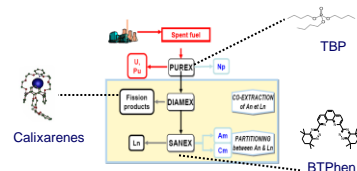


## INTRODUCTION:

The management of nuclear wastes remains a major problem for future generations, particularly the storage of highly radiotoxic wastes. The minor actinides [MA] are the main contributors to the long term radiotoxicity. The transmutation of MA leads to an important decrease in waste radiotoxicity but requires the separation of MA from the lanthanides [Ln] that are neutrophages. The partitioning of MA from Ln is particularly difficult because of trivalent Ln and actinides Ac have very similar properties. A family of new bis-triazine ligands were recently found to be remarkably selective extracting agents for the MA/Ln separation. However, their effectiveness decreases on going from a central pyridine ring (BTP) to a phenantroline (BTPhen) or bipyridine (BTBP) and finally to a terpyridine unit (BTTP).

We use several advanced NMR techniques in order to fully characterize Ac and Ln ions and their complexes with new promising extracting agents.

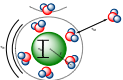


Strategy for the Nuclear Fuel Cycle in the 21<sup>st</sup> Century.

## First approach : use of relaxivity to determine the stoichiometry of complexes.

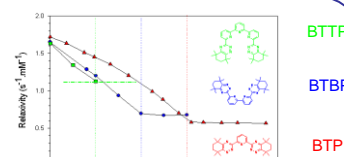
The dispersion of the longitudinal relaxation time  $T_1$  of the solvent nuclei with the magnetic field (NMRD) yields information on the magnetic properties and on the dynamic behavior of paramagnetic species. The relaxation rates  $1/T_{1,2}$  (or relaxivities) depend on (1) the solvation state, (2) the rotational correlation time  $\tau_r$ , (3) the electronic relaxation  $\tau_{el}$  and (4) the solvent exchange time  $\tau_m$ .

$$\left(\frac{1}{T_1}\right)_{\text{solvent}} = f(B_0, \tau_r, \tau_{el}) \left[ \frac{1}{\tau_m} = \frac{1}{\tau_r} + \frac{1}{\tau_{el}} + \frac{1}{\tau_m} \right]$$



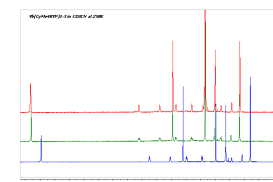
NMRD titrations are very useful for the determination of the stoichiometry of complexes. The relaxivity decreases when a ligand is added from paramagnetic centers until a plateau is reached when the complex is fully formed.

**BTP forms a tris-complex, BTBP forms a more solvated bis-complex and only a soluble 1:1 complex can be formed with BTTP.**



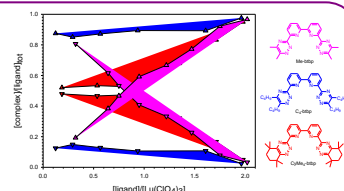
New J. Chem. 2006, 30, 1171

## Second approach: speciation in solution by NMR titration of diamagnetic complexes.



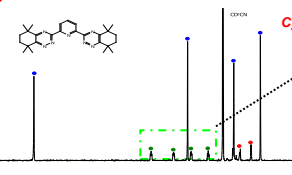
Recording the NMR spectra of solution's diamagnetic  $\text{Lu}(\text{ClO}_4)_3$  vs ligand concentration leads to the speciation in solution.

Only a tris-complex is formed with BTP (left) whereas hydrophobic effects are observed with BTBP. For which, the species distribution depends on the alkyl chain length (right).



## Third approach: NMR spectroscopy of paramagnetic compounds.

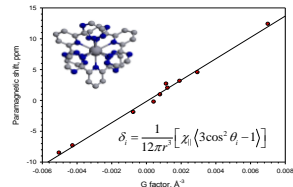
The chemical shifts induced by paramagnetic ions depend on (1) the through space dipolar interaction between the nuclear spins and the unpaired electronic spins and/or (2) the contact contribution due to electronic spin densities delocalized into the ligand orbitals and thus on the partial covalency of the coordination bonds.



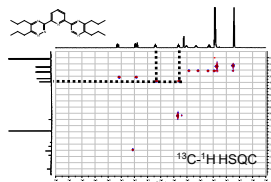
Cyclohexenyl groups are rigidified by complexation.



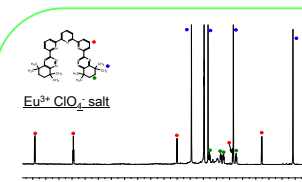
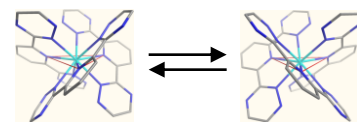
A good correlation between calculated and experimental paramagnetic shifts is obtained (right). BTP forms highly compact and symmetric tris-complexes. These very crowded and stable structures are highly hydrophobic units which are very well extracted.



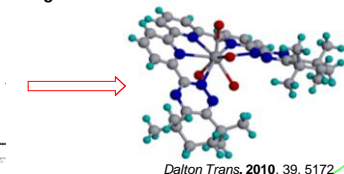
Rigid propyl chains ?



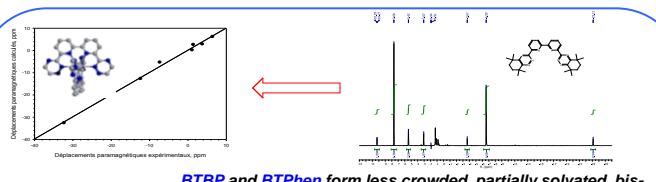
Surprisingly, all alkyl  $\text{CH}_2$  protons are different (left). Are propyl chains rigid ? No change are observed upon heating to 423 K. BTP forms two helical enantiomers (right). The alkyl protons are connected to an asymmetric center and are all inequivalents.



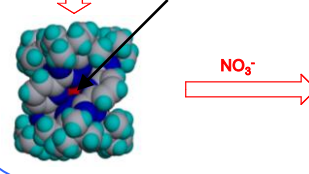
Only a poorly extractible 1:1 species is formed in nitrate media with BTTP due to the competition between nitrate ions and BTTP ligand for the metallic ions center.



Dalton Trans. 2010, 39, 5172



BTBP and BTPhen form less crowded, partially solvated, bis-complexes with enough room for a nitrate ion that penetrates the coordination sphere and deforms the structure.



J. Am. Chem. Soc. 2011, 133, 13093

## Conclusions

NMR is a hardly broached research field in actinide science. We showed that NMR and relaxivity are useful techniques to determine the stoichiometry of complexes, to know their speciation in solution and to obtain information about solvation states. Furthermore, the dipolar paramagnetic shifts lead to the solution structures and conformations of Ln and Ac complexes. These information help to better understand the properties of selective extracting agents for the Ac/Ln separations.

## Acknowledgements

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