Complexation of lanthanides and actinides with aromatic nitrogen donor ligands: thermodynamic and kinetic studies

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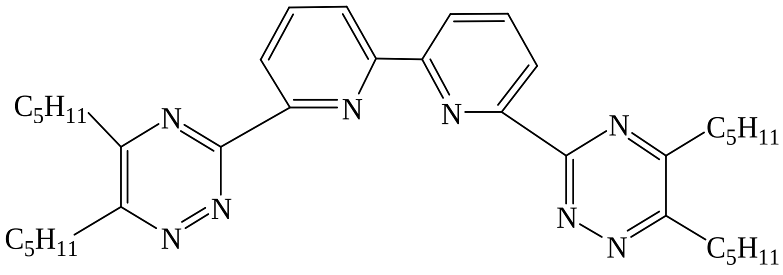
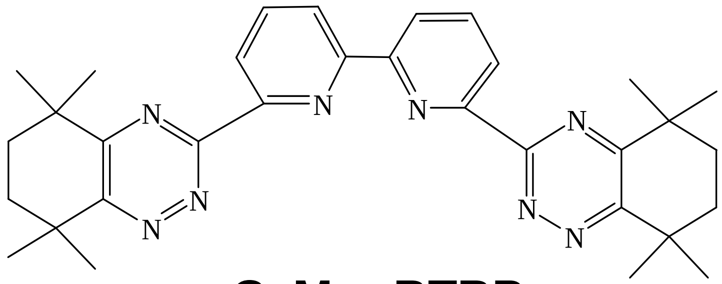
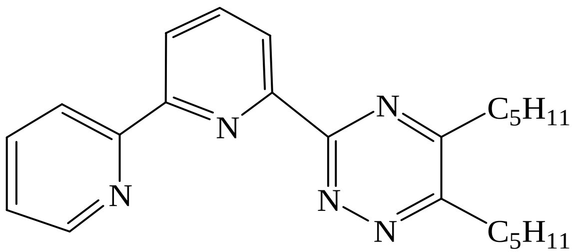
Compounds studied



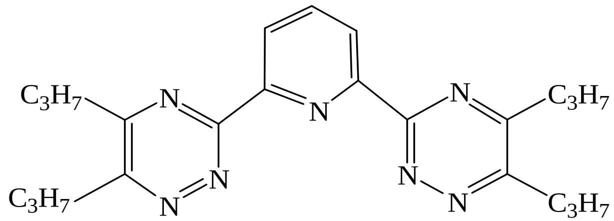
C_5-BTBP



$CyMe_4$-BTBP



C_5-*hemi*-BTP



n-Pr-BTP

Metal ions

La^{3+}, Nd^{3+}, Eu^{3+}, Gd^{3+}, Er^{3+}, Yb^{3+}, Th^{4+} and UO_2^{2+}

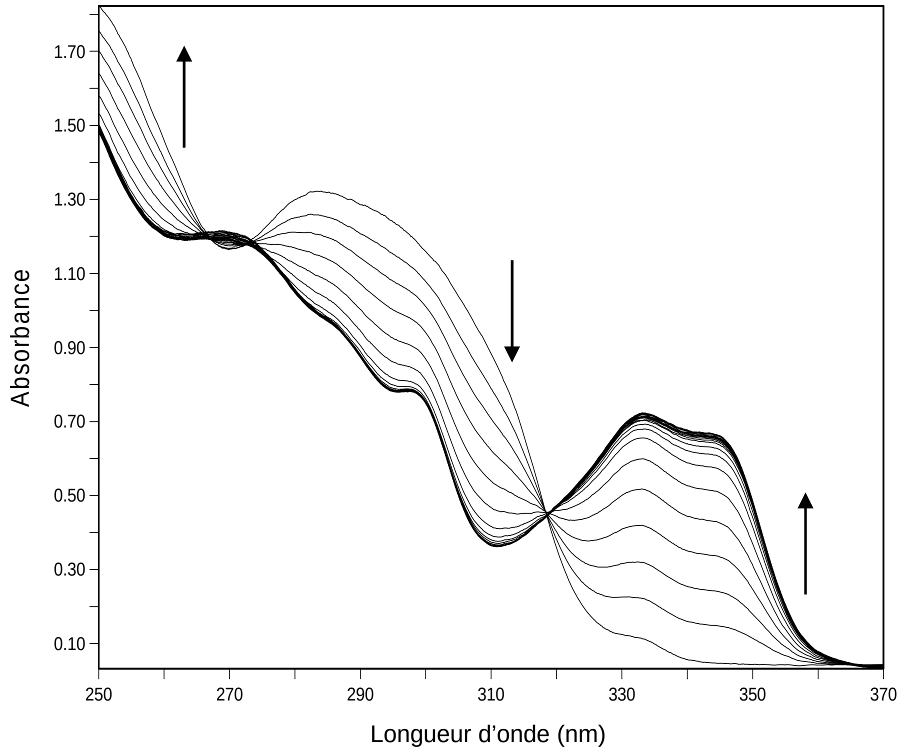
Thermodynamic study

Spectrophotometric titrations

- **Solvent: methanol**
- **T = 25°C**
- **Background electrolyte:**

  Et_4NNO_3 (I = 10^{-2} M)
- **Lanthanides and actinides nitrates**
- **Addition of metal solution into 2 mL of ligand solution**

<u>Interpretation</u>: program Specfit



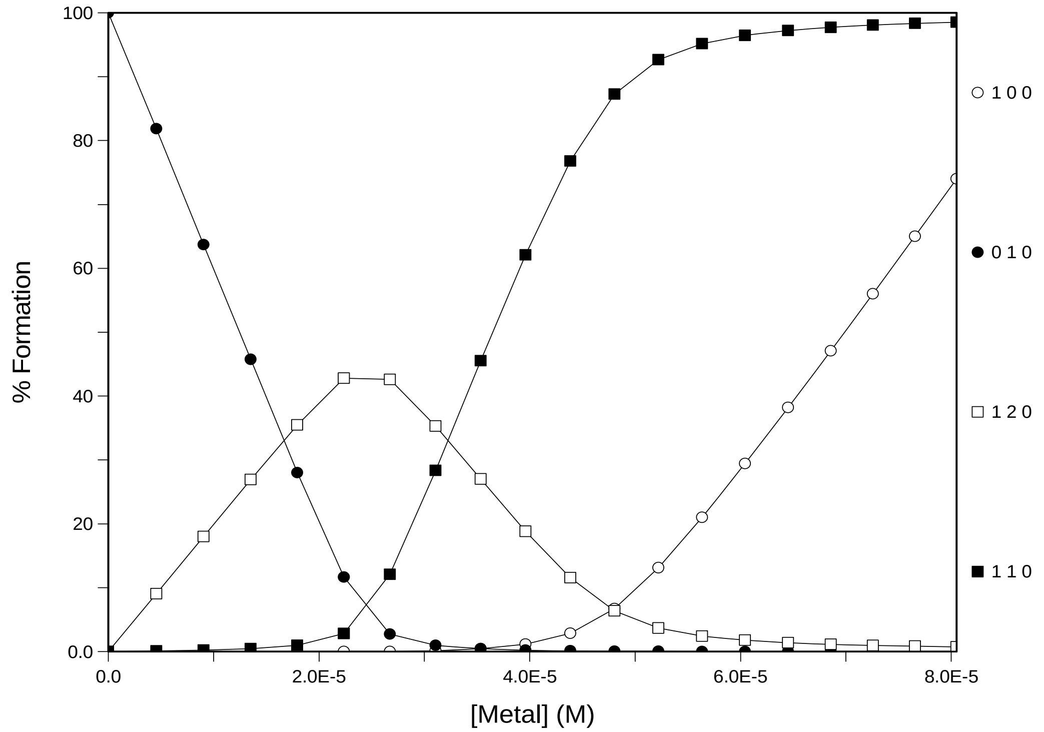
Complexation of Eu^{3+} with C_5-BTBP
($C_L = 5 \times 10^{-5}$ M; $0 \leq C_M/C_L \leq 1.8$)

Complex stability constants (log β) with BTBP's

Cations	Complexes (M:L)	C_5-BTBP	$CyMe_4$-BTBP
La^{3+}	1:1 1:2	4.8 10.0	4.4 8.8
Nd^{3+}	1:1 1:2	5.0 10.8	n.d.
Eu^{3+}	1:1 1:2	5.7 11.3	6.5 11.9
Gd^{3+}	1:1 1:2	4.15 10.2	n.d.
Er^{3+}	1:1 1:2	7.4 13.4	n.d.
Yb^{3+}	1:1 1:2	8.0 13.9	5.9
Th^{4+}	1:1	3.94	n.d.
UO_2^{2+}	1:1	5.92	n.d.

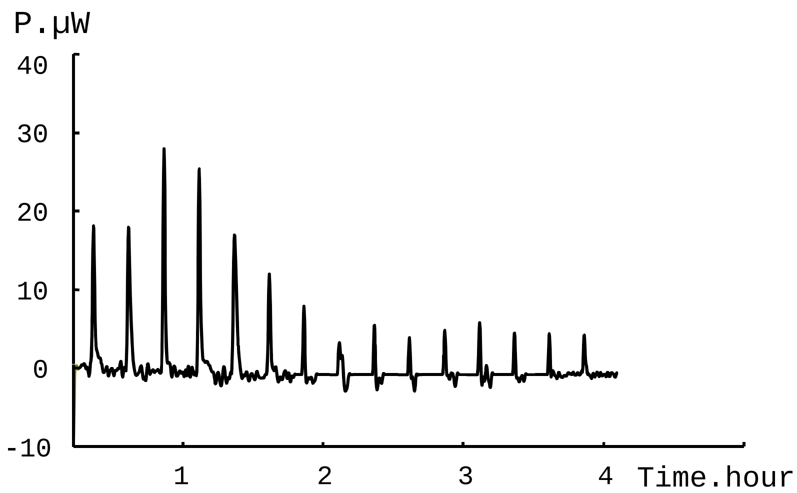
- **Complexes ML and ML_2 (with lanthanides) and ML (with actinides)**
- **C_5-BTBP: increase of stability within the lanthanides series**

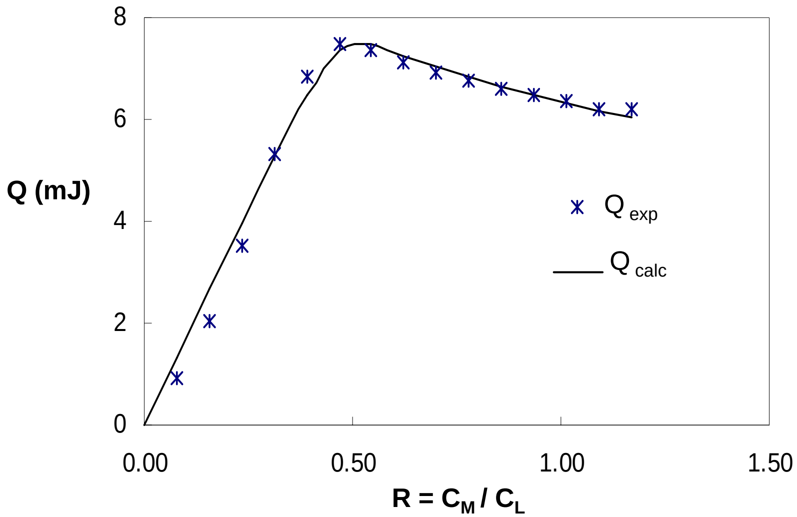
Distribution of all the species present in the system Yb^{3+}/C_5-BTBP in methanol at 25°C ($C_L = 10^{-5}$ M).



Microcalorimetric studies

- Solvent: methanol
- T = 25°C
- Europium nitrate
- Background electrolyte : Et_4NNO_3 (I = 10^{-2} M)





Titration of 2.7 ml C_5-BTBP (2.5 $\times 10^{-4}$ M) by injection of 15×15 µL $Eu(NO_3)_3$
($0 \leq R = C_M/C_L \leq 1.2$)

Overall thermodynamic complexation parameters

Complexes (M : L)	log β	$-\Delta G$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	$T\Delta S$ (kJ mol^{-1})
1 : 1	5.6 (5.7)*	32	12	20
1 : 2	10.5 (11.3)*	60	28	32
Stepwise	4.9	30	16	12

* Spectrophotometric determination

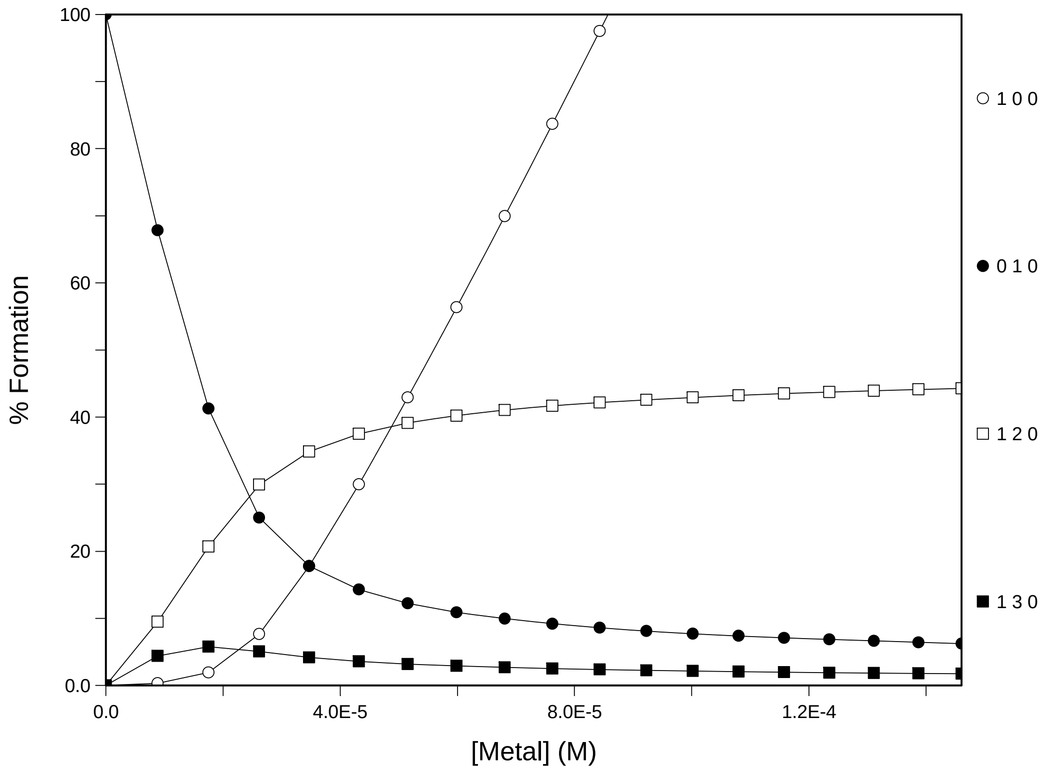
- **Excellent agreement with spectrophotometric results**
- **Formation of ML and ML_2: enthalpy and entropy origins**

Complex stability constants (log β) with BTP's

Cations	Complexes	C_5-*hémi*-BTP	*n*-Pr-BTP
La^{3+}	1:1	2.8	3.7
Nd^{3+}	1:1	3.01	n.d.
Eu^{3+}	1:1 1:2 1:3	3.6 - -	- 9.50 14.2
Gd^{3+}	1:1	3.6	n.d.
Er^{3+}	1:1	4.18	n.d.
Yb^{3+}	1:1 1:2 1:3	4.19 - -	- 10.3 14.3
Th^{4+}	1:1	3.9	n.d.
UO_2^{2+}	1:1	3.6	n.d.

- ML complexes for C_5-*hemi*-BTP and *n*-Pr-BTP with La^{3+}
- ML_2 + ML_3 complexes for *n*-Pr-BTP with Eu^{3+} and Yb^{3+}
- ML species less stable for C_5-*hemi*-BTP than for C_5-BTBP
- Increase of stability in the lanthanide series

Distribution of all the species present in the system Yb^{3+}/*n*-Pr-BTP in methanol at 25°C ($C_L = 10^{-5}$ M)

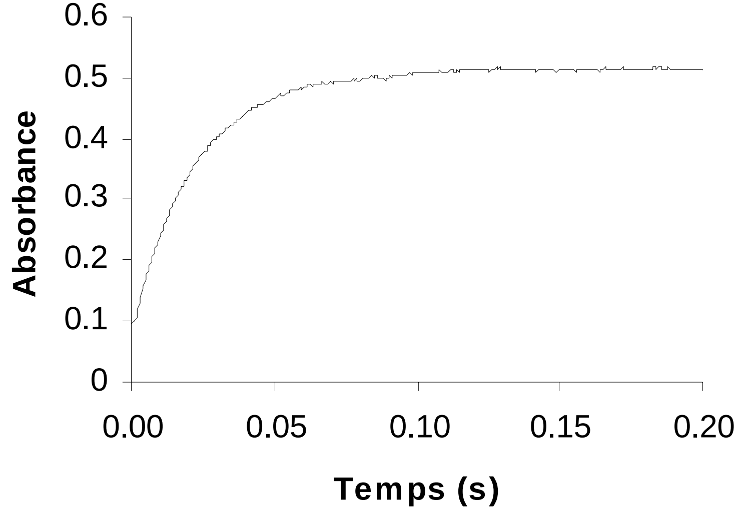


Kinetics studies

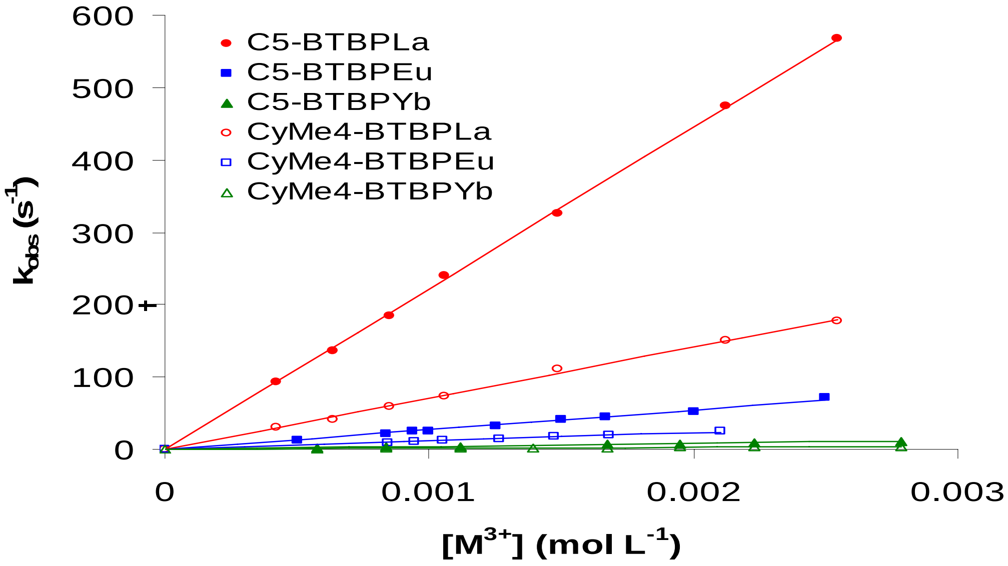
Stopped-flow spectrophotometric studies

- Solvent: methanol
- T = 25°C
- La^{3+}, Eu^{3+}, Yb^{3+} nitrates
- Background electrolyte: Et_4NNO_3 ($I = 10^{-2}$ M)
- Selected wavelength: 345 nm
- Metal ion in excess: pseudo first order

Complexation of Eu^{3+} (1.25×10^{-3} M) with C_5-BTBP (1.04×10^{-4} M)



Fitted by one exponantial → k_{obs}



Rate constants of formation k_f (L mol^{-1} s^{-1}) with BTBP

Lanthanides	C_5-BTBP	$CyMe_4$-BTBP
La^{3+} Eu^{3+} Yb^{3+}	223×10^3 27.0×10^3 4.07×10^3	70.5×10^3 11.5×10^3 1.4×10^3

- Decrease of the rate constants in the series
- lower rate constants with $CyMe_4$-BTBP

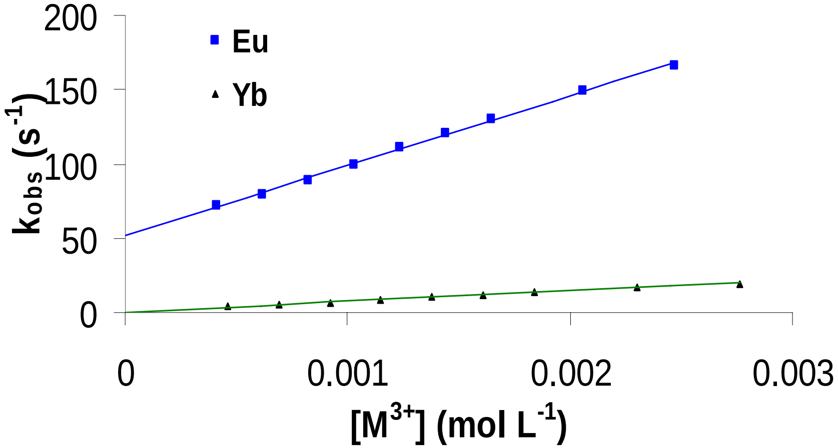
Proposed mechanism with BTBP's

$$M^{3+}_{solvated} + BTBP \underset{k_d}{\overset{k_f}{\rightleftarrows}} [\text{outer-sphere - complex}] \quad \text{(fast)}$$

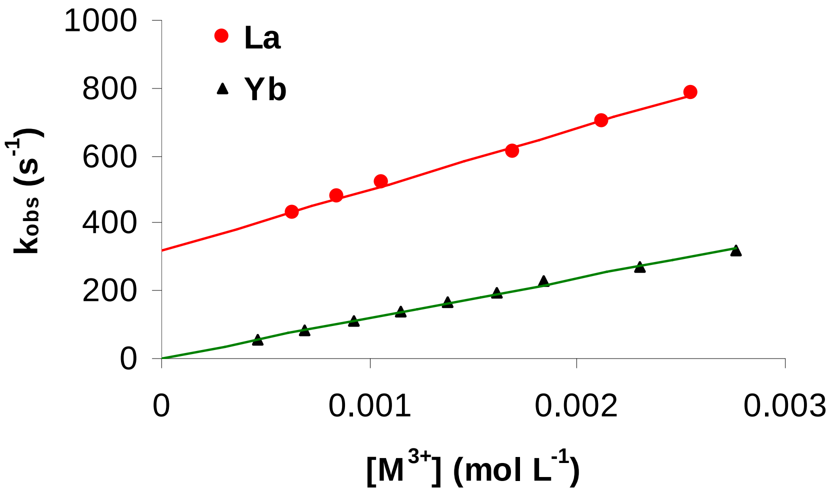
$$[\text{outer - sphere}] \underset{k'_d}{\overset{k'_f}{\rightleftarrows}} [M(BTBP)]^{3+} \quad \text{(slow)}$$

$$[M(BTBP)]^{3+} + BTBP \underset{k''_d}{\overset{k''_f}{\rightleftarrows}} [M(BTBP)_2]^{3+} \quad \text{(not quantifiable)}$$

C_5-*hemi*-BTP



***n*-Pr-BTP**



$$k_{obs} = k_f \times [M^{3+}] + k_d$$

Formation (k_f) and dissociation (k_d) rate constants

Lanthanides		C_5-*hemi*-BTP	*n*-Pr-BTP
La^{3+}	k_f (L mol^{-1} s^{-1})	*	182×10^3
	k_d (s^{-1})	*	318
Eu^{3+}	k_f (L mol^{-1} s^{-1})	46.9×10^3	*
	k_d (s^{-1})	51.9	*
Yb^{3+}	k_f (L mol^{-1} s^{-1})	7.0×10^3	118.7×10^3
	k_d (s^{-1})	0.5	

* *Kinetic traces could not be interpreted*

- **Highest values of k_f and k_d corresponding to one single step with La^{3+}/n-Pr-BTP and Eu^{3+}/C_5-*hemi*-BTP**

Proposed mechanism for C_5-*hemi*-BTP with Eu^{3+} and Yb^{3+} and for *n*-Pr-BTP with La^{3+}

$$M^{3+}_{solvated} + L \underset{k_d}{\overset{k_f}{\rightleftarrows}} \text{[outer sphere - complex]} \quad \text{(fast)}$$

$$\text{[outer sphere – complex]} \underset{k'_d}{\overset{k'_f}{\rightleftarrows}} [M(L)]^{3+} \quad \text{(slow)}$$

C_5-*hemi*-BTP $\beta = k'_f / k'_d$

- **Good agreement with spectrophotometric data**

Eu^{3+}: log β = 3.0 (3.6)[s]

Yb^{3+} : log β = 4.15 (4.19)[s]

Proposed mechanism for *n*-Pr-BTP with Yb^{3+}

$$Yb^{3+}_{solvated} + n\text{-Pr-BTP} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [\text{outer sphere - complex}] \quad \text{(fast)}$$

$$[\text{outer sphere - complex}] \underset{k'_d}{\overset{k'_f}{\rightleftharpoons}} [Yb(n\text{-Pr-BTP})]^{3+} \quad \text{(fast)}$$

$$[Yb(n\text{-Pr-BTP})]^{3+} + n\text{-Pr-BTP} \underset{k''_d}{\overset{k''_f}{\rightleftharpoons}} [Yb(n\text{-Pr-BTP})_2]^{3+} \quad \text{(slow)}$$

$$[Yb(n\text{-Pr-BTP})_2]^{3+} + n\text{-Pr-BTP} \underset{k'''_d}{\overset{k'''_f}{\rightleftharpoons}} [Yb(n\text{-Pr-BTP})_3]^{3+} \quad \text{(not quantifiable)}$$

Conclusions

➢ Thermodynamic studies

Absorption spectrophotometry and microcalorimetry

* **BTBP: ML and/or ML_2 with Ln(III); ML with Th^{4+} and UO_2^{2+}.**
* **C_5-*hémi*-BTP: ML with Ln(III).**
* ***n*-Pr-BTP: ML with La^{3+}; ML_2 + ML_3 with Eu^{3+} et Yb^{3+}.**

* **Increase of stability in the series (lanthanidic contraction)**

➢ Kinetic studies

Absorption spectrophotometry: stopped flow

* **Different mechanisms (2 to 4 steps) according to the ligand and the cation**
* **Rate constants determined for only one step**
* **Rate constants of formation and of dissociation determined for C_5-*hemi*-BTP and *n*-Pr-BTP**

Acknowledgements

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