2	0,1	—	—

Table 3/4: Paramagnetic shift contributions for ¹H and ¹³C calculated from parameters of the BLEANEY separations for 300K in [ppm].

FERMI contact contributions to the paramagnetic shift in lanthanide complexes can be found all over the complex. Their size depends mainly on the physical properties of the respective metal ion. Unpaired electron density can propagate over covalent bonds and is delocalised over the conjugated aromatic system and decays rapidly in the aliphatic decorations of the ligands.

Ongoing studies aim to extend the presented results on actinide complexes to elucidate the origin of the ligands' selectivity. Investigations on the first Americium complex are already completed.

Literature:

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