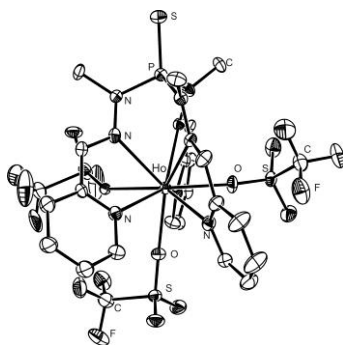


Solution Behaviour of f-Element Coordination Compounds

Löble, M., Karlsruhe/D, Fernández, I./Esp, Almería, Vitova, T., Karlsruhe/D,
Denecke, M.A., Karlsruhe/D, Breher, F., Karlsruhe/D

Prof. Dr. Frank Breher, Karlsruhe Institute of Technology (KIT), Institute of
Inorganic Chemistry, Engesserstrasse 15, D-76131 Karlsruhe, Germany.

Lanthanide coordination compounds consisting of N-Donor ligands have attracted considerable attention because of the rich spectrum of use in catalysis^[1], medicine^[2], in molecular magnetic compounds^[3] and for their spectroscopic properties.^[4] Especially in metal extraction processes like reprocessing of spent nuclear fuels, N-Donor ligands are thought to play a decisive role by removing long-lived isotopes of the minor actinides Americium and Curium from high-level radioactive waste (partitioning).^[5] This operation is followed by the transmutation of the actinides to short-lived isotopes. To understand the selectivity of existing extraction agents for actinide cations over their chemically similar lanthanide counterparts, to improve their performance and to develop new extraction ligands, a complete understanding of the bonding situation between the cation and the ligand, the influence of counter anions and the behaviour and properties of all existing species in solution is of crucial importance. We therefore prepared two easily accessible chelating ligand systems^[6] to study mononuclear and homobinuclear coordination compounds of *f*-elements.



We will present the synthesis and characterization of two κ^6 / κ^8 -N-donor ligands $\text{PS}(\text{N}^{\text{Me}}\text{NC}(\text{H})\text{Py})_3$ (L^1) and $[\text{B}(\text{N}^{\text{Me}}\text{NC}(\text{H})\text{Py})_4]^-$ (L^2), providing intrinsically well-defined 1:1 and 1:2 (ligand : metal) coordination compounds.^[7] Several complexes of trivalent 4*f* metal cations such as lanthanum and middle-sized lanthanides will be presented. All complexes of the general formula $[\text{Ln}(\text{L}^1)](\text{OTf})_3$ (see Ho compound on the left) and $[\text{Ln}_2(\text{L}^2)](\text{OTf})_5$ have been characterized in detail using various spectroscopic methods like XRD,

TRLFS and XAS either in the solid state or in solution. By combination with several advanced NMR techniques like ¹H¹⁹F-HOESY, PGSE, low temperature ¹⁹F-NMR, ¹³⁹La-NMR and ¹H⁸⁹Y-HMQC we were able to get first insights concerning the aggregation, dynamic behaviour and structural properties of these compounds in solution. These results represent initial efforts of a broader initiative to understand the solution behaviour of *f*-element coordination compounds.

References:

- [1] F. T. Edelman, *Chem. Soc. Rev.* **2009**, 38, 2253. [2] M. Woods, D. E. Woessner, A. D. Sherry, *Chem. Soc. Rev.* **2006**, 35, 500. [3] C. Benelli, D. Gatteschi, *Chem. Rev.* **2002**, 102, 2369. [4] J.-C. G. Bünzli, V. Eliseeva, *Chem. Soc. Rev.* **2010**, 39, 189. [5] Z. Kolarik, *Chem. Rev.* **2008** 108, 4208. [6] I. Kuzu, I. Krummenacher, J. Meyer, F. Armbruster, F. Breher, *Dalton Trans.* **2008**, 5836. [7] M. Loeble, T. Vitova, M. A. Denecke, I. Fernández, F. Breher, *in preparation*.