Karlsruhe Institute of Technology

Institute for Nuclear Waste Disposal (INE)

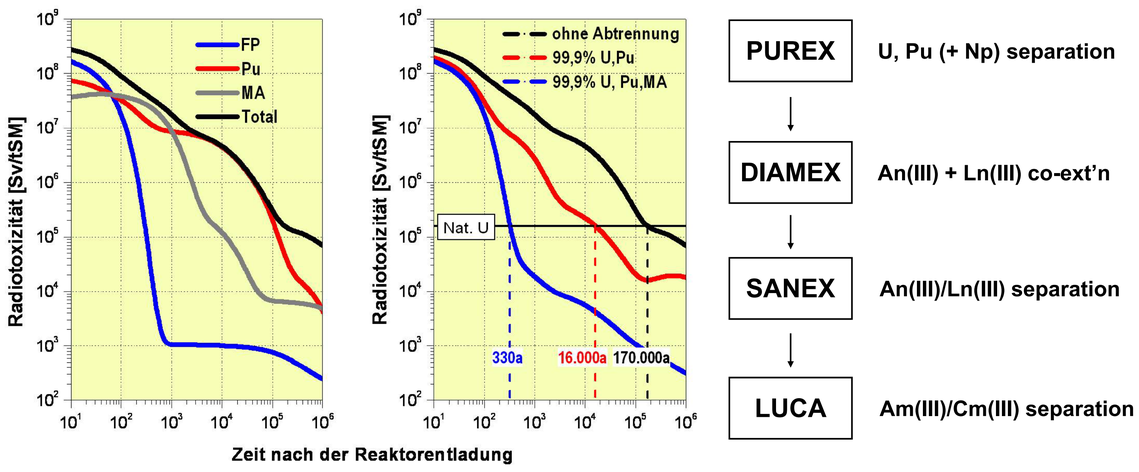
A comparative NMR study of complexes of trivalent actinides and lanthanides with partitioning relevant N-donor ligands

Christian Adam,[1,2] Andreas Geist,[1] Petra J. Panak,[1,2] Melissa A. Denecke,[1] Peter Kaden[1]

[1] Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), P.O. Box 3640, 76021 Karlsruhe, Email: christian.adam@kit.edu
[2] University of Heidelberg, Institute for Physical Chemistry, c/o KIT-INE, P.O. Box 3640, 76021 Karlsruhe

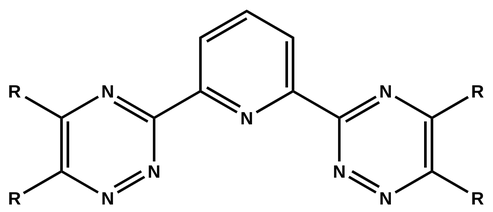
Objectives

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. Rational design in ligand development for liquid-liquid extraction is desirable.



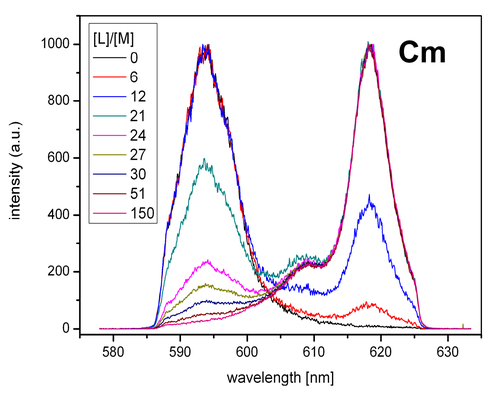
Background

Fundamental understanding on a molecular level of the origin of the selectivity of extracting ligands is necessary in order to develop new or further improve already established extraction systems.

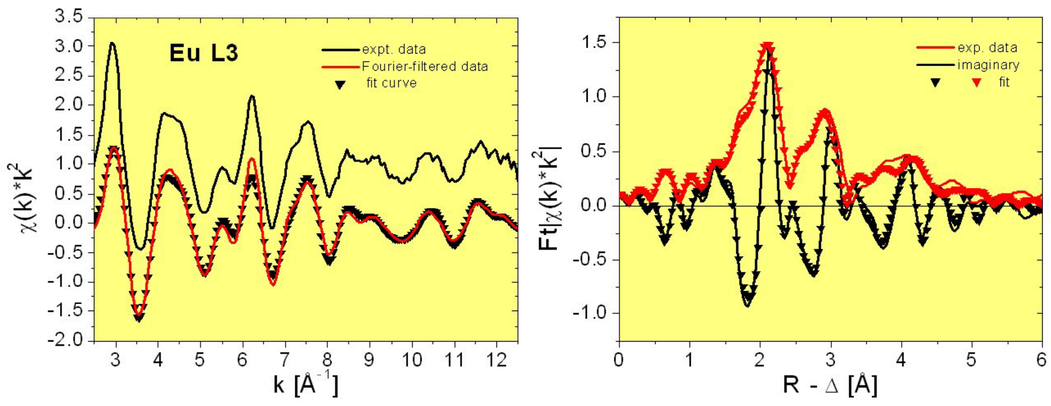


BTP
(2,6-di(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine)

TRLFS



Eu-L3-EXAFS



NMR theory

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

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

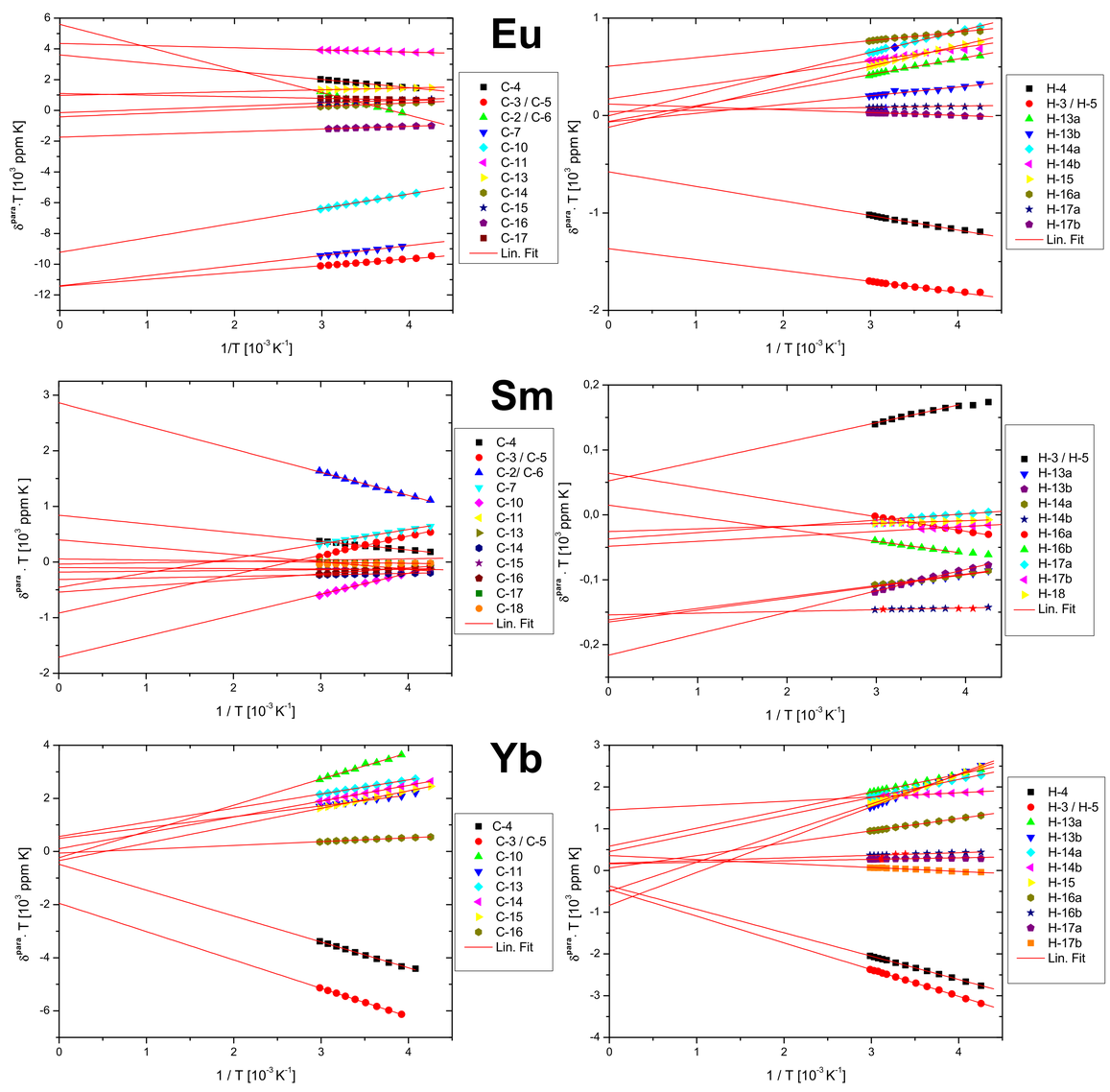
Paramagnetic contributions can be separated from the overall observed chemical shift by referencing to a isostructural diamagnetic complex. Subsequent splitting into a FERMI contact (δ^{FCS}) and a pseudo contact or dipolar part (δ^{PCS}) can be achieved by application of variable temperature measurements.

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

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.

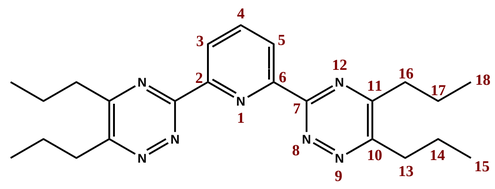
Results

Contributions to paramagnetic shift via temperature dependent measurements following BLEANEY methodology of complexes of the form $[Ln(nPrBTP)_3](NO_3)_3$. Error bars are smaller than the depicted symbols.



^{1}H	Europium [ppm]		Samarium [ppm]		Ytterbium [ppm]	
Position	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	—	—

^{13}C	Europium [ppm]		Samarium [ppm]		Ytterbium [ppm]	
Position	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	—	—



Eu:
FERMI contact shift contribution stronger than pseudo contact part

Sm:
Overall small contributions
FERMI contact and dipolar contribution are equal

Yb:
Only small FERMI contact but strong dipolar contribution detectable
PRE effects in core structure

Literature:

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