Nuclear magnetic resonance applied to actinide ions and their complexes: in search of covalency effects.

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The aim: use NMR for determining

- the stoichiometry
- the solvation state
- the solution structure … of Ln and Ac complexes

The approach

- nuclear magnetic relaxation dispersion (NMRD) titration
- nuclear magnetic spectroscopy (NMR) of
  - diamagnetic complexes
  - paramagnetic complexes

The ultimate goal

- *covalency effects in actinide complexes*

A (very) quick remainder of nuclear magnetic resonance

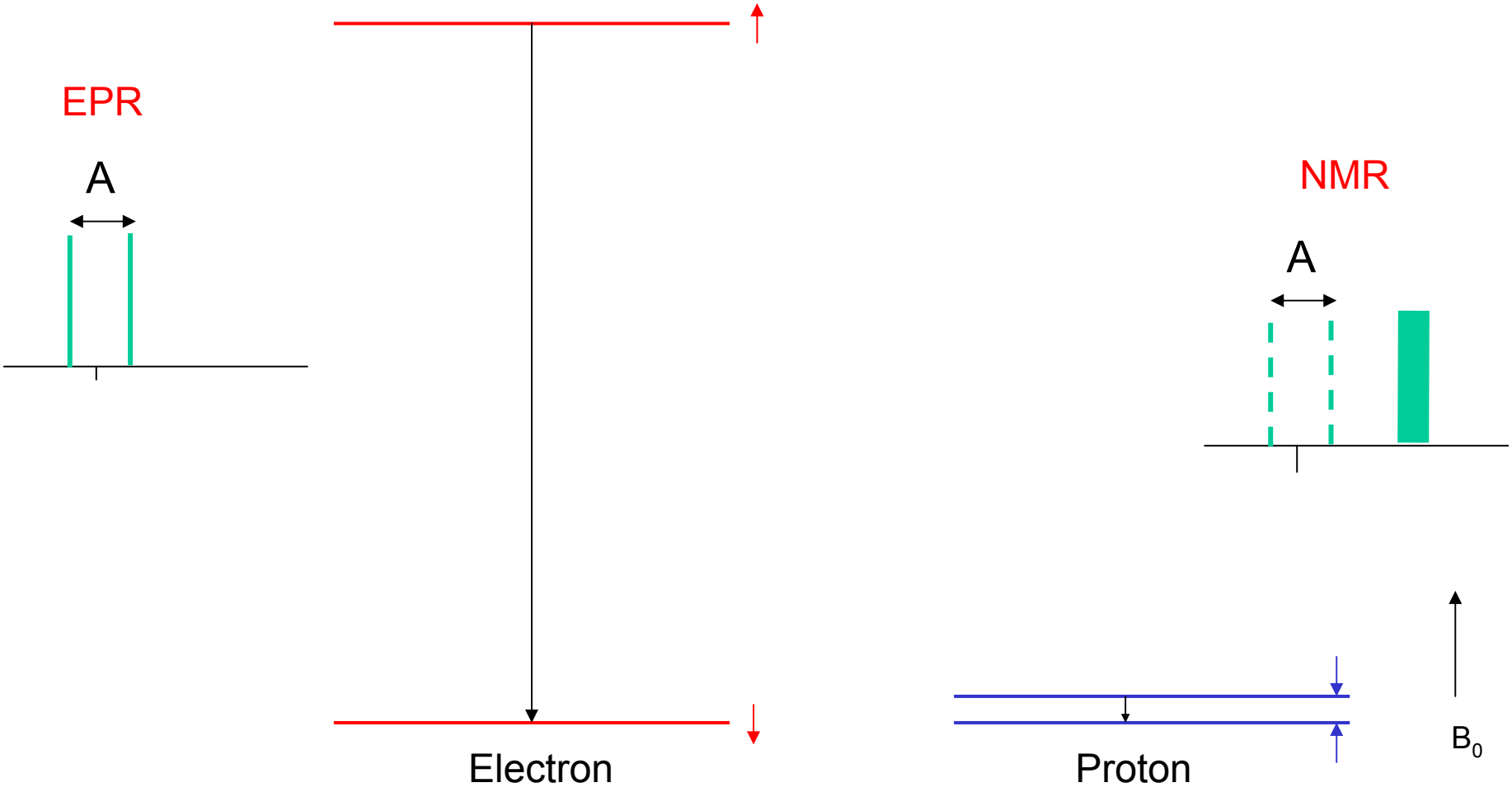
Paramagnetic metal complexes

The NMR spectrum of the H atom

$$|\gamma_e| = 658\,|\gamma_H|$$

$$g_e\,\mu_B = 658\,g_H\,\mu_N$$

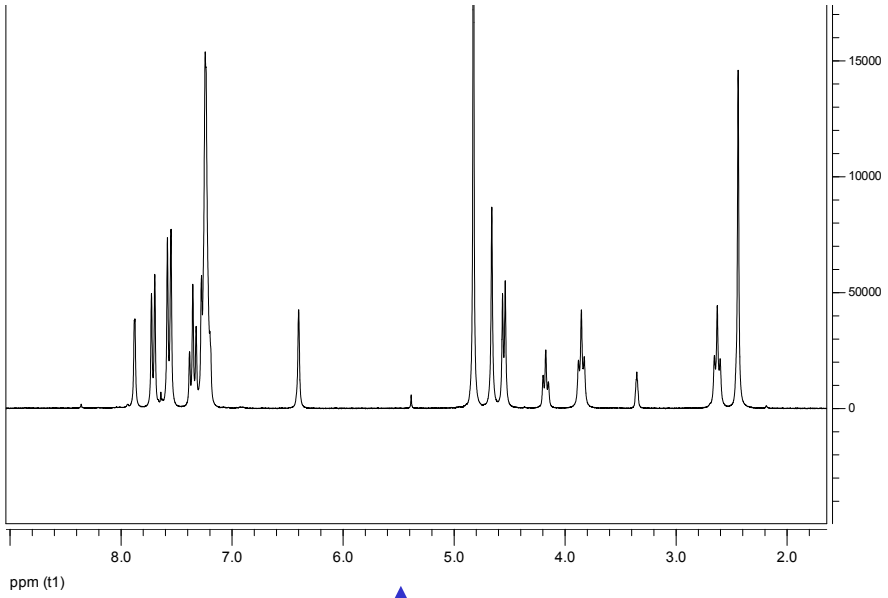
e^-: better interaction with matrix



Nuclear magnetic resonance of actinides: two approaches

Two Approaches

- *Spectroscopy*
- *Relaxometry (NMRD)*

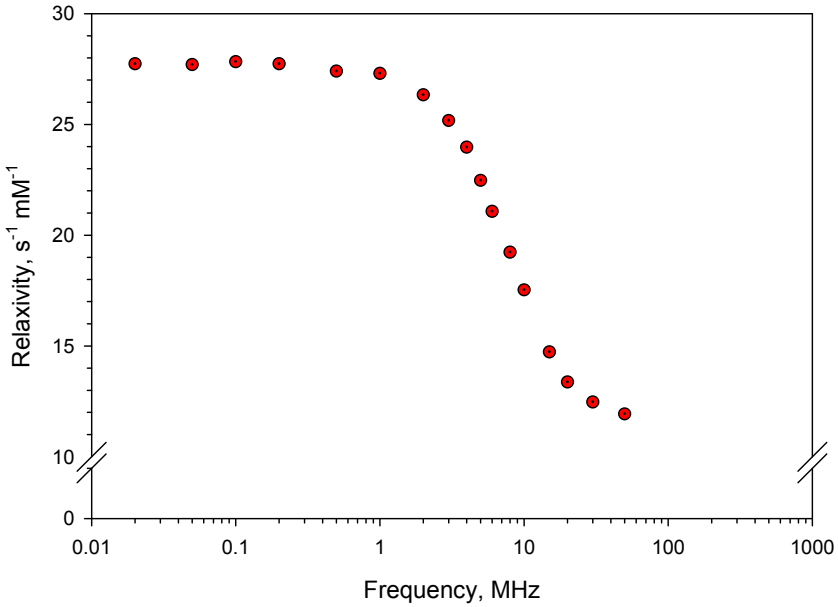


Molecule

Paramagnetic shifts

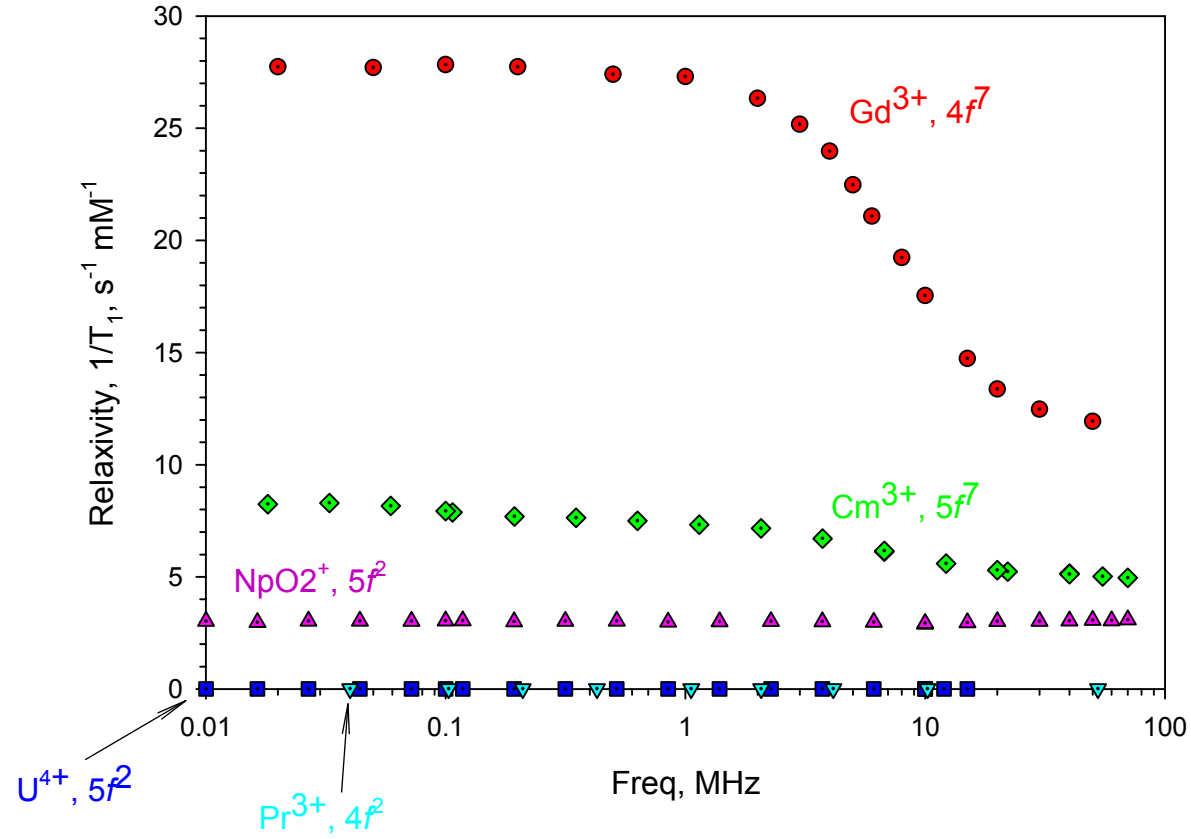
Solvent

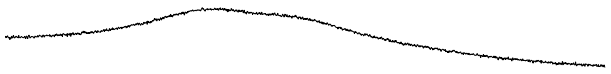
Relaxation rate vs. frequency (or field)



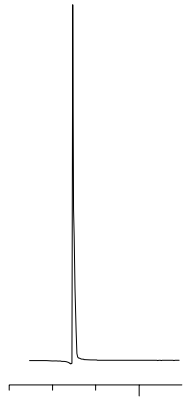
Nuclear magnetic relaxation dispersion: which metal ion?

Water $1/T_1$ dispersion with B_0





GdDTPA



U(IV)DOTA

Nuclear magnetic relaxation dispersion: which metal ion?

1444 cm^{-1} 46% $^3H_4$

1288, 1301,1311 cm^{-1}

44-45% $^3H_4$

U^{4+}

468, 504 cm^{-1} 45% $^3H_4$

150, 157 cm^{-1} 47% $^3H_4$

0 cm^{-1} 47% $^3H_4$

Energy, cm^{-1}

35.7

13.4

Δ : 0.6 cm^{-1}

0

$J_z = \pm 1/2$

Gd^{3+} **Cm^{3+}**

Small zero field splitting → long electronic relaxation time → large NMR ^1H peaks

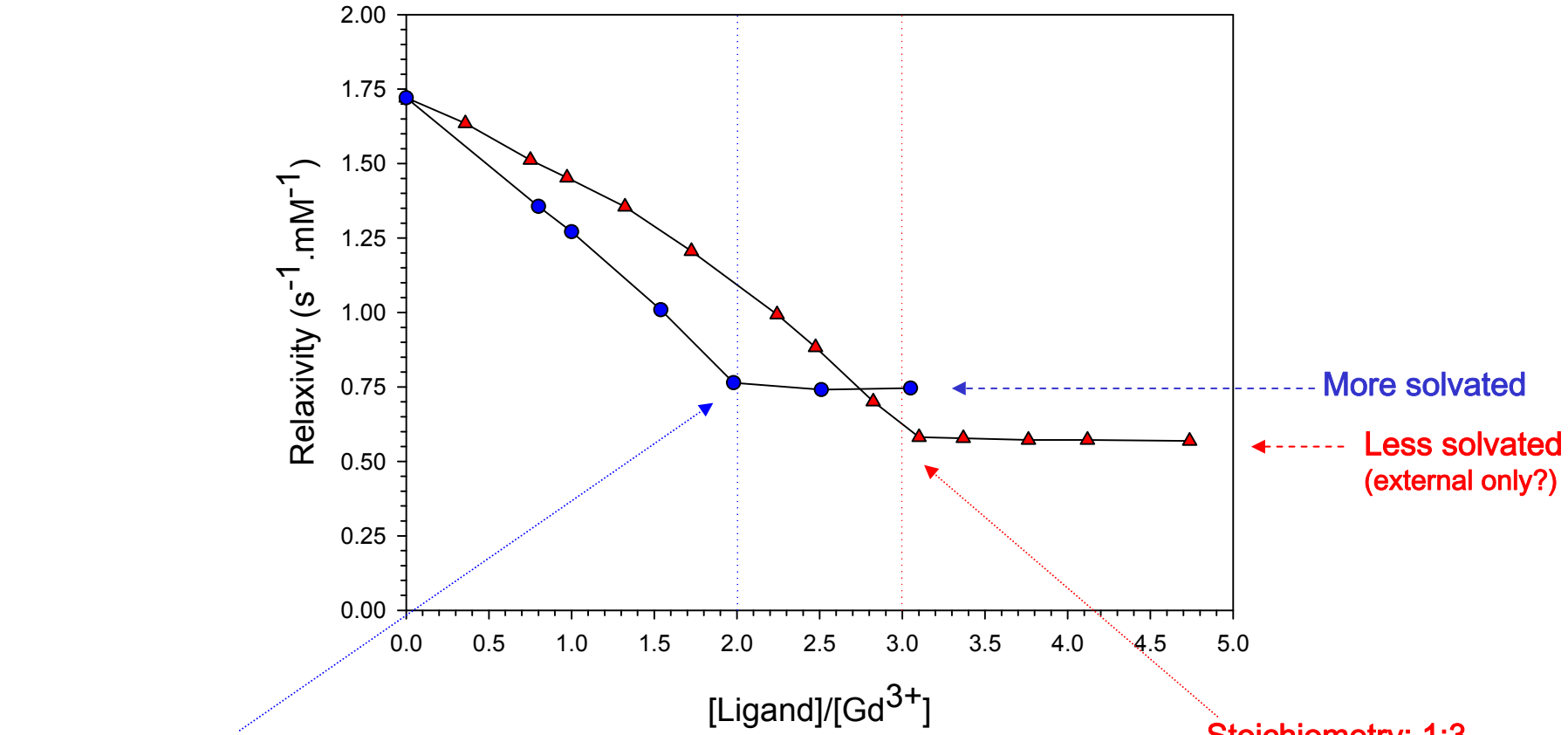
V. Vallet et al. 2009, Univ. of Lille

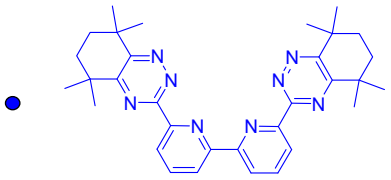
P. Lindqvist-Reis *et al., J. Phys. Chem.* B **2006**, *110*, 5279
N. Edelstein et al. J. Chem. Phys. **1968**, *48*, 2110

Stoichiometry and solvation

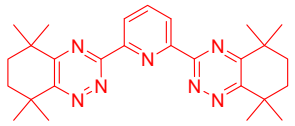
Paramagnetic metal complexes

Maximum stoichiometry of complexes





$(Me_4cy)_2BTBP$



$(Me_4cy)_2BTP$

ClO_4^-, in anhydrous acetonitrile

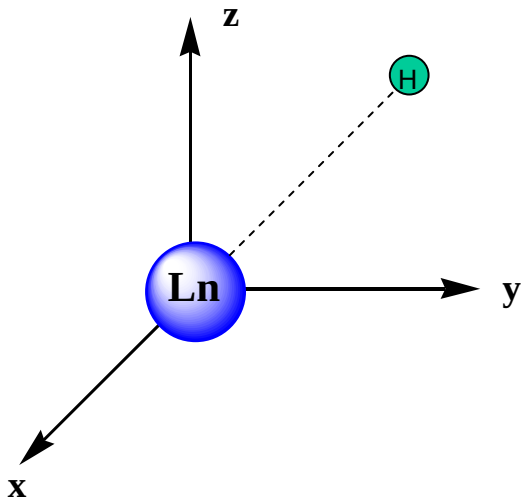
New J. Chem. **2006**, *30*, 1171

Solution structures by NMR

Paramagnetic metal complexes

Dipolar shifts

A through space interaction between magnetic moments



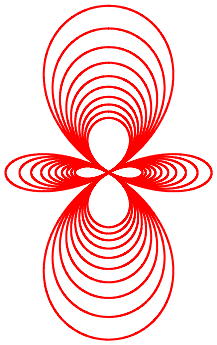
Axial symmetry

$$\delta_i = (\chi_{\parallel} - \chi_{\perp}) \left\langle \frac{3\cos^2\theta_i - 1}{r_i^3} \right\rangle$$

Requirements:

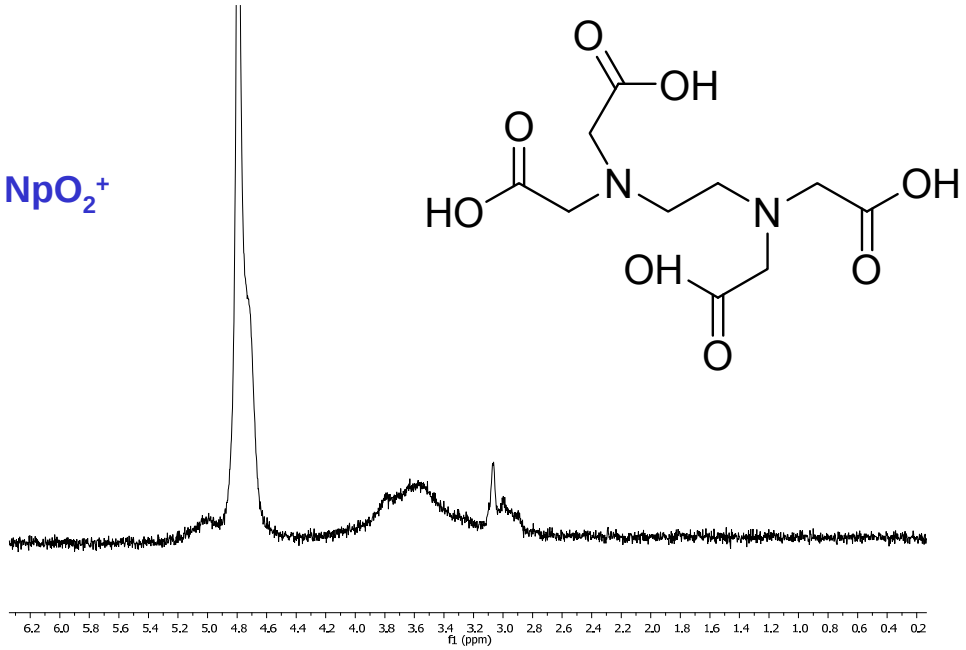
- One single species
- Axial symmetry
- Rigidity

$$\delta_i = \frac{1}{12\pi}\left[\left(\chi_{zz} - \frac{\chi_{xx}+\chi_{yy}}{2}\right)\left\langle \frac{3\cos^2\theta_i - 1}{r_i^3}\right\rangle + \frac{3}{2}\left(\chi_{xx} - \chi_{yy}\right)\left\langle \frac{\sin^2\theta_i \cos 2\psi_i}{r_i^3}\right\rangle\right]$$

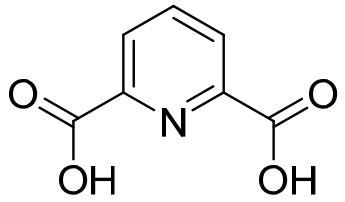


Which orientation of the susceptibility tensor ?

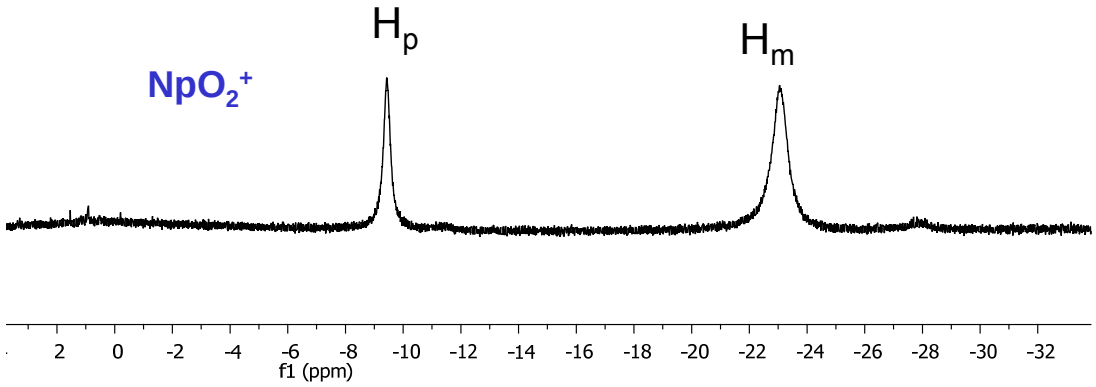
Which ligand ?



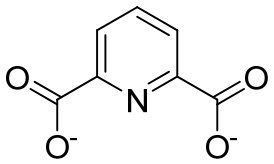
Not rigid enough ?
No symmetry ?



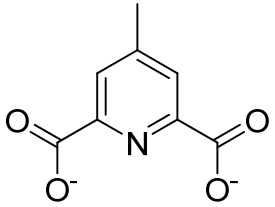
DPA



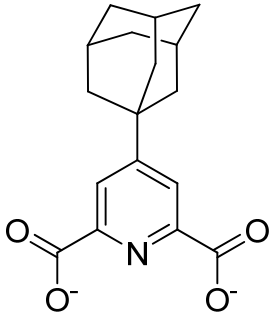
Which ligand ?



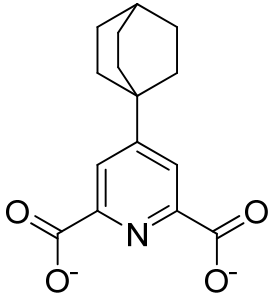
DPA



MDPA

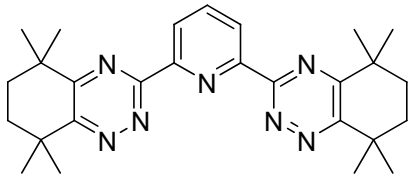


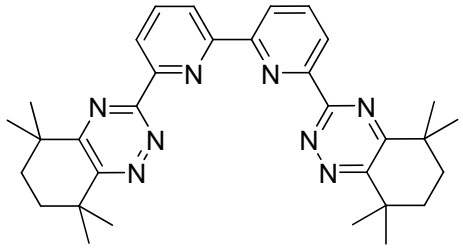
AdamDPA

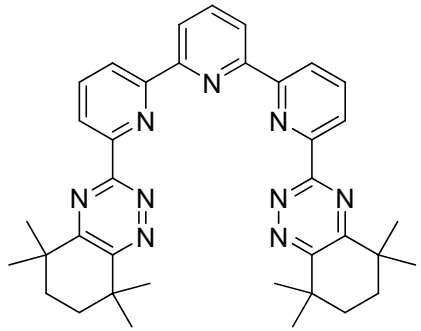


BicyDPA

- High stability in water
- High symmetry: C_3
- Lanthanide complexes: known crystallographic structure

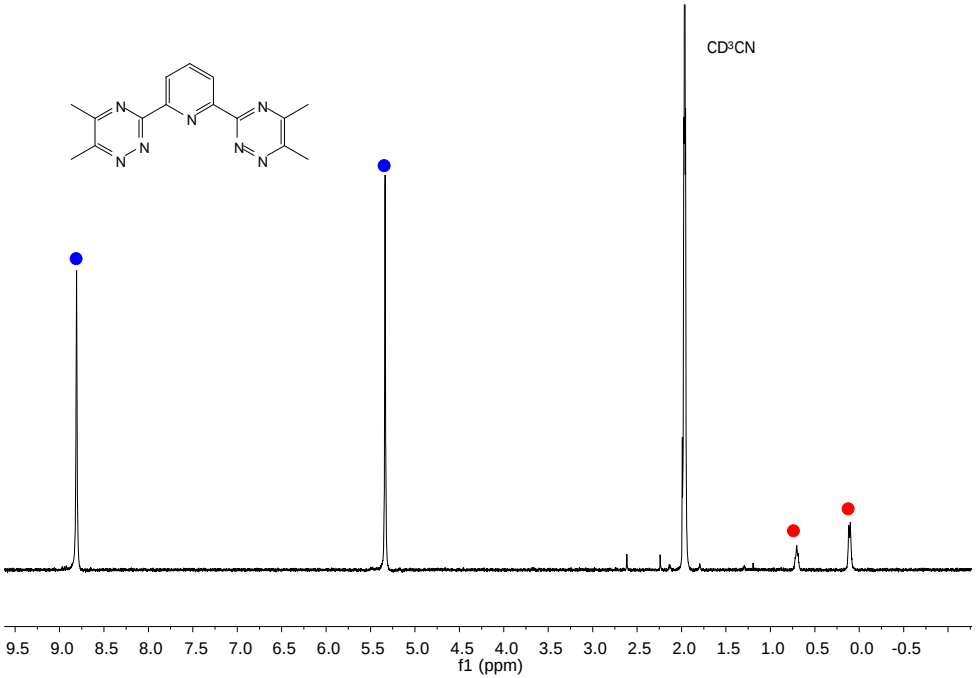


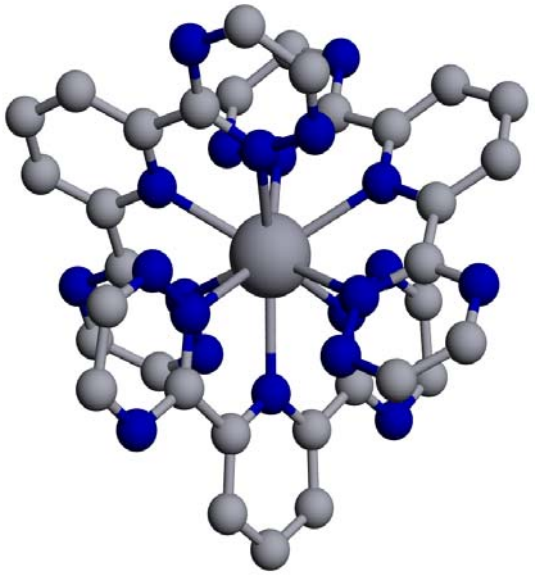




- High stability in CH_3CN
- High symmetry: C_3 or C_2
- Lanthanide complexes: known or unknown crystallographic structure

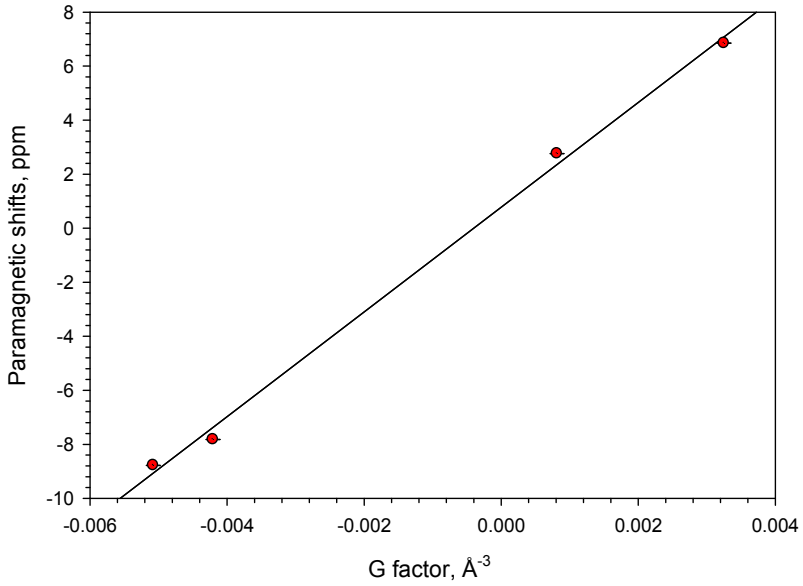
Yb^{3+} tris-complex with BTP in anhydrous acetonitrile





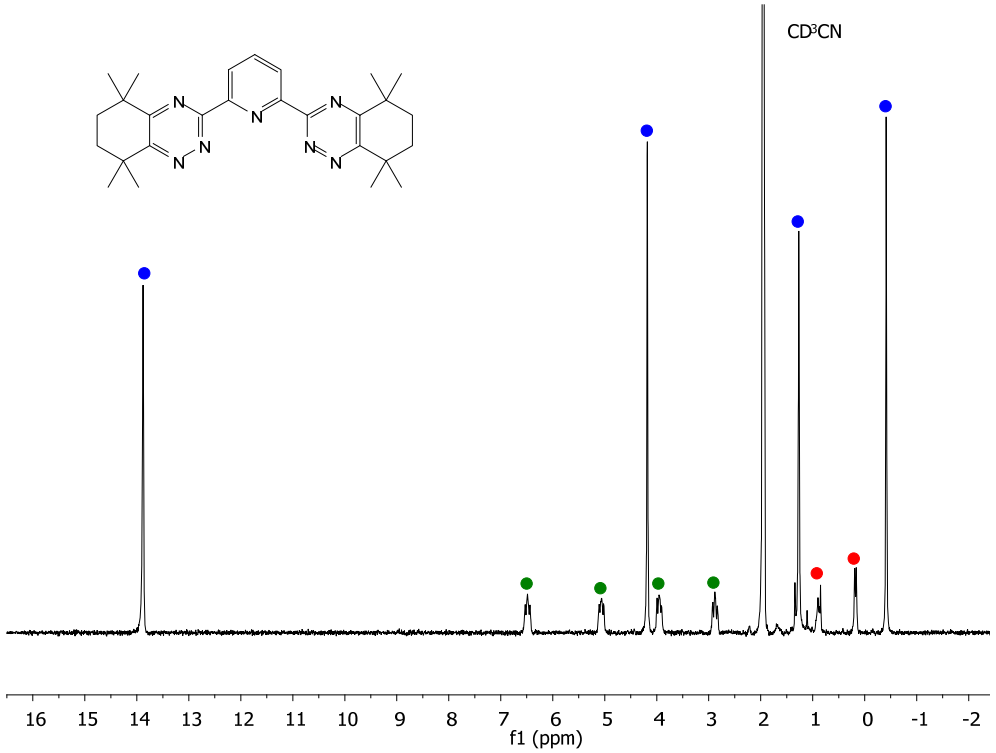
$$\delta_i = \frac{1}{3N}\left(\chi_{zz} - \chi_{xx}\right)\left\langle \frac{3\cos^2\theta_i - 1}{r_i^3} \right\rangle$$

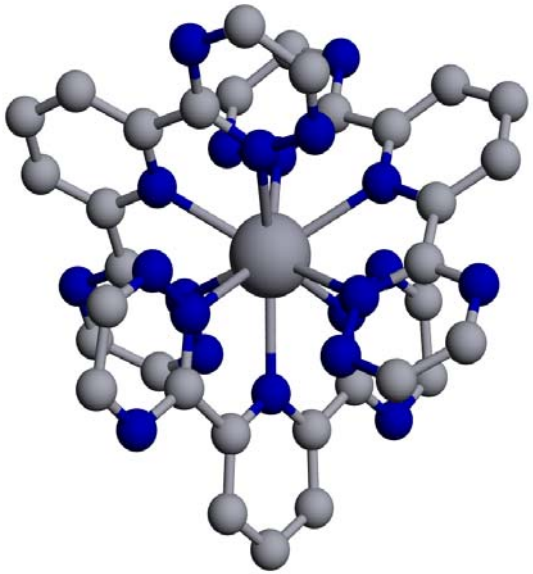
C_3 axis, the ideal case



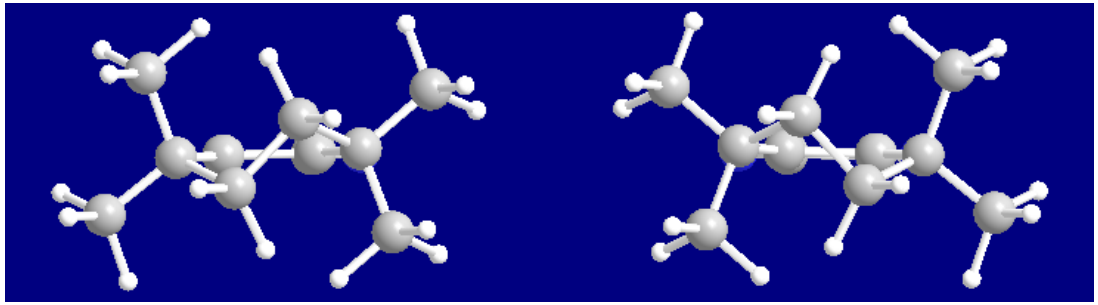
ClO_4^-, in anhydrous acetonitrile

Yb^{3+} tris-complex with crowded BTP in anhydrous acetonitrile

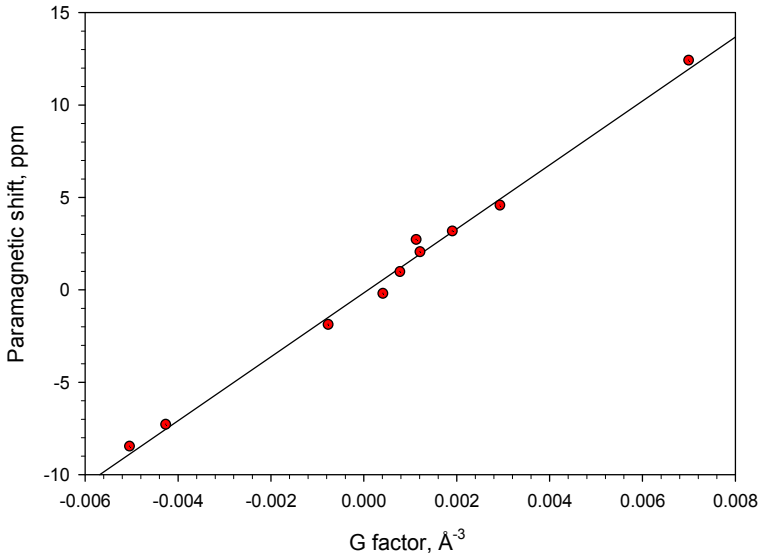




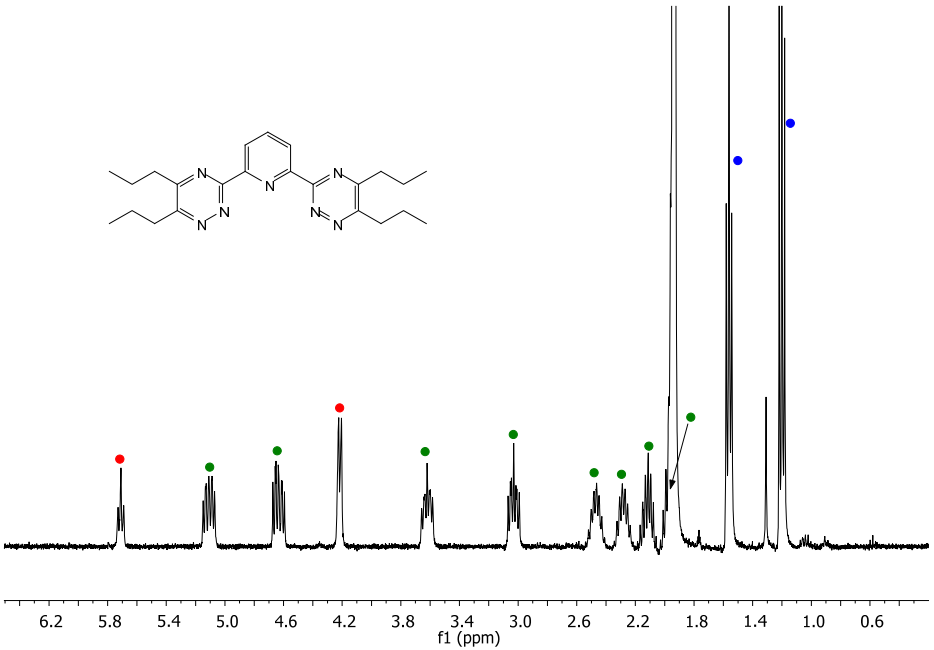
Rigid cyclohexenyl groups



ClO_4^-, in anhydrous acetonitrile

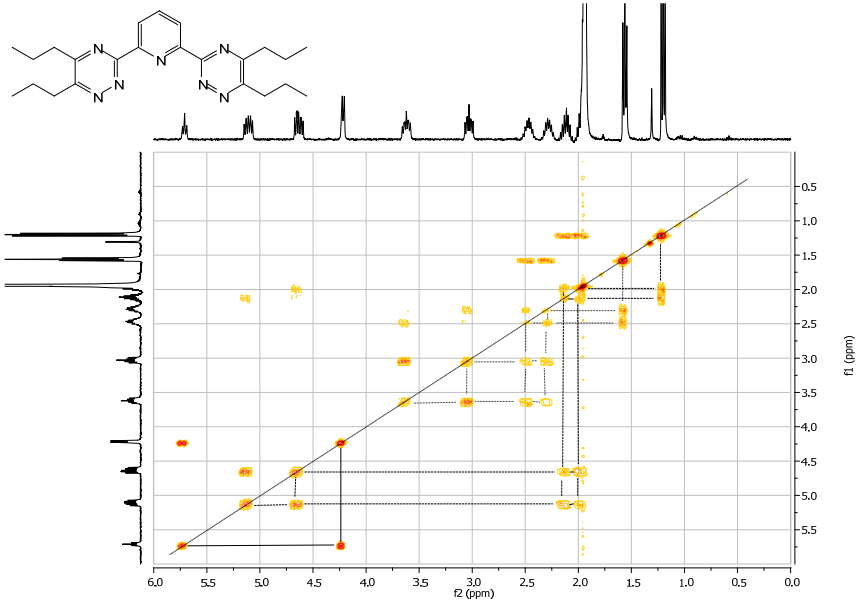


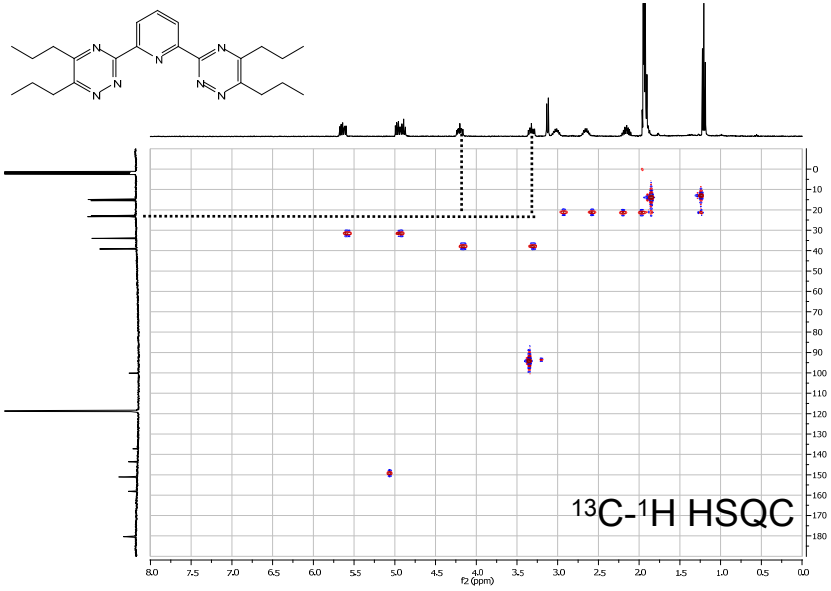
$Eu(Pr_4BTP)_3$: rigid alkyl substituents

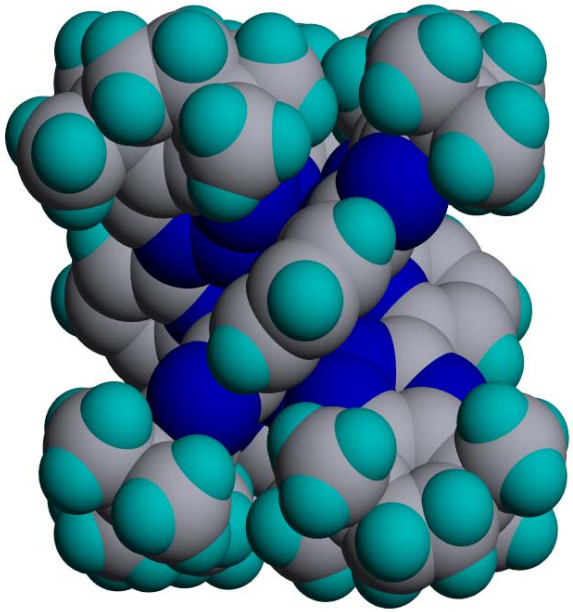


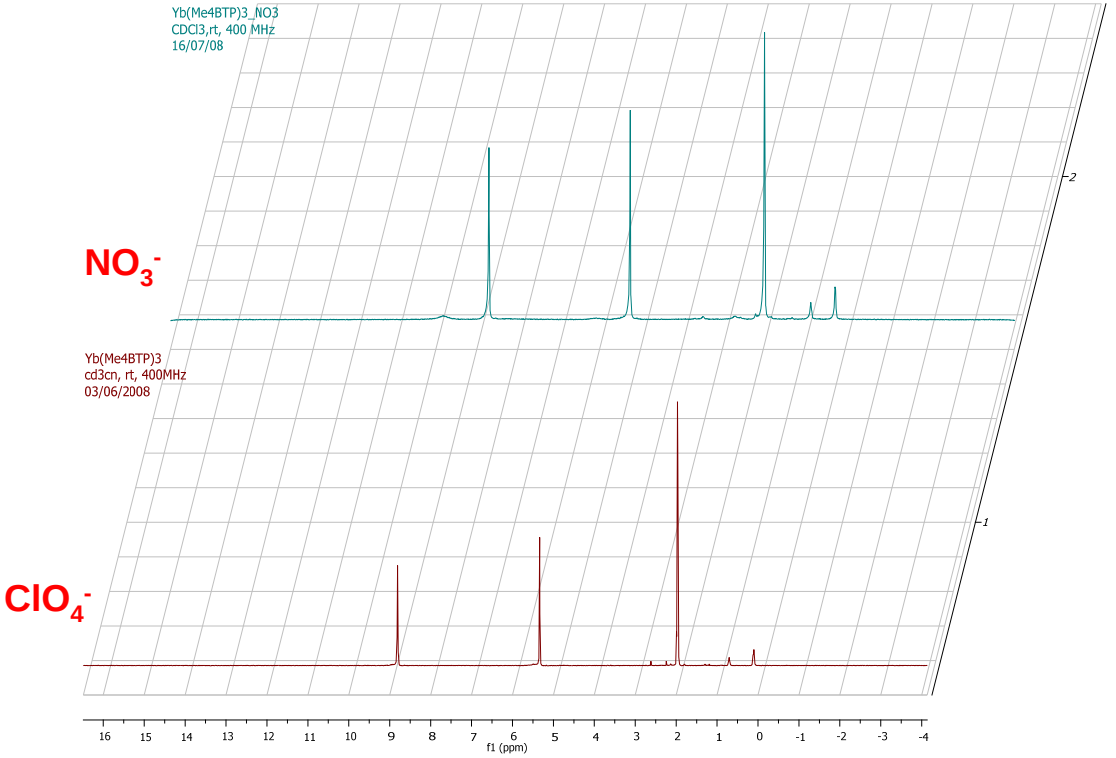
Rigid propyl chains !!!

ClO_4^-, in anhydrous acetonitrile
No change upon heating





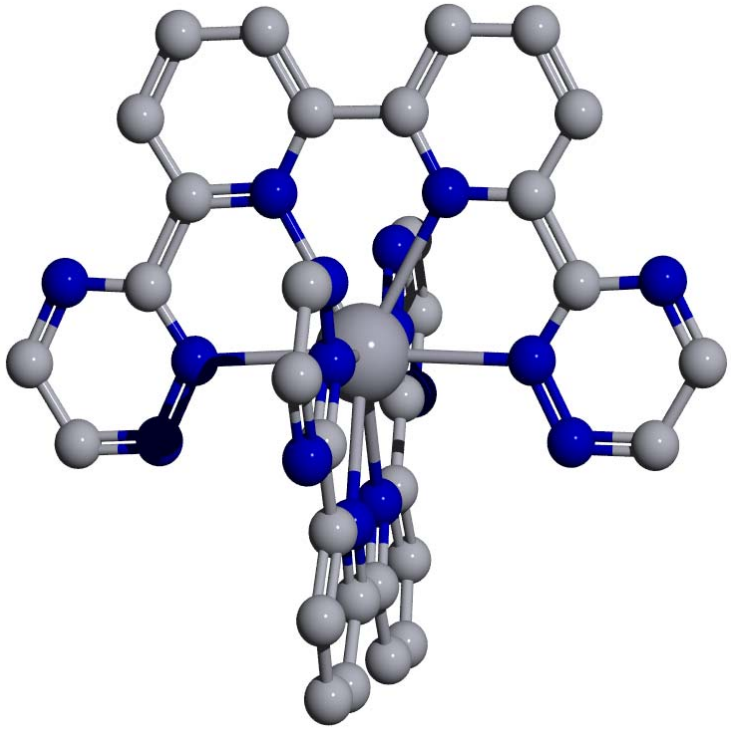




Highly compact structure

- **slow inversion of cyclohexenyl groups**
- **slow rotation of aliphatic chains**
- **NO_3^- : not coordinated**

The BTBP complexes

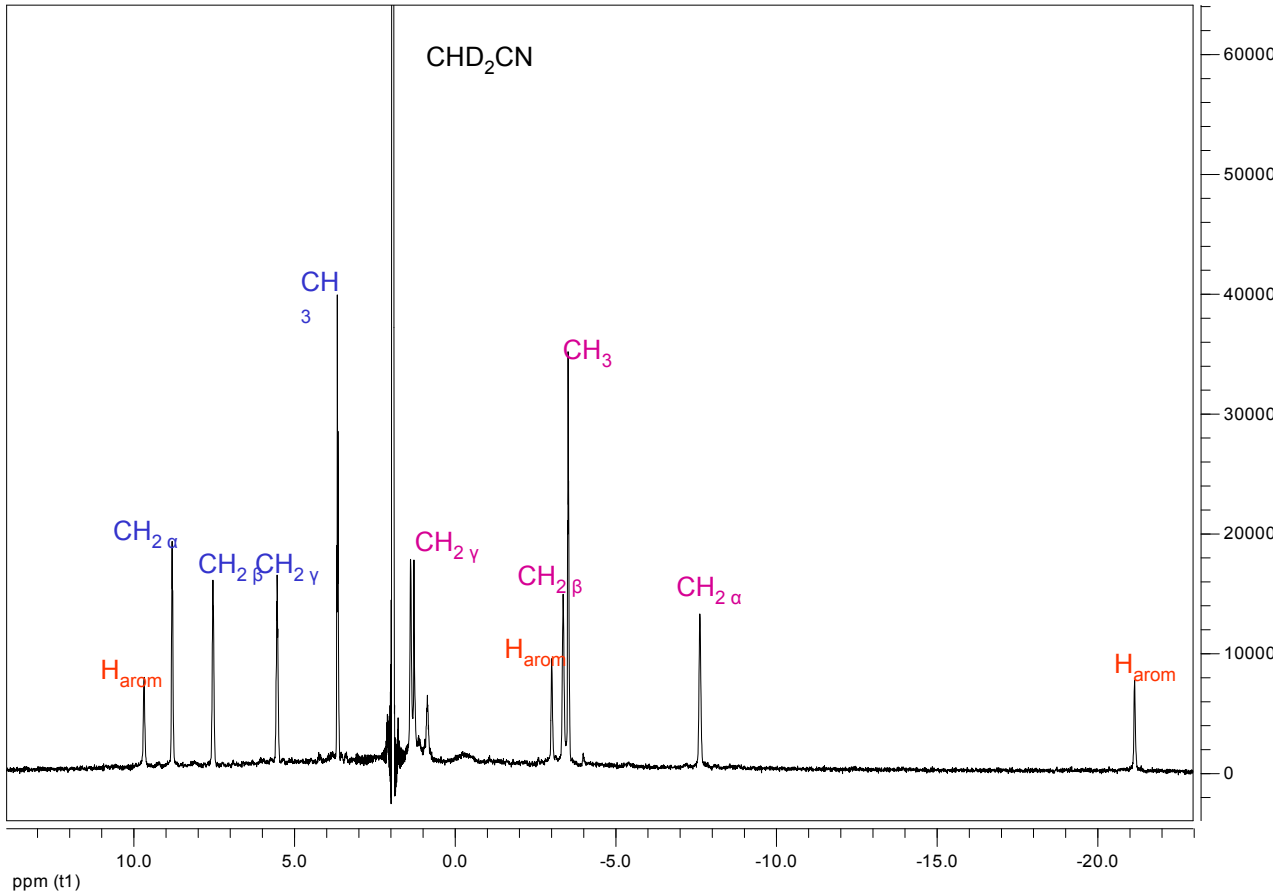


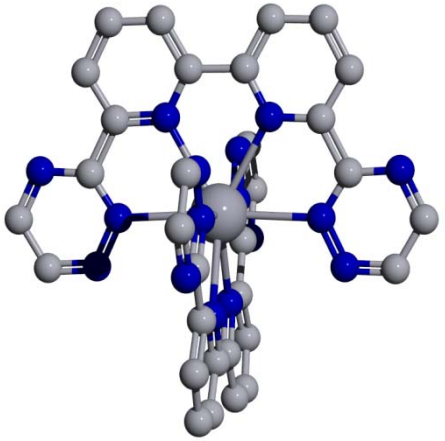
Bis-complex: no crystallographic structure

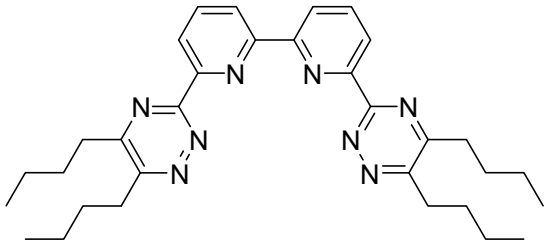
→ Molecular modeling

- Force field with Hay and Cundary parameters
- Full optimization with SPARKLE Yb(III) parameters in MOPAC 2009

Yb^{3+} bis-complex with BTBP: mobile alkyl substituents



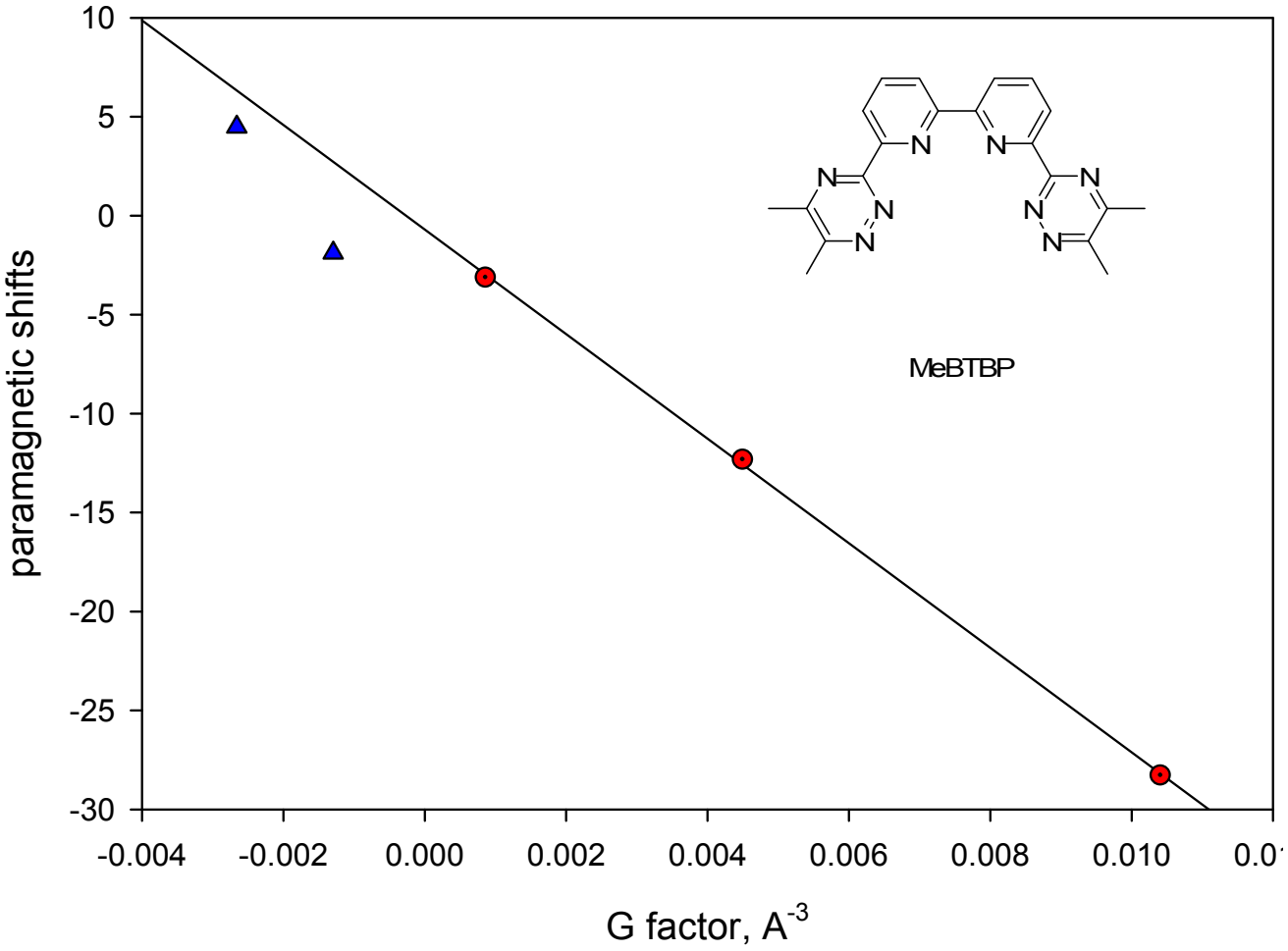


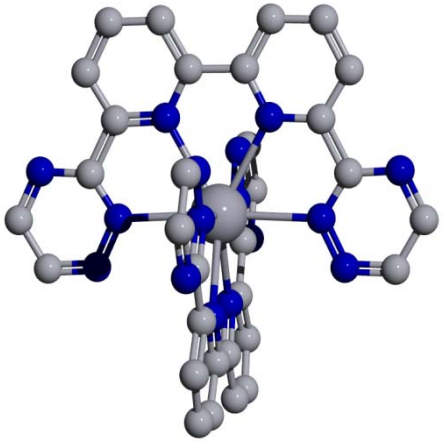


C4-bipyBTP

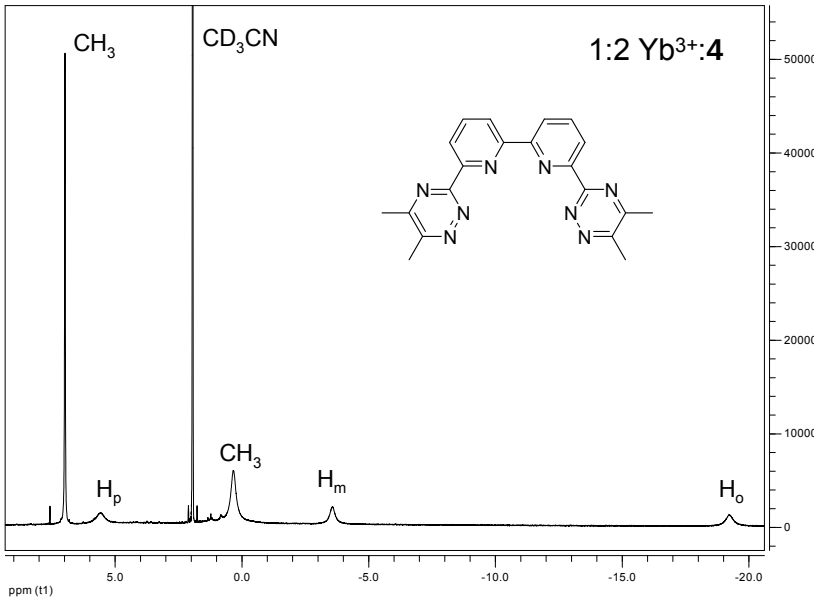
ClO_4^-, in anhydrous acetonitrile

Dipolar shifts V. High symmetry, Yb^{3+} complex





Yb^{3+} BTBP complexes: NO_3^- *vs.* ClO_4^-

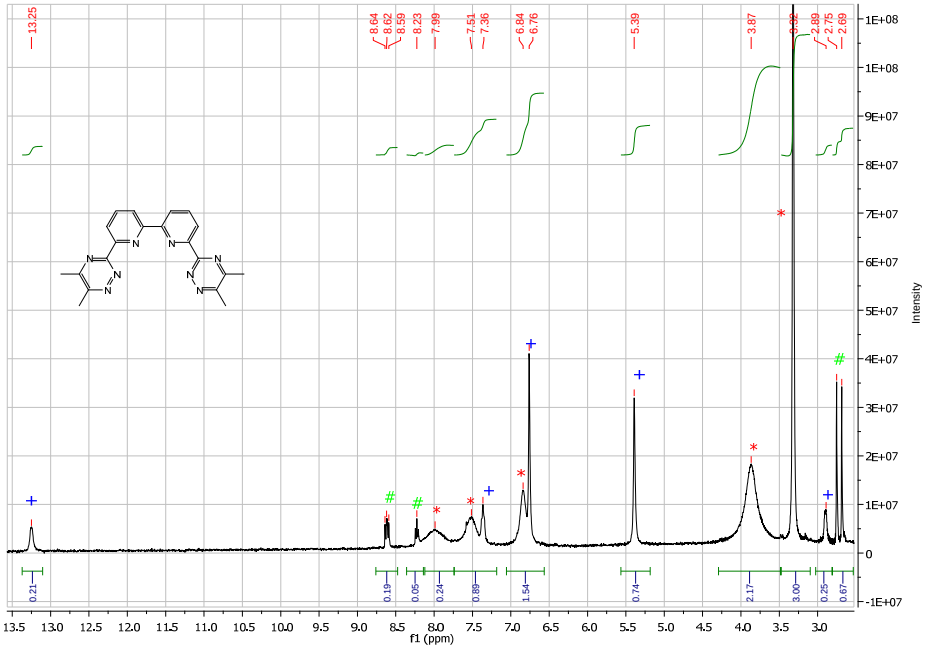


ClO_4^-

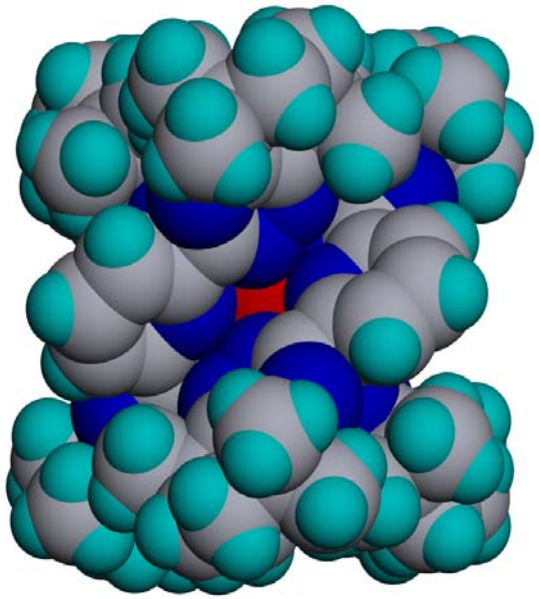
NO_3^-

No symmetry

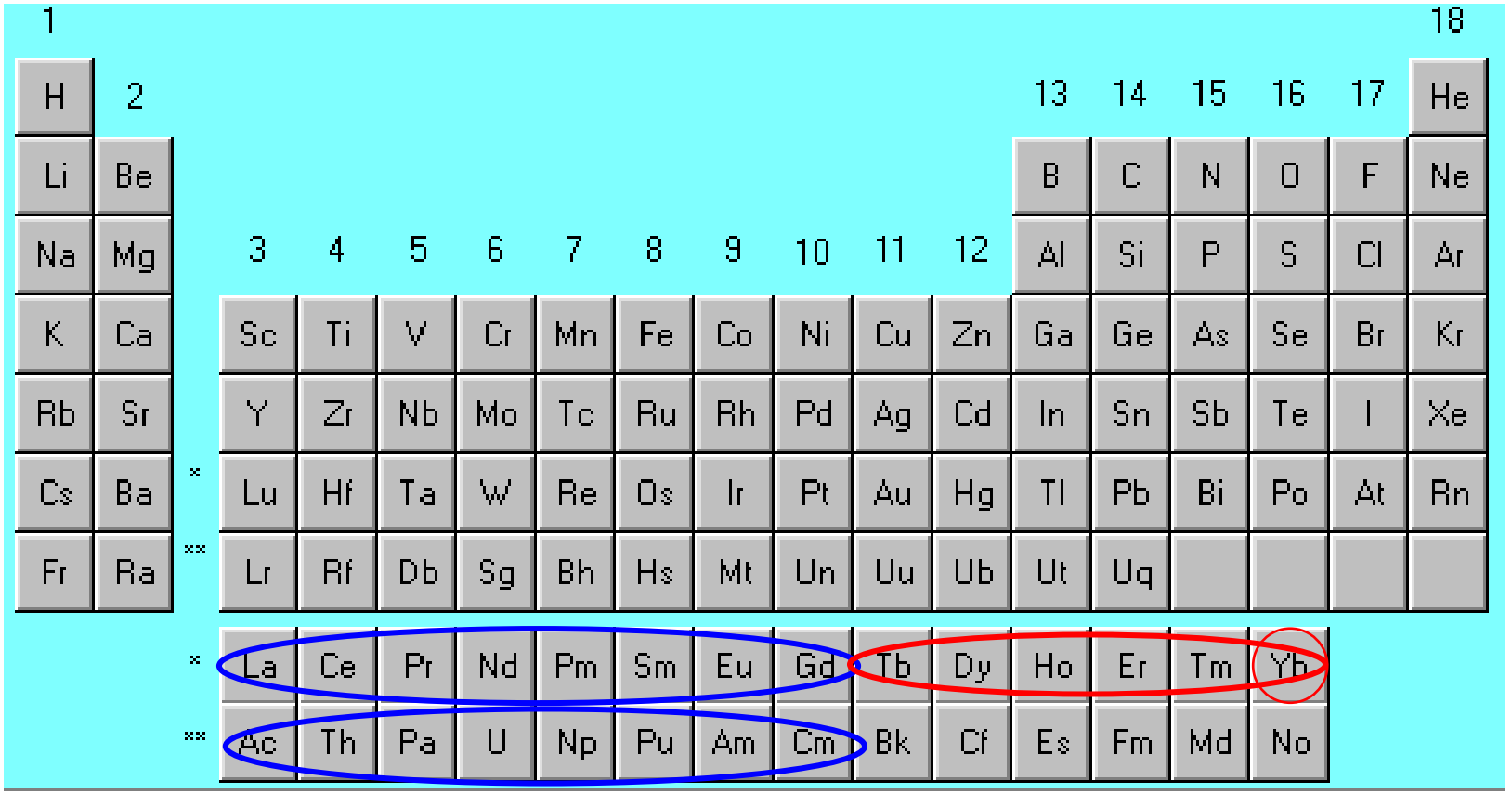
Structure ?



- Partially solvated
- Model, solution : similar structure (ClO_4^-)
- Different NMR spectra for ClO_4^- and NO_3^- !!!
- Less crowded
  - flexible cyclohexenyl substituents
  - flexible alkyl chains



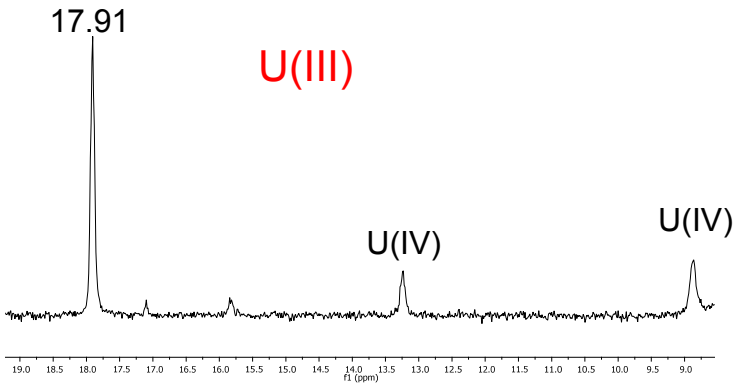
Which lanthanide or actinide ion ?

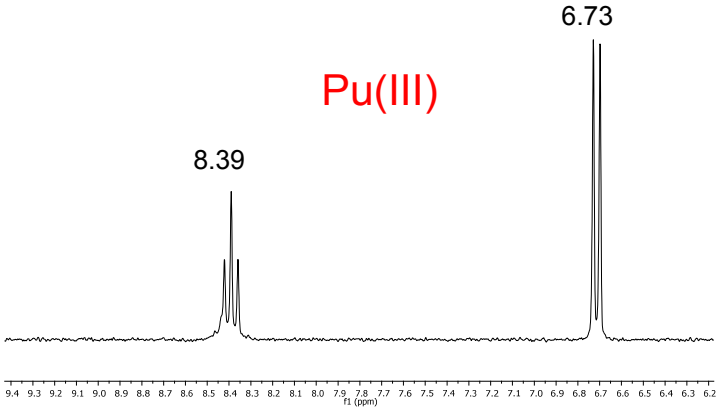


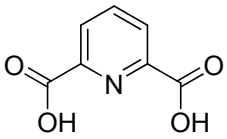
Small paramagnetic shifts

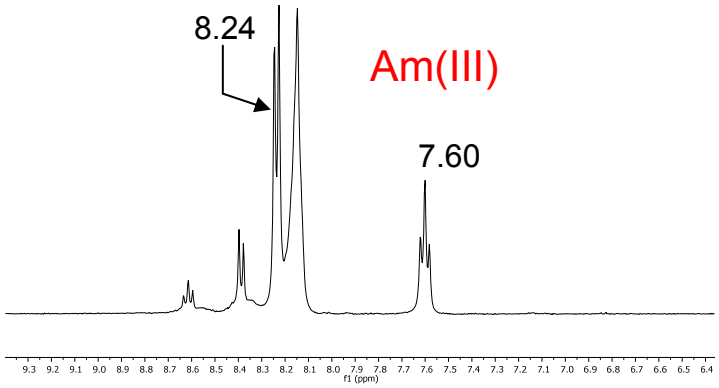
- Small magnetic moments
- Small anisotropy for 1:3 complexes

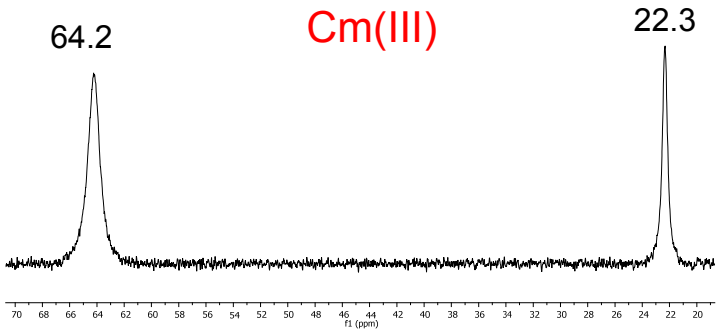
Actinide DPA complexes: small magnetic anisotropy

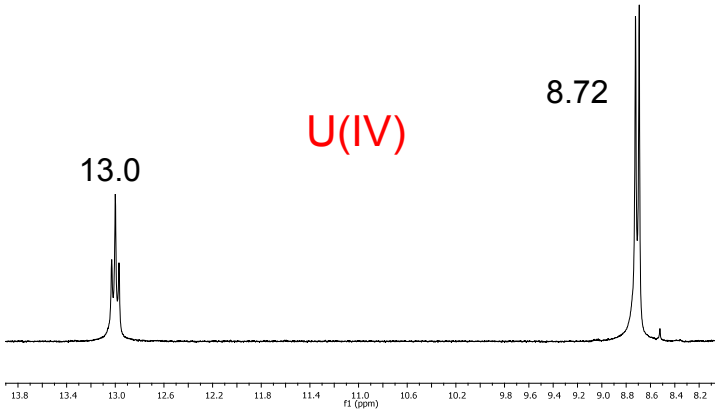


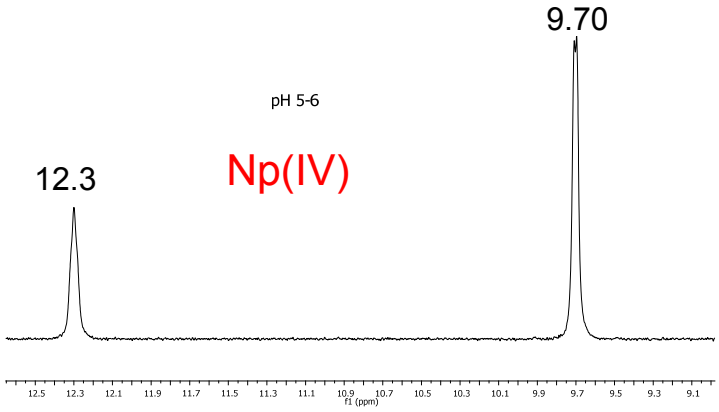


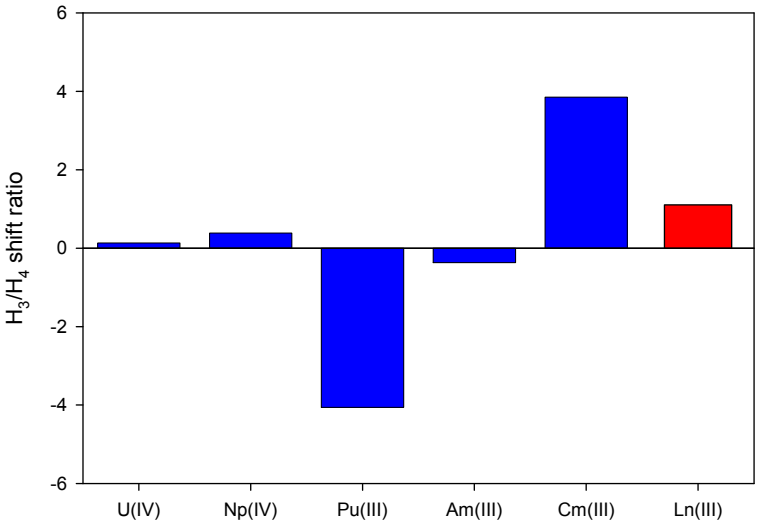












Incorrect shift ratio

→ contact shift

Unpaired spin density through the ligand system due to covalence / polarization

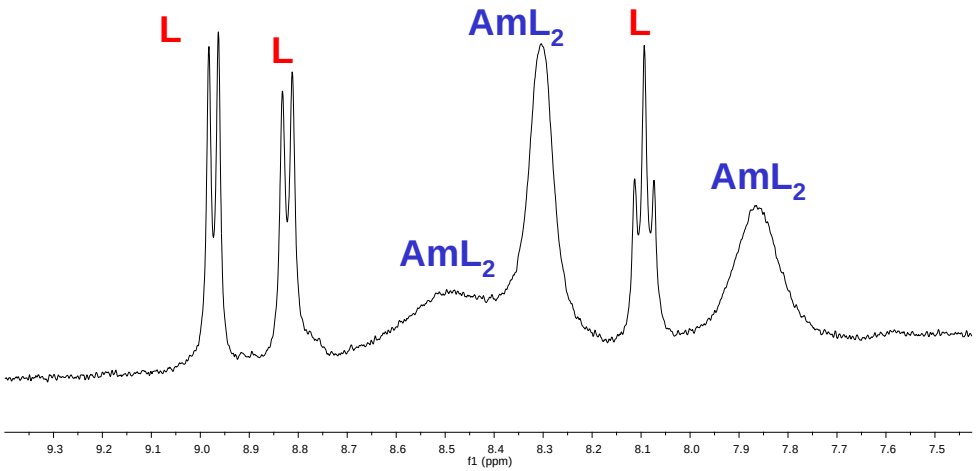
$$\delta_i = \frac{A}{\hbar}\frac{\mu_B}{3\gamma_I kT} < S_Z >$$

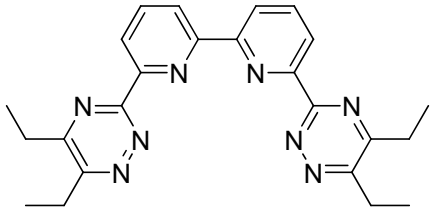
$$A = \frac{2\mu_0}{3}\hbar\gamma_I g_e \mu_B \rho$$

$$\rho : spin\ \ density$$
$$= \psi_{-1/2}(0)^2 - \psi_{1/2}(0)^2$$

$<S>_z$: thermal average of the value of S

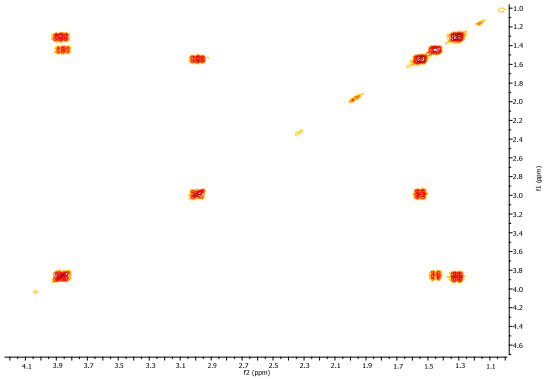
What about the actinides ?



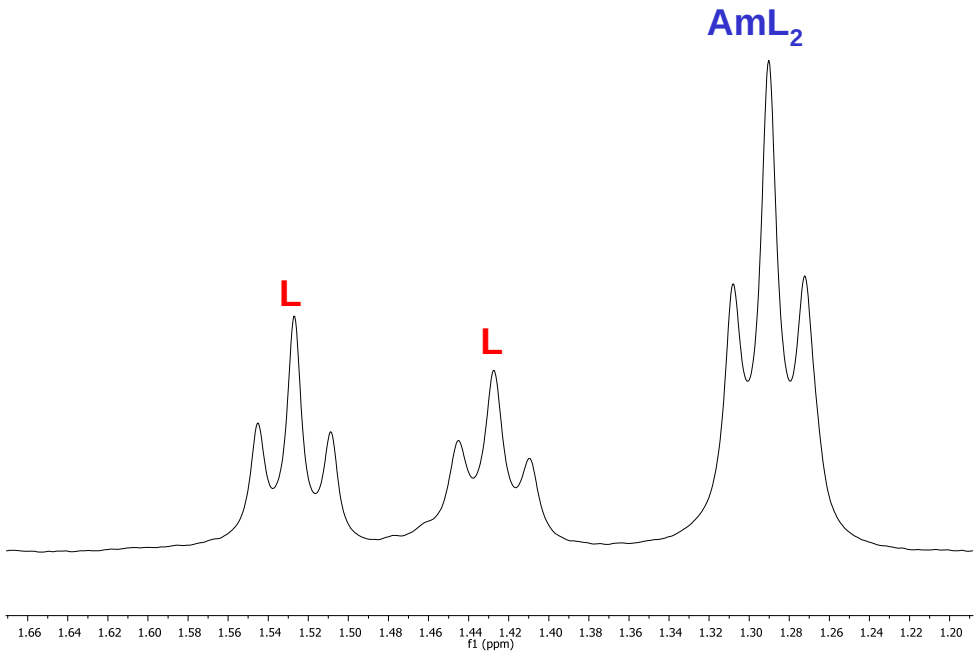


1:2 $Am(NO_3)_3$:ligand mixture

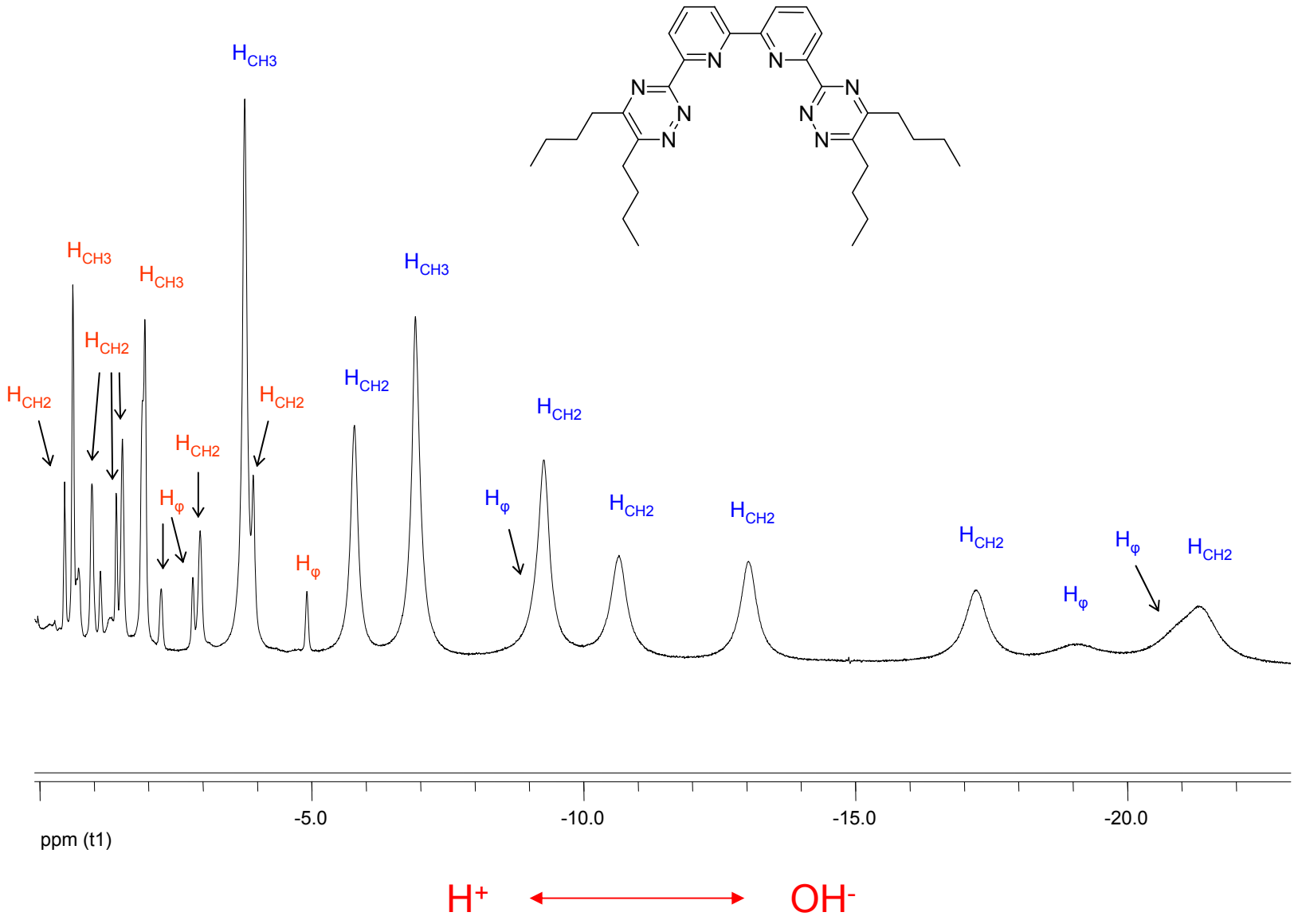
In acetonitrile



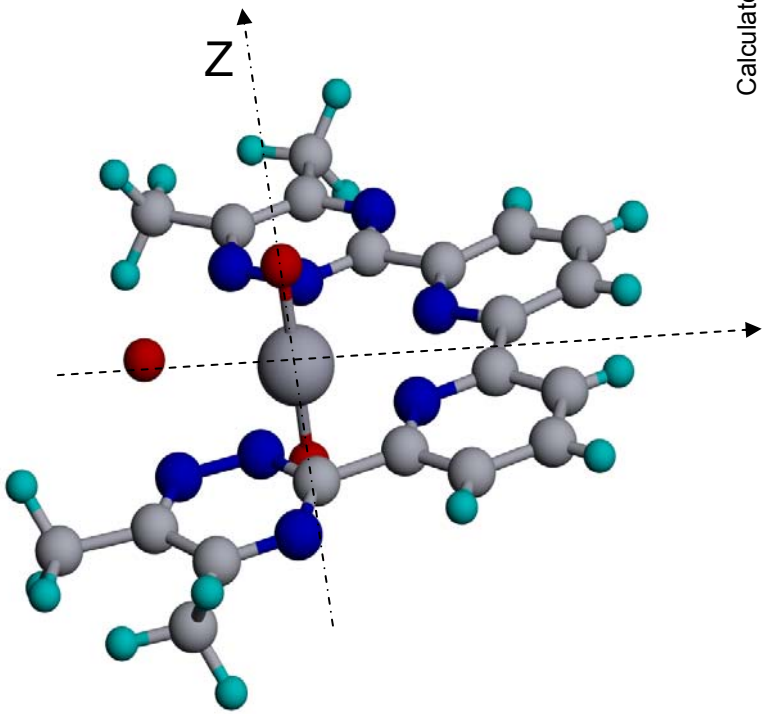
COSY alkyl peaks

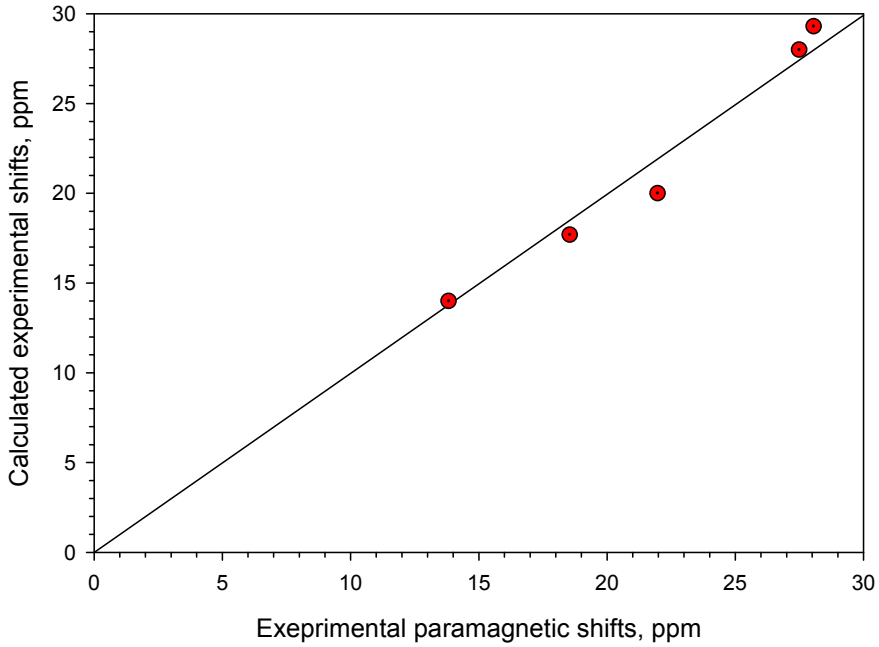


NpO_2^+ - C_4BTBP in CH_3CN



NpO_2^{2+} - C_1BTBP in CH_3CN: a dipolar interaction





Thank you

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