Actinide reCycling by SEParation and Transmutation
FP7 Collaborative Project 211267

Studies on the Interaction of a Novel 6,6''-bis(1,2,4-triazin-3-yl)-2,2':6',2''-terpyridine Ligand with Lanthanide(III) Ions and Americium(III)

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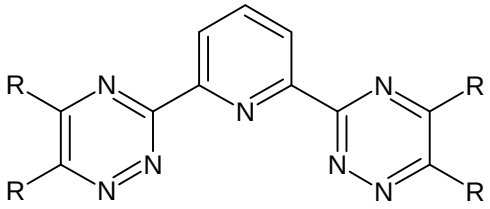
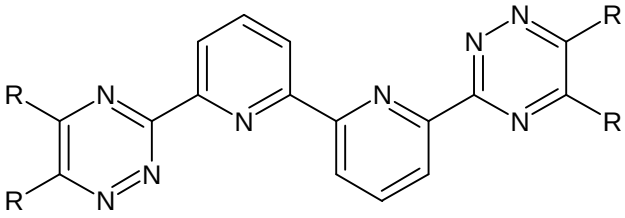
Introduction



BTPs



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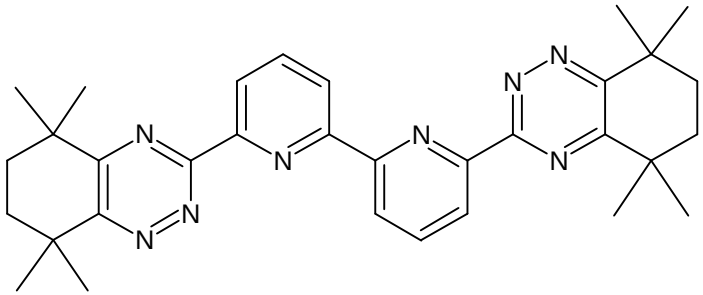
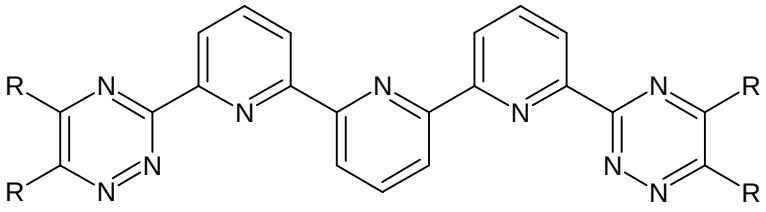


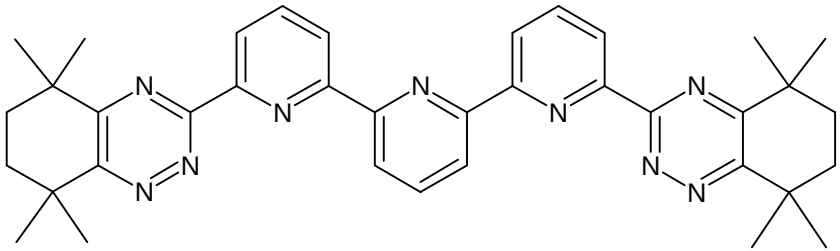
CyMe$_4$-BTBP

D. Magnusson et al. *Solvent Extr. Ion Exch.*, 2009, **27**, 97

Introduction

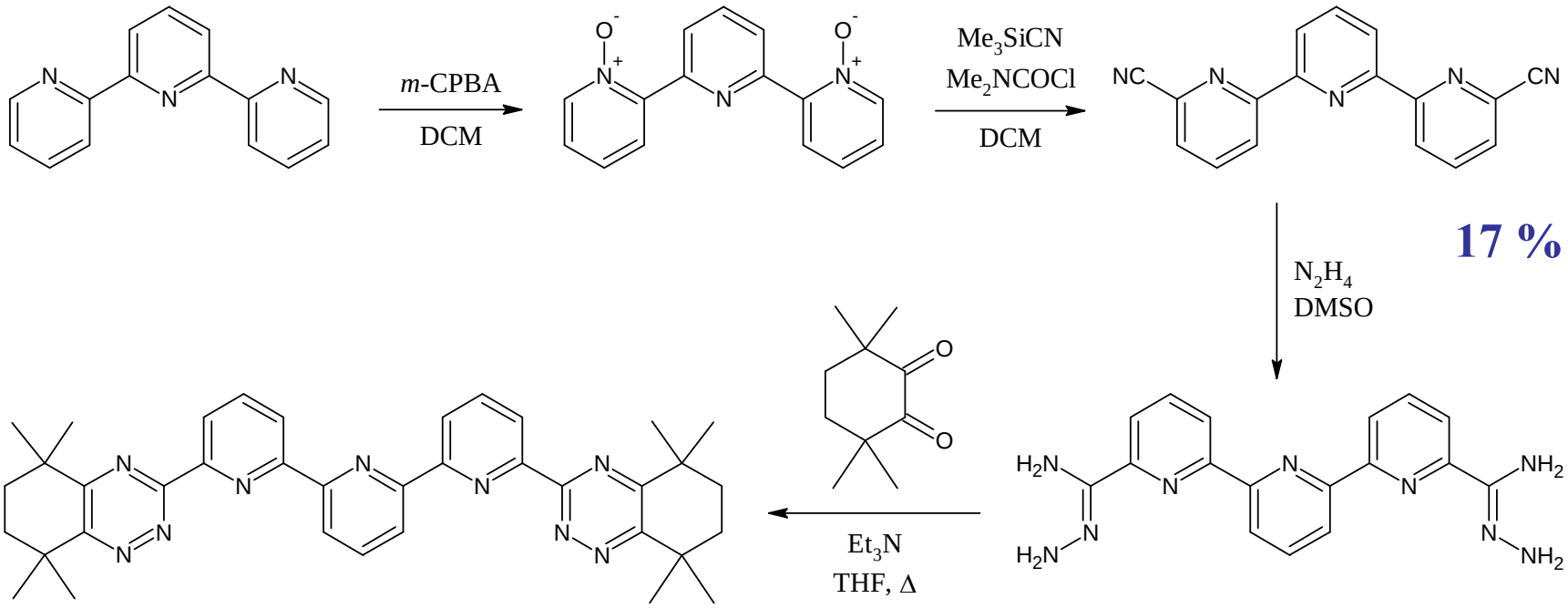


BTTPs

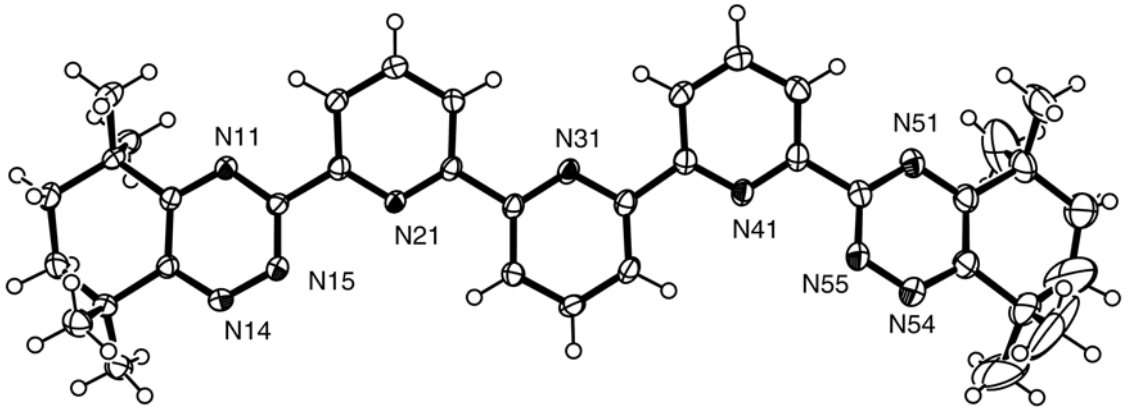


$CyMe_4$-BTTP

Synthesis of $CyMe_4$-BTTP

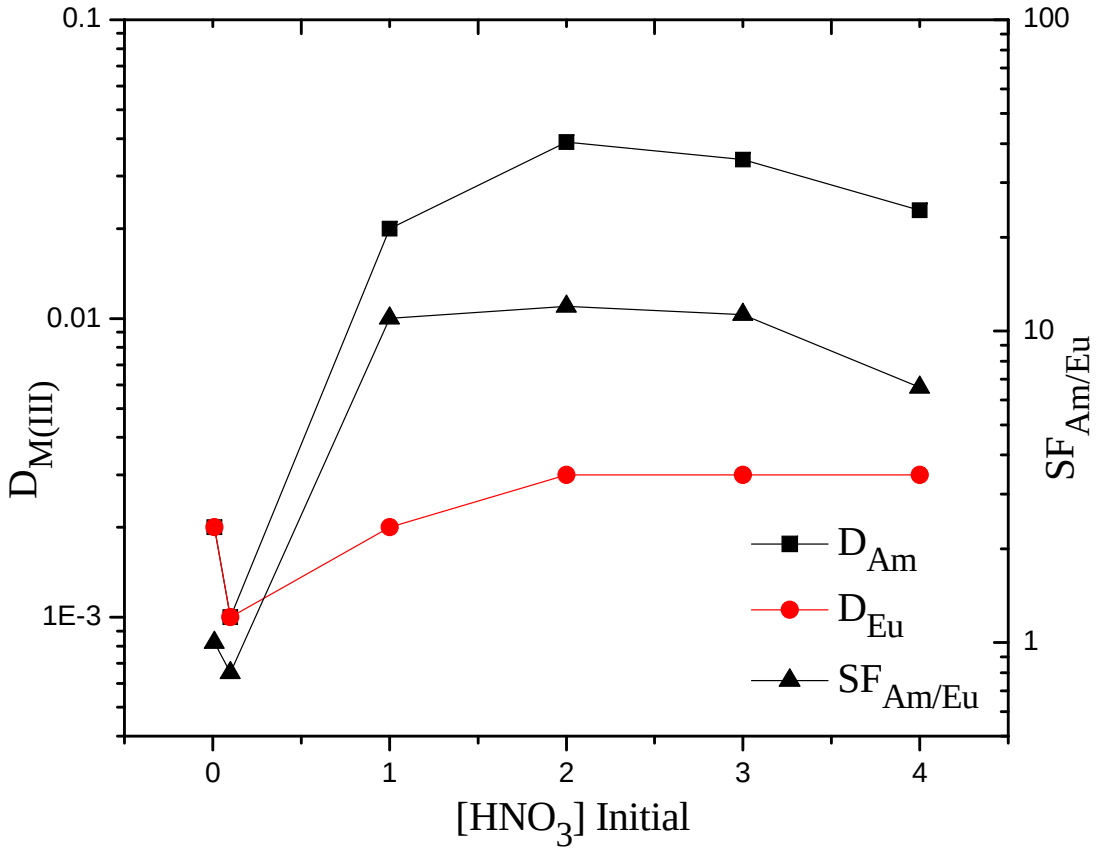


X-Ray Crystal Structure of $CyMe_4$-BTTP



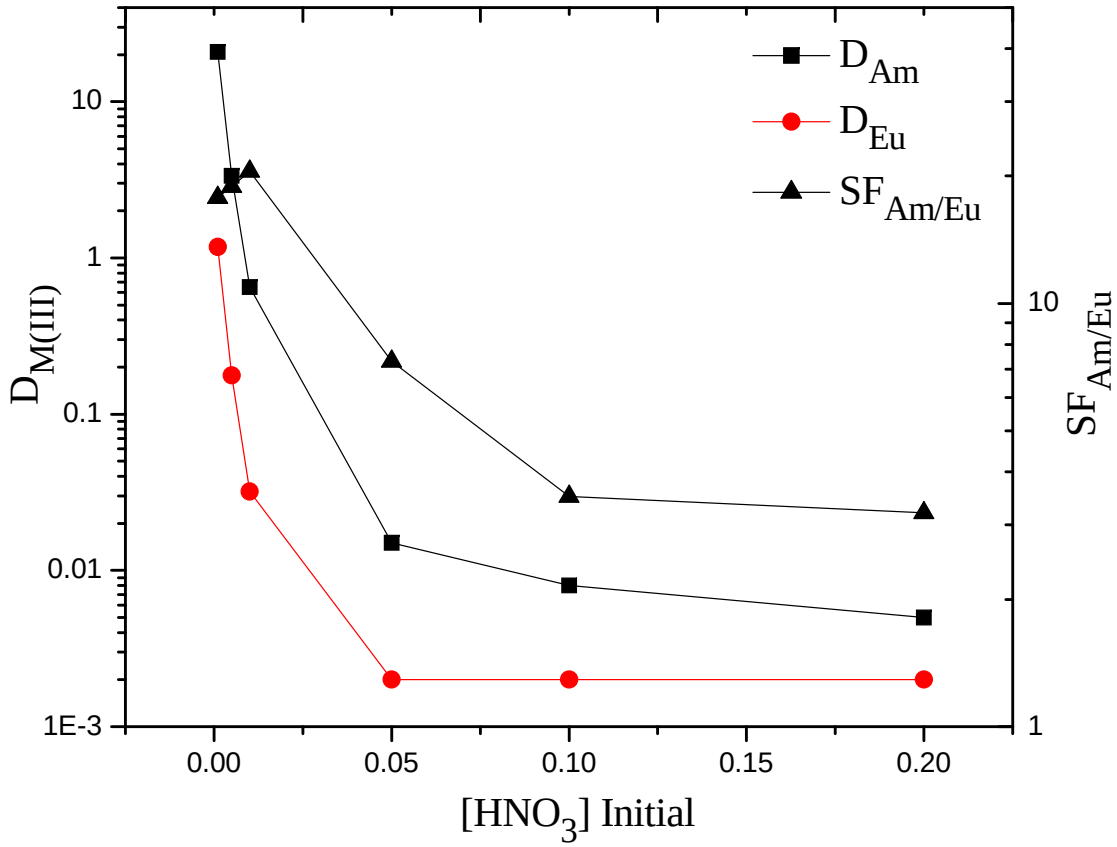
***cis – trans – trans - cis* arrangement of donor atoms**

Solvent Extraction Studies



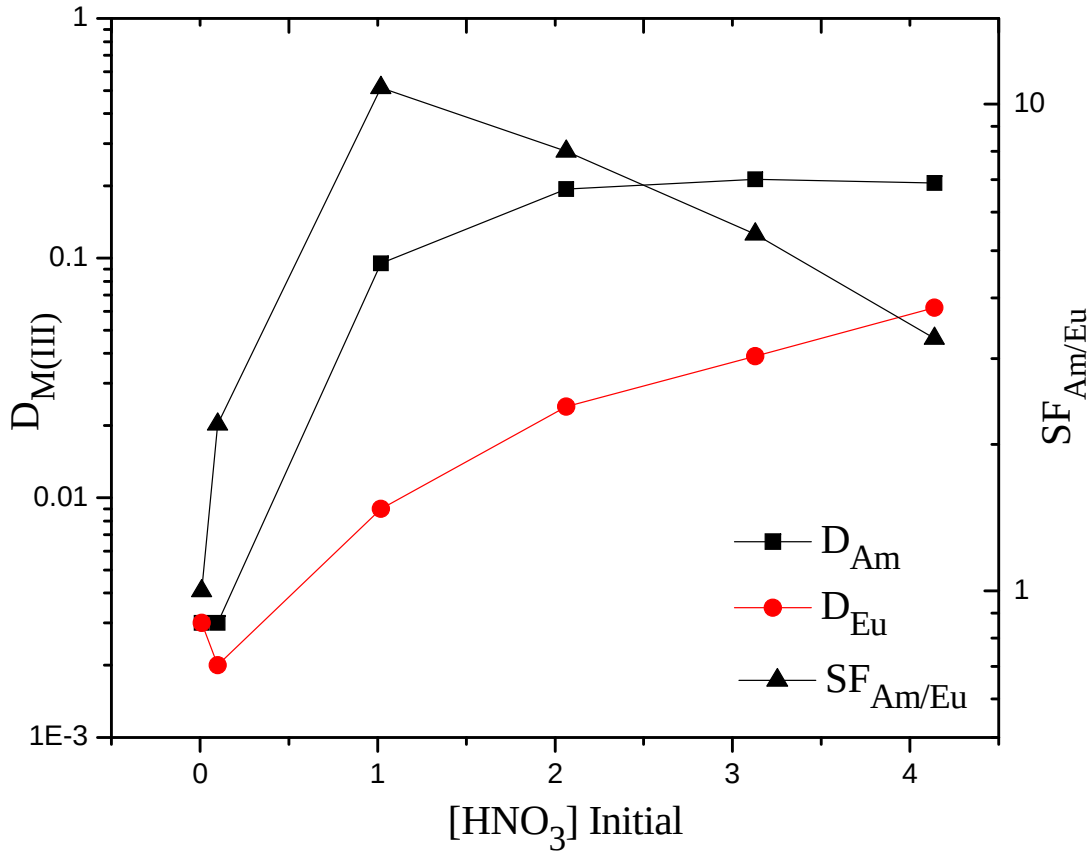
Extraction of Am(III) and Eu(III) from HNO_3 by $CyMe_4$-BTTP (0.01 M) in 1-octanol

Solvent Extraction Studies



Extraction of Am(III) and Eu(III) from HNO_3 by $CyMe_4$-BTTP (0.01 M) + 2-bromohexanoic acid (1 M) in 1-octanol

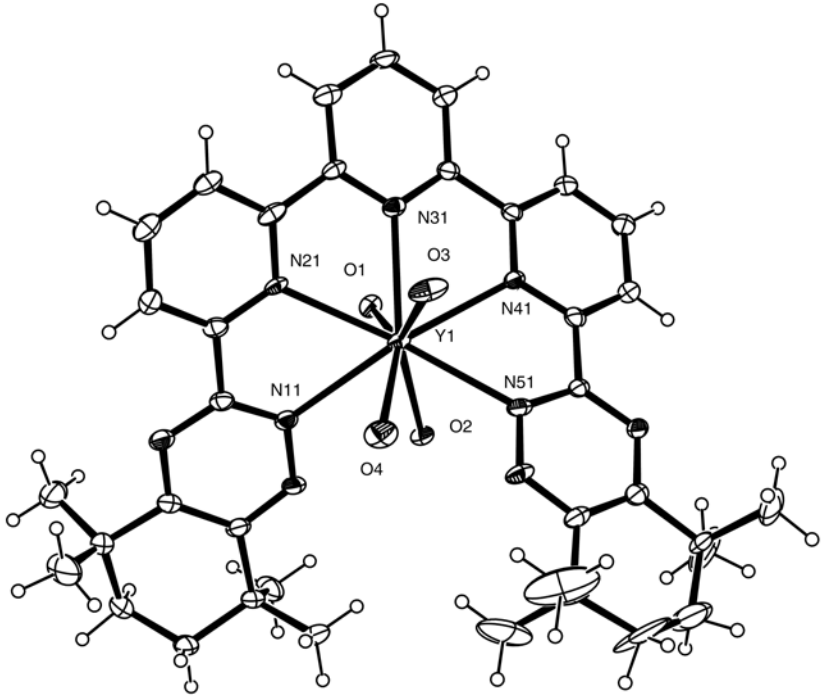
Solvent Extraction Studies



Extraction of Am(III) and Eu(III) from HNO_3 by $CyMe_4$-BTTP (0.01 M) + DMDOHEMA (0.25 M) in 1-octanol

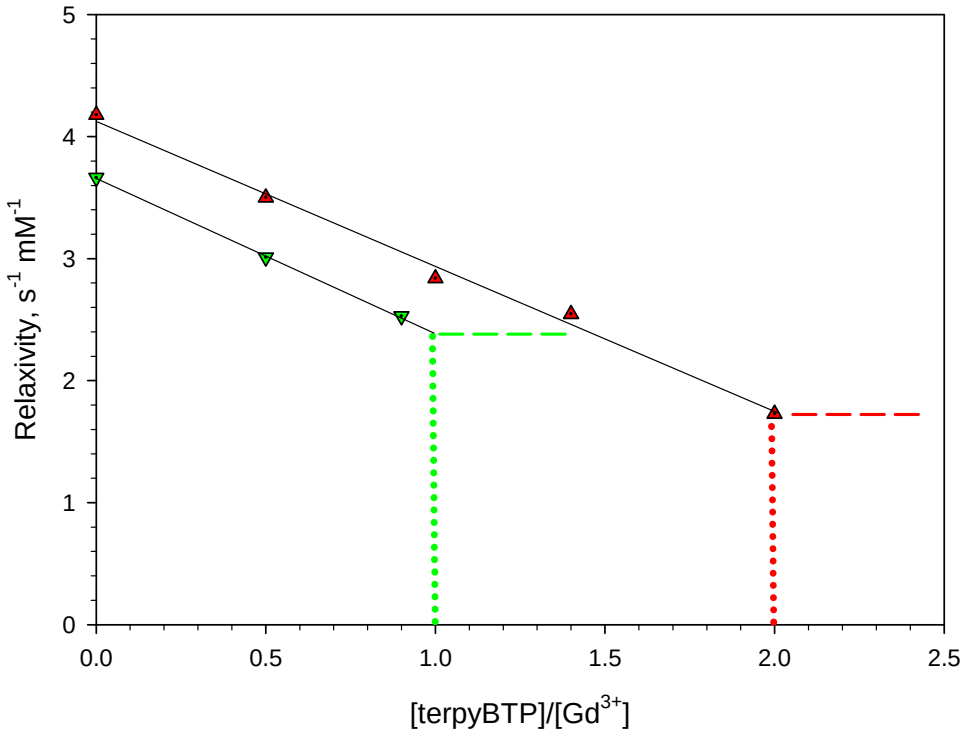
Metal Complexes of $CyMe_4$-BTTP

Yttrium(III) complex:



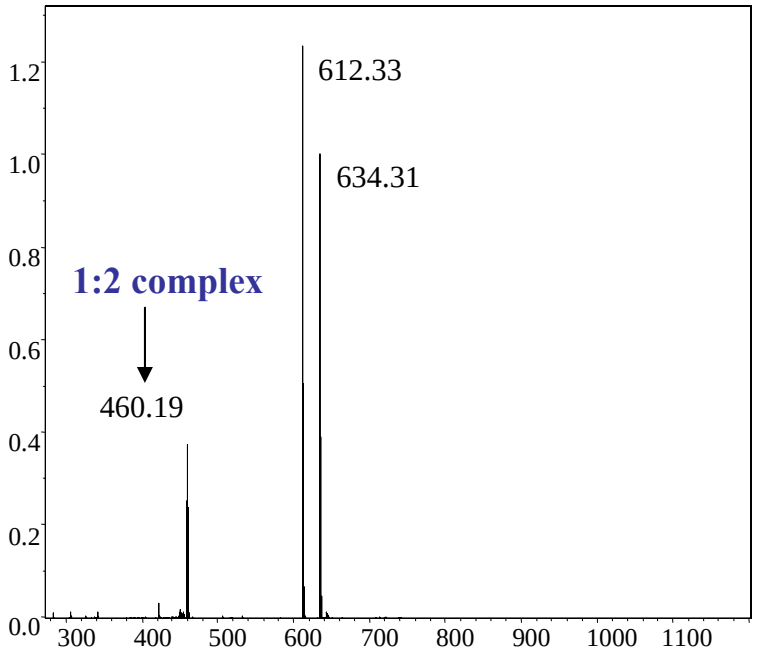
$CyMe_4$-BTTP (1 eq) + $Y(ClO_4)_3$ (0.5 eq) in DCM/CH_3CN

Solution-Phase NMR Studies of Lanthanide Complexes



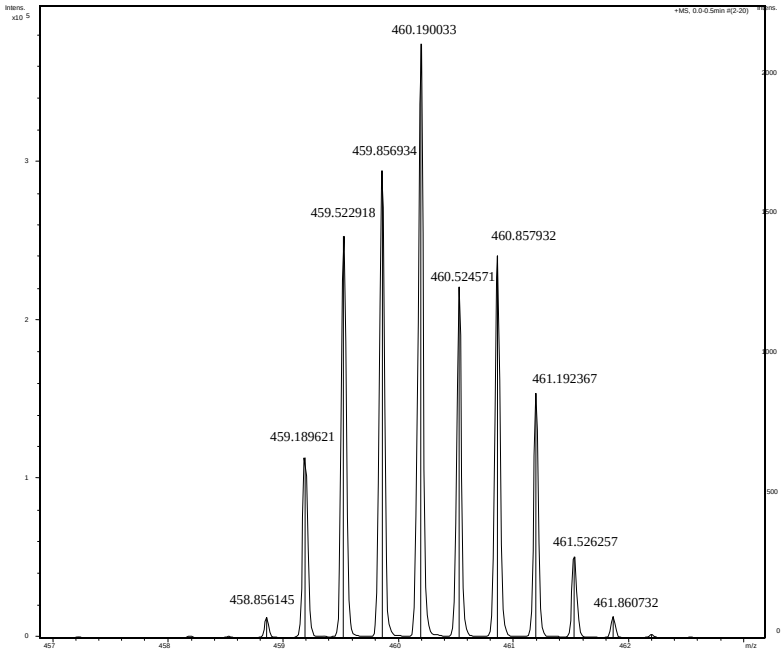
Nuclear Magnetic Relaxation Dispersion Titration of Gd^{3+} by $CyMe_4$-BTTP in anhydrous CD_3CN (▲ = perchlorate salt, ▼ = nitrate salt)

Mass Spectrometry Studies of Lanthanide Complexes

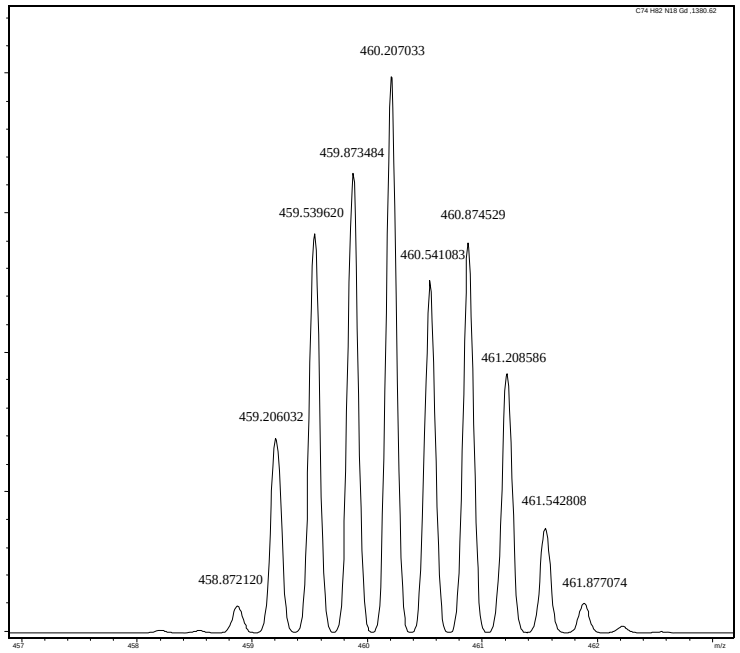


Electrospray Mass Spectrum of a $CyMe_4$-BTTP:$Gd(ClO_4)_3$ mixture (2.5:1 ratio)

Mass Spectrometry Studies of Lanthanide Complexes

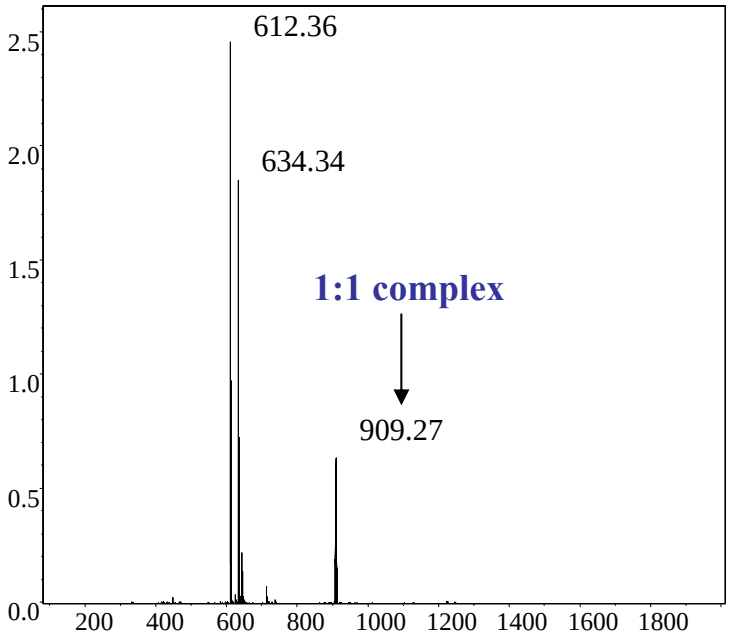


Expanded view of the mass peak at m/z = 460.19



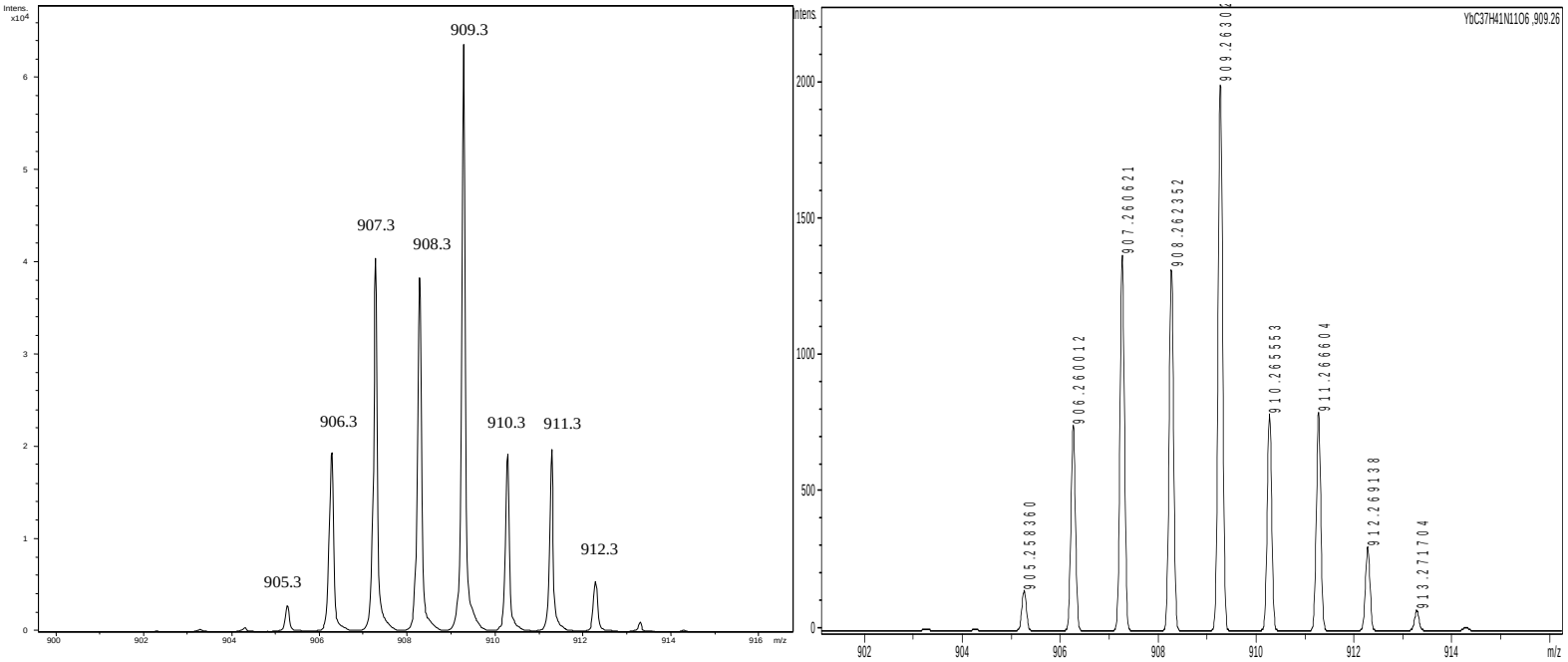
Computer simulation of the isotope distribution pattern of $Gd(CyMe_4\text{-}BTTP)_2^{3+}$

Mass Spectrometry Studies of Lanthanide Complexes



Electrospray Mass Spectrum of a $CyMe_4$-BTTP:$Yb(NO_3)_3$ mixture (1:1 ratio)

Mass Spectrometry Studies of Lanthanide Complexes

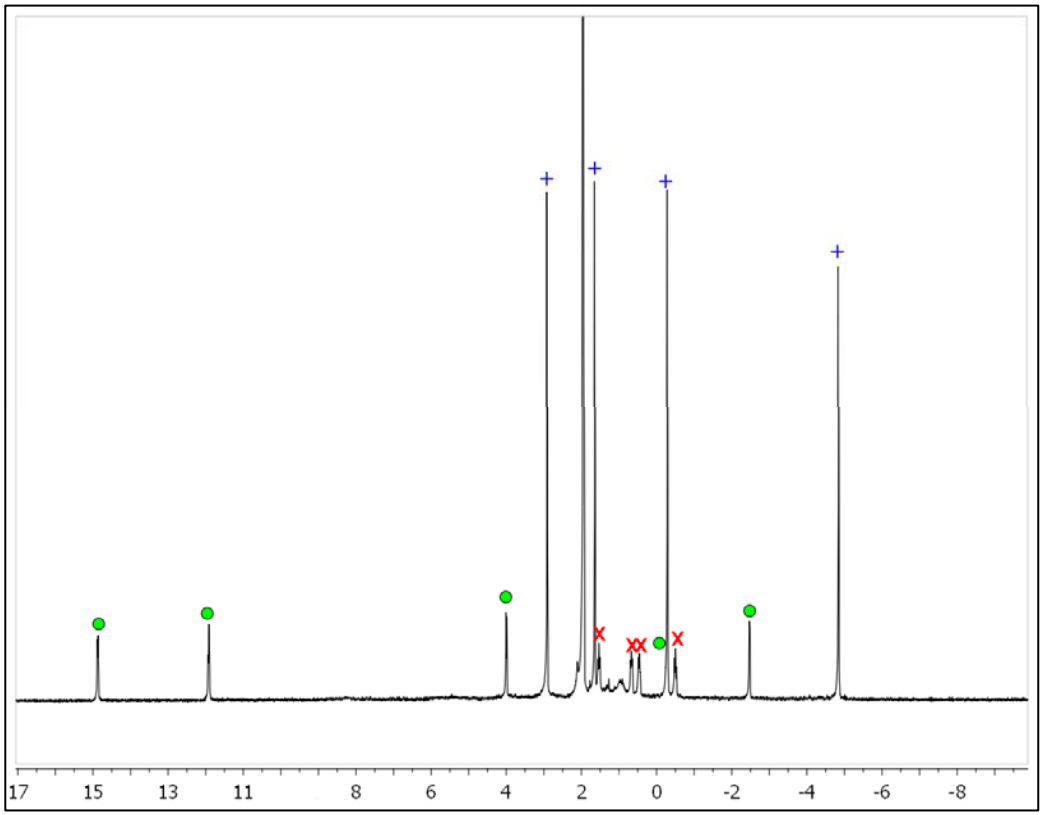


Expanded view of the mass peak at m/z = 909.27

Computer simulation of the isotope distribution pattern of $[Yb(CyMe_4\text{-}BTTP)(NO_3)_2]^+$

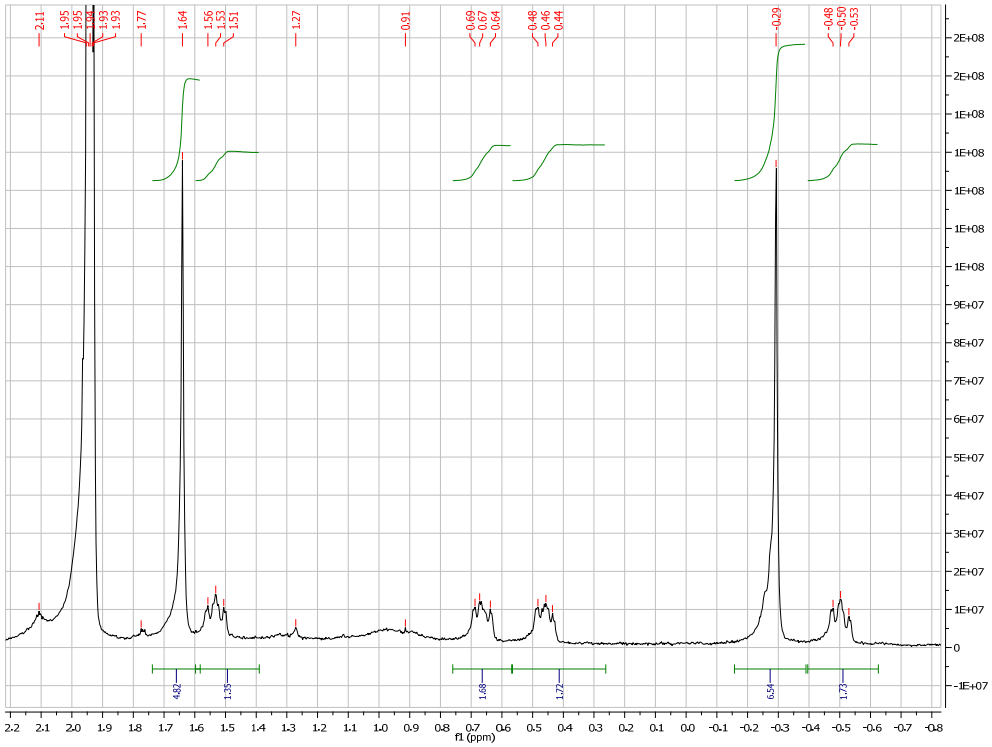
Solution-Phase NMR Studies of Lanthanide Complexes

● = pyridine protons
+ = methyl protons
x = methylene protons



^{1}H NMR spectrum of a 2:1 mixture of $CyMe_4$-BTTP and $Eu(ClO_4)_3$ in anhydrous CD_3CN at 25 °C

Solution-Phase NMR Studies of Lanthanide Complexes



Expanded view of the methylene resonances in the ^{1}H NMR spectrum of a 2:1 mixture of $CyMe_4$-BTTP and $Eu(ClO_4)_3$

Solution-Phase NMR Studies of Lanthanide Complexes

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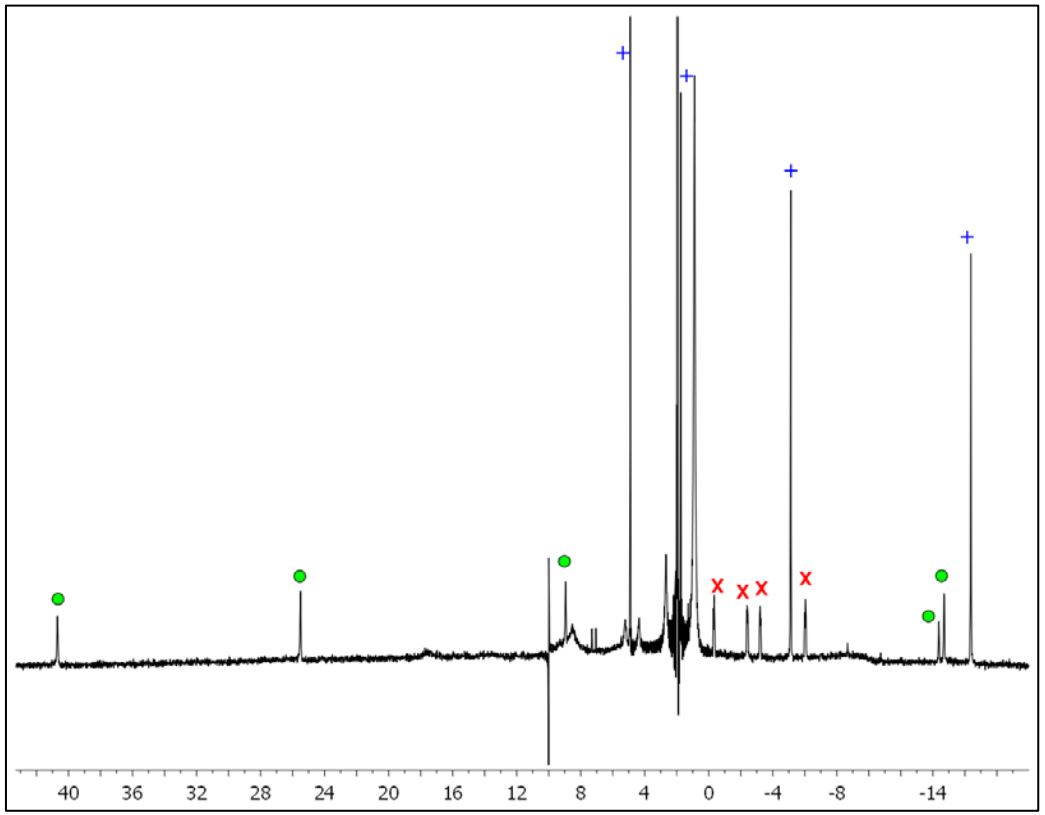
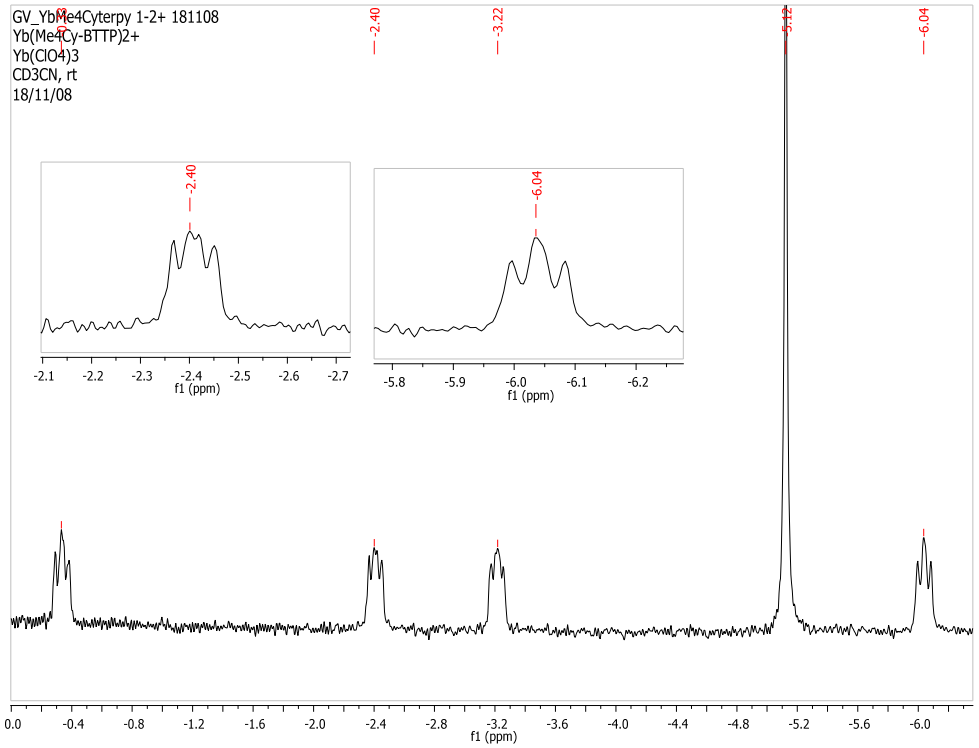


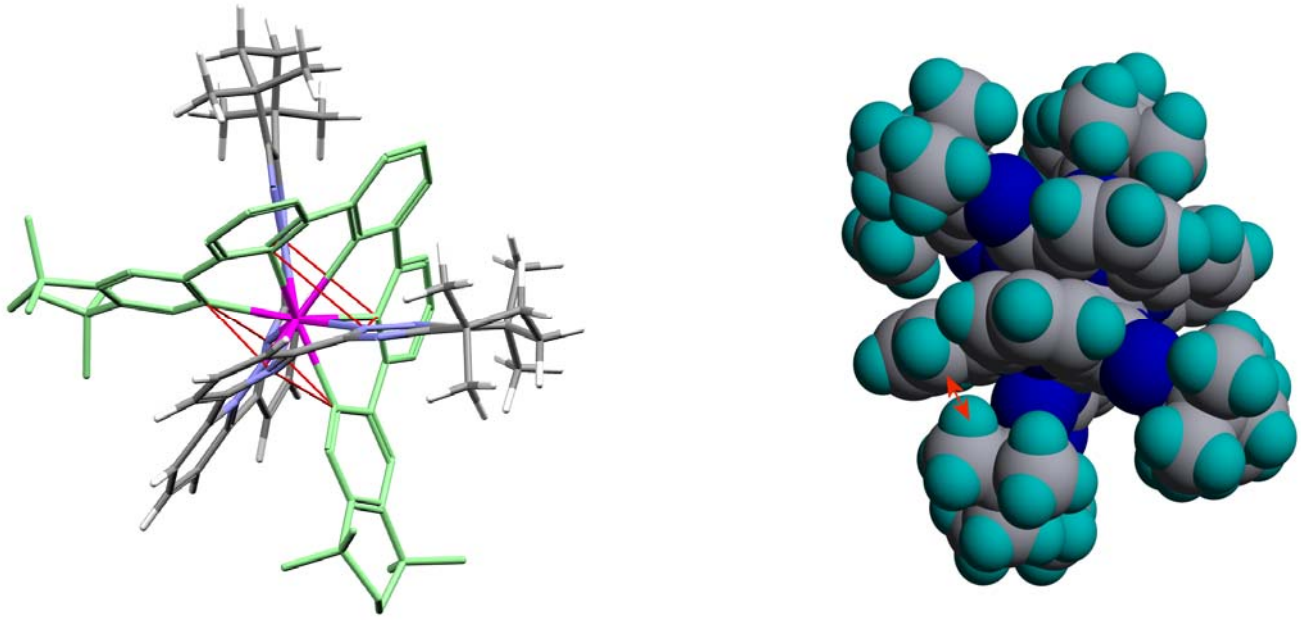
^{1}H NMR spectrum of a 2:1 mixture of $CyMe_4$-BTTP and $Yb(ClO_4)_3$ in anhydrous CD_3CN at 25 °C

Solution-Phase NMR Studies of Lanthanide Complexes



Expanded view of the methylene resonances in the ^{1}H NMR spectrum of a 2:1 mixture of $CyMe_4$-BTTP and $Yb(ClO_4)_3$

Optimized Solution Structure of Ytterbium bis-Complex



Two views of the optimized structure of $Yb(CyMe_4\text{-}BTTP)_2^{3+}$ obtained by force-field calculations. The two square faces of the square antiprism are shown in red.

Optimized Solution Structure of Ytterbium bis-Complex

Induced paramagnetic shifts calculated from:

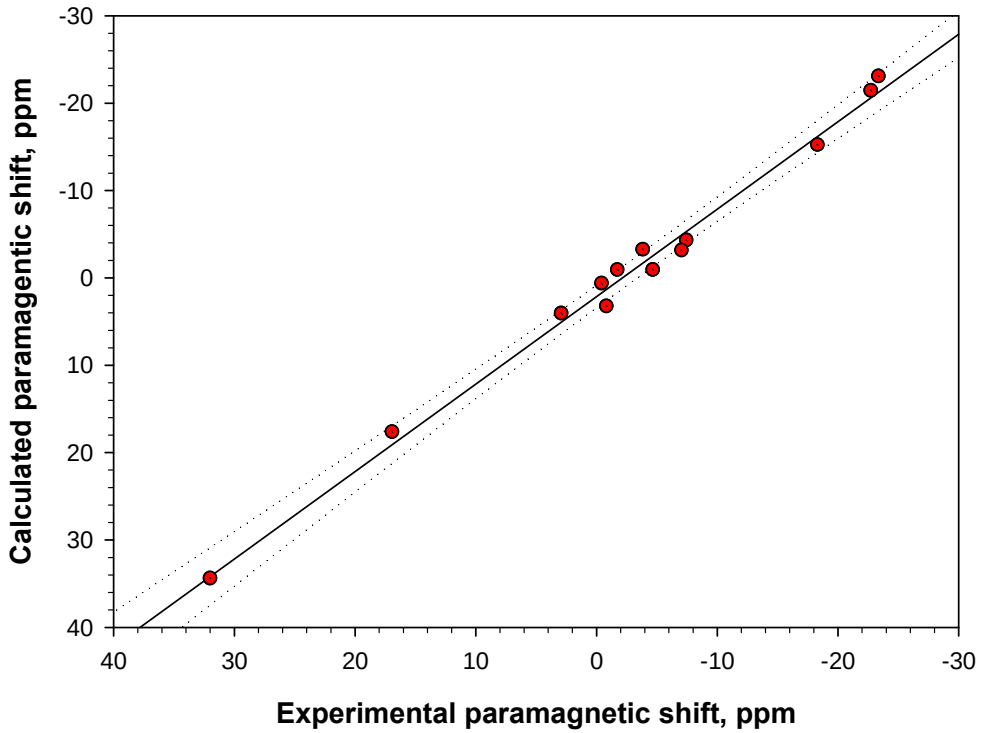
$$\delta_i = \frac{1}{12\pi r^3}\left[\left(\chi_{zz} - \frac{1}{2}\left(\chi_{xx} + \chi_{yy}\right)\right)\left\langle 3\cos^2\theta_i - 1\right\rangle + \left(\chi_{xx} - \chi_{yy}\right)\left\langle \sin^2\theta_i \cos 2\psi_i \right\rangle\right]$$

δ_i = induced paramagnetic shift of nucleus i

χ_{xx}, χ_{yy} and χ_{zz} = magnetic susceptibility terms

r_i, θ_i and ψ_i = polar coordinates of proton i

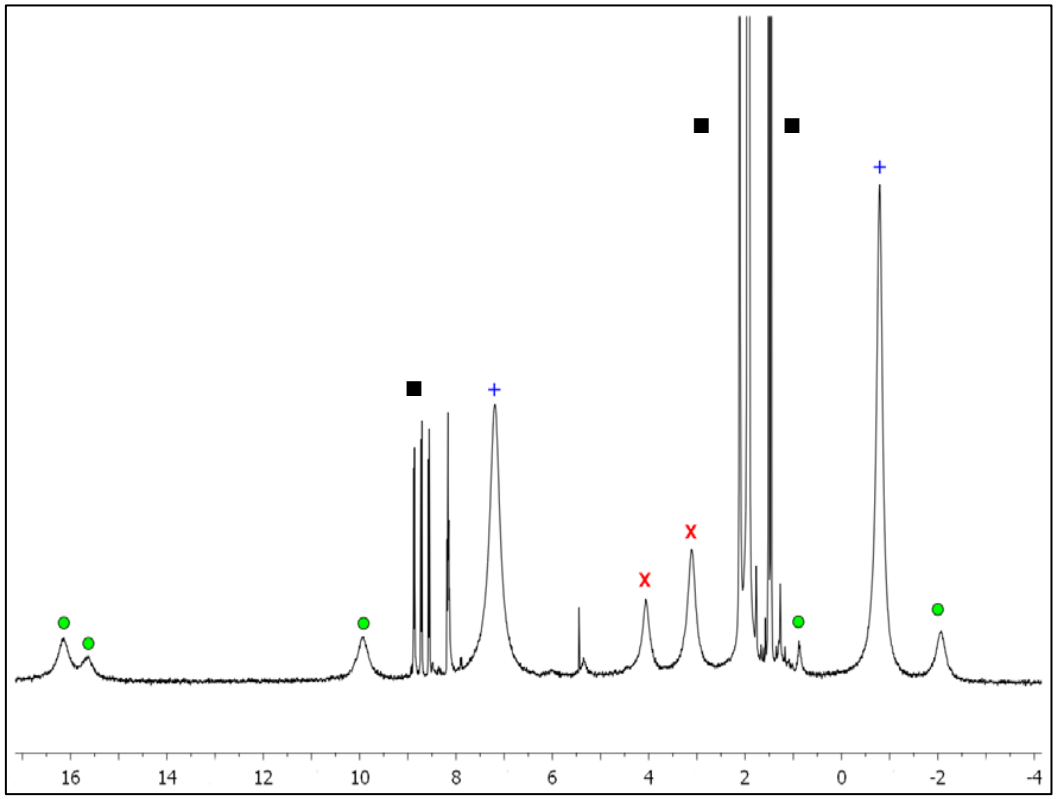
Optimized Solution Structure of Ytterbium bis-Complex



Correlation between the calculated and experimental paramagnetic shifts in the ^{1}H NMR spectrum of [Yb(CyMe$_4$-BTTP)$_2$(ClO$_4$)$_3$]. 99 % intervals indicated by dotted lines.

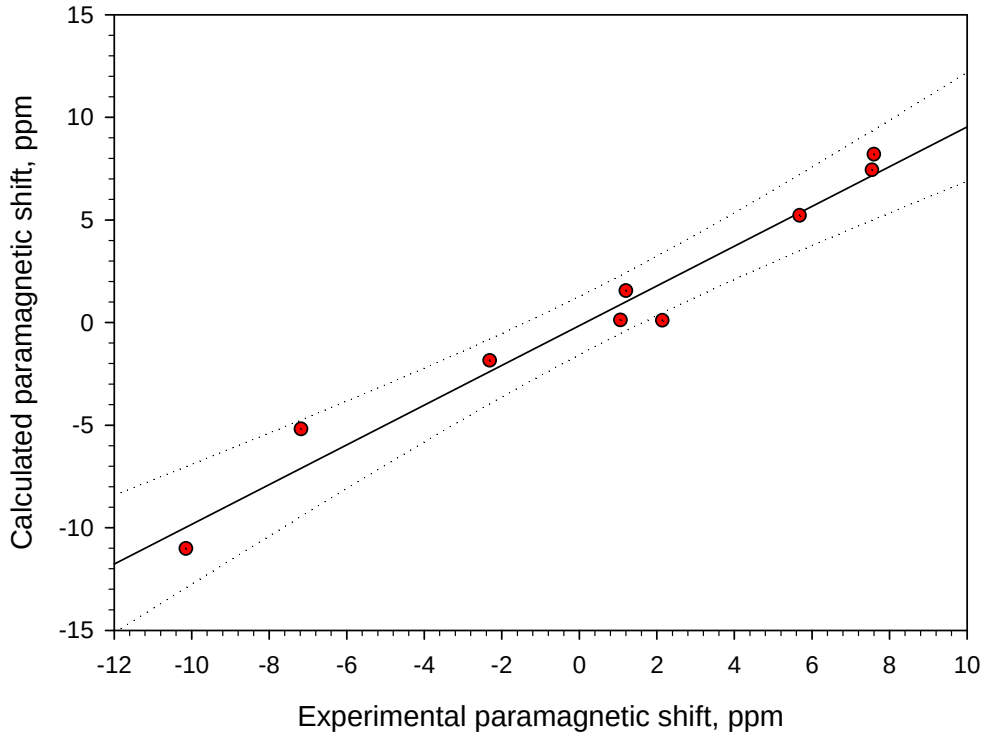
Solution-Phase NMR Studies of Lanthanide Complexes

● = pyridine protons
+ = methyl protons
x = methylene protons
■ = free ligand



^{1}H NMR spectrum of a 1:1 mixture of $CyMe_4$-BTTP and $Yb(NO_3)_3$ in anhydrous CD_3CN at 25 °C

Optimized Solution Structure of Ytterbium mono-Complex



Correlation between the calculated and experimental paramagnetic shifts in the ^{1}H NMR spectrum of [Yb(CyMe$_4$-BTTP)(NO$_3$)$_3$]. 99 % intervals indicated by dotted lines.

Conclusions

- **Low DAm values but good separation factors (SFAm/Eu) are observed for $CyMe_4$-BTTP in 1-octanol.**
- **Higher DAm values obtained with 2-bromohexanoic acid at low acidity.**
- **With lanthanide perchlorates, $CyMe_4$-BTTP forms highly-crowded 1:2 complexes - aliphatic rings conformationally immobile.**
- **With lanthanide nitrates, $CyMe_4$-BTTP forms less crowded 1:1 complexes – aliphatic rings conformationally mobile.**
- **Nitrate ions compete with the ligand for coordination sites on the metal – less hydrophobic 1:1 complexes.**
- **Solution structure of 1:2 complex with $Yb(ClO_4)_3$ determined – metal adopts bicapped square antiprism geometry.**

Acknowledgments

COLLABORATORS:

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Michael Drew (Reading)

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Michal Sypula (Jülich)

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Nouri Bouslimani (Liege)
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EURATOM

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