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Anionic effects observed in complexes of trivalent lanthanides with partitioning relevant N-donor ligands

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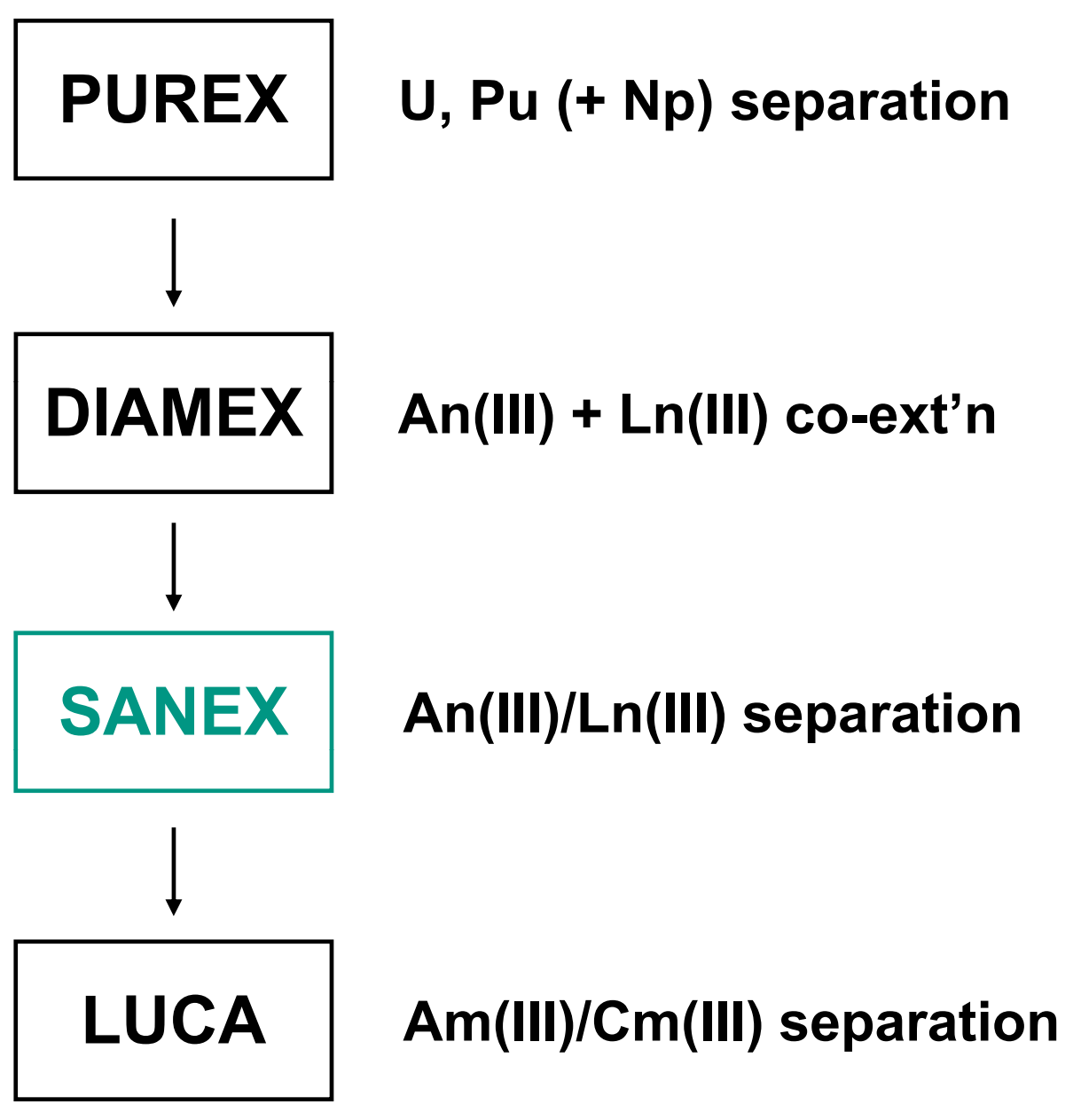
Objectives

In current reprocessing strategies, spent nuclear fuel is dissolved in nitric acid. Therefore ligands for all partitioning steps need a certain stability against acidic conditions. To facilitate a potential SANEX process co-extraction of nitrates is desirable, as otherwise charge compensating lipophilic anions are necessary.

Liquid-liquid extractions with BTPs from nitric acid solutions give outstanding separation factors of actinides over lanthanides. Previous studies showed strong dependence on charge compensating ions, but direct correlation to the hardness or size of the anion could not be determined.



PUREX U, Pu (+ Np) separation

DIAMEX An(III) + Ln(III) co-ext'n

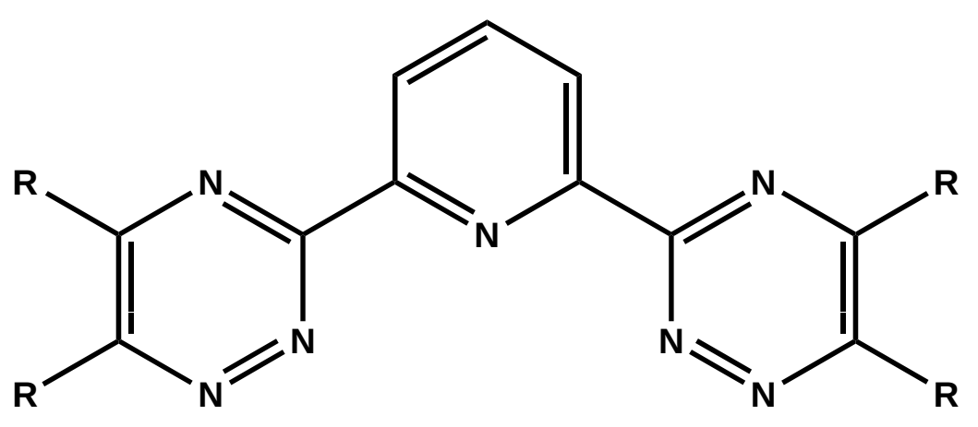
SANEX An(III)/Ln(III) separation

LUCA Am(III)/Cm(III) separation

Background

TRLFS studies of Eu and Cm BTP complexes with various anion concentrations show different thermodynamic stabilities with respect to the anion used.

Liquid-liquid **extraction studies** confirm dependence on charge compensating anion in solution.



BTP
(2,6-di(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine)

DFT calculations (TURBOMOLE, BP86, AVTZP-quality) of complexes with D_{3h} geometry slightly overestimate bond lengths [Å]. However, trends for distances of the anion to the metal centre develop in opposite directions along the lanthanide series, while ligand-metal distances follow the cation size.

	free complex			Chloride				Nitrate				
Ln	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

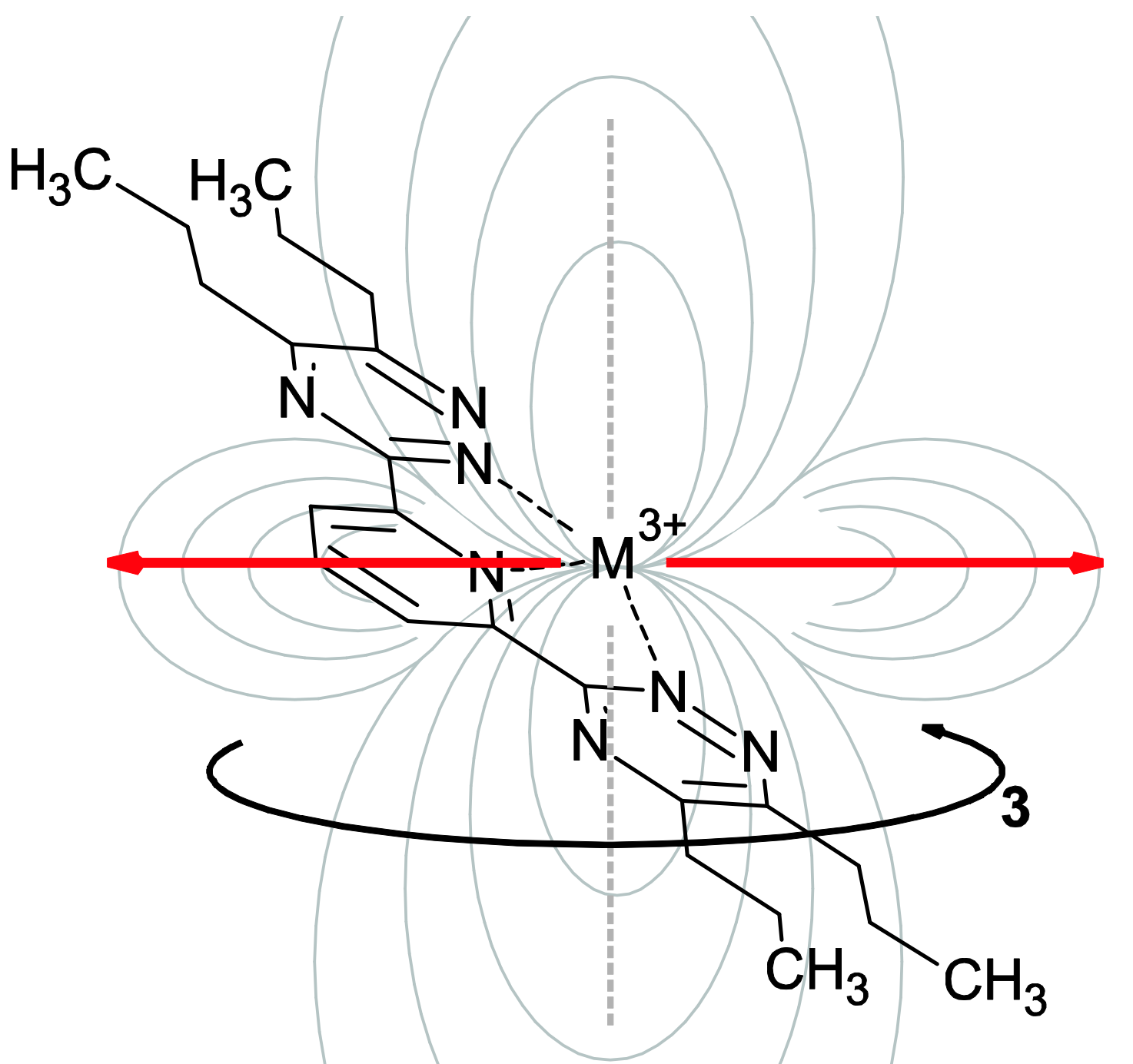
NMR theory

To fully describe the contributions to the overall chemical shift of a nucleus in a complex, knowledge about solvent and anion effects on the structure is necessary.

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

Diamagnetic complexes:
Direct influence on electronical structure of the ligand in the complex is accessible by subtraction of chemical shifts of two samples which only differ in the anion.

Paramagnetic complexes:
Observed changes in chemical shifts depend additionally on the PCS isosurface on which a nucleus is located. Small structural changes lead to elevated effects on the chemical shift. To quantify this paramagnetic effect precise knowledge about the relative amount of PCS to FCS in the observed complex is necessary. Changes will be attributed to distance dependent PCS. FCS is estimated to be constant.



Only relative shifts are accessible. Their size and content of information depend on the chosen reference compound. Here complexes with triflate as anion are selected, since triflate was expected not to insert into the complex.

Results

BTP ligands lead to sterical hindrance in direct proximity to the central metal ion
Anions compete against N-donor ligands

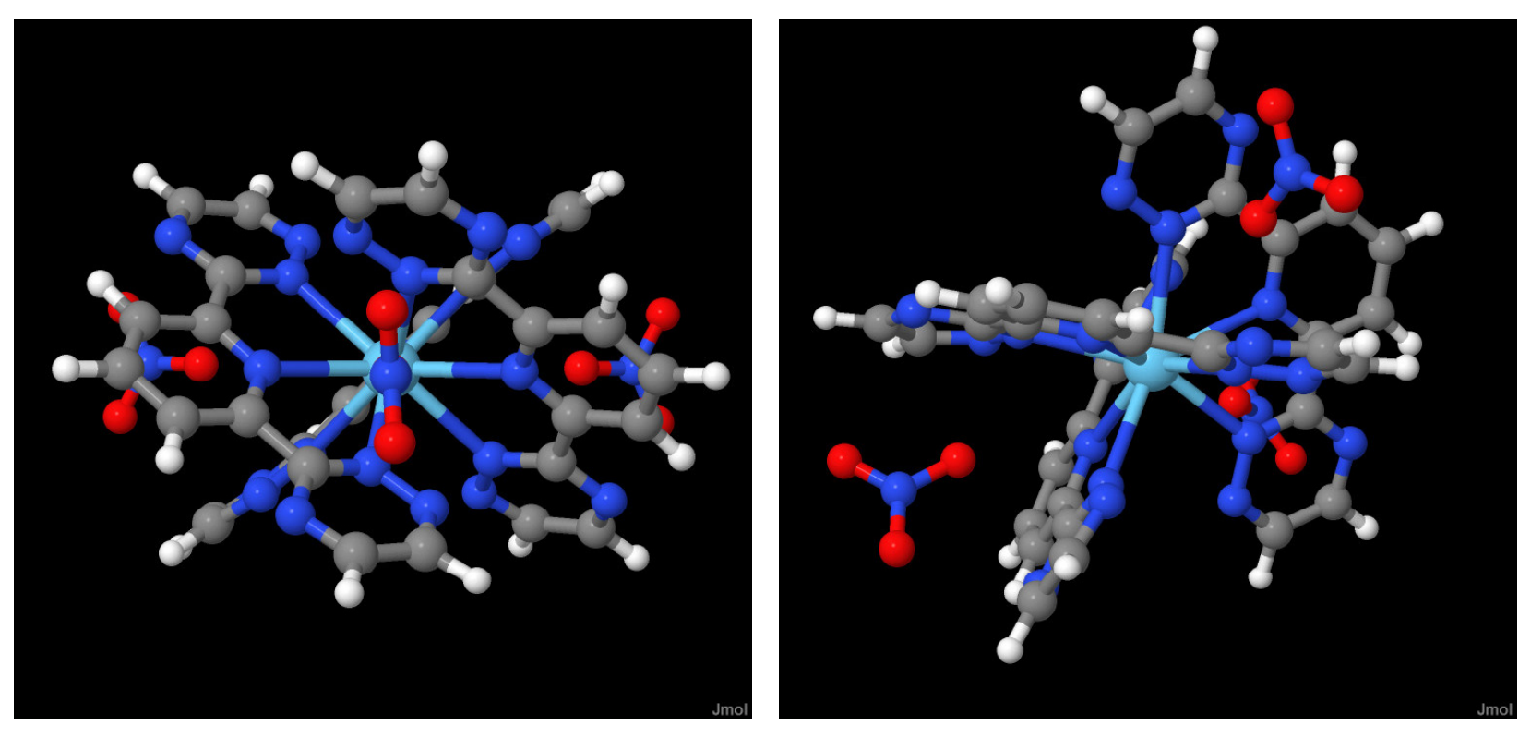
Lutetium complexes:
Lutetium is the smallest metal ion

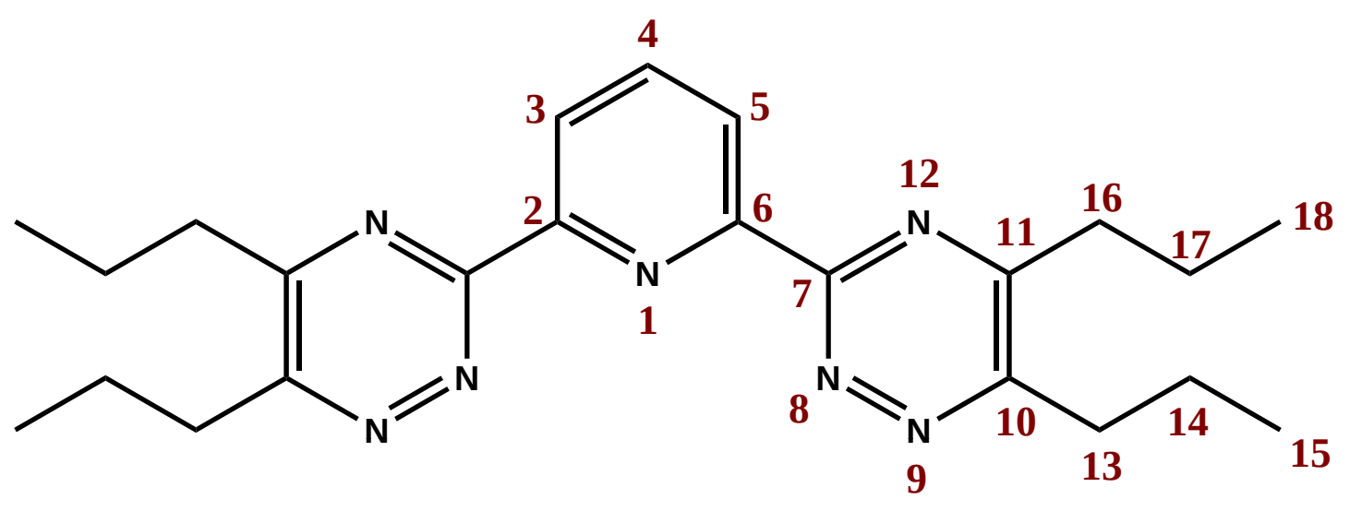
NO_3^- – increase of electron density in the ligand, inserts deeply into the pockets while displacing BTP

Cl^- – decrease in electron density, more efficient complexation of ligands, competition anion against ligand

ClO_4^- – (soluble) complexes incorporate anion by decreasing complexation efficiency (more shielding) to increase solubility

Lu	NO_3^- [Hz]		Cl^- [Hz]		ClO_4^- [Hz]	
Position	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
4	-5,8	-4	12,9	25	-23,1	—
3, 5	-7,1	-10	9,9	5	-14,5	—
2, 6	—	-1	—	-9	—	—
7	—	-1	—	-5	—	—
10	—	-7	—	8	—	—
11	—	-6	—	14	—	—
13a	10,9	-5	13,6	-5	-15,7	—
13b	-7,7		-1,4		—	—
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	—





Paramagnetic lanthanides
In addition to the effects in the Lu complexes paramagnetic shifts arise from different PCS isosurfaces for different distances of the observed nuclei to the metal ion.

Sm	NO_3^- [Hz]		Cl^- [Hz]		ClO_4^- [Hz]	
Position	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
4	-3,3	3	13,5	28	-14,5	—
3, 5	-3,9	-7	10,5	6	-8,8	-2
2, 6	—	-5	—	-10	—	—
7	—	-0	—	-3	—	3
10	—	-2	—	10	—	-11
11	—	1	—	18	—	-21
13a	-1,4	-5	0,7	-6	-1,9	4
13b	19,9		18,9		-8,3	

Eu	NO_3^- [Hz]		Cl^- [Hz]		ClO_4^- [Hz]	
Position	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
4	-10,3	14	4,3	35	-19,6	—
3, 5	2,6	-6	10,9	12	-14,8	—
2, 6	—	-3	—	-6	—	—
7	—	-23	—	-12	—	-11
10	—	16	—	29	—	16
11	—	0	—	14	—	18
13a	-37,8	-17	-16,0	-8	13,8	-0
13b	-17,4		6,4		-16,5	

Yb	NO_3^- [Hz]		Cl^- [Hz]		ClO_4^- [Hz]	
Position	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
4	36,9	20	35,9	36	-11,2	—
3, 5	28,2	15	31,3	16	-47,4	—
2, 6	—	—	—	—	—	—
7	—	—	—	—	—	—
10	—	-38	—	1	—	—
11	—	-35	—	-2	—	—
13a	-135,2	-21	-73,2	-6	76,8	—
13b	161,2		146,5		—	—

Samarium and Europium complexes:
Complexes have approx. the same size, paramagnetic effects are very small, corresponds to small PCS of Sm/Eu.

Ytterbium complexes:
Effects are more pronounced, *NO_3^-* shows higher shift towards positive values than *Cl^-*.

Conclusion
For a full description of all influences on the electron density distribution on the ligand and in consequence for the description of all contributions to the chemical shifts of all NMR active nuclei a concise knowledge of all anion and solvent effects is necessary.

Separation of paramagnetic components of the additional chemical shifts will help to measure distance effects of certain anions with even better accuracy.

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