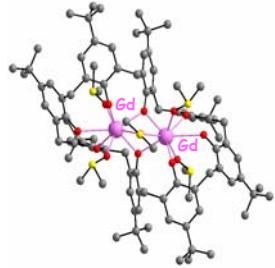
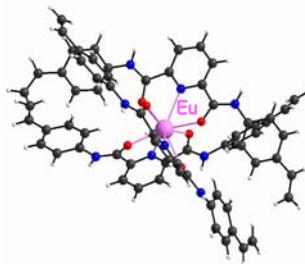


## f - Elements



$4f_{z^3}$



Master degree course, SCGC

Jean-Claude Bünzli  
2006

Faculty of basic sciences  
Laboratory of lanthanide supramolecular  
chemistry



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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## Appendices



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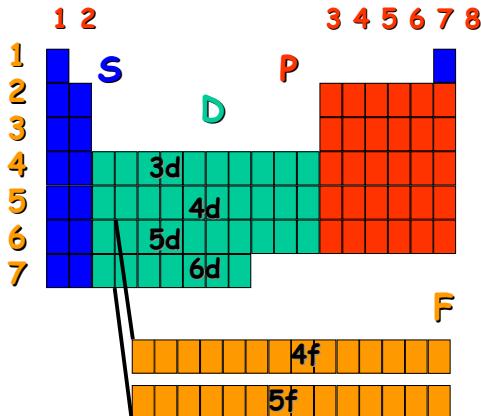
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## Pedagogical objective

- Overview of f-elements properties, with reference to their uses in daily life and high technology applications
- Mainly focused on 4f-elements

### Pre-requisites

Coordination chemistry  
Quantum chemistry



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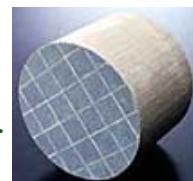
## Chapter 1 f-Atoms and Ions

### Table of Contents



Nuclear fuel rod assembly

- 1.1 Definitions and discovery
- 1.2 Occurrence of 4f elements
- 1.3 Basic properties
  - 1.3.1 Electronic configuration
  - 1.3.2 Oxidation states of 4f elements
  - 1.3.3 Oxidation states of 5f elements
- 1.4 Radioactivity of 5f elements



Particle filter for Diesel exhaust gases



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## Chapter 1. f-Atoms and Ions

### 1.1 Definitions and discovery

Lanthanides: 58-71      **Ln**

Actinides: 90-103      **An**

Parent elements La and Ac often included in **Ln** and **An**

Rare earths: Sc, Y, La + Ce-Lu

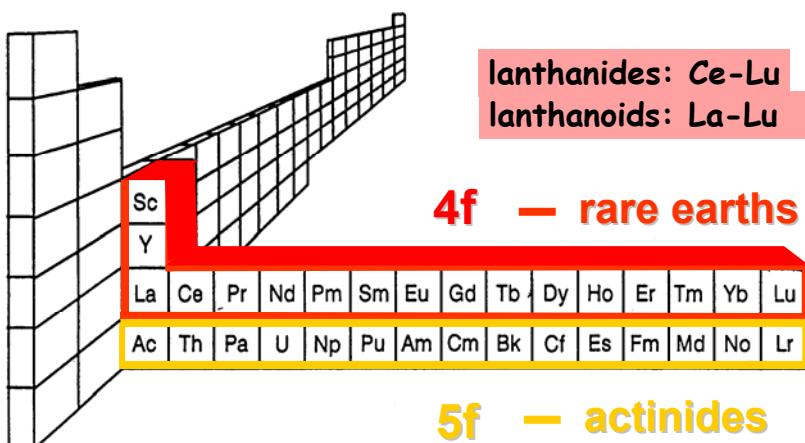
Discovery of rare earths

1794 (Y) - 1947 (Pm)

Discovery of actinides

1789 (U) - 1971 (Lr)

Naturally occurring: Ac, Th, Pa, U, (Np, Pu)



Yttrium was discovered in 1794 by Johan Gadolin, in Åbo (Turku)



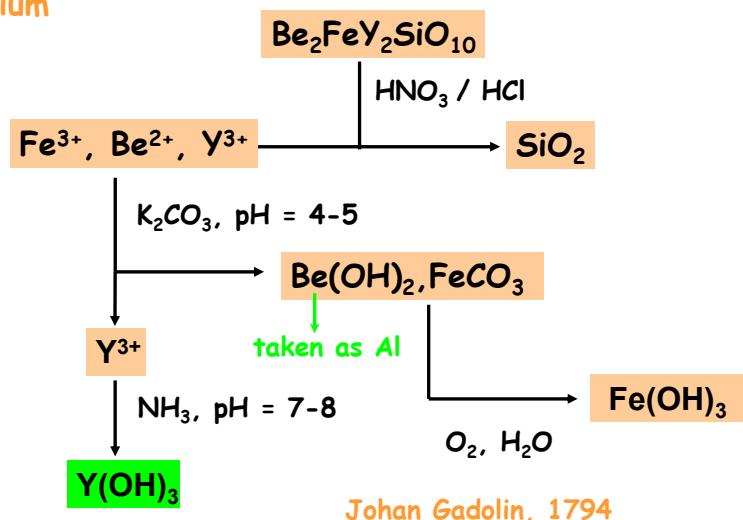
### Discovery of yttrium (1794)

- 1787 Carl Axel Arrhenius, an artillery lieutenant and amateur geologist, finds a black mineral in a quarry near Ytterby, 30 km from Stockholm.
- 1788 B. R. Geijer (Stockholm) describes the mineral ( $d = 4.2$ ) and names it ytterbite, presently known as gadolinite, with formula  $\text{Be}_2\text{FeY}_2\text{SiO}_{10}$ .
- 1792 J. Gadolin (1760-1852) studies the mineral and publishes a 19-page report in 1794 in the Proceedings of the Royal Swedish Academy of Sciences, concluding to the presence of a new "earth", which he names yttrium.

Subsequent work revealed that yttrium contained the oxides of 10 other elements.



### Chemical separation of yttrium



### Discovery of cerium (1804)

- 1751 The mineralogist Cronstedt finds a peculiar heavy stone near Batnäs.
- 1803 W. Hisinger and J. J. Berzelius analyse this stone and find it contains an unknown “earth” they name **ceria** after the recently discovered planet **Ceres**. Their finding is published in 1804 in a 24-page report and confirmed by the German chemist Klaproth.

The silicate material has a variable composition close to  $(Ce, La)_3M^{II}H_3Si_3O_{13}$  and is presently named **cerite** ( $M = Ca, Fe$ ).



### Other rare earths (1839-1947)

Most of the other rare earths have been discovered by further analysing the two initial minerals, gadolinite and cerite.

The main techniques were fractional precipitation and crystallisation, as well as flame spectroscopy (absorption and emission).

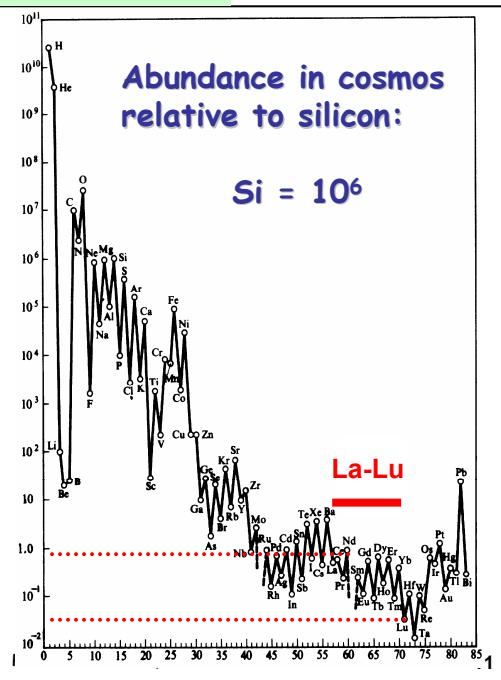
These operations were tedious: for instance, 20 tons were needed to produce 82 µg of element 61 by ion-exchange separation techniques (61 = radioactive **promethium**), that is a fraction equal to  $4 \times 10^{-12}$  !



## Chapter 1 f-Atoms and Ions

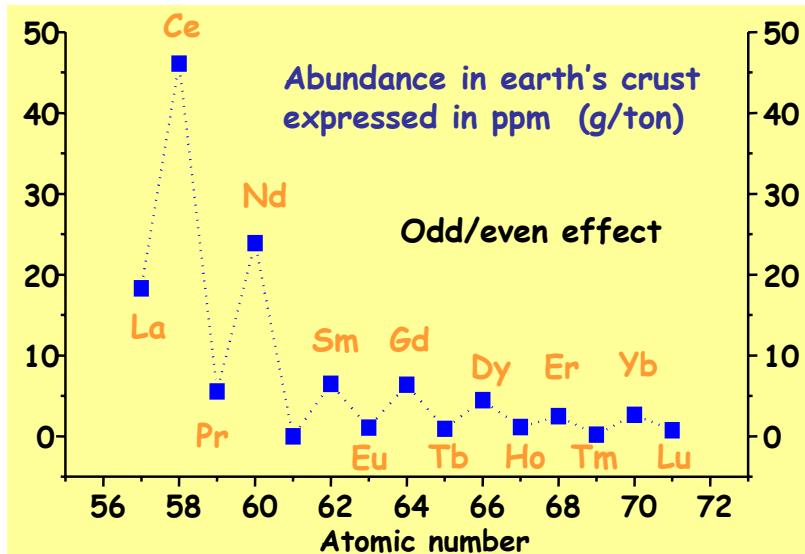
### 1.2 Occurrence of 4f elements

The elements are "rare" but not rarer than many others, such as Au, Pt, Pd, Rh, for instance



## Chapter 1 f-Atoms and Ions

### Natural abundance



## Chapter 1 f-Atoms and Ions

### Main resources (4f elements)

#### Cerium group (lighter elements)

Bastnasite	$\text{Ln}(\text{CO}_3)\text{F}$	65-70%
Monazite	$\text{LnPO}_4$	50-75%
Cerite	$(\text{Ce}, \text{La})_3\text{M}^{\text{II}}\text{H}_3\text{Si}_3\text{O}_{13}$	50-70%

#### Yttrium group (heavier elements)

Xenotime	$\text{LnPO}_4$	55-65%
Gadolinite	$\text{Ln}_2\text{M}_3\text{Si}_2\text{O}_{10}$	35-50%
Euxenite	$\text{Ln}(\text{Nb}, \text{Ta})\text{TiO}_6 \times \text{H}_2\text{O}$	15-35%



## Chapter 1 f-Atoms and Ions

### Main resources (4f elements)

World resources are estimated to 83 million metric tons  
for a present usage of about 40'000 metric tons a year

China	50 % (?)
Russia	25 % (?)
USA	10 %
Australia	5 %
Other	10 %



## Applications of 4f-elements

### • Catalysts

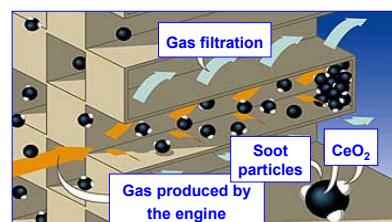
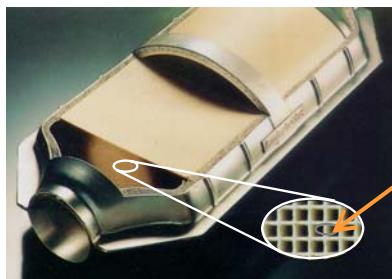
- cracking of hydrocarbons
- conversion of exhaust gases (gasoline and diesel)

### • Metallurgy

- Steel production (removal of O, S)
- Nodular graphite
- Hardener (e.g. in magnesium)

### • Materials

- High temperature superconducting ceramics
- Electronic devices (capacitors, O<sub>2</sub>-sensors)
- Magnets (Sm<sub>5</sub>Co, Nd<sub>5</sub>Fe)
- Neutron moderators in nuclear reactors
- Hydrogen storage with metal hydrides



**EOLYS®**  
Soot emission of Diesel engines reduced by 99.9 %



## Chapter 1 f-Atoms and Ions

### • Optics and lighting

- Polishing powders
- Protection against sun (sunglasses)
- Lasers, particularly Nd YAG
- Phosphors for displays (incl. electrolumin. displays)
- Fluorescent lamps

### • Medicine

- Seasickness (Ce oxalate), thromboses (Nd oxalate)
- X-ray intensifying screens
- NMR imaging
- Cancer radio- and photo-therapy
- Laser surgery (Nd YAG laser)
- Luminescent immunoassays

### • Science

- Shift reagents, luminescent and magnetic probes
- Catalysts for organic chemistry



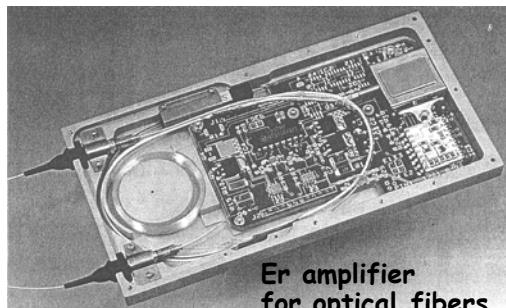
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## Chapter 1 f-Atoms and Ions



fluorescent lamps



Er amplifier  
for optical fibers



rechargeable batteries



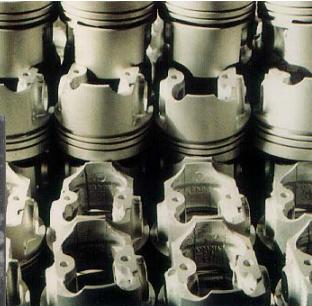
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## Chapter 1 f-Atoms and Ions



pigments



Re-inforced  
cast Al pistons

MRI images



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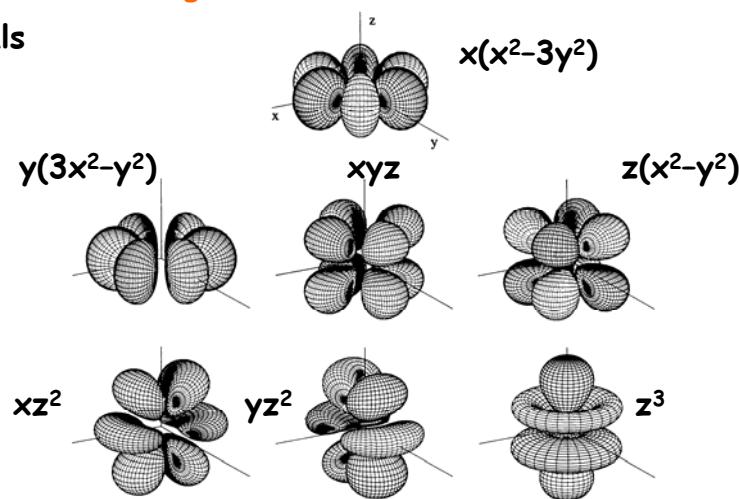
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## Chapter 1 f-Atoms and Ions

### 1.3 Basic properties

#### 1.3.1 Electronic configuration

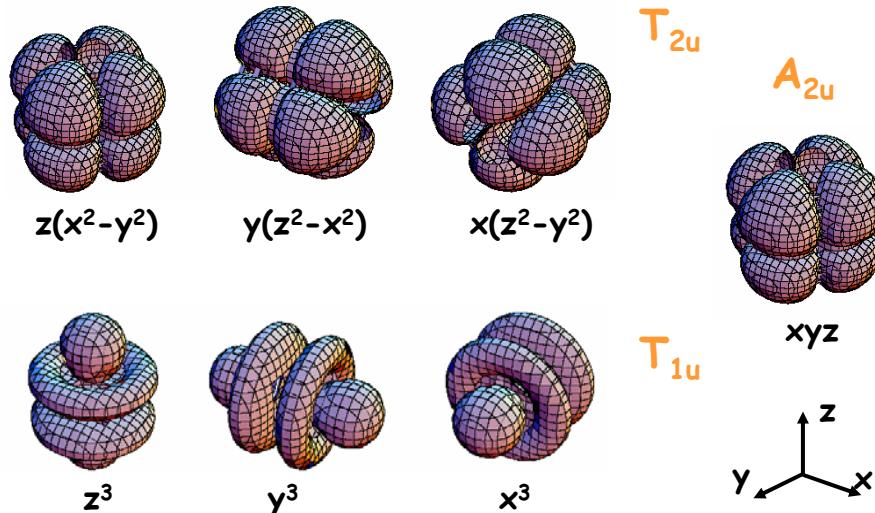
##### 4f-orbitals



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## 4f-orbitals (in octahedral symmetry)



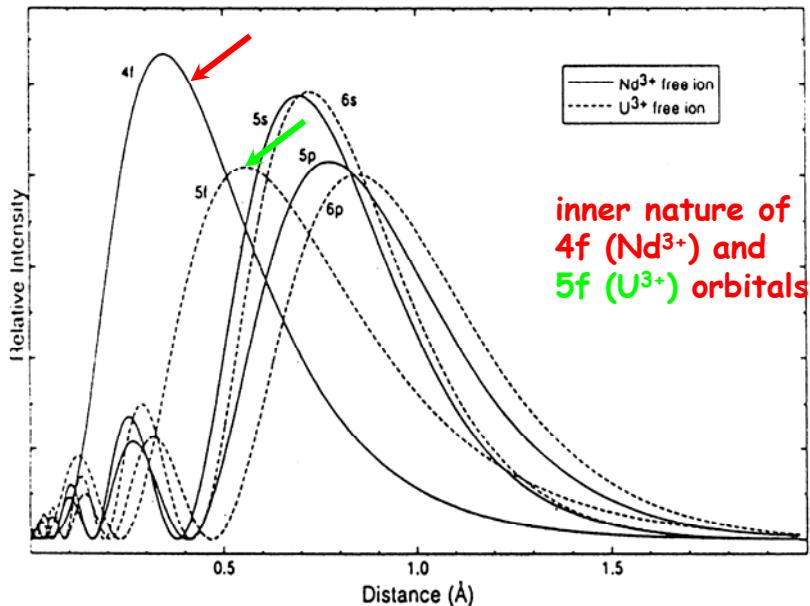
## Lanthanides

- Sc, Y and La introduce the 3d, 4d and 5d transition series:  $nd^1(n+1)s^2$     n=3 (Sc), 4 (Y) and 5 (La)
- The energy of the 4f orbitals decreases abruptly beyond La: -0.95 eV for La, -5 eV for Nd ! which leads to the filling of the 4f shell
- The 4f orbitals lie outside the Xe electronic structure for La, but inside the Xe electronic structure for the other Ln elements

## Actinides

- Similarly, the 5f orbitals are also “inner orbitals”

## Chapter 1 f-Atoms and Ions



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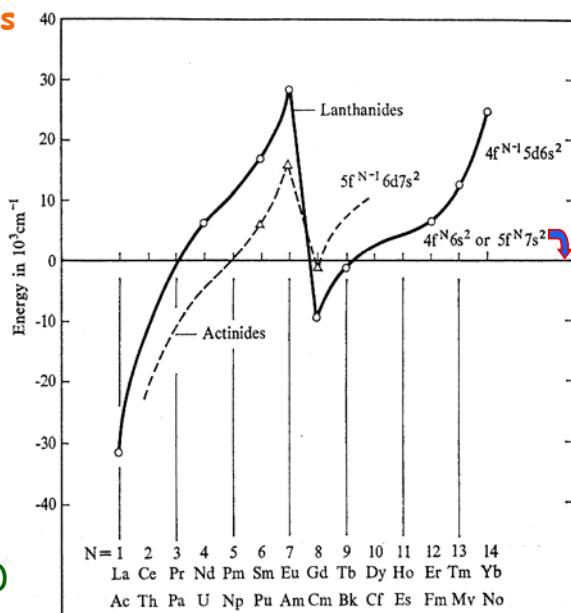
## Chapter 1 f-Atoms and Ions

### 1.3.2 Oxidation states of 4f elements

$\text{Ln}^0$      $4f^{N-1} 5d^1 6s^2$   
 La, Ce, Gd, Lu  
 $4f^N 6s^2$   
 Pr-Eu, Tb-Yb

$\text{Ln}^{II}$      $4f^{N-1} 5d^1$   
 La, Gd  
 $4f^N$   
 Ce-Eu, Tb-Y  
 $4f^{N-1} 6s^1$   
 Lu

$\text{Ln}^{III}$      $4f^{N-1}$  (no exception)

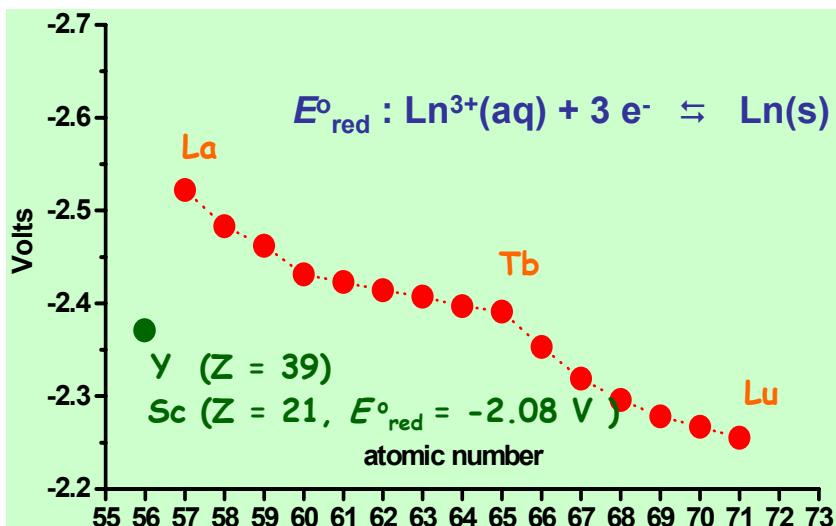


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**Oxidation states of 4f elements**

- The more stable oxidation state of Ln is +3



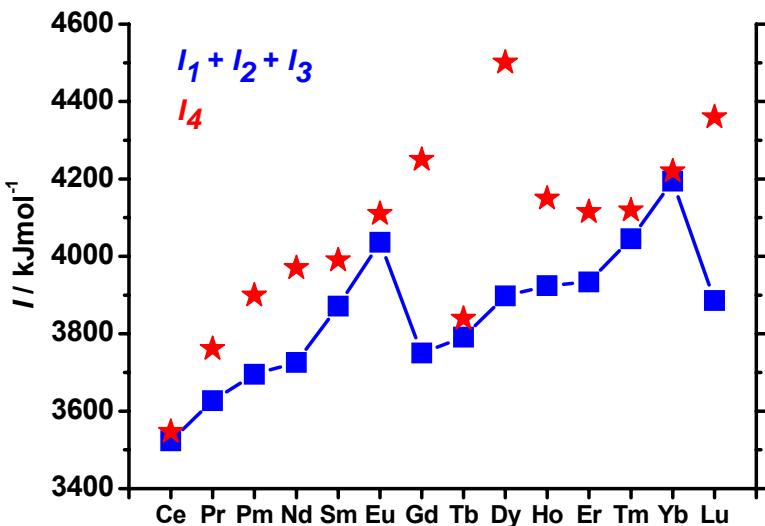
Main reason: the fourth ionization energy is larger than the sum of the first three ones; this extra energy cannot, in most cases, be compensated by bond formation

**Explanation:**

Upon ionization, all of the valence orbitals (4f, 5d, 6s) are stabilized, but to variable degrees.

4f orbitals are stabilized most and 6s least.

After removal of three electrons, the remaining are very tightly bound



### Oxidation states of 4f elements

- **Ce, Pr, Nd and Tb** may have +4 oxidation state  
 $E^0_{\text{red}}$  for  $\text{Ln}^{4+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ln}^{3+}(\text{aq})$  in acidic solutions:  
 +1.72 V for  $\text{Ce}^{4+}$ , stable in water  
 +3.20 V for  $\text{Pr}^{4+}$ , oxidises water  
 +3.10 V for  $\text{Tb}^{4+}$ , oxidises water
- **Sm, Eu, and Yb** have a relatively stable +2 state  
 $E^0_{\text{red}}$  for  $\text{Ln}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ln}^{2+}(\text{aq})$  in acidic solutions:  
 -0.35 V for  $\text{Eu}^{2+}$ , stable in water  
 -1.15 V for  $\text{Yb}^{2+}$ , reduces water  
 -1.56 V for  $\text{Sm}^{2+}$ , reduces water

Chapter 1 f-Atoms and Ions

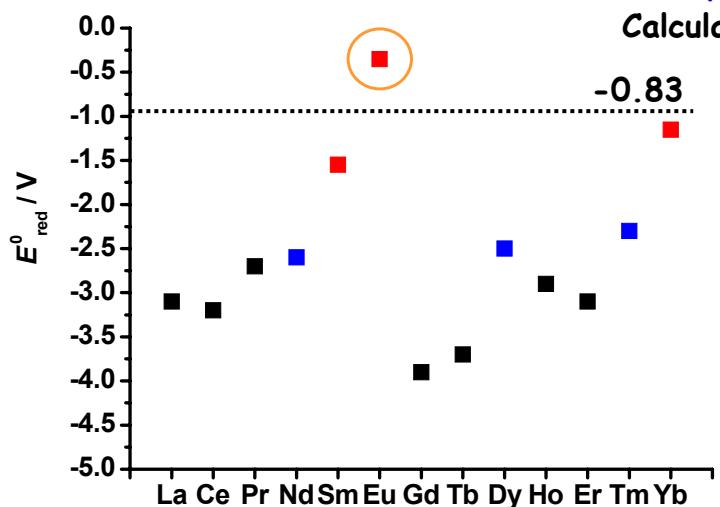


In water

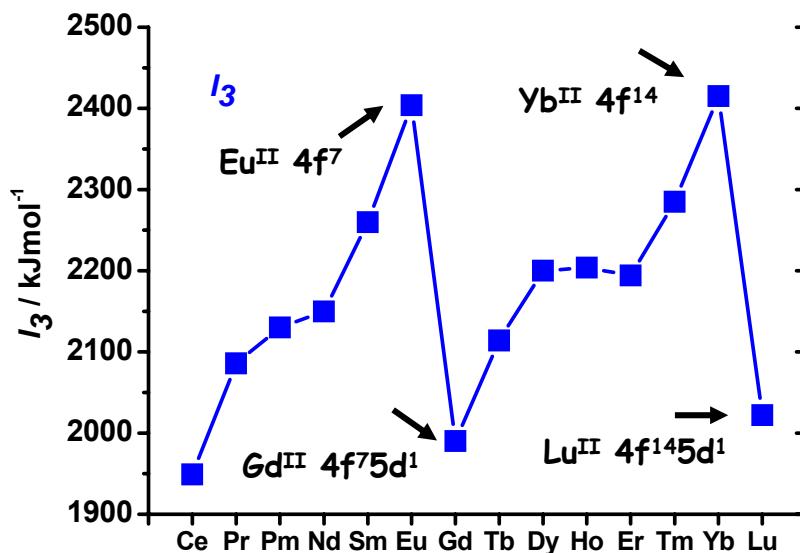
In thf

Calculated

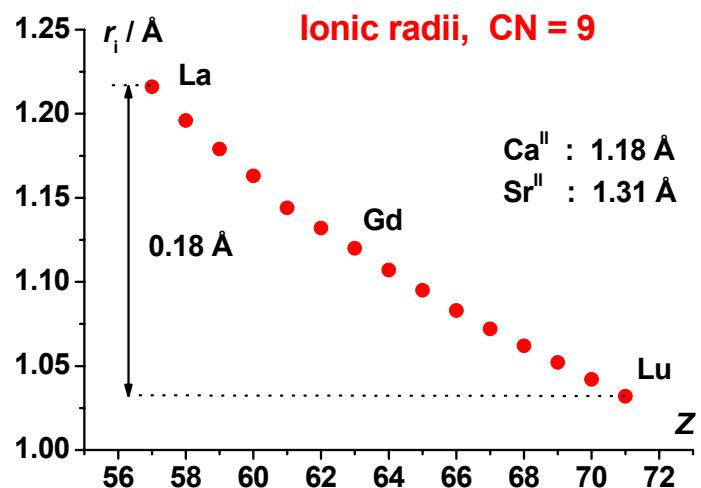
-0.83



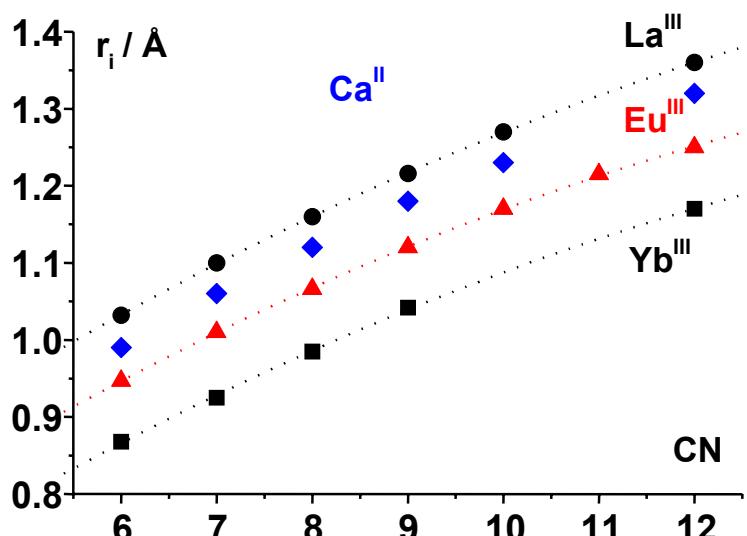
Chapter 1 f-Atoms and Ions



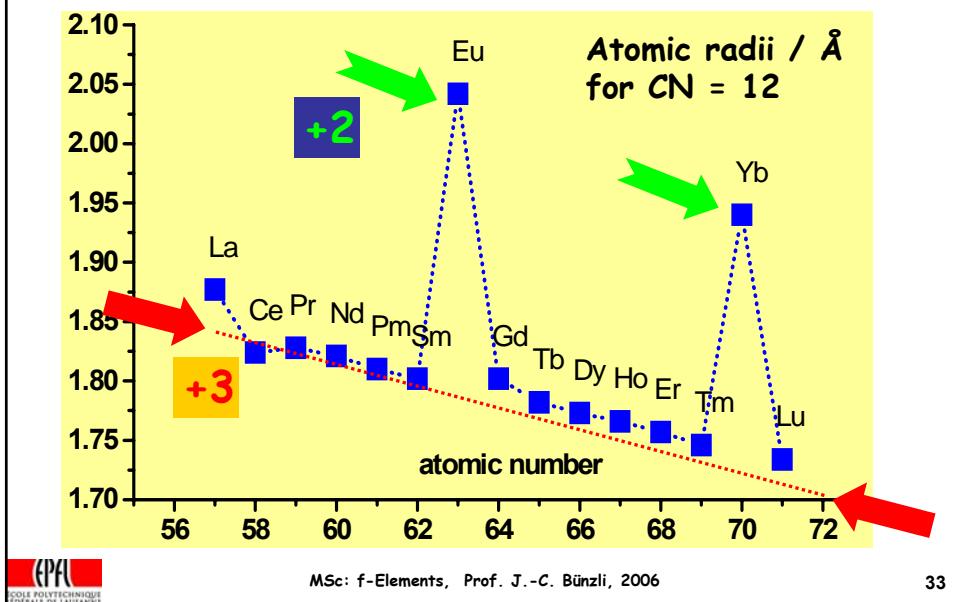
## Ionic radii: lanthanide contraction



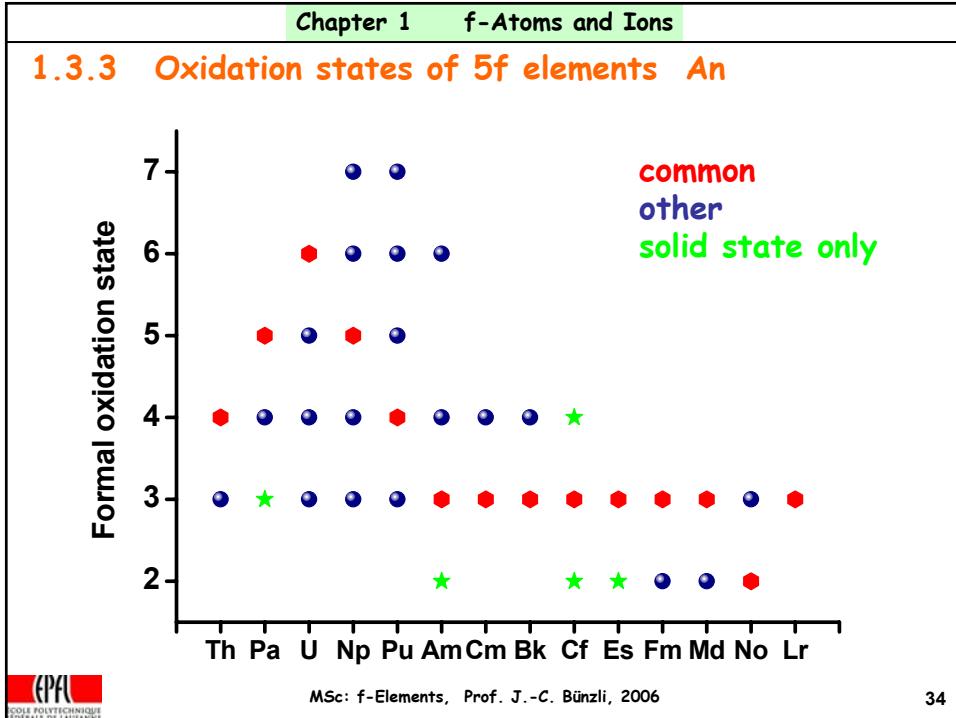
## Ionic radii: variation with coordination number CN



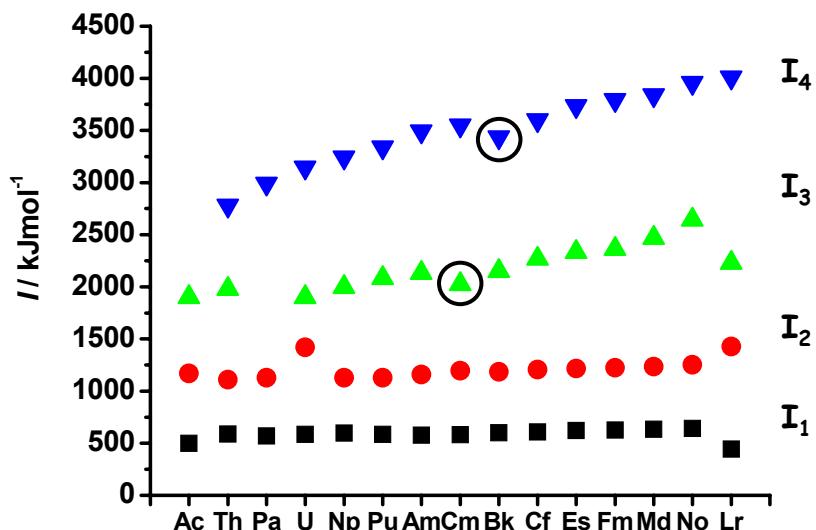
## Oxidation states in the 4f metals



## 1.3.3 Oxidation states of 5f elements An

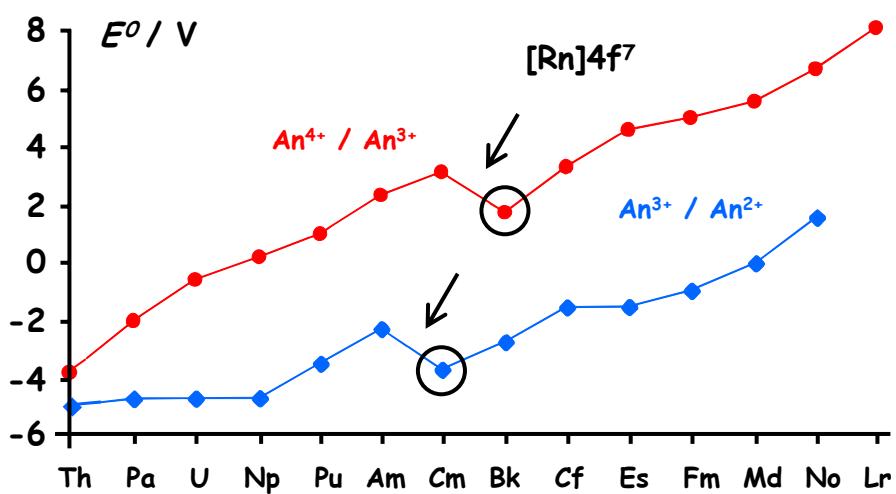


Chapter 1 f-Atoms and Ions



Chapter 1 f-Atoms and Ions

Reduction potentials of 5f elements



- The stability of  $An^{IV}$  decreases along the series  
Quite stable for Th, Pa, U, Np.  
Only found in solution with fluoride for Am, Cm, Bk  
The drop in  $E^0$  ( $An^{4+}/An^{3+}$ ) at Bk reflects the stability of  $[Rn]5f^7$  ( $Bk^{IV}$ ). 
- The trend in  $E^0$  ( $An^{3+}/An^{2+}$ ) parallels the one in  $E^0$  ( $An^{4+}/An^{3+}$ ).  
The stability of  $An^{II}$  increases across the series.  
Note that the discontinuity appears at Cm, reflecting the stability of  $[Rn]5f^7$  ( $Cm^{II}$ ).
- The greater range of oxidation numbers of An elements compared with Ln is due to the nature of 5f orbitals



### Influence of relativity on f-orbitals

$$m = \frac{m_0}{\sqrt{1 - (\frac{v}{c})^2}} \quad \text{mass of a particle moving with velocity } v$$

### Effects are important for heavy elements

For U(1s) :  $m = 1.35m_0$ , leads to contraction of 1s

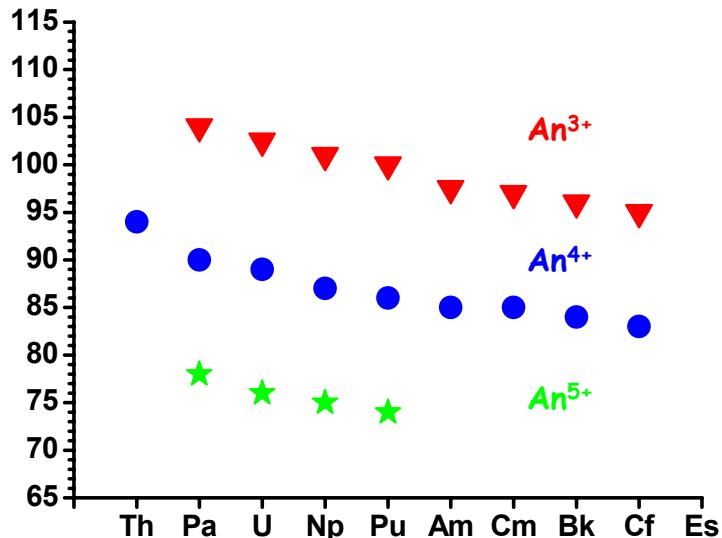
On the contrary d and f orbitals are expanded and destabilized.

5f orbitals are more destabilized than 4f; they are more weakly bound and more chemically active, henceforth the larger range of oxidation numbers (and, also, larger covalency of the bonds)



## Chapter 1 f-Atoms and Ions

### Ionic radii: actinide contraction

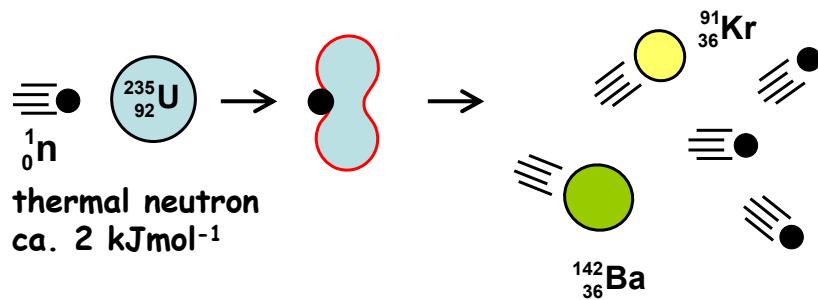


## Chapter 1 f-Atoms and Ions

### 1.4 Radioactivity of the actinides

All of the An isotopes are radioactive, mostly  $\alpha$  emitters.

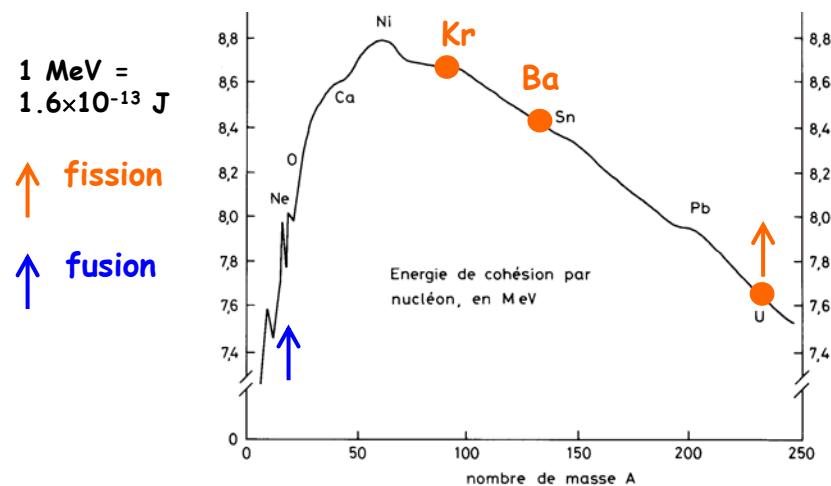
$Z$	El.	$A$	$t_{1/2}$ (* $\beta^-$ , EC)	$Z$	El.	$A$	$t_{1/2}$
90	Th	232	$1.40 \times 10^{10}$ y	96	Cm	244	$18.11$ y
91	Pa	231	$3.25 \times 10^4$ y	97	Bk	247	$1.38 \times 10^3$ y
92	U	235	$7.04 \times 10^8$ y	98	Cf	249	351 y
		238	$4.47 \times 10^9$ y	99	Es	252	472 d
93	Np	236	$1.55 \times 10^5$ y*	100	Fm	257	100.5 d
94	Pu	239	$2.41 \times 10^4$ y	101	Md	258	56 d
		244	$8.26 \times 10^7$ y	102	No	259	1 h ( $\alpha$ + EC)
95	Am	241	$4.32 \times 10^2$ y	103	Lr	262	3.6 h

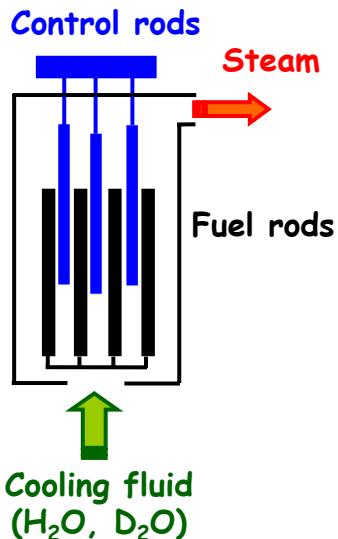
**Nuclear fission**

A large nucleus is split into two smaller (and more stable) ones by collision with a thermal neutron.

The process releases several neutrons, which in turn collide with other nuclei, initiating the "chain reaction", provided a "critical mass" exists, i.e. a minimum amount of the fissile product.

The nucleus mass is smaller than the sum of the masses of its constituting particles (neutrons, protons), due to the nuclear forces. Henceforth the concept of "cohesion energy", usually given per nucleon:



**Nuclear power generation**

**Best natural isotope:**  $^{235}\text{U}$   
**Natural abundance:** 0.72 %,  
 henceforth the need for  
 enrichment.

**Fuel:**  $\text{UO}_2$  enriched to 2-3%  
 $^{235}\text{U}$ , under the form of  
 pellets stuffed into Zr tubes

**Control rods:** boron nitride or  
 graphite (absorb neutrons)

The cooling fluid also acts as  
 moderator, slowing down the  
 produced neutrons (boric acid  
 added).

**Isotope separation**

- Gaseous diffusion of  $\text{UF}_6$  through Al or Ni membranes (pore size 10-25 nm). Graham's law:

$$\nu_{\text{diff}} \propto \frac{1}{\text{MW}} \quad \alpha = \frac{\nu_{\text{diff}}(^{235}\text{UF}_6)}{\nu_{\text{diff}}(^{238}\text{UF}_6)} = \sqrt{\frac{352}{349}} = 1.0043$$

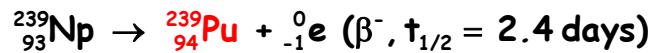
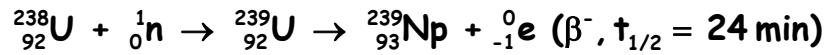
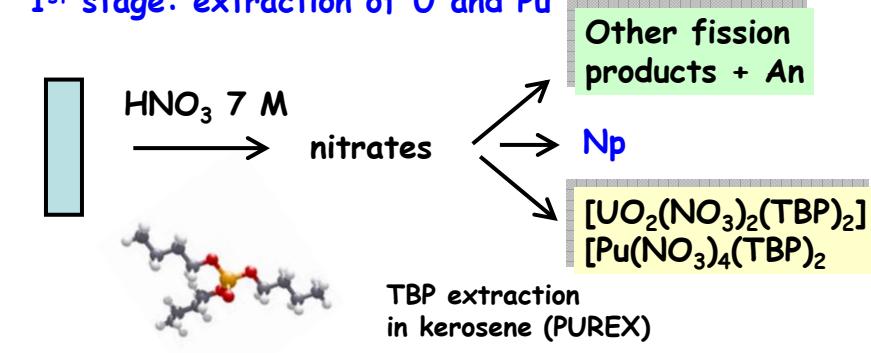
3000 passes needed (large and expensive fluorine-resistant plants) for 90% enrichment

- Centrifugation of  $\text{UF}_6$  ( $^{238}\text{UF}_6$  concentrates near the walls)
- Laser separation (now abandoned)  
 Ionization energy of  $^{235}\text{U}$  slightly different from  $^{238}\text{U}$   
 Laser with wavelength tuned for ionizing  $^{235}\text{U}$  produces  $^{235}\text{U}^+$  which is collected on an electrode



**Fuel reprocessing and treatment**

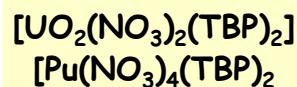
$^{238}\text{U}$  produces  $^{239}\text{Pu}$ , which can also be used as fuel


**1<sup>st</sup> stage: extraction of U and Pu**


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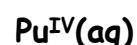
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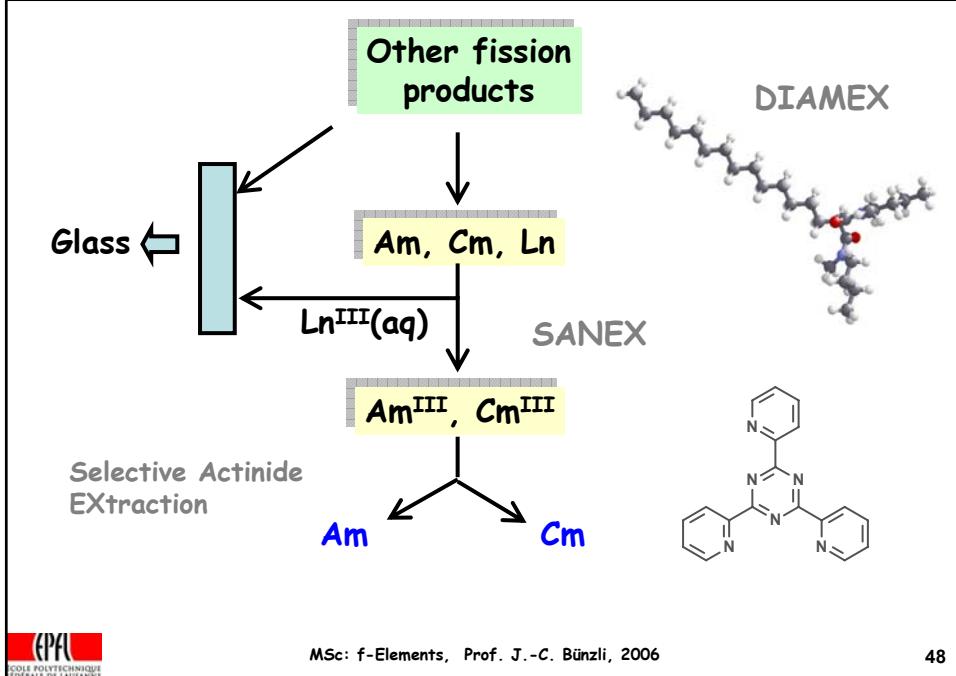
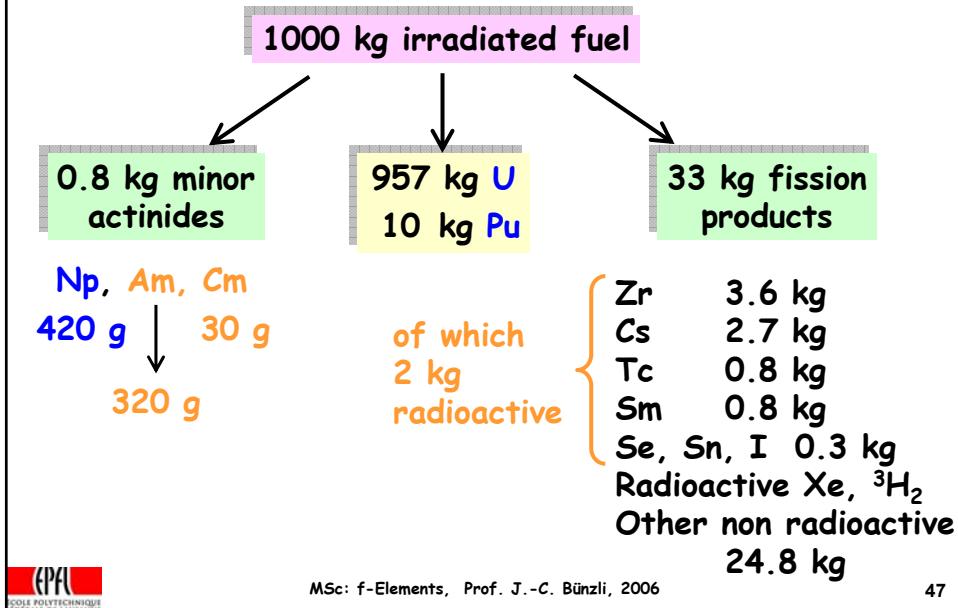
PUREX



Plutonium-Uranium  
Refining by EXtraction

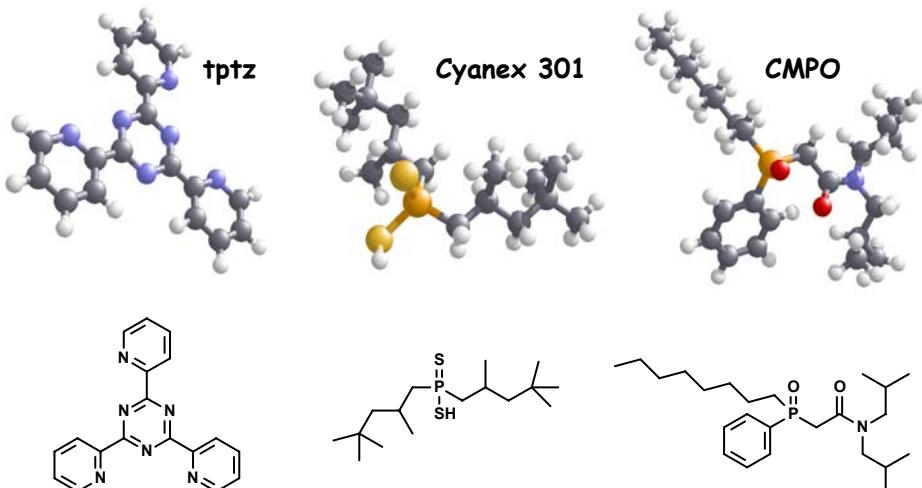
$\text{Fe}^{\text{II}}$



2<sup>nd</sup> stage: separation of radioactive wastes

Chapter 1 f-Atoms and Ions

Some extraction molecules for An/Ln separation  
exploiting the difference in hard/soft behavior

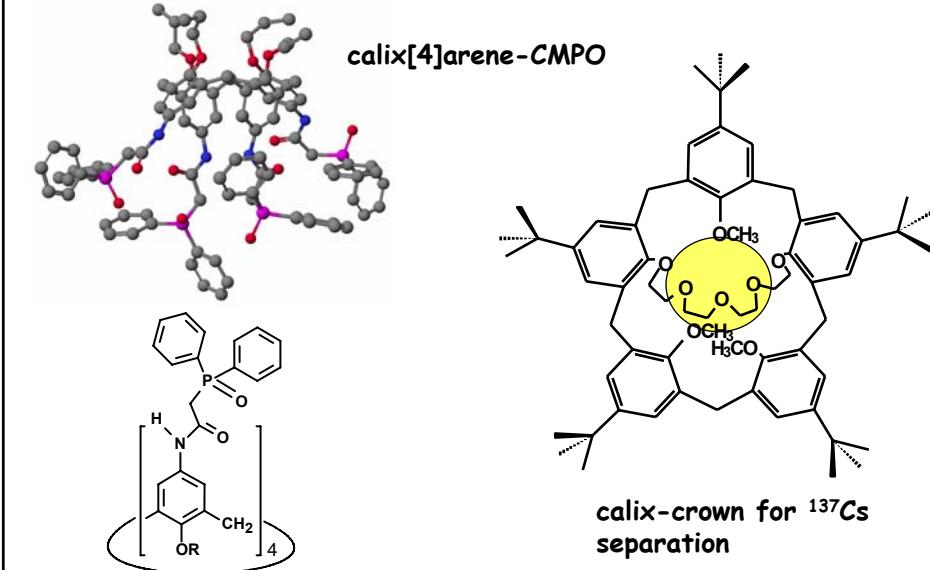


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Chapter 1 f-Atoms and Ions

Some extraction molecules for selective separation



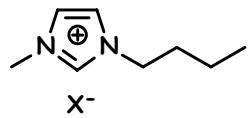
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## Future developments

**Grouped separation allowing separation of all An which are then inserted into a matrix and irradiated by high- velocity neutrons (breeder reactor) - if politically accepted.**

## Ionic liquids

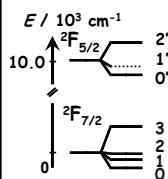
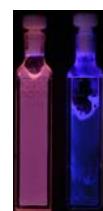


Reprocessing plant in La Hague



## Chapter 2 Physico-chemical properties

- 2.1 Electronic levels
- 2.2 Magnetism
- 2.3 Electronic absorption spectra
- 2.4 Luminescence spectra



## Chapter 2 Physico-chemical properties

### 2.1 Electronic levels

#### 2.1.1 Electronic structure of 4f elements

(Summary from the BSc course "Coordination chemistry")

Russel-Saunders coupling usually works well

$$(2S+1)\Gamma \quad \text{Spectroscopic term}$$

$$\downarrow \qquad \qquad \qquad \text{Multiplicity} = (2S+1) \times (2L+1)$$

$$\begin{array}{ccccccccccccc} S & P & D & F & G & H & I & J & K & \dots \\ 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & = L \end{array}$$

→ spin multiplicity

$$(2S+1)\Gamma_J \rightarrow J = L+S, L+S-1, \dots, |L-S|$$

$$\text{Spectroscopic level, multiplicity} = (2J+1)$$



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## Chapter 2 Physico-chemical properties

Hund's rules for ground state:

- Spin multiplicity must be the highest possible ( $S_{\max}$ )
- If more than one term have the highest multiplicity, the term with the highest value of  $L$  is the ground state ( $L_{\max}$ )
- The ground level has  $J_{\min}$  if the subshell is less than half filled,  $J_{\max}$  if the subshell is more than half filled

Example:  $\text{Nd}^{3+}, 4f^3$

$$S_{\max} = 3 \times \frac{1}{2} = 3/2$$



$$L_{\max} = 6 \quad J = 15/2, \dots, 9/2$$

3 2 1 0 -1 -2 -3  $m_l$  ( $\ell = 3$ )

$4I_{9/2}$



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$Ln^{3+}$	$4f^n$ , $n$	Ground level	Color	Magnetic moment exp.	Magnetic moment calc.
Ce	1	$^2F_{5/2}$	colorless	2.3-2.5	2.54
Pr	2	$^3H_4$	green	3.4-3.6	3.58
Nd	3	$^4I_{9/2}$	lilac	3.5-3.6	3.62
Pm	4	$^5I_4$	pink	n.a.	2.68
Sm	5	$^6H_{5/2}$	yellow	1.4-1.7	0.85
Eu	6	$^7F_0$	pale pink	3.3-3.5	0
Gd	7	$^8S_{7/2}$	colorless	7.9-8.0	7.94
Tb	8	$^7F_6$	colorless	9.5-9.8	9.72
Dy	9	$^6H_{15/2}$	yellow	10.4-10.6	10.6
Ho	10	$^5I_8$	yellow	10.4-10.7	10.6
Er	11	$^4H_{15/2}$	rose	9.4-9.6	9.58
Tm	12	$^3H_6$	pale green	7.1-7.5	7.56
Yb	13	$^2F_{7/2}$	colorless	4.3-4.9	4.54



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Chapter 2 Physico-chemical properties					
Spin-orbit coupling constants for aqua-ions					
$Ln^{III}$	$\lambda_{4f}$	$\zeta_{4f}$	$Ln^{III}$	$\lambda_{4f}$	$\zeta_{4f}$
Ce	625	625	Tb	-285	1710
Pr	370	740	Dy	-483	1932
Nd	295	885	Ho	-535	2140
Sm	232	1160	Er	-793	2380
Eu	221	1326	Tm	-1315	2630
Gd	207	1450	Yb	-2940	2940

$$\lambda = \pm \frac{\zeta}{2s} \quad \text{for } s \neq 0$$

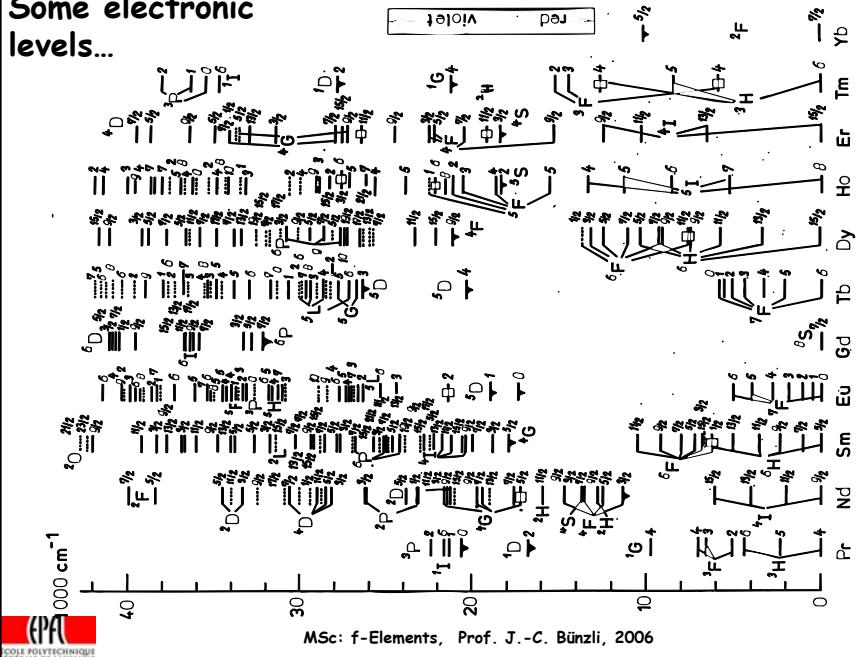


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### Some electronic levels...



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## Chapter 2 Physico-chemical properties

### Ligand field effects

They are very weak, a few hundreds  $\text{cm}^{-1}$  as compared to a few thousands for spin-orbit coupling, and  $10^4 \text{ cm}^{-1}$  for electron repulsion.

Example:  $\text{Yb}^{3+}$  ( $^2\text{F}_{7/2}$  and  $^2\text{F}_{5/2}$ ) in  $D_3$  symmetry

Since  $J$  is half-integer, double group  $D'_3$  has to be used



- a) Determine the reducible representation with rotation formula

$$\chi_a^J = \frac{\sin(J + \frac{1}{2})\alpha}{\sin \frac{\alpha}{2}}$$

- b) Use reduction formula

$$a_i = \frac{1}{h} \sum_R g_R \cdot \chi_r^{(R)} \cdot \chi_i^{(R)}$$



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**Chapter 2 Physico-chemical properties**

$C_2$ , $\alpha = 180^\circ$	$J = 5/2$	$\sin(540)/\sin(90) = 0$
	$J = 7/2$	$\sin(720)/\sin(90) = 0$
$C_2R$ , $\alpha = 540^\circ$	$J = 5/2$	$\sin(1620)/\sin(270) = 0$
	$J = 7/2$	$\sin(2160)/\sin(270) = 0$
$C_3$ , $\alpha = 120^\circ$	$J = 5/2$	$\sin(360)/\sin(60) = 0$
	$J = 7/2$	$\sin(480)/\sin(60) = 1$
$C_3^2$ , $\alpha = 240^\circ$	$J = 5/2$	$\sin(720)/\sin(120) = 0$
	$J = 7/2$	$\sin(960)/\sin(120) = -1$



**Chapter 2 Physico-chemical properties**

$D_3'$	$E$	$R$	$C_3$	$C_3^2$	$3C_2$	$3C_2R$
( $h=12$ )				$C_3^2R$	$C_3R$	
$\Gamma_1$	$A_1$	+1	+1	+1	+1	+1
$\Gamma_2$	$A_2$	+1	+1	+1	+1	-1
$\Gamma_3$	$E$	+2	+2	-1	-1	0
$\Gamma_4$		+2	-2	+1	-1	0
$\Gamma_5$	{}	+1	-1	-1	+1	+i
$\Gamma_6$		+1	-1	-1	+1	-i
$J=7/2$		+8	-8	+1	-1	0
$J=5/2$		+6	-6	0	0	0

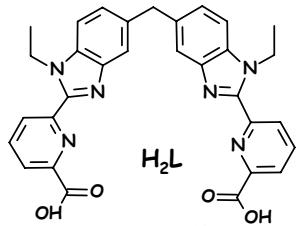


$J = 7/2: 3\Gamma_4 + \Gamma_{5,6}$

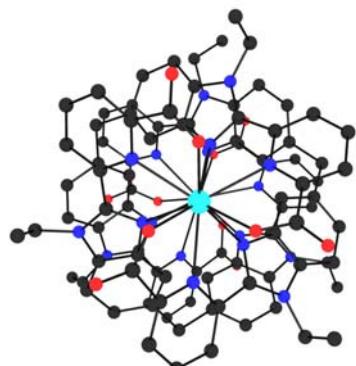
$J = 5/2: 2\Gamma_4 + \Gamma_{5,6}$



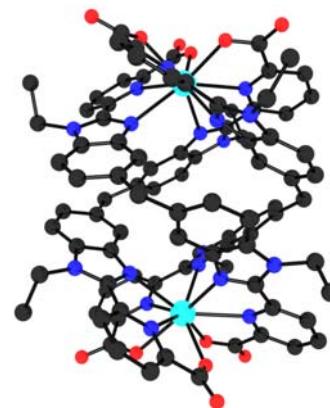
## Chapter 2 Physico-chemical properties



self-assembly process in water  
yields triple-stranded helicate



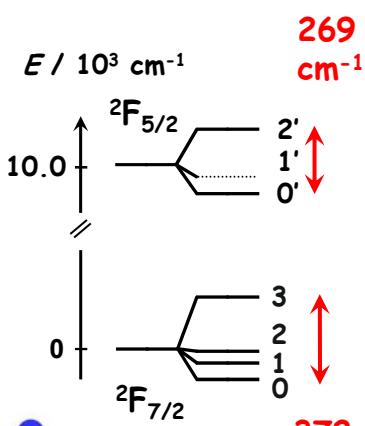
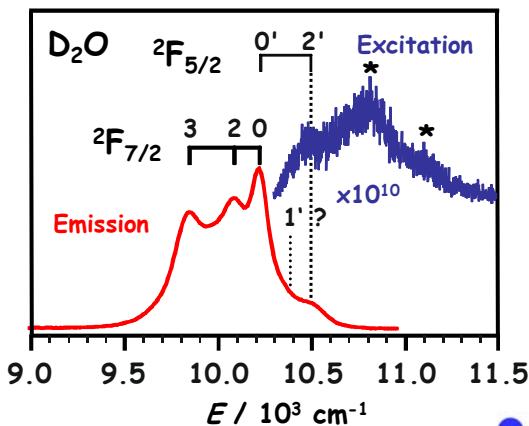
$\approx \text{D}_3$   
symmetry



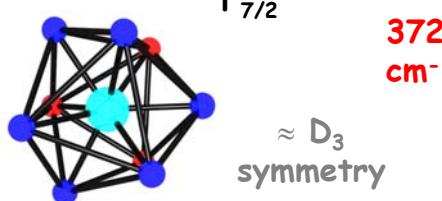
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F. Gonçalves e Silva, J.-C. G. Bünzli  
et al. J. Chem. Phys. A 2002, 106, 1670.



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## Chapter 2 Physico-chemical properties

**Number of levels**

$$\frac{(4\ell + 2)!}{N!(4\ell + 2 - N)!} = \frac{14!}{N!(14-N)!}$$

Number of f electrons	Number of terms $2s+1L$	Number of levels $2s+1L_J$	Number of LF sublevels $2s+1\Gamma_x$
1      13	1	2	14
2      12	7	13	91
3      11	17	41	364
4      10	47	107	1001
5      9	73	198	2002
6      8	119	295	3003
7	119	327	3432



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## Chapter 2 Physico-chemical properties

### 2.1.2 Electronic structure of 5f elements

An	Atom [Rn]xxx	An <sup>3+</sup>	An <sup>4+</sup>	An	Atom [Rn]xxx	An <sup>3+</sup>	An <sup>4+</sup>
Ac	6d <sup>1</sup> 7s <sup>2</sup>	[Rn]	-	Bk	5f <sup>9</sup> 7s <sup>2</sup>	5f <sup>8</sup>	5f <sup>7</sup>
Th	6d <sup>2</sup> 7s <sup>2</sup>	5f <sup>1</sup>	[Rn]	Cf	5f <sup>10</sup> 7s <sup>2</sup>	5f <sup>9</sup>	5f <sup>8</sup>
Pa	5f <sup>2</sup> 6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>2</sup>	5f <sup>1</sup>	Es	5f <sup>11</sup> 7s <sup>2</sup>	5f <sup>10</sup>	5f <sup>9</sup>
U	5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>3</sup>	5f <sup>2</sup>	Fm	5f <sup>12</sup> 7s <sup>2</sup>	5f <sup>11</sup>	5f <sup>10</sup>
Np	5f <sup>4</sup> 6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>4</sup>	5f <sup>3</sup>	Md	5f <sup>13</sup> 7s <sup>2</sup>	5f <sup>12</sup>	5f <sup>11</sup>
Pu	5f <sup>6</sup> 7s <sup>2</sup>	5f <sup>5</sup>	5f <sup>4</sup>	No	5f <sup>14</sup> 7s <sup>2</sup>	5f <sup>13</sup>	5f <sup>12</sup>
Am	5f <sup>7</sup> 7s <sup>2</sup>	5f <sup>6</sup>	5f <sup>5</sup>	Lr	5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>14</sup>	5f <sup>13</sup>
Cm	5f <sup>7</sup> 6d <sup>1</sup> 7s <sup>2</sup>	5f <sup>7</sup>	5f <sup>6</sup>				



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## Chapter 2 Physico-chemical properties

Deciphering the electronic structure needs the use of an adequate scheme for spin-orbit coupling.

The coupling is much greater than for 4f elements, so that Russel-Saunders scheme does not work.

Interpretation of magnetic and optical data is therefore more difficult than for 4f elements.

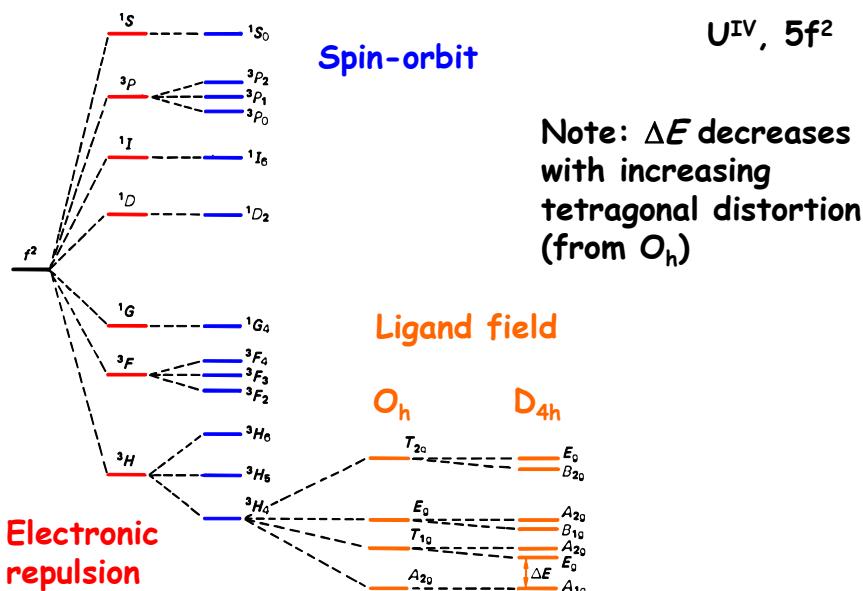
Sometimes, however, Russell-Saunders coupling scheme is used as a first approach.

Example: U<sup>IV</sup>, 5f<sup>2</sup>

Ground level:  $^3H_4$   
SO levels:  $^3H_4$ ,  $^3H_5$ ,  $^3H_6$



## Chapter 2 Physico-chemical properties



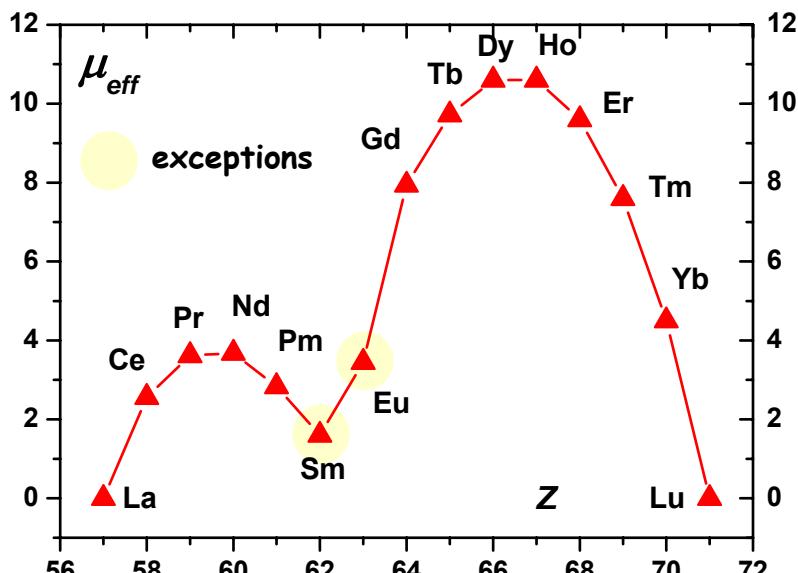
## 2.2 Magnetism

When Russell-Saunders scheme for spin-orbit coupling is valid and when the ground state is pure and well separated from excited states, the following formulae are well adapted to predict the effective magnetic moment:

$$\mu_{\text{eff}} = \frac{\sqrt{3RT \cdot \chi_M}}{N_A \cdot \beta} = 2,828\sqrt{\chi_M \cdot T}$$

$$\mu_{\text{eff}} = g_J \sqrt{(J(J+1)}$$

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$



### Actinides

- More complicated behavior: large  $\zeta_{5f}$  (see Table below) and RS coupling scheme for spin-orbit is not applicable.
- $U^{VI}$  compounds  $[Rn]5f^0 ({}^1S_0)$  should be diamagnetic, but they often display temperature-independent paramagnetism (TIP) because of the mixing of excited states with the ground state.
- $U^{IV}$  compounds:  $[Rn]5f^2 ({}^3H_4)$ . Predicted  
 $g_J = 1 + (4 \times 5 + 1 \times 2 - 5 \times 6) / 2 \times 4 \times 5 = 1 - 0.2 = 0.8$   
 $\mu_{eff} = 0.8 \times (4 \times 5)^{1/2} = 3.6$   
measured for  $[U(NCS)_8]^{4-}$ : 2.9

### Spin-orbit coupling constants for some trivalent actinides

$f^n$	$Ln^{III}$	$\zeta_{4f}/cm^{-1}$	$An^{III}$	$\zeta_{5f}/cm^{-1}$
$f^3$	Nd	885	U	1666
$f^4$	Pm	1070	Np	2070
$f^5$	Sm	1160	Pu	2292
$f^6$	Eu	1326	Am	2548
$f^7$	Gd	1450	Cm	2968

Moreover, interelectronic repulsion is only about 2/3 that of  $Ln$  ions, therefore j-j coupling should be used.

## 2.3 Electronic absorption spectra

### 2.3.1 General considerations: selection rules

Laporte's rule:  $\Delta \ell = \pm 1$  (ed)       $\Delta \ell = \pm 0$  (md)

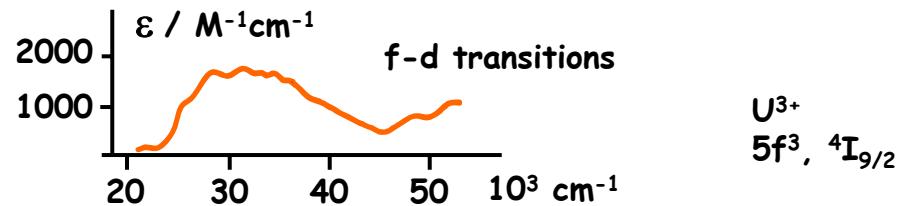
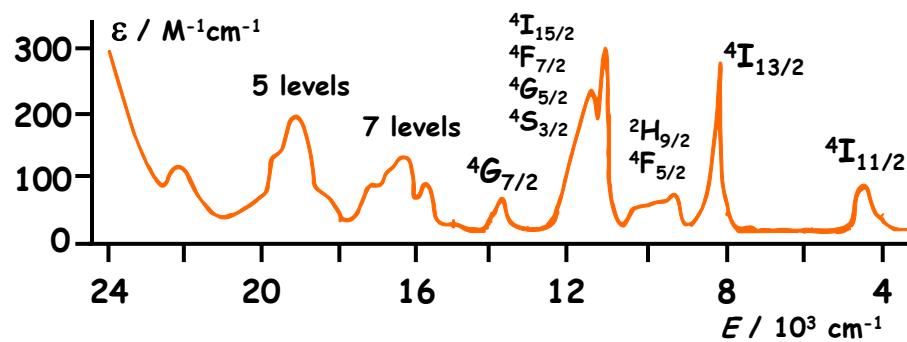
Spin rule:       $\Delta S = 0$  (ed)       $\Delta S = \pm 1$  (md)

Rules on L and J: depend on the specific ion

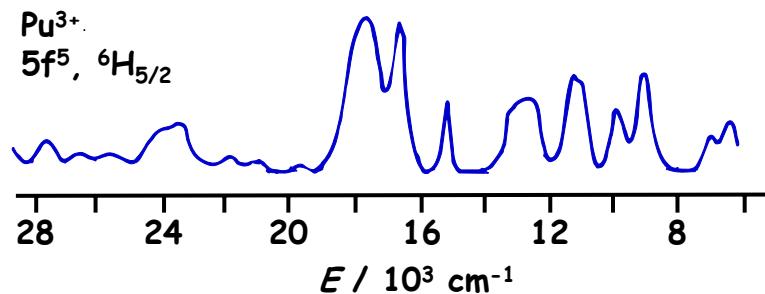
Symmetry rule:  $\Gamma_{op} \subset \Gamma_i \times \Gamma_f$

### 2.3.2 Spectra of $An^{III}$ aquo ions

They contain f-f transitions ( $100-300 M^{-1}cm^{-1}$ ) and more intense f-d absorptions ( $1000-3000 M^{-1}cm^{-1}$ ), ( $5f^N \rightarrow 5f^{N-1}6d$ ).



## Chapter 2 Physico-chemical properties



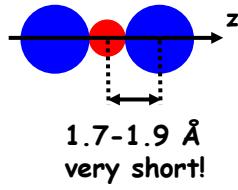
### 2.3.3 Uranyl spectrum

$\text{U}^{\text{VI}}$ : main compounds

$\text{UF}_6$ ,  $\text{UCl}_6$ ,  $\text{UOF}_4$ ,  $\text{UOMe}_6$ , and  $\text{UO}_2^{2+}$  compounds



Uranyl :



Linear molecule

Vibrational frequencies:  
 $920\text{-}990 \text{ cm}^{-1} \quad \nu_{as}$   
 $850\text{-}900 \text{ cm}^{-1} \quad \nu_s$   
 $240\text{-}260 \text{ cm}^{-1} \quad \delta_s$

Bonding, MO model, symmetry  $D_{\infty h}$ :

$\text{U}^{\text{VI}}$ :  $[\text{Rn}]5f^06d^0$ , these a.o. can be implied in bonding

**6d**

$\sigma_g (d_{z2})$

$\pi_g (d_{xz}, d_{yz})$

$\delta_g (d_{xy}, d_{x^2-y^2})$

**5f**

$\sigma_u (f_{z3})$

$\pi_u (f_{xz2}, f_{yz2})$

$\delta_u (f_{xyz}, f_{z(x^2-y^2)})$

$\phi_u (f_{x(x^2-3y^2)}, f_{y(3x^2-y^2)})$



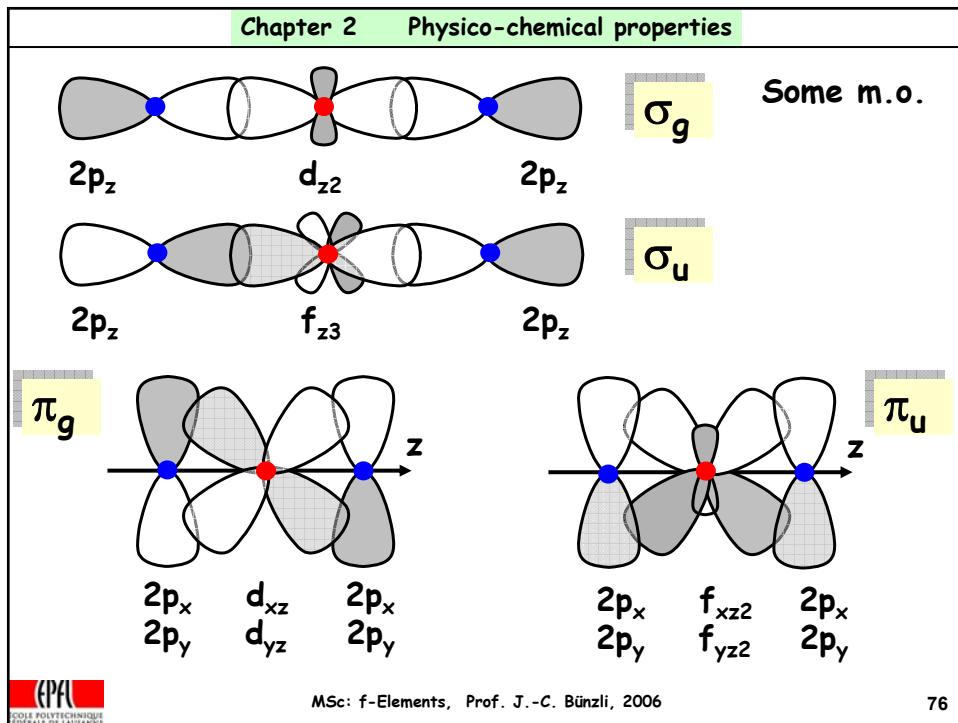
Chapter 2 Physico-chemical properties										
D <sub>∞h</sub>	E	2 C <sub>∞</sub> <sup>ρ</sup>	...	∞σ <sub>v</sub>	i	2 S <sub>∞</sub> <sup>ρ</sup>	...	∞σ' <sub>v</sub>		h = ∞
Σ <sub>g</sub> <sup>+</sup>	1	1	...	+1	+1	1	...	+1		x <sup>2</sup> +y <sup>2</sup> , z <sup>2</sup>
Σ <sub>g</sub> <sup>-</sup>	1	1	...	-1	+1	1	...	-1	R <sub>z</sub>	
Π <sub>g</sub>	2	2cosφ	...	0	+2	-2cosφ	...	0	R <sub>x</sub> , R <sub>y</sub>	xy, xz
Δ <sub>g</sub>	2	2cos2φ	...	0	+2	+2cos2φ	...	0		x <sup>2</sup> -y <sup>2</sup> , xy
Φ <sub>g</sub>	2	2cos3φ	...	0	+2	-2cos3φ	...	0		
...	...	...	...	...	...	...	...	...		
Σ <sub>u</sub> <sup>+</sup>	1	1	...	+1	-1	-1	...	-1	z	z <sup>3</sup> , z(x <sup>2</sup> +y <sup>2</sup> )
Σ <sub>u</sub> <sup>-</sup>	1	1	...	-1	-1	-1	...	+		
Π <sub>u</sub>	2	2cosφ	...	0	-2	+2cosφ	...	0	x, y	xz <sup>2</sup> , yz <sup>2</sup>
Δ <sub>u</sub>	2	2cos2φ	...	0	-2	-2cos2φ	...	0		xyz, x(x <sup>2</sup> -y <sup>2</sup> )
Φ <sub>u</sub>	2	2cos3φ	...	0	-2	+2cos3φ	...	0		x(x <sup>2</sup> -3y <sup>2</sup> ), y(3x <sup>2</sup> -y <sup>2</sup> )
...	...	...	...	...	...	...	...	...		

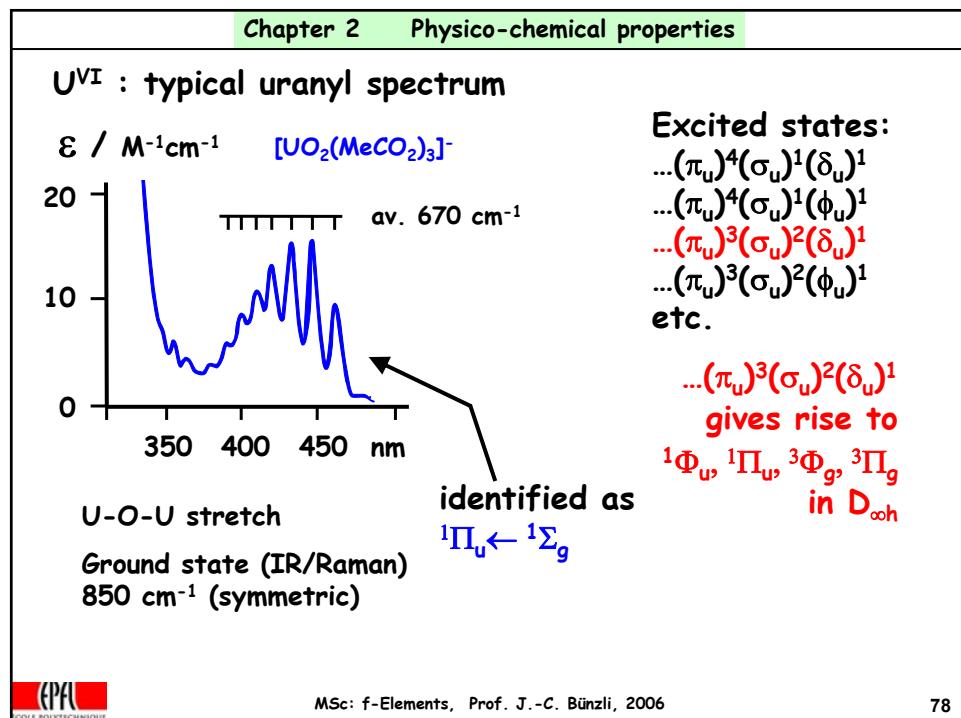
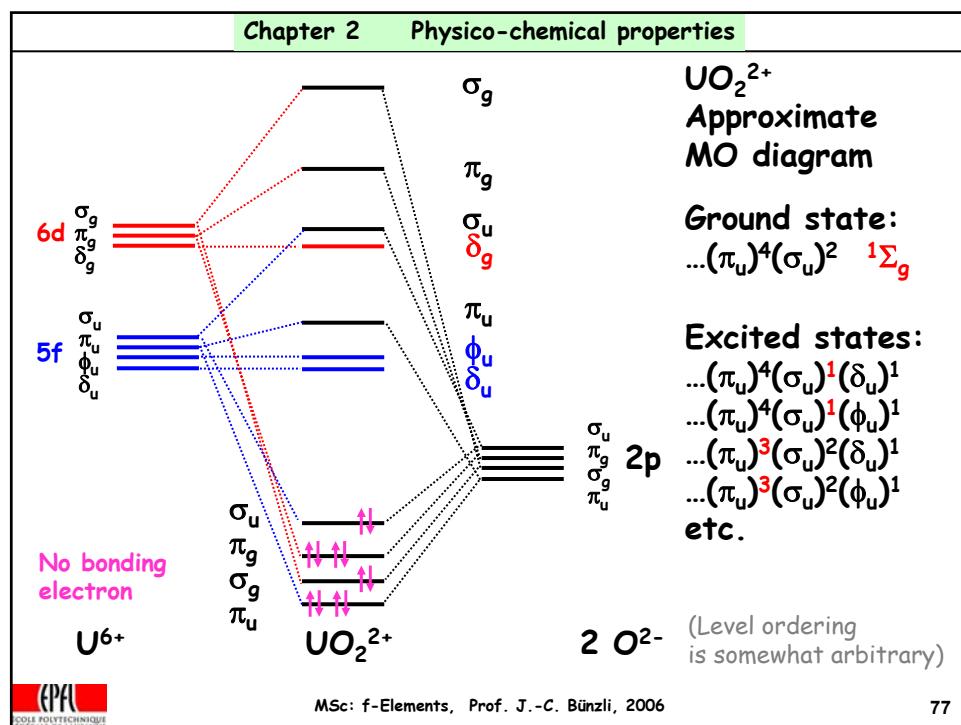
Symmetry-adapted 2p(O) orbitals:  $\sigma_g + \sigma_u + \pi_g + \pi_u$   
Therefore  $\delta_g$ ,  $\delta_u$ ,  $\phi_u$  are non bonding orbitals

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## Chapter 2 Physico-chemical properties

### 2.3.4 $\text{Ln}^{\text{III}}$ ions

**f-f transitions**       $\epsilon < 10 \text{ M}^{-1}\text{cm}^{-1}$

- Narrow bands
- Barycenters of LF sublevels are not much dependent on the nature of the  $\text{Ln}^{\text{III}}$  environment therefore energy of the transitions is more or less constant (but not LF splitting!)

Electric dipole transitions are forbidden

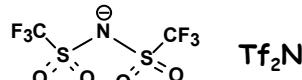
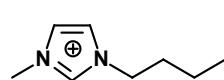
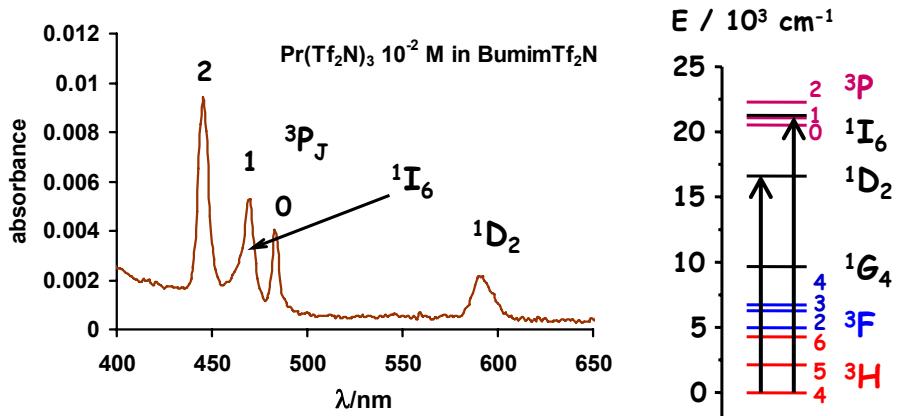
Magnetic dipole transitions are allowed, but very weak

The number of components for a given  $(2S+1)L'_J \leftarrow (2S+1)L_J$  transition depends on the site symmetry.

Some transitions are **hypersensitive**, i.e. very sensitive to small changes in the  $\text{Ln}^{\text{III}}$  environment



## Chapter 2 Physico-chemical properties

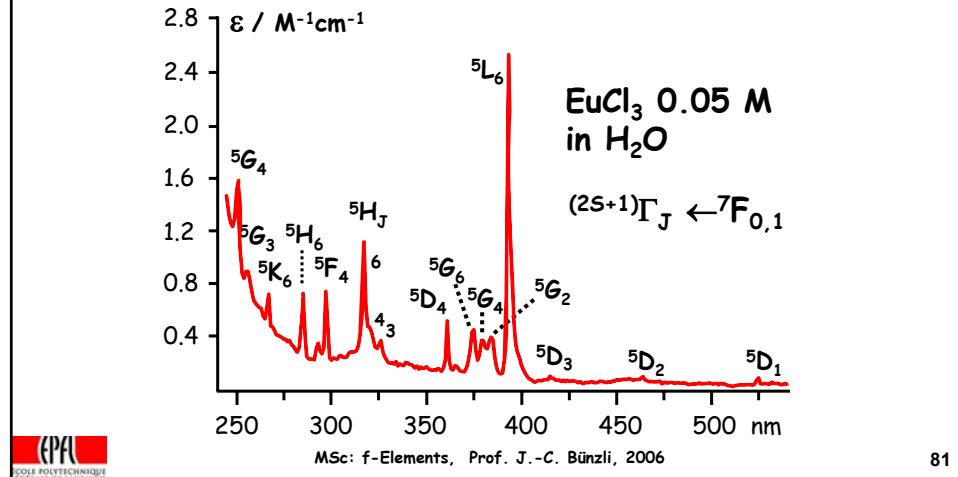


## Chapter 2 Physico-chemical properties

### Europium(III), $4f^6$

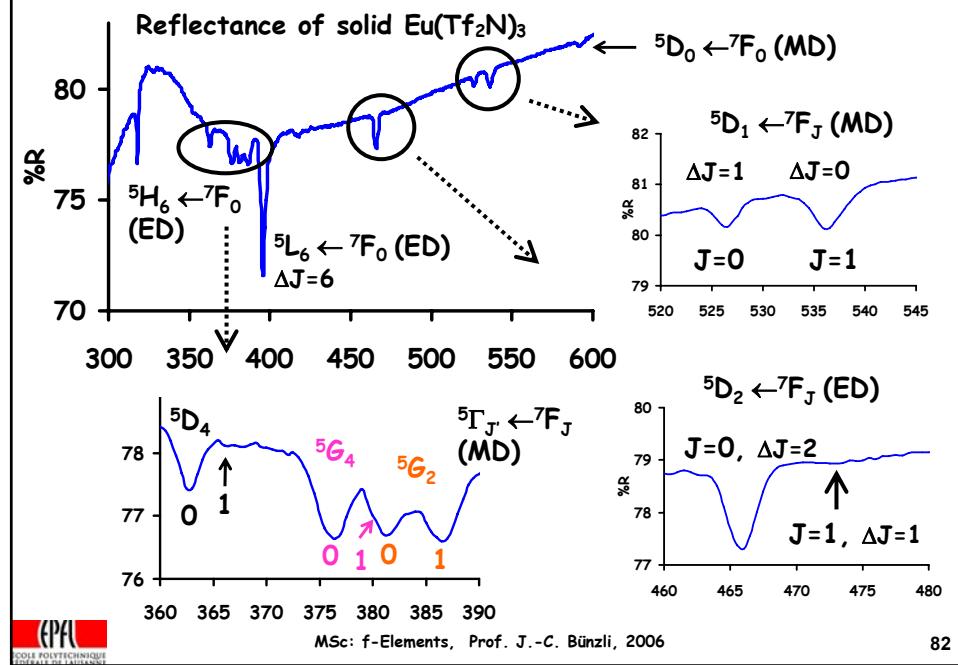
Special selection rules (also valid for  $4f^8$ ,  $Tb^{III}$ ):

- ED:  $\Delta L, \Delta J = 0, 2, 4, 6 \quad \} \quad 0-0$
- MD:  $\Delta L = 0, \Delta J = 0, \pm 1 \quad \} \quad \text{forbidden}$



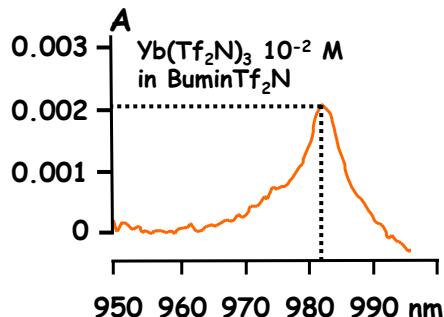
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## Chapter 2 Physico-chemical properties



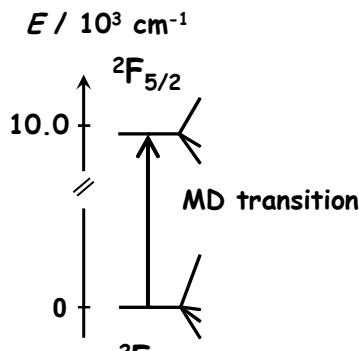
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## Chapter 2 Physico-chemical properties



**Absorption coefficient:**

$$\varepsilon = 0.00203 / 0.01 \times 0.1 = \\ 2.03 \text{ M}^{-1}\text{cm}^{-1}$$



Yb<sup>III</sup> 4f<sup>13</sup>,  $2F_{7/2}$

**Conclusion: RS scheme O.K. for Ln<sup>III</sup> ions**



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## Chapter 2 Physico-chemical properties

### Hypersensitivity

Some f-f transitions are particularly sensitive to changes in symmetry and/or in the inner coordination sphere. They display shifts of their maxima, splittings, and intensity variation.

Some examples:

Pr <sup>III</sup>	$3F_2 \leftarrow 3H_4$	5200 cm <sup>-1</sup>
Nd <sup>III</sup>	$2H_{9/2}, 4F_{5/2} \leftarrow 4I_{9/2}$	17300 cm <sup>-1</sup>
Eu <sup>III</sup>	$5D_2 \leftarrow 7F_0, 5D_1 \leftarrow 7F_1$	21500, 18700 cm <sup>-1</sup>
Ho <sup>III</sup>	$5G_6 \leftarrow 5I_8, 5H_6 \leftarrow 5I_8$	22100, 27700 cm <sup>-1</sup>
Er <sup>III</sup>	$2H_{11/2} \leftarrow 4I_{15/2}$	19200 cm <sup>-1</sup>
Tm <sup>III</sup>	$1G_4 \leftarrow 3H_6$	21300 cm <sup>-1</sup>

The mechanism has been discussed at length: it arises from the mixing of the 4f states with ligand states

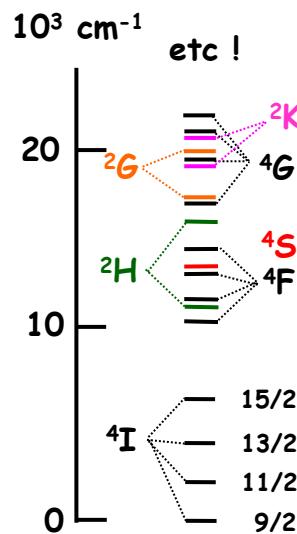
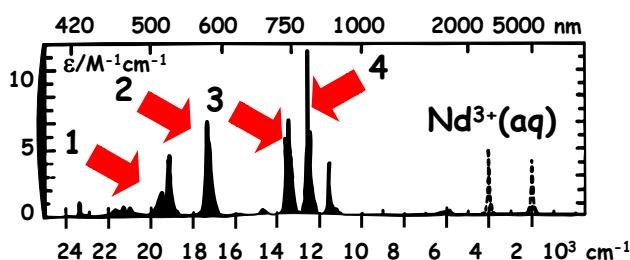
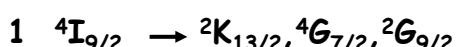
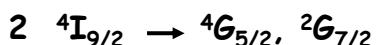
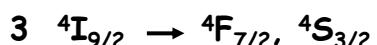
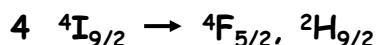


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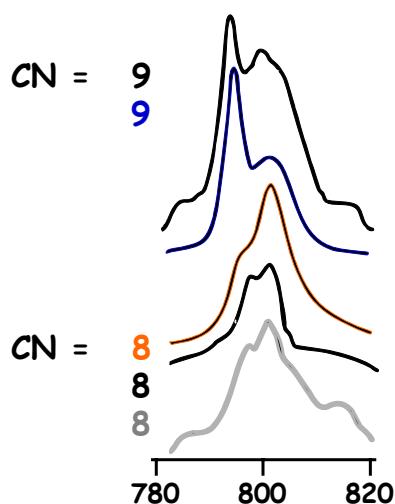
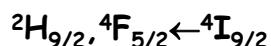
## Chapter 2 Physico-chemical properties

### Transitions of Nd<sup>III</sup>:



## Chapter 2 Physico-chemical properties

### Nd<sup>III</sup> hypersensitivity



$Nd(BrO_3)_3 \times 9H_2O$  (solid)

$[Nd(H_2O)_9]^{3+}$  0.05 M /  $H_2O$

$[Nd(H_2O)_9]^{3+}$  0.05 M /  $HCl$  11 M

$NdCl_3 \times 6H_2O$  (solid)

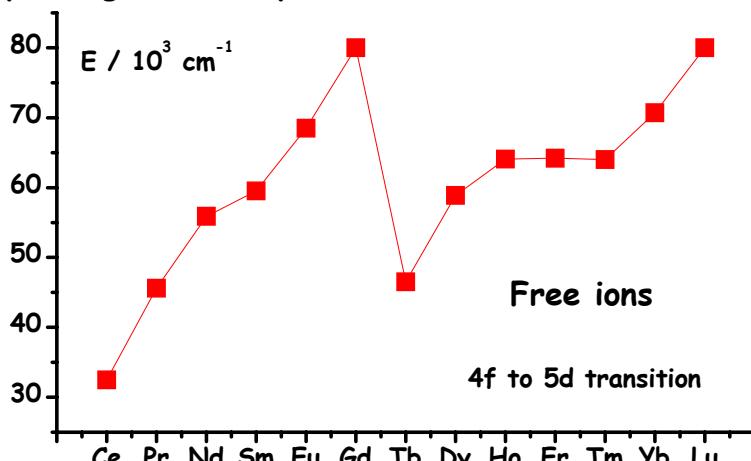
$Nd_2(SO_4)_3 \times 8H_2O$  (solid)

## Chapter 2 Physico-chemical properties

### f-d Transitions

Allowed by Laporte's rule,  $\approx 100\text{-}1000 \text{ M}^{-1}\text{cm}^{-1}$

Highly energetic, except for  $\text{Ce}^{\text{III}}$ ,  $\text{Pr}^{\text{III}}$ , and  $\text{Tb}^{\text{III}}$

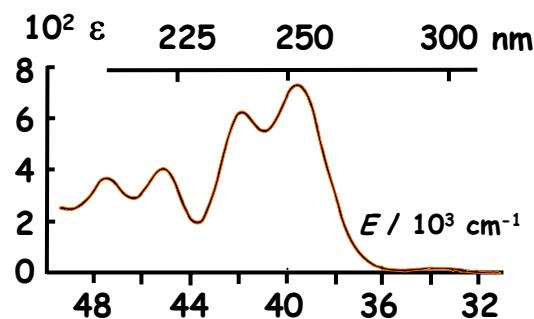


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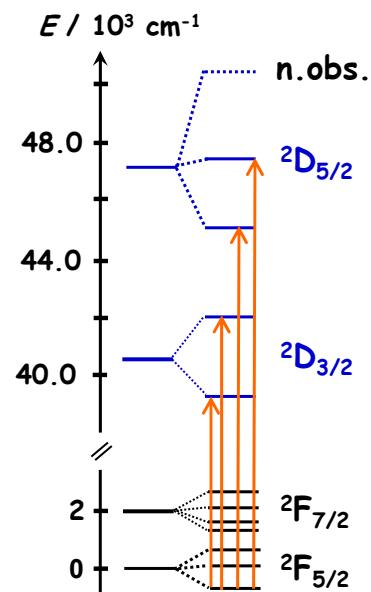
87

## Chapter 2 Physico-chemical properties

$[\text{Ce}(\text{H}_2\text{O})_9]^{3+}$ ,  $\text{D}_{3\text{h}}$  symmetry



$\text{Ce}^{3+} [\text{Xe}]5\text{d}^1$  generates two levels,  $^2\text{D}_{3/2}$  and  $^2\text{D}_{5/2}$



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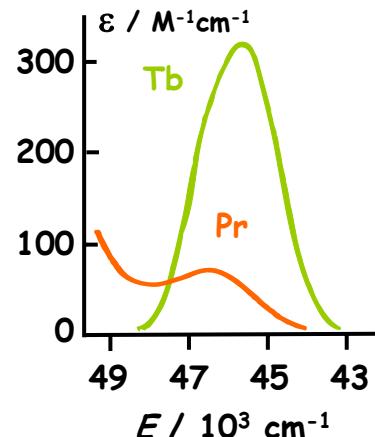
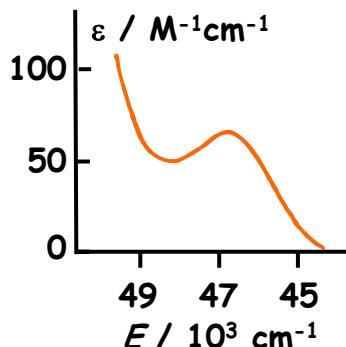
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Chapter 2 Physico-chemical properties

Observed f-d transitions for  $\text{LnBr}_3$  in anhydrous EtOH:

$\text{Ln}^{\text{III}}$  (aq)

- Ce    312 nm (  $800 \text{ M}^{-1}\text{cm}^{-1}$  )  
 Pr    228 nm (  $1500 \text{ M}^{-1}\text{cm}^{-1}$  )  
 Tb    231 nm (  $500 \text{ M}^{-1}\text{cm}^{-1}$  )

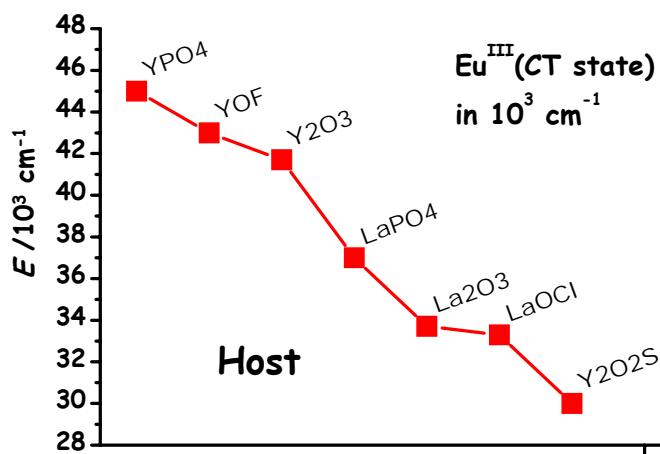


MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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Chapter 2 Physico-chemical properties

Charge transfer transitions  
Allowed by Laporte's rule,  $\approx 200\text{-}500 \text{ M}^{-1}\text{cm}^{-1}$

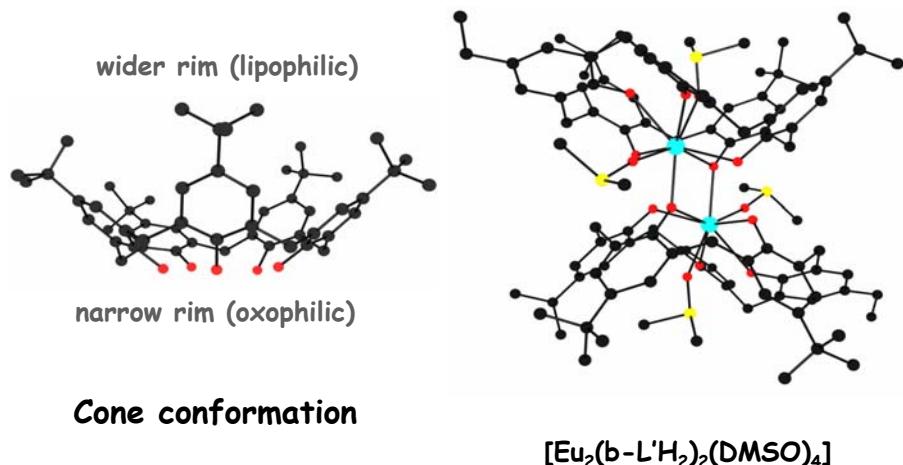


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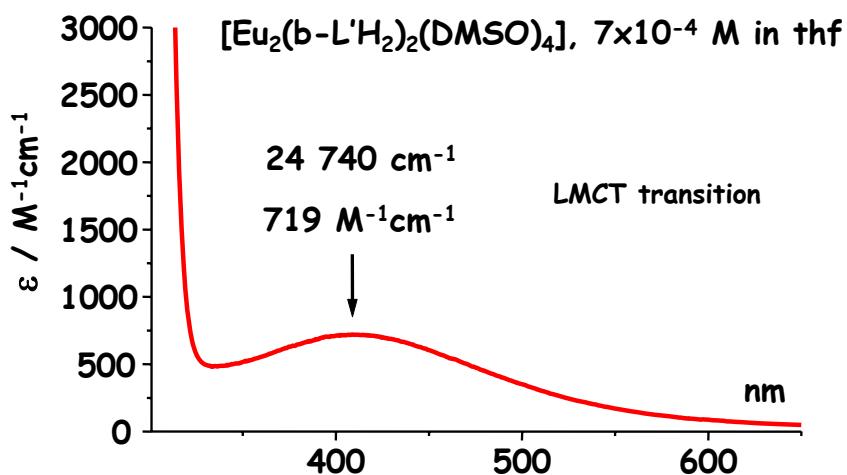
Charge transfer in bimetallic complexes with calix[n]arenes  
 $p$ -tert-butylcalix[5]arene ( $b\text{-L}'\text{H}_5$ )



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Chapter 2 Physico-chemical properties

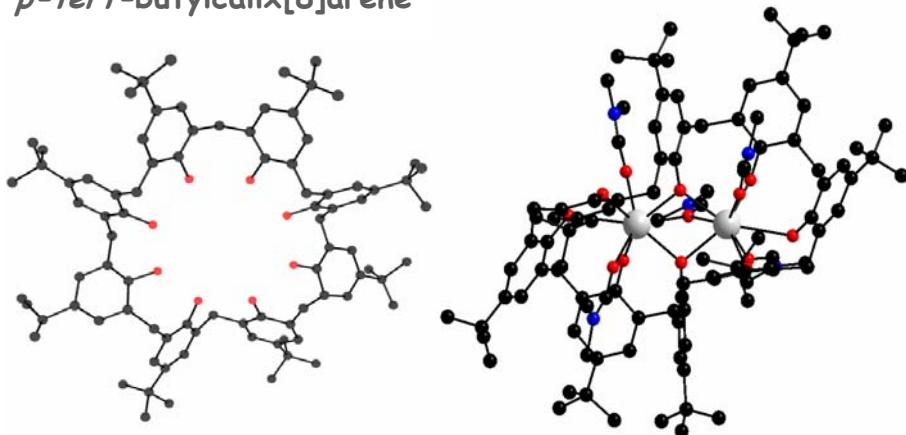


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*p*-tert-butylcalix[8]arene



"undulated" conformation

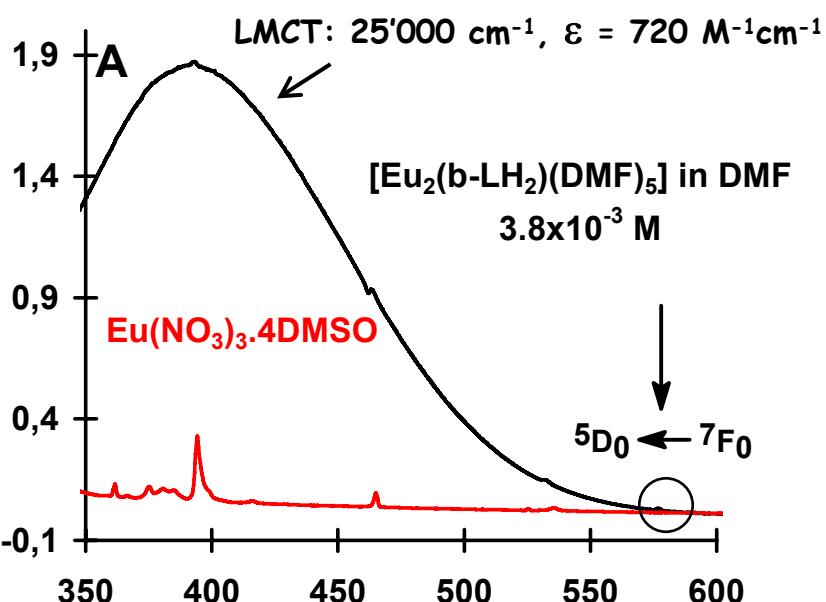
$[\text{Eu}_2(\text{b-LH}_2)(\text{dmf})_5]$



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Chapter 2 Physico-chemical properties



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## Chapter 2 Physico-chemical properties

### Intensity stealing

Overlap between LMCT and f-states leads to f-f transitions with larger intensities, e.g.  ${}^5D_0 \leftarrow {}^7F_0$

Replacing *p-tbut* by  $SO_3H$  (*s-LH<sub>8</sub>*) and  $NO_2$  (*n-LH<sub>8</sub>*) leads to LMCT states with higher energy and to a reduced intensity stealing

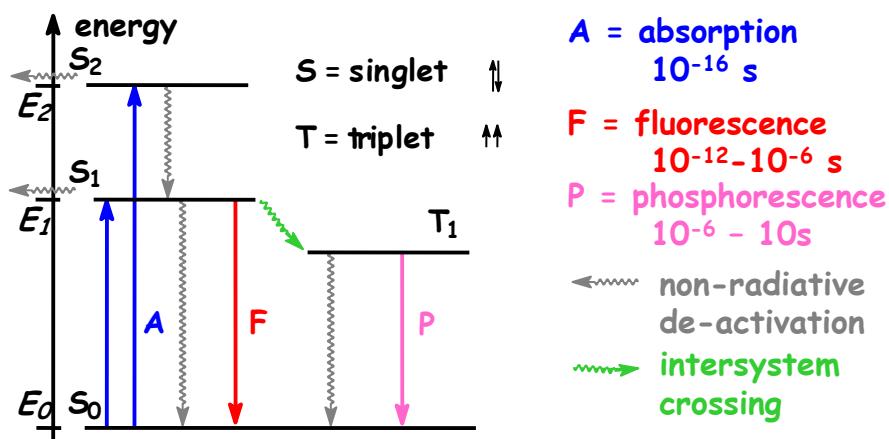
Cmpnd	MLCT/cm <sup>-1</sup>	0-0/cm <sup>-1</sup>	$\varepsilon / M^{-1}cm^{-1}$
Eu <sub>2</sub> (b-LH <sub>2</sub> )	24740	17330	5.0
Eu <sub>2</sub> (s-LH <sub>2</sub> )	30300	17322	1.4
Eu <sub>2</sub> (n-LH <sub>2</sub> )	not located	17319	0.8
[Eu(H <sub>2</sub> O) <sub>9</sub> ] <sup>3+</sup>	-	17212	0.001

## Chapter 2 Physico-chemical properties

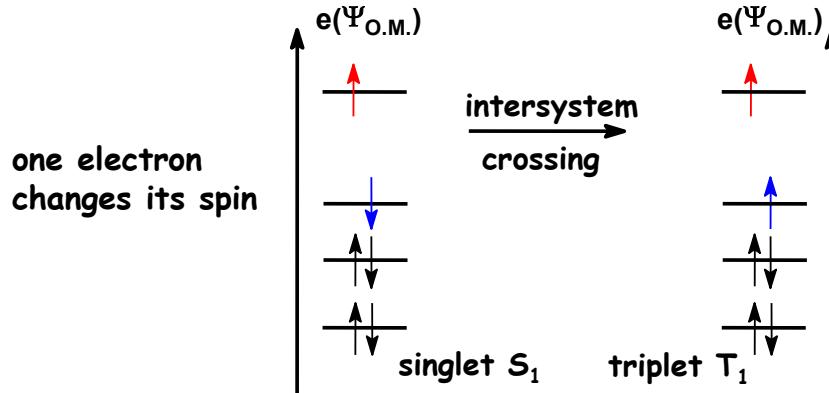
### 2.4 Luminescence spectra

#### 2.4.1 Basics of luminescence

Jablonski's diagram (organic molecules)



## Chapter 2 Physico-chemical properties



Fluorescence : without spin change  
Phosphorescence : with spin change



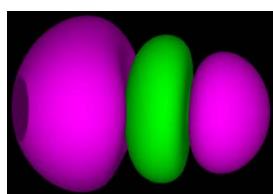
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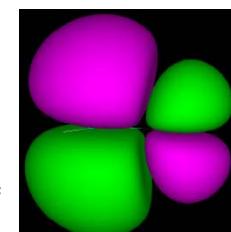
## Chapter 2 Physico-chemical properties

### The states involved

#### $\sigma\pi^*$ states

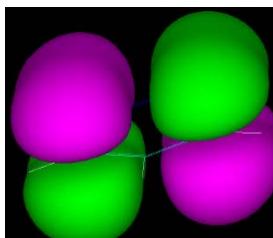


$\sigma$

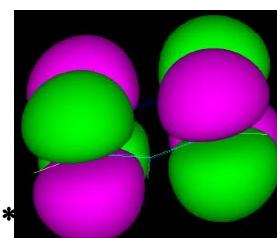


$\pi^*$

#### $\pi\pi^*$ states



$\pi$



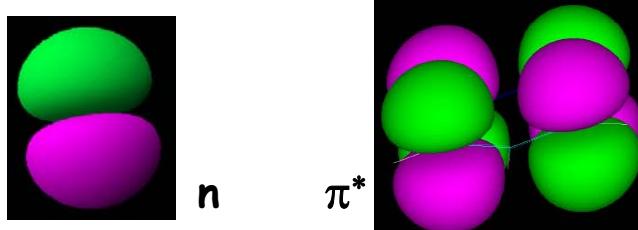
$\pi^*$



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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### $n\pi^*$ states



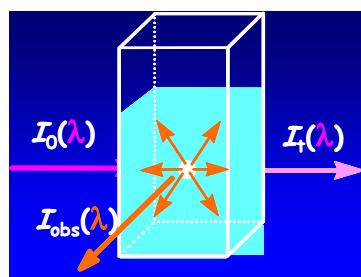
### Charge transfer states

$4f^n \rightarrow 4f^{n+1}L^{-1}$  (reduction of the metal ion)  
 $4f^n \rightarrow 4f^{n-1}L^{+1}$  (oxidation of the metal ion)

### Quantum yield :

$$Q = \frac{I_{\text{ém}}}{I_{\text{abs}}} = \frac{\text{number of emitted photons}}{\text{number of absorbed photons}} = f(T)$$

The quantum yield increases when temperature decreases



$$Q = \frac{I_{\text{em}}}{I_0 - I_t}$$

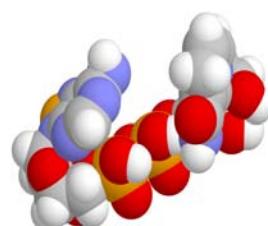
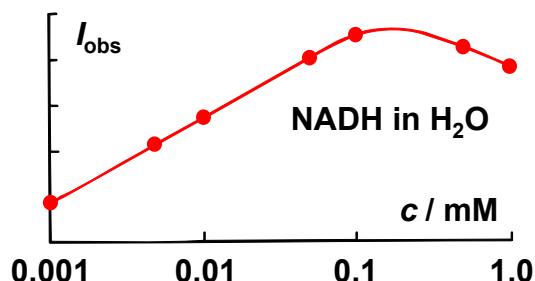
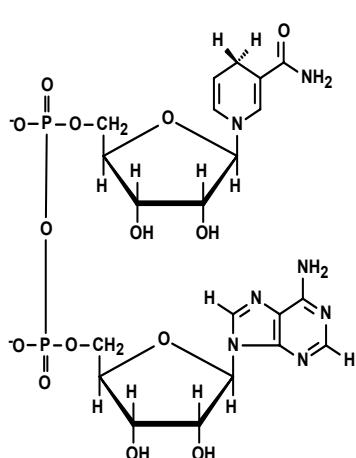
What is the relationship between  $I_{obs}$  and concentration ?

$$I_{obs} = K \cdot Q \cdot I_0 \cdot \varepsilon \cdot b \cdot c = \text{constant} \cdot c$$

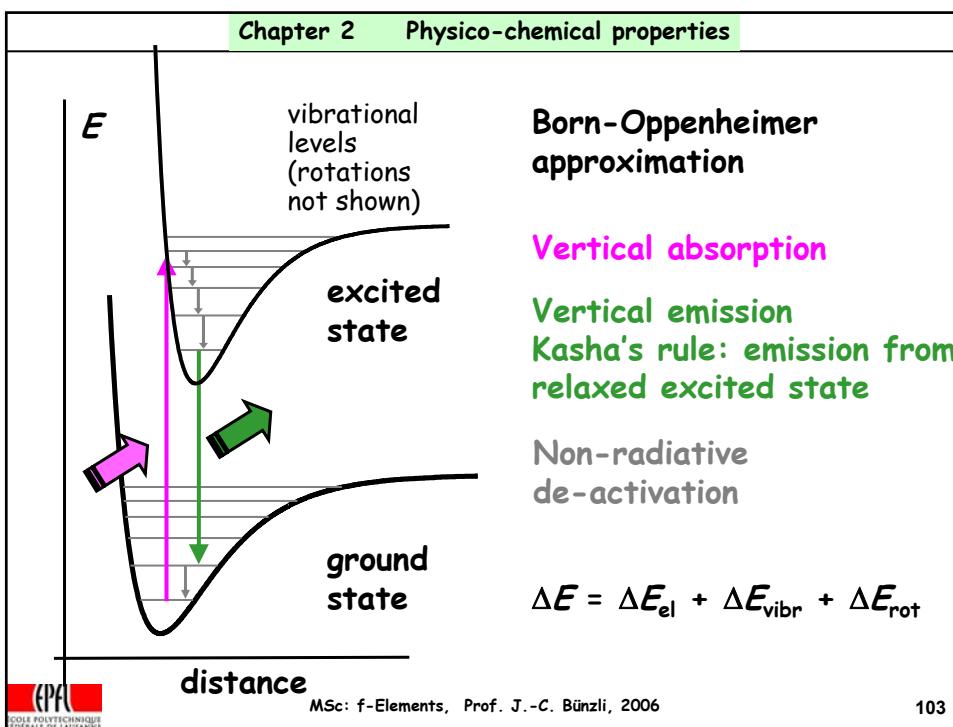
if  $\varepsilon \cdot b \cdot c \leq 0,05$

The condition on  $\varepsilon bc$  stems from the fact that only the first term of a series development is retained in demonstrating this formula.

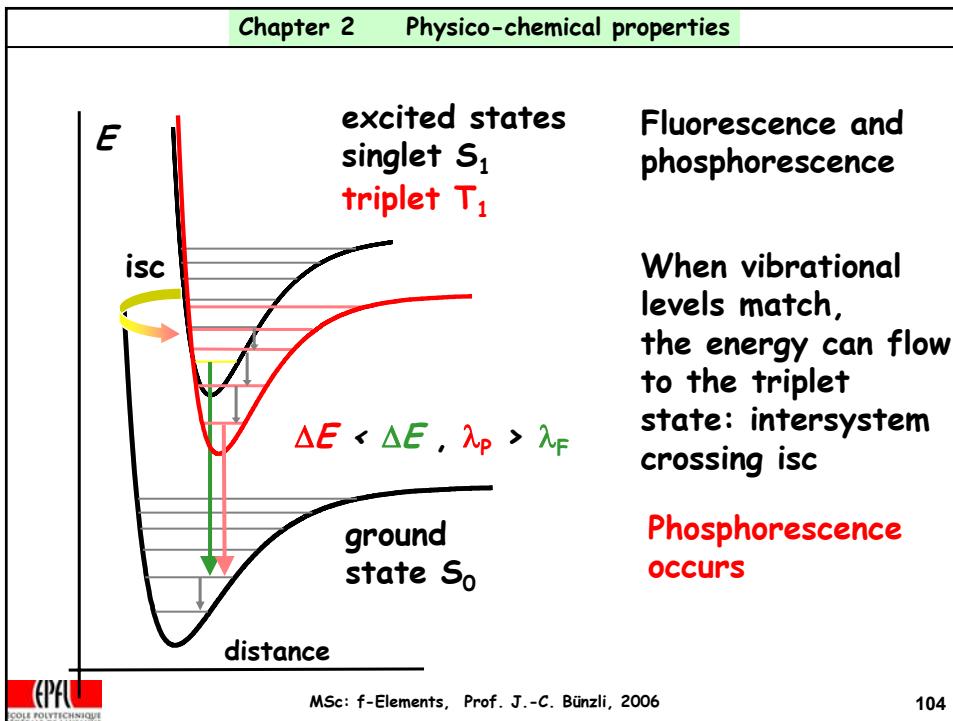
Example of a calibration curve showing the inner-filter effect



## Chapter 2 Physico-chemical properties



## Chapter 2 Physico-chemical properties



## Chapter 2 Physico-chemical properties

### Time dependence of the emitted light

If  $N^*$  is the number of excited molecules at time  $t$ :

$$-\frac{dN^*}{dt} = k_r \cdot N^*$$

$k_r$  = radiative rate constant ( $s^{-1}$ )

$$-\frac{dN^*}{N^*} = k_r \cdot dt$$

Integration between  $\{N_0^*; t_0\}$  and  $\{N^*; t\}$  gives

$$N^* = N_0^* \cdot e^{-k_r t}$$

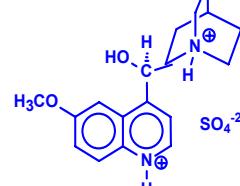
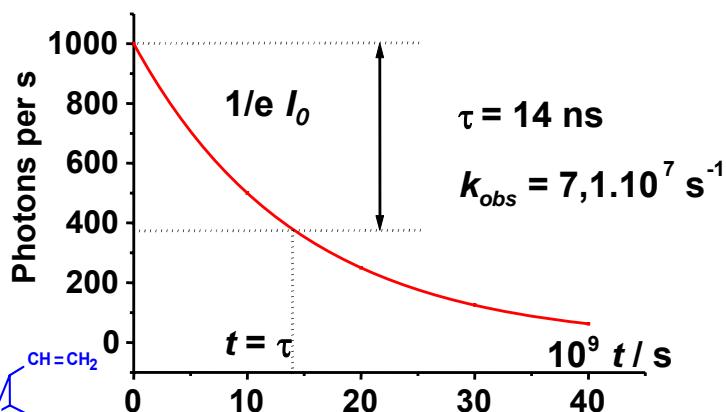
$$I(t) = I_{t=0} \cdot e^{-k_r t}$$

The lifetime of the excited level is given by:

$$\tau = 1/k_{obs} \text{ (s)}$$

During this time, a fraction  $1/e$  of the excited molecules return to the ground state ( $e = 2,73$ )

## Chapter 2 Physico-chemical properties



Quinine sulfate in water

In absence of non-radiative de-activation ( $Q = 1$ ),  
 $k_{\text{obs}} = k_r$

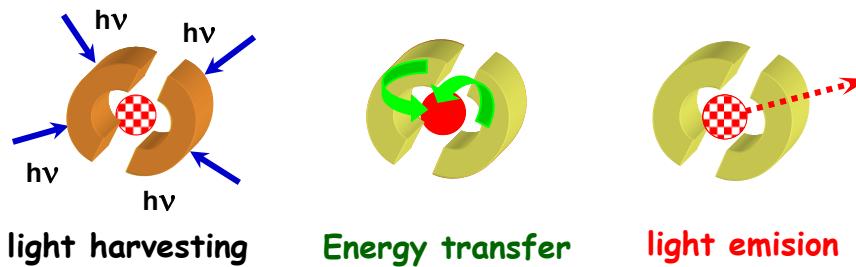
In presence of non-radiative de-activation ( $Q < 1$ ),  
 $k_{\text{obs}} = k_r + k_{\text{nr}}$ , therefore

$$Q = \frac{k_r}{k_{\text{obs}}} = \frac{k_r}{k_r + k_{\text{nr}}} = \frac{\tau_{\text{obs}}}{\tau_r}$$

#### 2.4.2 The special case of 4f-elements

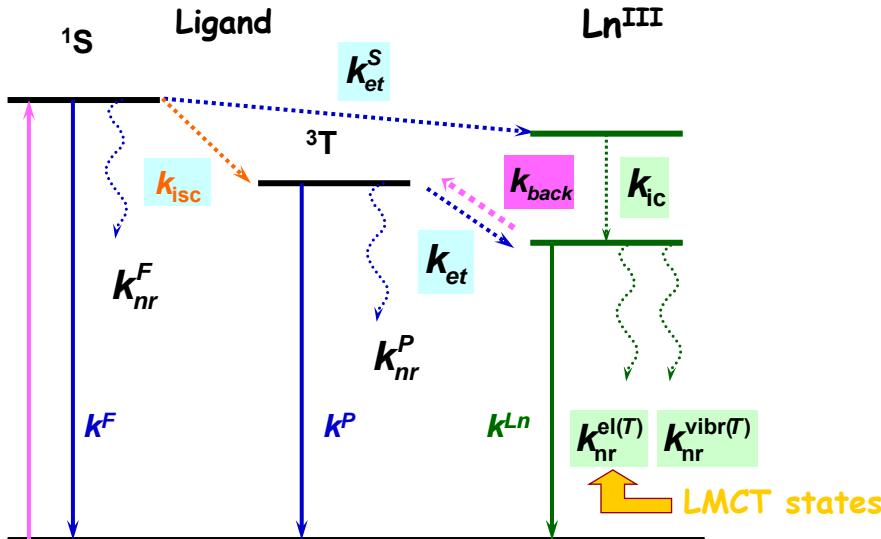
In view of the weak f-f oscillator strengths, direct excitation of  $\text{Ln}^{\text{III}}$  luminescence is not very efficient, unless powerful lasers are used. Therefore the need for sensitisation (antenna effect).

Indirect excitation, called **sensitisation** is achieved through lattice or attached ligands



The excited states of  $\text{Ln}^{\text{III}}$  ions are usually long-lived with lifetimes in the range  $\mu\text{s}$  to  $\text{ms}$ , so that the ligands triplet state plays a major role in the energy transfer.

## Energy migration paths



$$Q_{\text{Ln}}^L = \eta_{\text{sens}} \cdot Q_{\text{Ln}}^{\text{Ln}} = \eta_{\text{isc}} \cdot \eta_{\text{et}} \cdot Q_{\text{Ln}}^{\text{Ln}}$$

intrinsic quantum yield

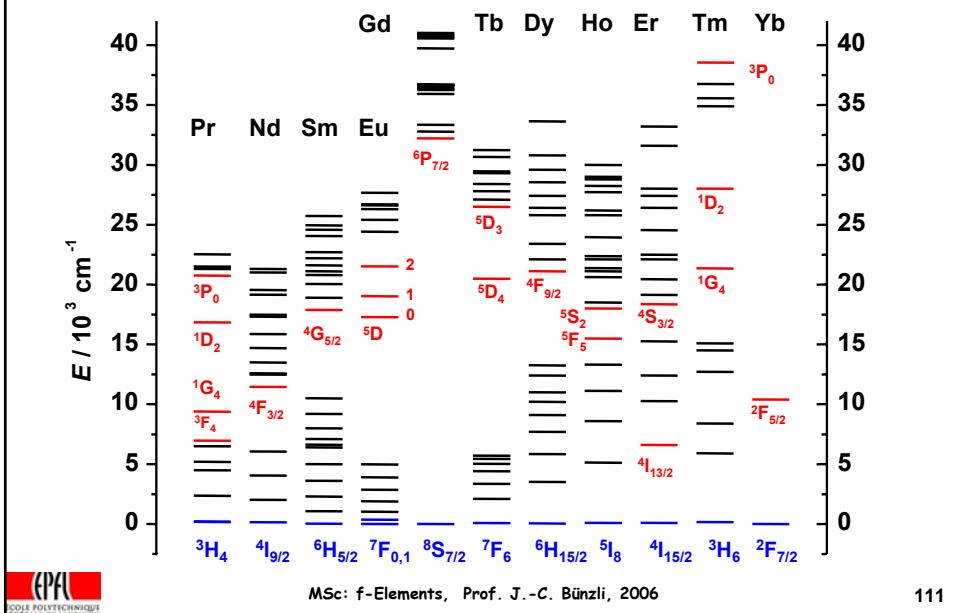
In the special case of  $\text{Eu}^{\text{III}}$ ,  $\tau_r$  may be estimated from:

$$\frac{1}{\tau_r} = 14.65 \cdot n^3 \cdot \left( \frac{I_{\text{tot}}}{I_{\text{md}}} \right) = \frac{\tau_{\text{obs}}}{\tau_r}$$

where  $n$  is the refractive index,  $I_{\text{tot}}$  the total emitted light intensity and  $I_{\text{md}}$  the intensity of the purely magnetic dipole transition  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ .

## Chapter 2 Physico-chemical properties

### 2.4.3 4f emission spectra

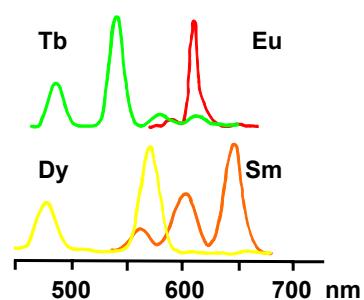


## Chapter 2 Physico-chemical properties

The smaller the gap between excited and ground state, the larger the contribution of non-radiative de-activation (particularly through vibrations).

$\text{Gd}^{\text{III}}$  is the best ion, but emits in the UV

$\text{Eu}^{\text{III}}$ ,  $\text{Tb}^{\text{III}}$  have often large intrinsic quantum yields and are used as luminescent probes.



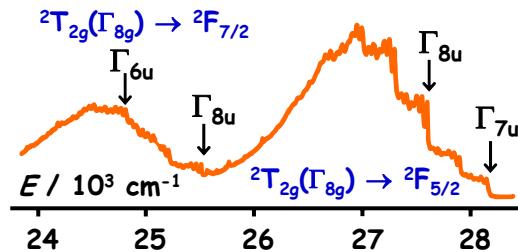
$\text{Pr}^{\text{III}}$  ( $1.33 \mu\text{m}$ ),  $\text{Nd}^{\text{III}}$  ( $1.06 \mu\text{m}$ ),  $\text{Er}^{\text{III}}$  ( $1.54 \mu\text{m}$ ), and  $\text{Yb}^{\text{III}}$  ( $0.98 \mu\text{m}$ ) have interesting emission bands in the NIR range, some of them are in the telecommunication window ( $1 - 1.6 \mu\text{m}$ )

Chapter 2 Physico-chemical properties

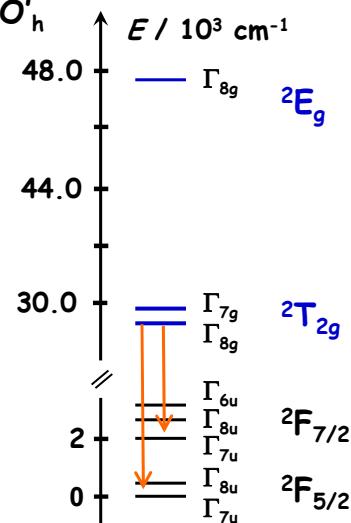
Cerium(III) in  $O_h$  symmetry

$Cs_2Na(Y:Ce)Cl_6$

Emission spectrum at 10 K, exc.  
 $50 \times 10^3 \text{ cm}^{-1}$



(E.P. Tanner et al. JACS 2003 125, 13225)



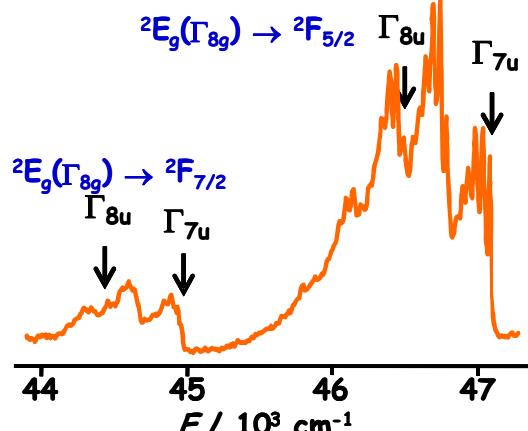
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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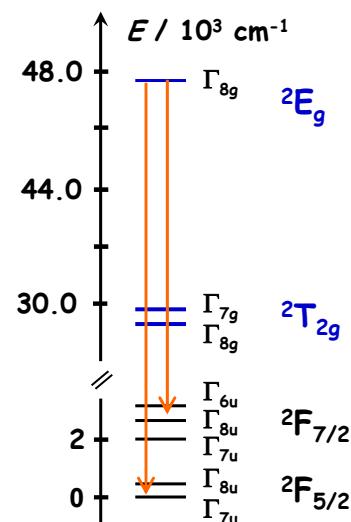
Chapter 2 Physico-chemical properties

$Cs_2Na(Y:Ce)Cl_6$

Emission spectrum at 10 K, exc.  
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(E.P. Tanner et al. JACS 2003 125, 13225)

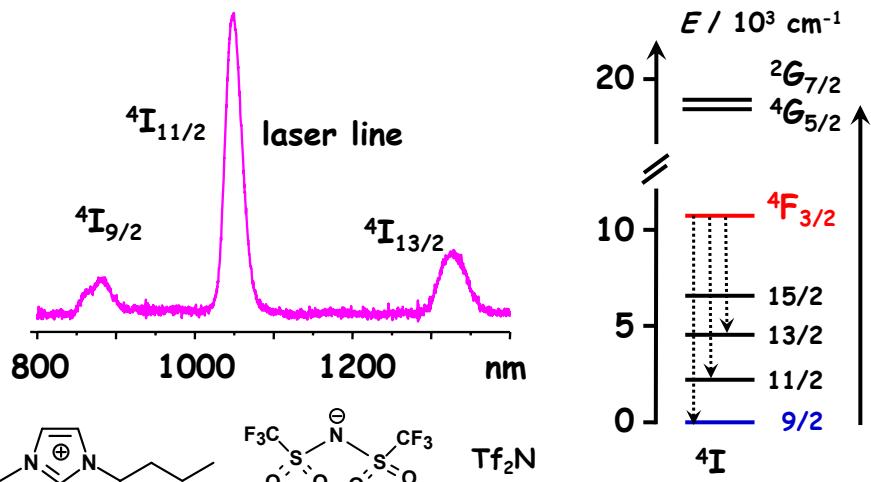


MSc: f-Elements, Prof. J.-C. Bünzli, 2006

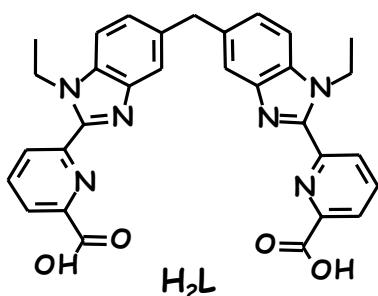
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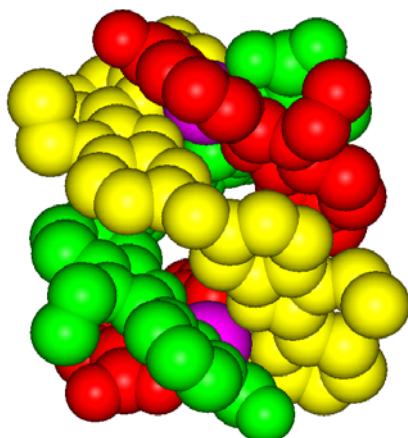
**Neodymium(III): Nd(NTf<sub>2</sub>)<sub>3</sub> in BumimNTf<sub>2</sub>**



Chapter 2 Physico-chemical properties



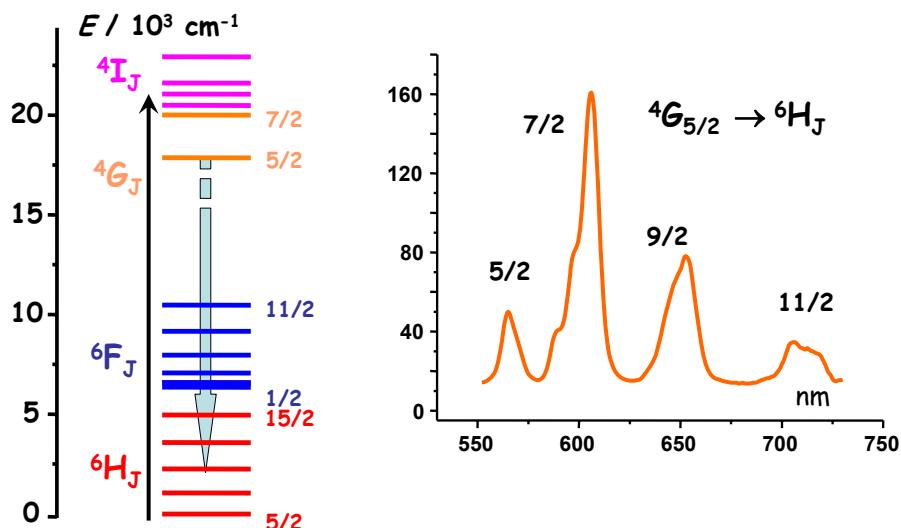
- $\log \beta_{23} = 51$  for Eu
- pEu = 21 (dota : 25)



Samarium emission spectrum:

## Chapter 2 Physico-chemical properties

### Samarium(III): $\text{Sm}_2\text{L}_3$ in $\text{H}_2\text{O}$

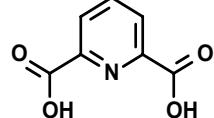
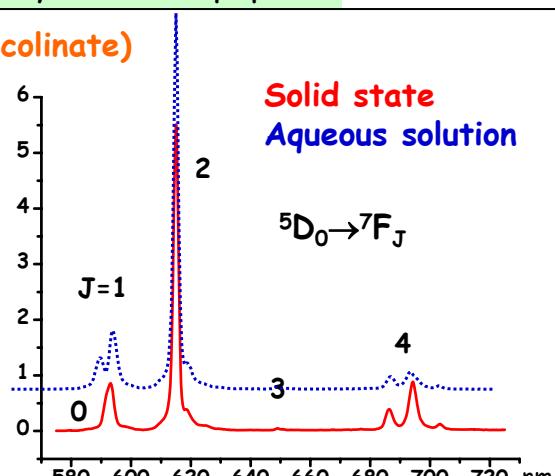
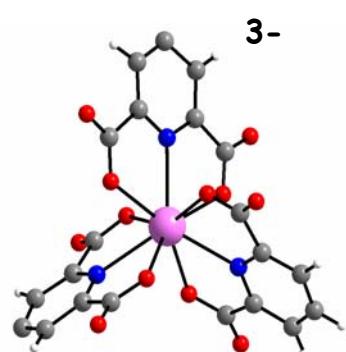


MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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## Chapter 2 Physico-chemical properties

### Europium(III): tris(dipicolinate)



$$\log K_i = 8.7, 8.1, \text{ and } 5.6 \quad (i = 1-3)$$

$$\tau(^5\text{D}_0) = 1.54 \text{ and } 1.67 \text{ ms}$$

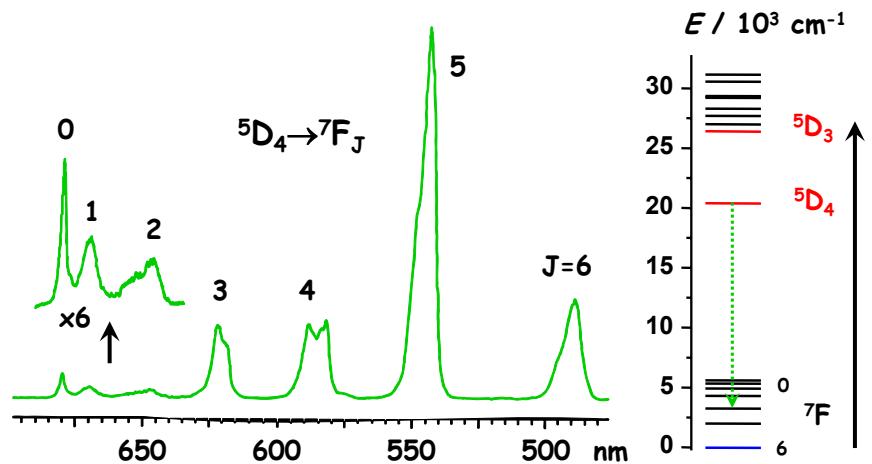


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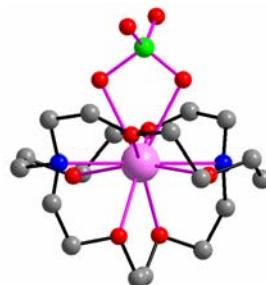
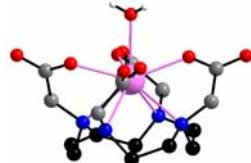
Chapter 2 Physico-chemical properties

Terbium(III):  $\text{Tb}(\text{NO}_3)_3$  in DMSO



## Chapter 3 Coordination chemistry

- 3.1 Properties of aqueous solutions (4f ions)
- 3.2 Properties of non-aqueous solutions (4f ions)
- 3.3 Properties of aqueous solutions (5f ions)
- 3.4 Macrocyclic complexes
  - 3.4.1 General principles
  - 3.4.2 4f complexes
  - 3.4.3 Some 5f complexes



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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## Chapter 3 Coordination chemistry

### 3.1 Properties of aqueous solutions (4f ions)

#### Co-ordination numbers in water

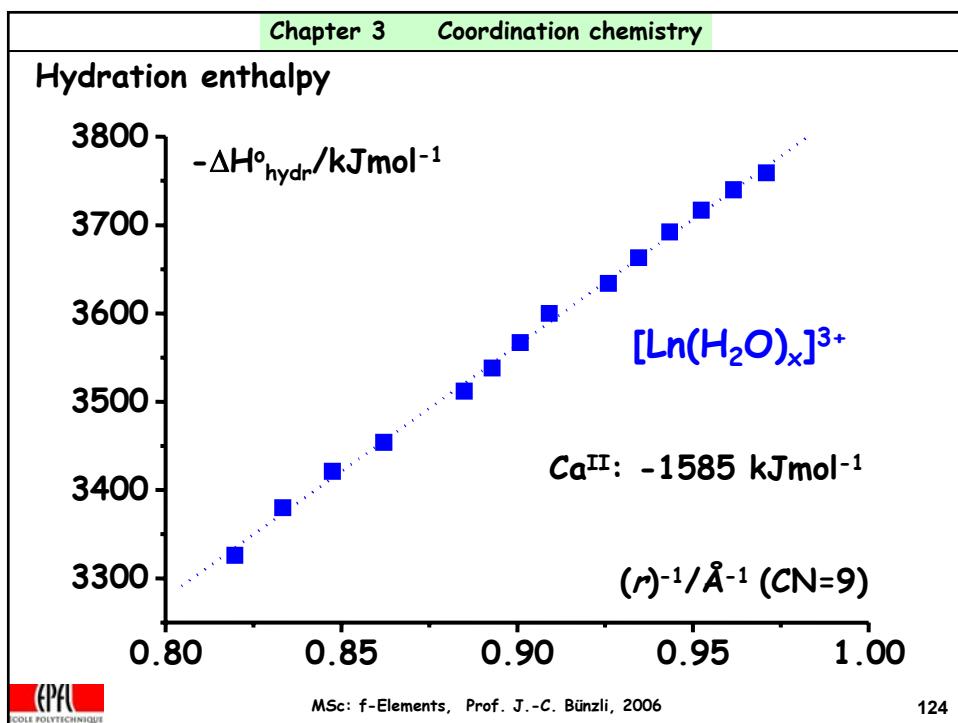
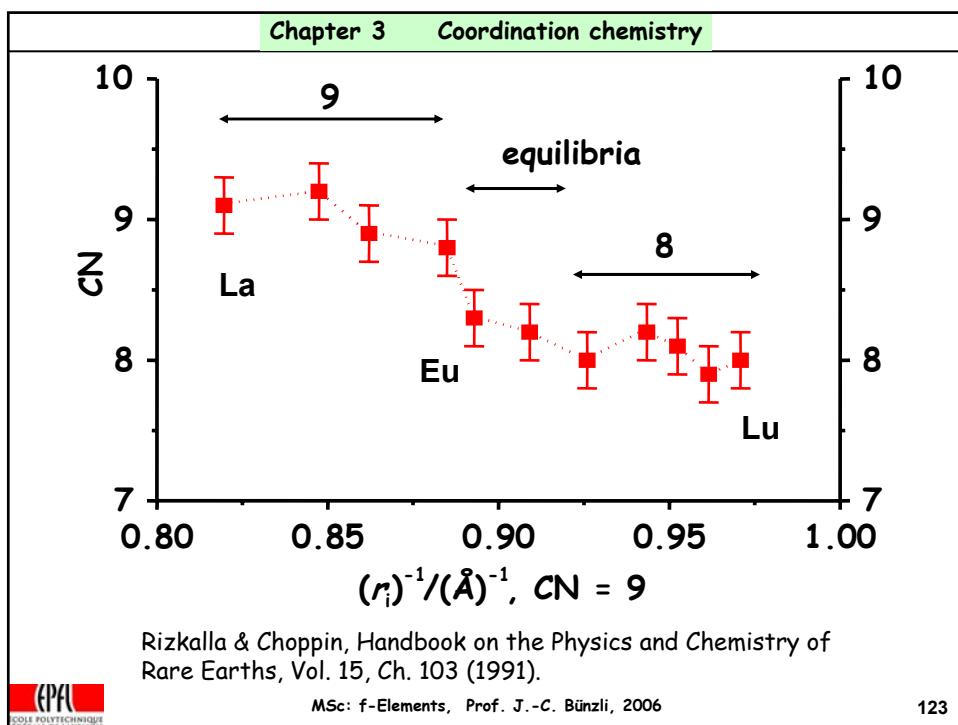
- In the solid state, CN = 9 from La-Lu as shown by the X-ray structures of bromates and ethylsulfates
- In solution, 8 or 9?  
Change along the series or not?
- Kinetic studies, optical data, NMR data, X-ray diffraction data, neutron diffraction data:

The CN changes from 9 (La-Nd) to 8 (Dy-Lu)  
with an intermediate number for Sm-Tb (equilibria)



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

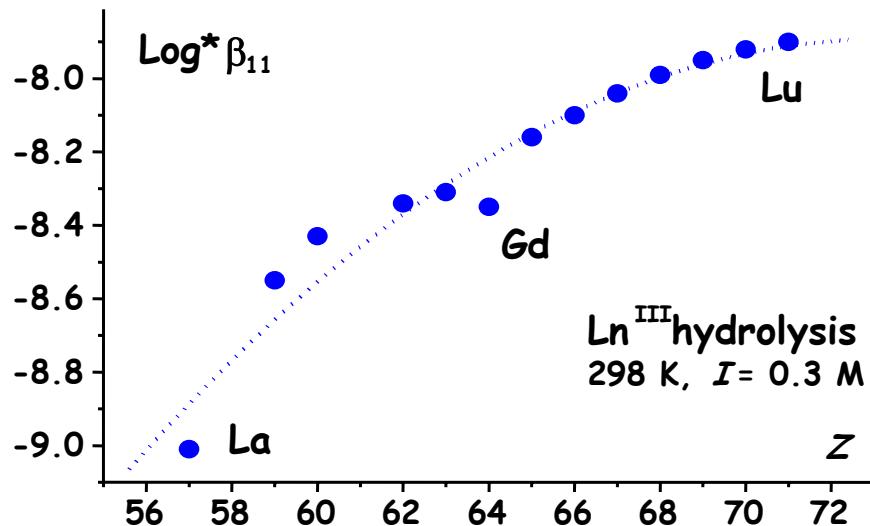
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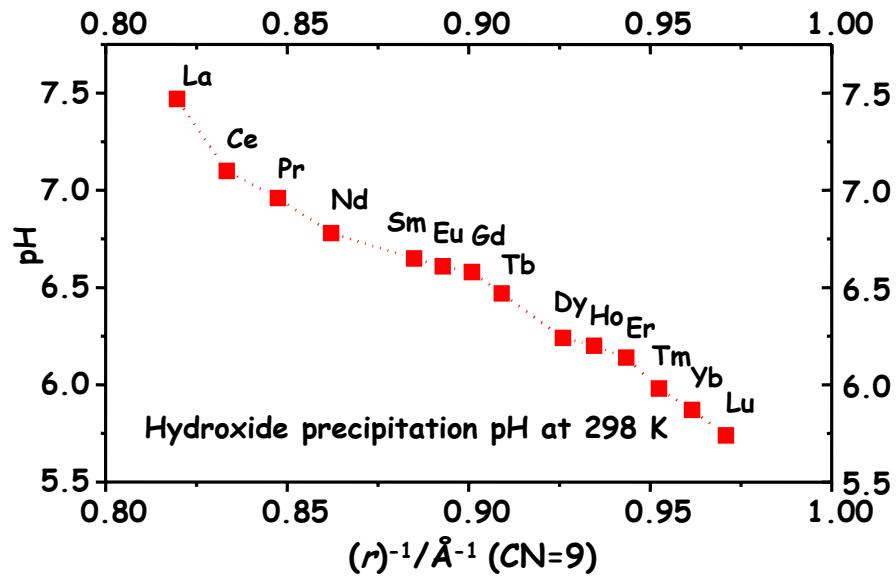


**Hydrolysis**

$$\text{*}\beta_{\ell,m} = \frac{[Ln_m(OH)_\ell(H_2O)_{(n-\ell)}]^{(3m-\ell)+}[H^+]^\ell}{[Ln(H_2O)_n]^{3+}}^m$$

**Example** Ligand L,  $\text{Log}K_1 = 3$ ,  $\text{pH} = 7$ ,  $\text{Log}^*\beta_{11} = -8$   
 $[L]_{\text{free}} = 10^{-3} \text{ M}$   
 $[LnL] : [LnOH] : [Ln_{\text{aq}}] = 45 : 45 : 10 \%$





### Kinetic aspects

$\text{Ln}^{\text{III}}$  ions are very labile in water

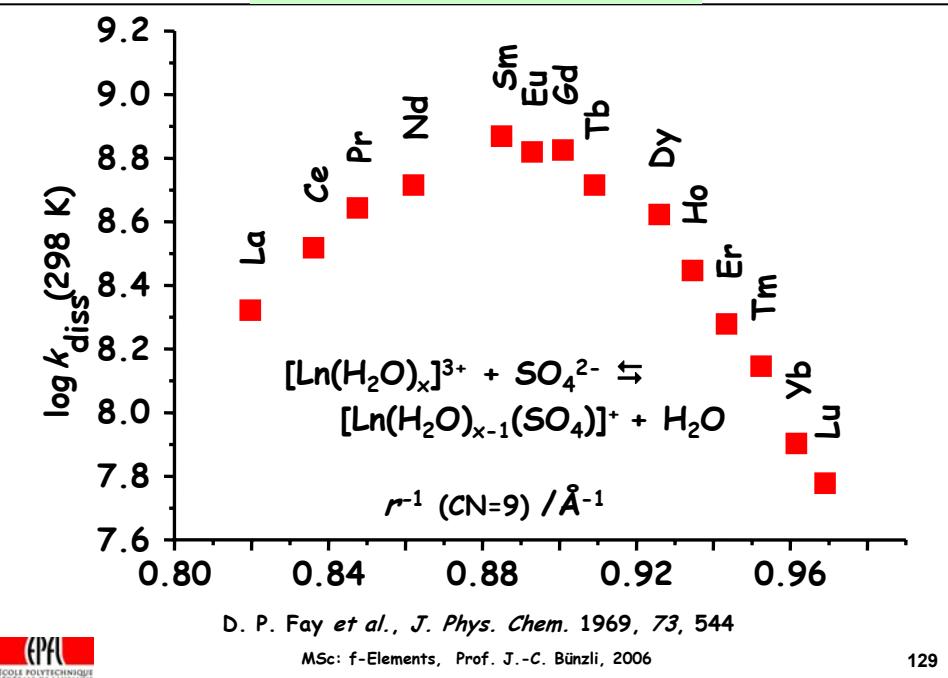


$k_{\text{ex}}$  for water exchange is in the range  $10^7$ - $10^9$  s<sup>-1</sup>

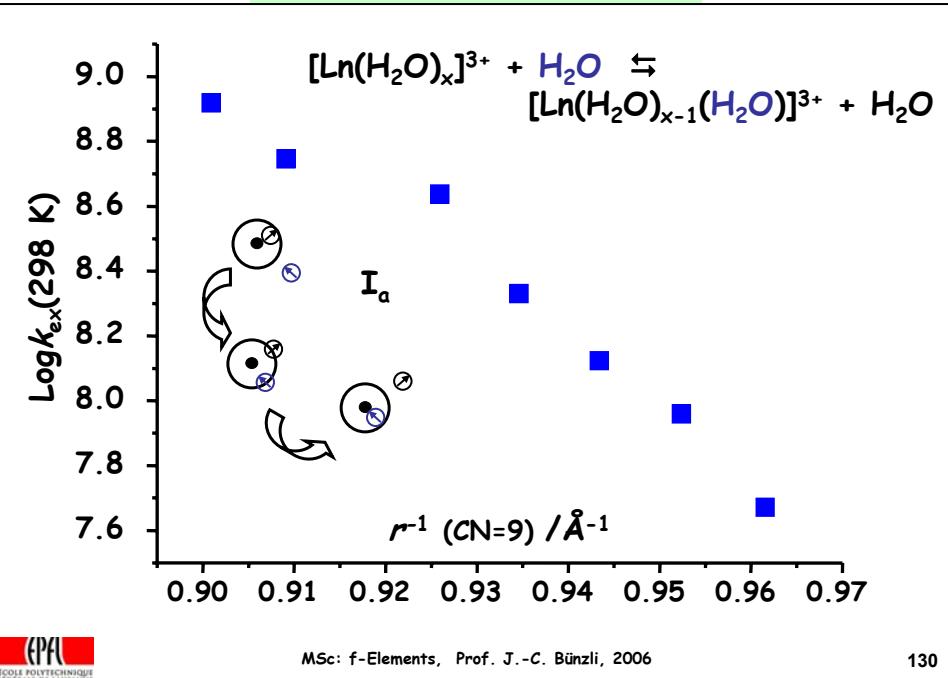
It has been measured by:

- EPR (Gd)
- NMR (<sup>17</sup>O and longitudinal  $1/T_1$  and transverse  $1/T_2$  relaxation times)
- Ultrasonic absorption spectroscopy

Chapter 3 Coordination chemistry



Chapter 3 Coordination chemistry



### 3.2 Properties of non-aqueous solutions (4f ions)

#### Acetonitrile

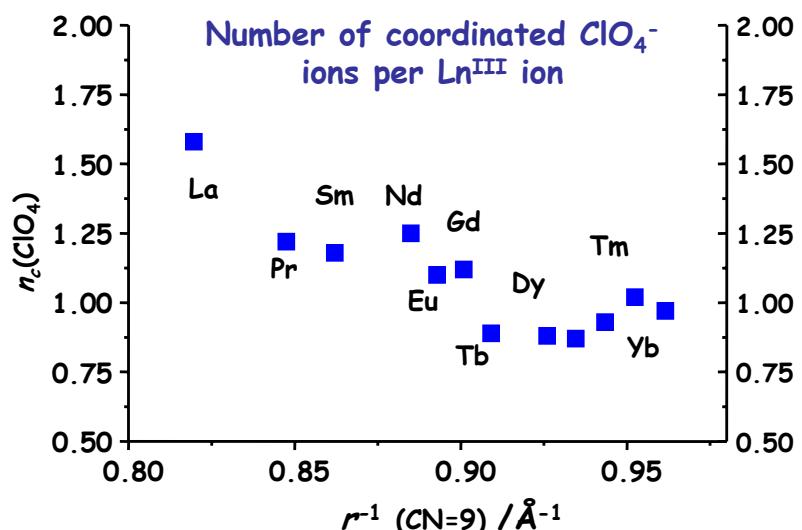
Most counterions are coordinated, at least partially.  
The solvation has been studied either by NMR or by vibrational spectroscopy (IR/Raman).

#### Anhydrous perchlorates:

Presence of       $[\text{Ln}(\text{MeCN})_x]^{3+}$   
 $[\text{Ln}(\text{ClO}_4)(\text{MeCN})_{x-2}]^{2+}$   
 $[\text{Ln}(\text{ClO}_4)_2(\text{MeCN})_{x-3}]^+$

#### Bis(perchlorato) species:

La 25 %, Pr 10 %, Tb-Lu 0 %



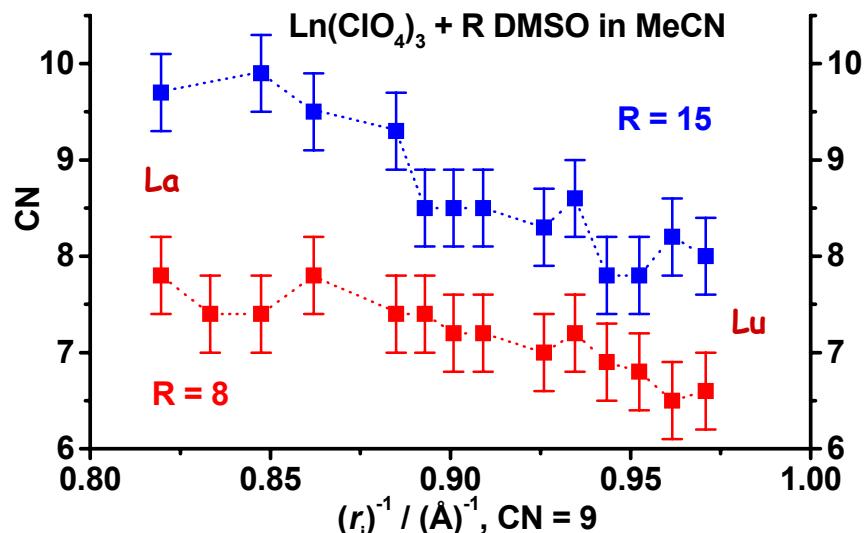
**LogK's in acetonitrile**

$$\text{Log} K_1(\text{ClO}_4^-) \quad \text{Log} K_3(\text{SO}_3\text{CF}_3^-)$$

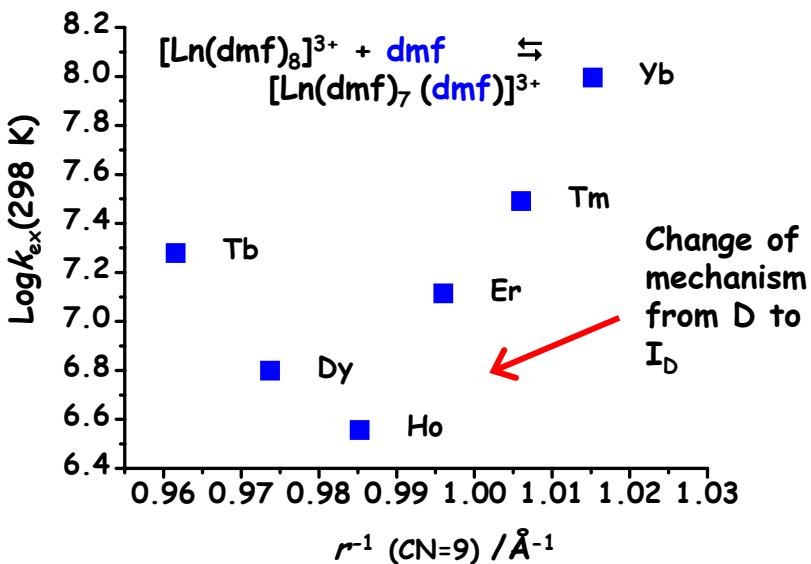
Tb	$1.9 \pm 0.4$	2.5	Di Bernardo et al. <i>Inorg. Chim. Acta</i> 1993, 207, 85
Dy	$1.8 \pm 0.4$	2.6	
Ho	$1.8 \pm 0.3$	2.5	
Er	$2.1 \pm 0.4$	2.5	
Tm	$2.7 \pm 0.5$	2.4	
Lu	$2.4 \pm 0.4$	2.3	



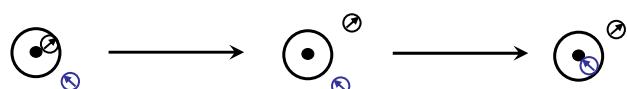
Bünzli, Milicic-Tang, Handbook on the Physics and Chemistry of Rare Earths, Vol. 21, Ch. 145 (1995)

**Perchlorates in presence of dimethylsulfoxide**

## Kinetic aspects

 $I_d$  mechanism

## Dissociative mechanism D

Activation thermodynamic parameters  
Activation volume

### 3.3 Properties of aqueous solutions (5f ions)

Far less data than for Ln ions, and many of them are extrapolated from Ln data.

A trend similar to Ln seems to prevail for An<sup>3+</sup>:

Am	CN = 9.0	Eu	CN = 8.3
Cm	8.9	Gd	8.2
Cf	8.2	Dy	8.0
Es	8.0	Ho	7.9

Hydration numbers (first + second coordination spheres) are between 14 and 16

Hydrolysis is also important with Log\*β<sub>11</sub> values between -3.8 for Fm(OH)<sup>2+</sup> to -7.4 for Np(OH)<sup>2+</sup>



### Dioxo actinide cations AnO<sub>2</sub><sup>2+</sup>

Uranyl solutions contain polymeric species at pH > 2:

[UO <sub>2</sub> (OH)] <sup>+</sup>	Log*β <sub>11</sub> = -5.72
[UO <sub>2</sub> (OH) <sub>2</sub> ]	Log*β <sub>12</sub> = -11.78
[(UO <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub> ] <sup>2+</sup>	Log*β <sub>22</sub> = -5.89

pH values required to achieve 50 % dimerization:

[AnO <sub>2</sub> ] <sup>2+</sup>	UO <sub>2</sub> <sup>2+</sup>	NpO <sub>2</sub> <sup>2+</sup>	PuO <sub>2</sub> <sup>2+</sup>
0.1 M	3.45	3.84	4.76
0.01 M	4.46	4.94	5.87
0.001 M	5.56	6.54	7.51



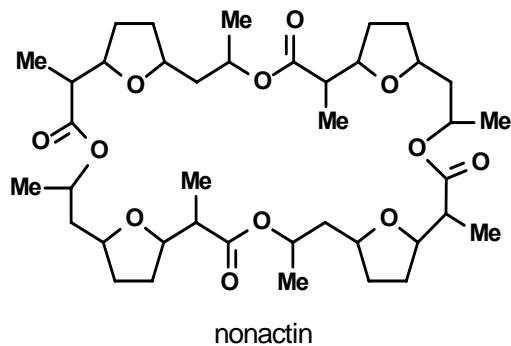
### 3.4 Macrocyclic complexes

#### 3.4.1 General principles

##### Historical outlook

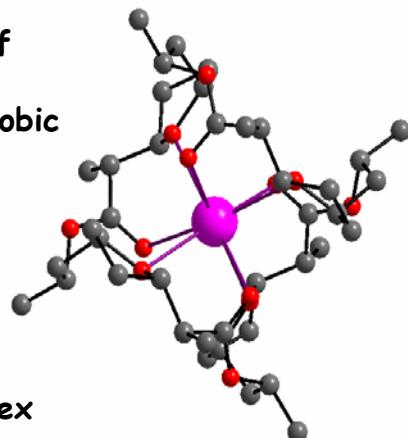
1955-1970

Discovery of nonactin (1955), a natural antibiotic



#### Natural ionophores

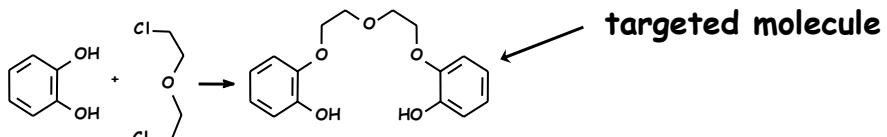
- Substances with the ability of transferring an ion from an aqueous phase into a hydrophobic phase
- Essential components of the transport of alkali cation though biological membranes
- 1967: crystal structure of the potassium-nonactin complex



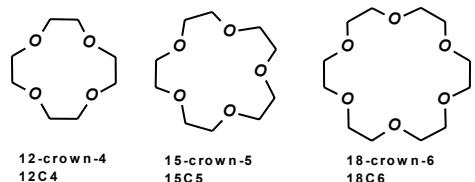
Globular complex with a polar cavity and an external hydrophobic envelope → elegant way to achieve lipid solubility of cations



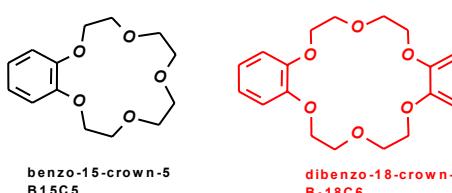
Chapter 3 Coordination chemistry



C.J. Pedersen, 1967



Serendipity helps  
the discovery of  
crown ethers!



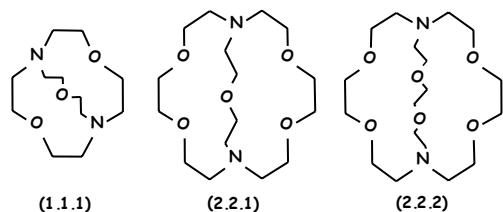
isolated molecule  
La, Ce complexes



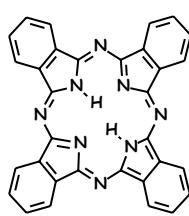
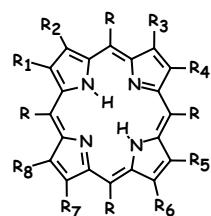
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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J.-M. Lehn, 1969  
cryptands



Porphyrins and  
phthalocyanines  
Mid 1965's



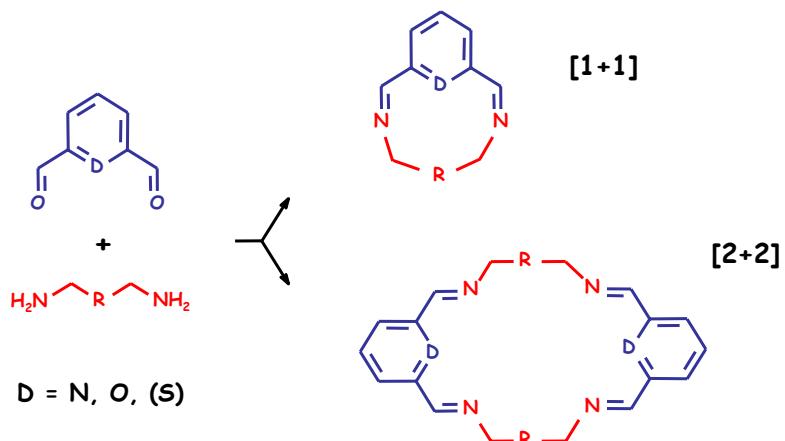
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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1970-1990

Schiff bases, late 1970's

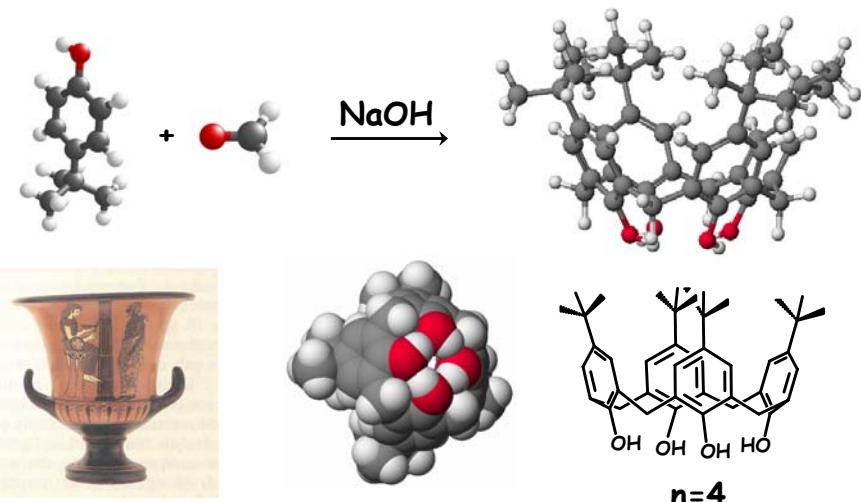


MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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Calix[n]arenes (Gutsche 1970)



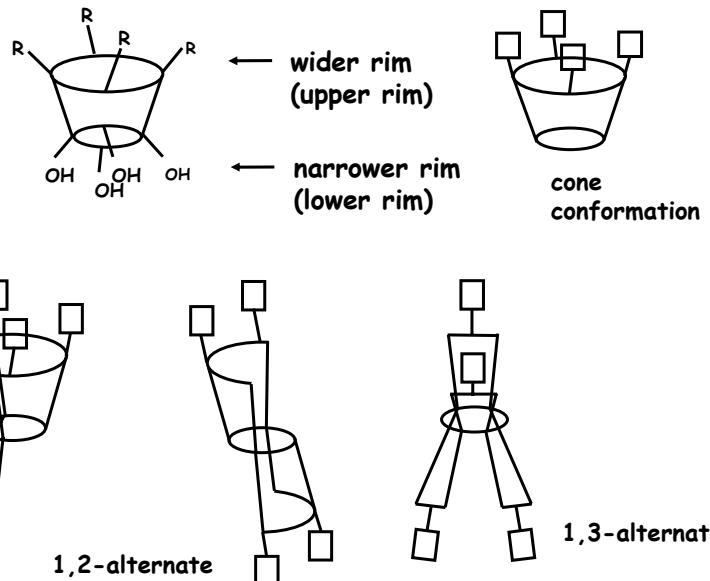
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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### Chapter 3 Coordination chemistry



David Gutsche

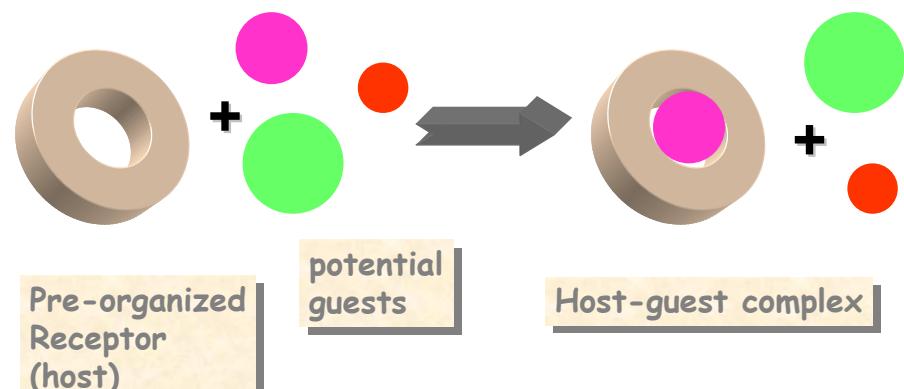


MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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### Chapter 3 Coordination chemistry

The lock and key principle (E. Fischer, 1894)



$$\Delta G_r < \Delta G_r^*, \Delta G_r$$

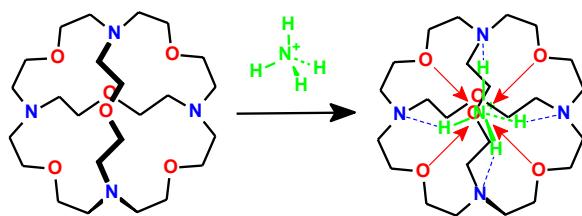


MSc: f-Elements, Prof. J.-C. Bünzli, 2006

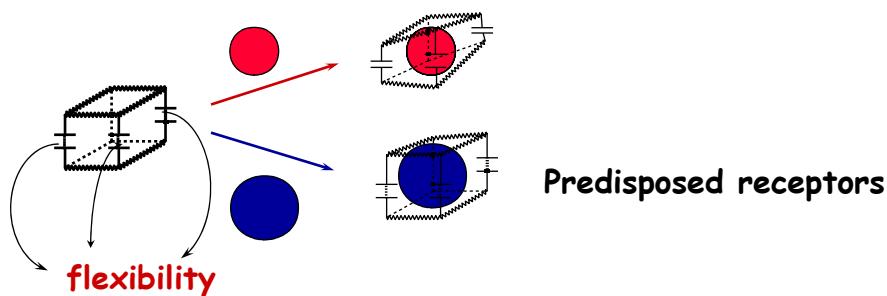
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- Steric complementarity
- Interaction matching (HSAB principle)
- Maximizing the number of interaction sites
- Maximizing bonding strength

**Cation recognition:**  
 Size (spherical cations)  
 Stereochemistry (e.g. d-elements)



### The induced fit concept (Koshland 1958)



**Finer recognition**

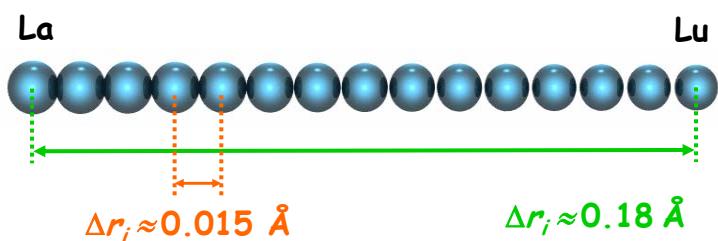
**Classes of ligands:**

- large flexible macrocycles
- macrocycles fitted with pendant arms

### 3.4.2 4f Complexes

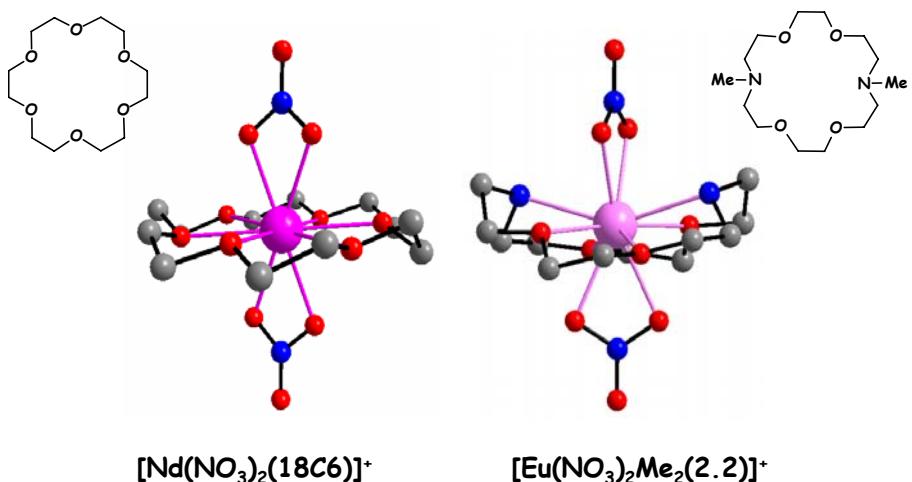
## A. The lock and key principle

For  $\text{Ln}^{\text{III}}$  ions, this principle is difficult to use because they are spherical, hard ions with similar properties

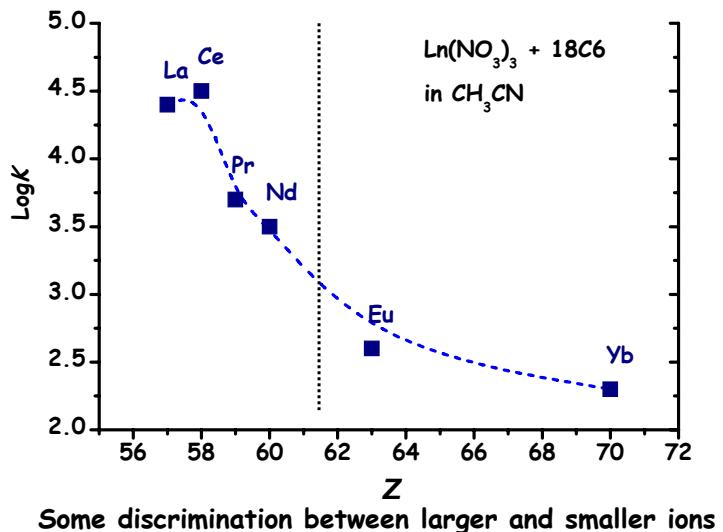


**Small differences in hardness and size**  
**Difficult to match the large coordination numbers (8-12)**

## $\text{Ln}^{\text{III}}$ ions and $18\text{C}6$ ether and $\text{Me}_2(2.2)$



Chapter 3 Coordination chemistry

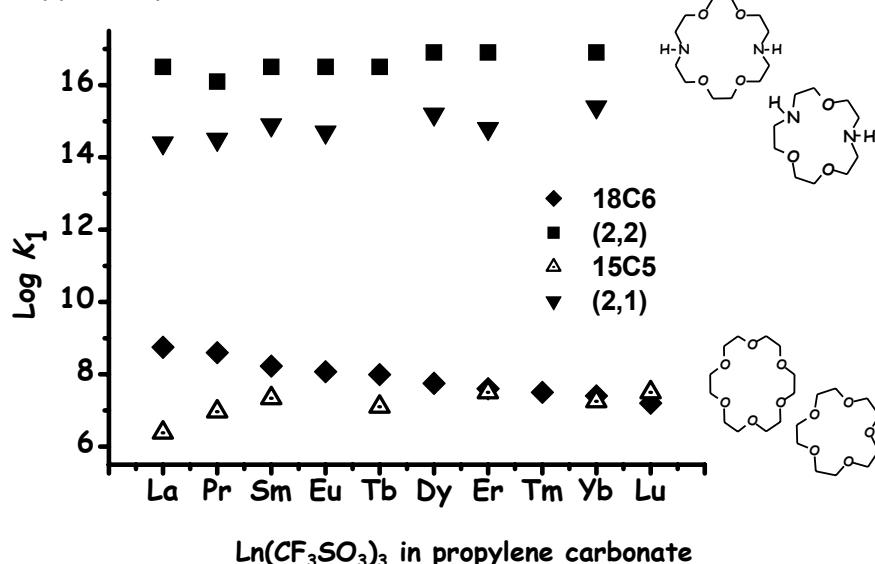


MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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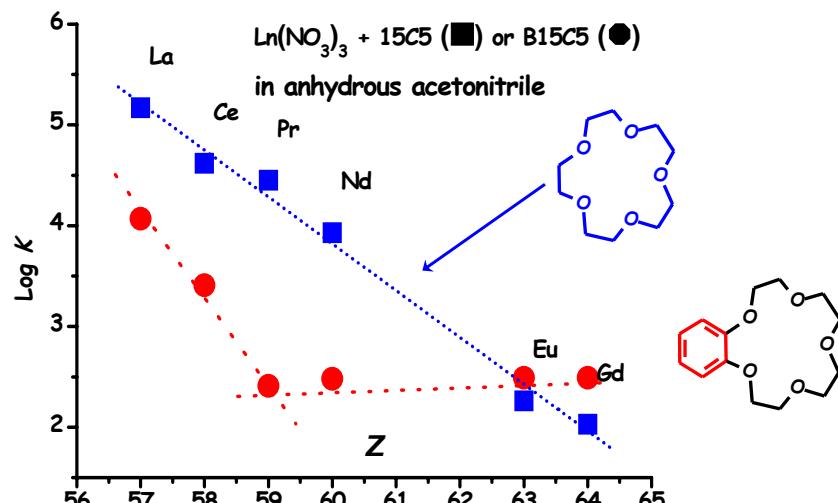
Effect of the donor atom



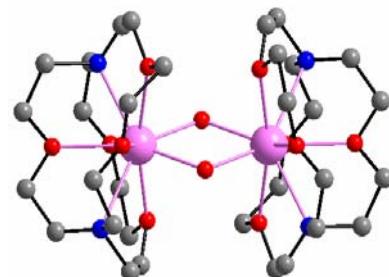
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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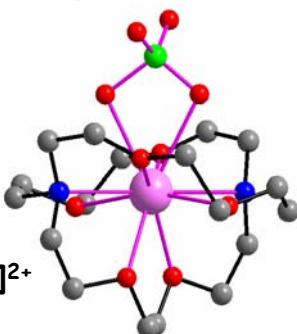
### Rigidifying the ligand induces more discrimination



### Simple cryptands



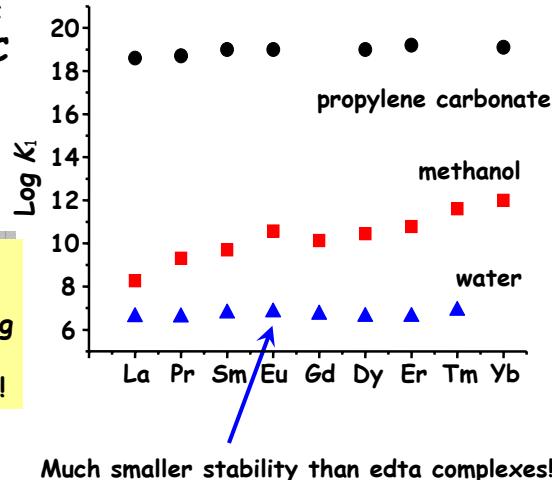
The receptors are less rigid than initially planned!



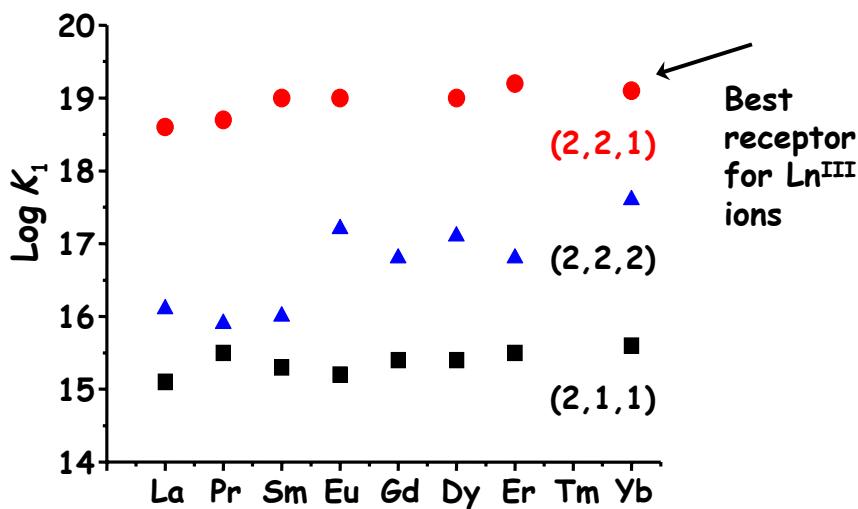
## Stability constants with (2.2.1): solvent influence



Thermodynamic considerations show the « recognition » being made by the solvent and not by the receptor!



Much smaller stability than edta complexes!

Stability constants ( $\text{Ln}(\text{CF}_3\text{SO}_3)_3$  in propylene carbonate)

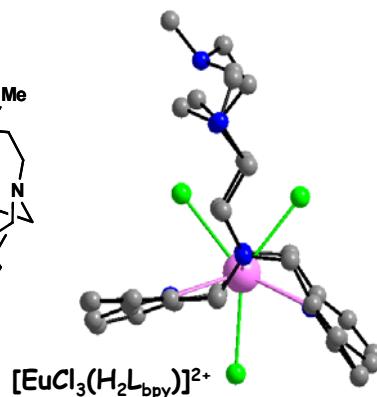
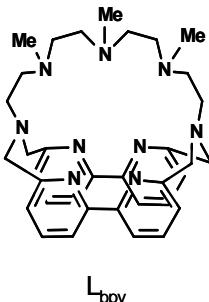
## Bioanalytical applications

- immunoassays with (bpy.bpy.bpy) cryptate as stain
- pH sensor (with  $\text{ClO}_4^-$ )

At pH < 7,  $\text{H}_2\text{L}^{2+}$   
(amine chain)

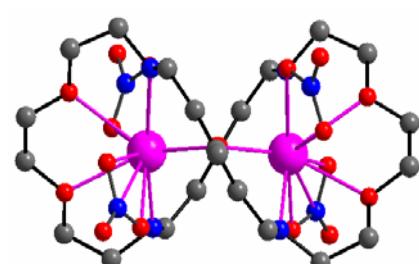
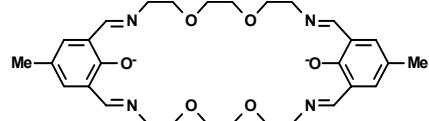
At pH = 7,  $\text{HL}^+$

At pH > 7, L  
amine chain  
coordinates  
and expels  $\text{H}_2\text{O}$



## B. The induced fit principle

### a) Large macrocycles

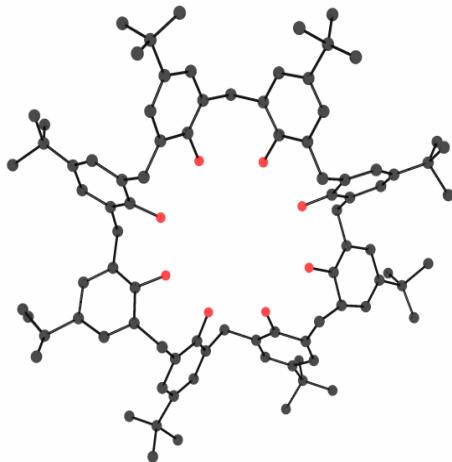


Large macrocycles  
may be flexible enough  
to wrap around metal ions  
as demonstrated by  
this ditopic Schiff base  
ligand

**Large calixarenes**

*p*-*tert*-butylcalix[8]arene  
**b-LH<sub>8</sub>**

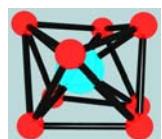
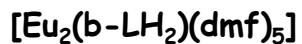
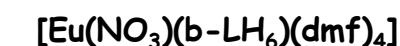
Undulated conformation



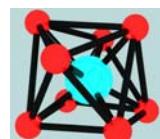
In presence of a weak base, KCO<sub>3</sub>, formation of 1:1 complexes with Ln(NO<sub>3</sub>)<sub>3</sub>

In presence of a stronger base, Et<sub>3</sub>N, formation of 2:1 bimetallic complexes

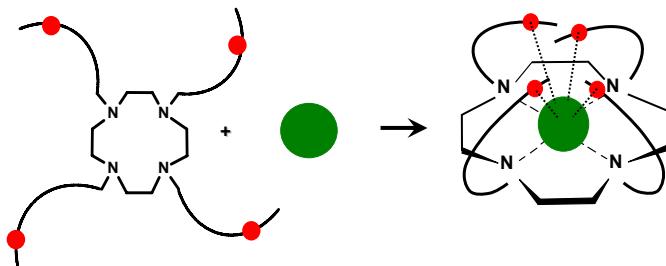
Eu-Eu : 369 pm



8-coordination:  
 distorted square  
 antiprism



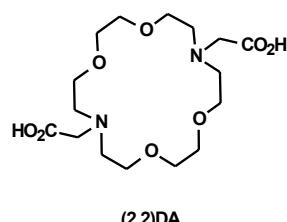
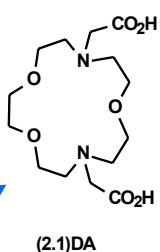
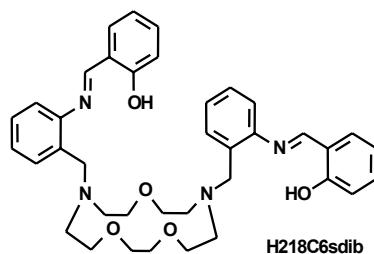
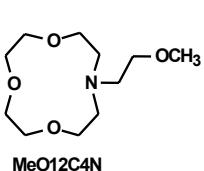
## b) Ligands with pendant arms



- Derivatized coronands
- Cyclen derivatives
- Derivatized calixarenes

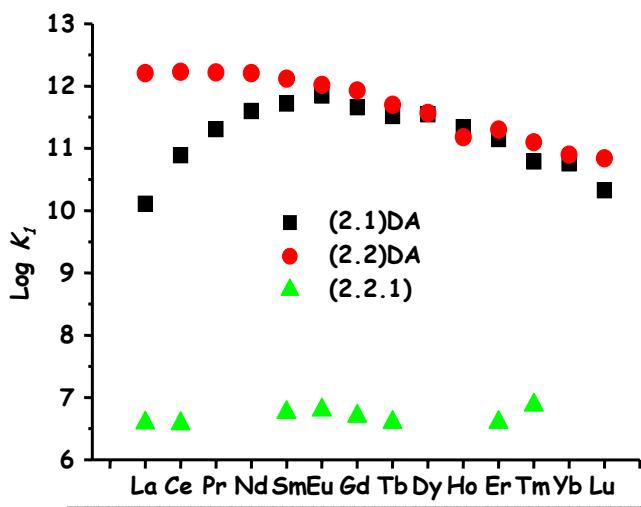
## • Lariat ethers

## Bibracchial lariat coronand



Chapter 3 Coordination chemistry

Stability constants in water (298 K)



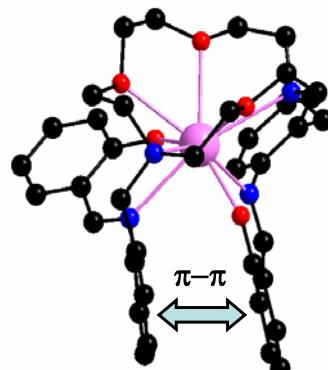
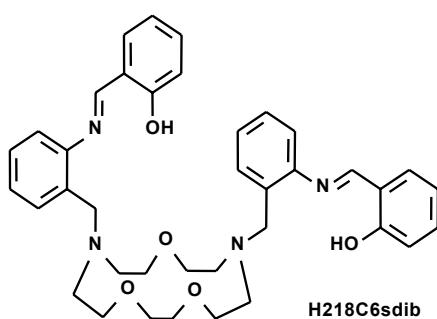
Induced fit versus lock-and-key principle !



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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Nd<sup>III</sup> sensitization

M. González Lorenzo, J.-C. G. Bünzli et al., *Inorg. Chem.*, 2003, 6946

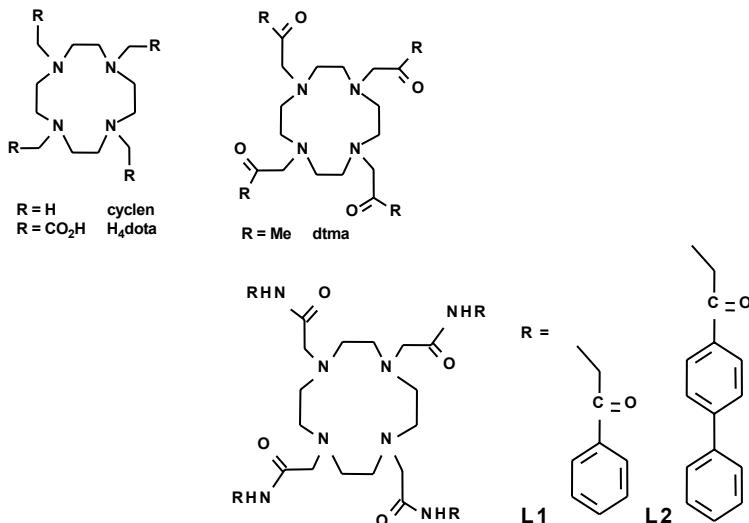


MSc: f-Elements, Prof. J.-C. Bünzli, 2006

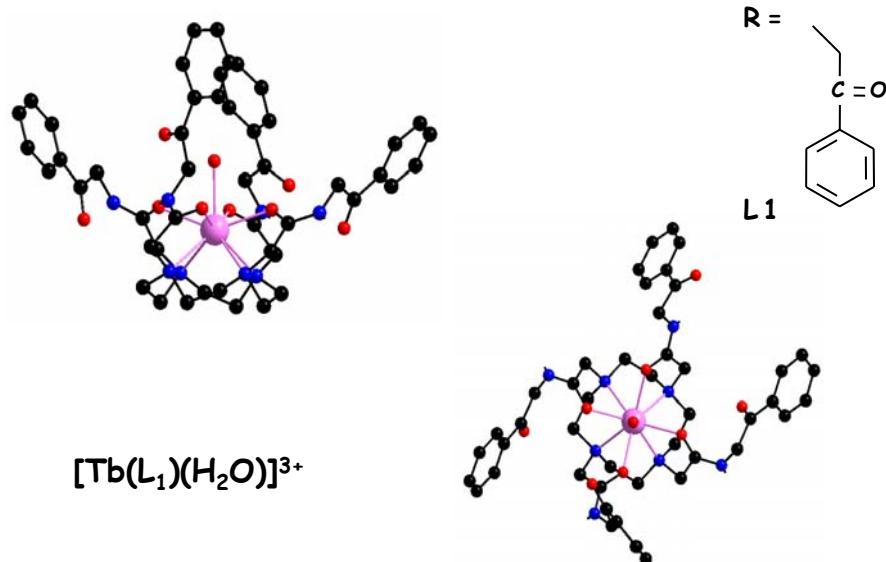
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Chapter 3 Coordination chemistry

- **Cyclen derivatives**



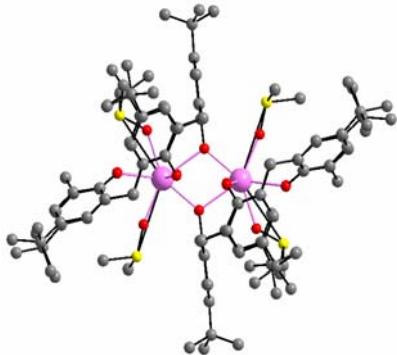
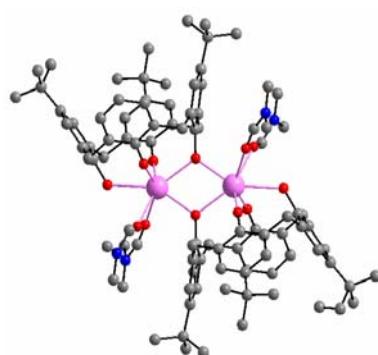
Chapter 3 Coordination chemistry



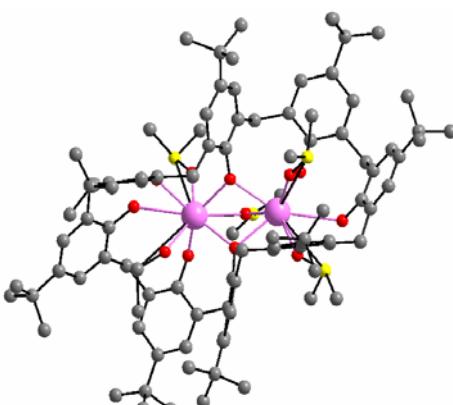
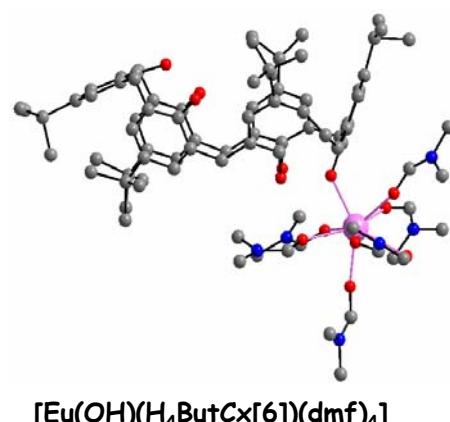
Chapter 3   Coordination chemistry

- Derivatized calix[n]arenes

The parent calixarenes are not well suited for  $\text{Ln}^{\text{III}}$  coordination:

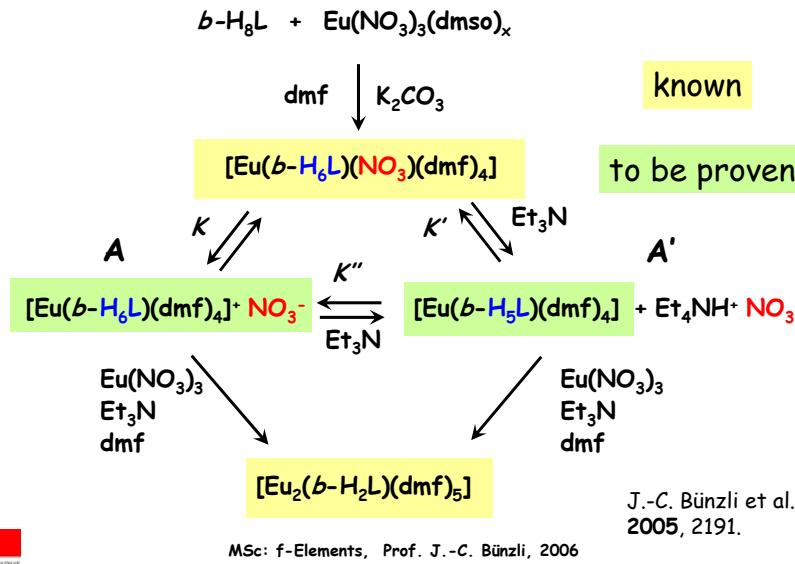


Chapter 3   Coordination chemistry



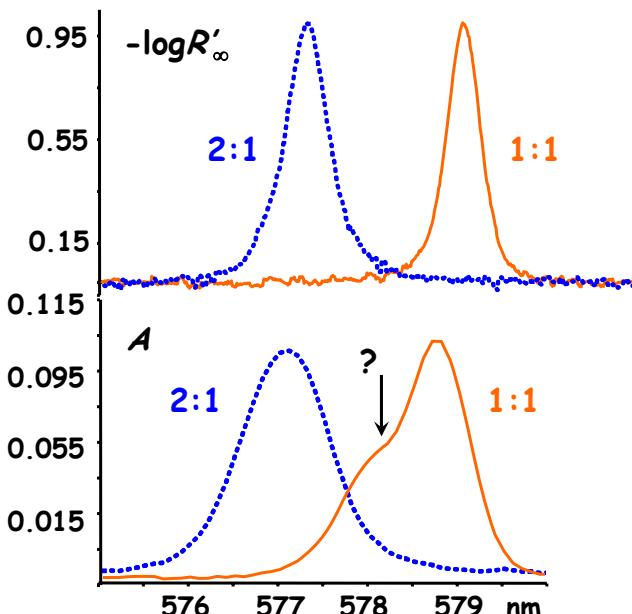
### Chapter 3 Coordination chemistry

Calix[8]arene: mechanistic study of the transformation of the 1:1 complex into the 2:1 complex



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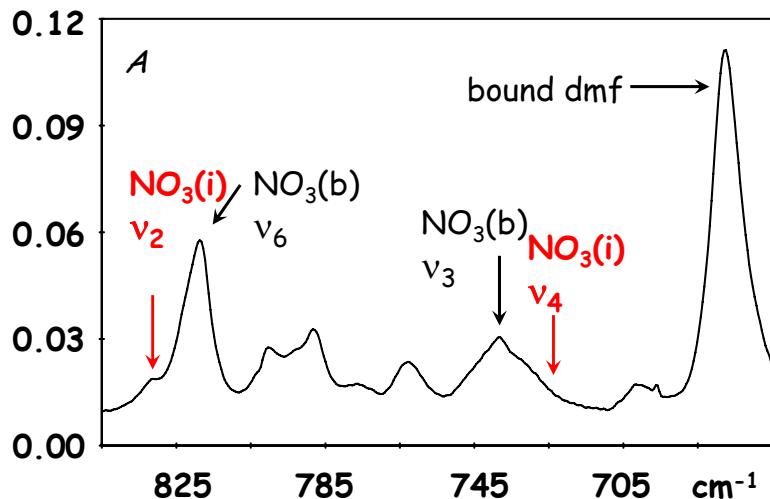
### Chapter 3 Coordination chemistry



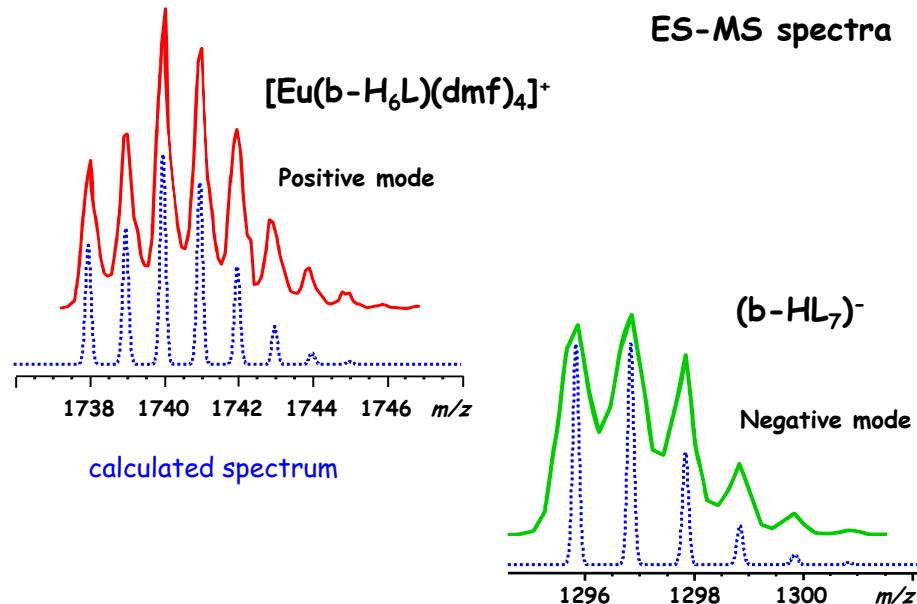
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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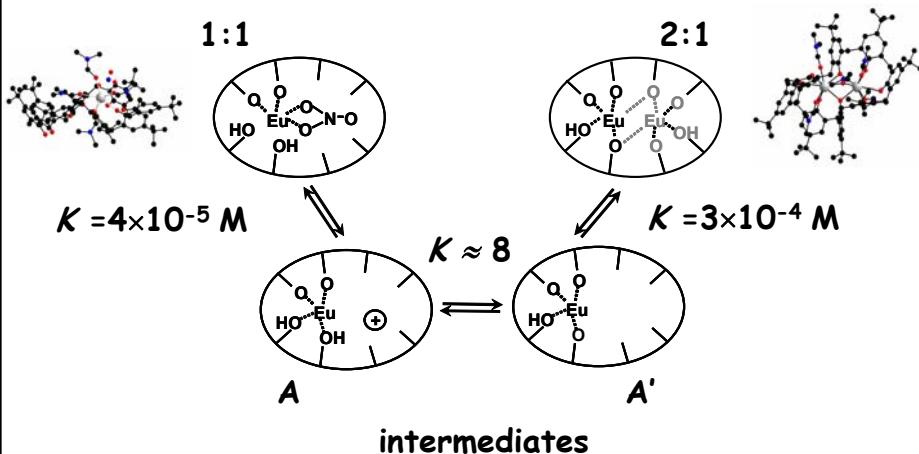
## IR spectrum of a solution of 1:1 complex in dmf



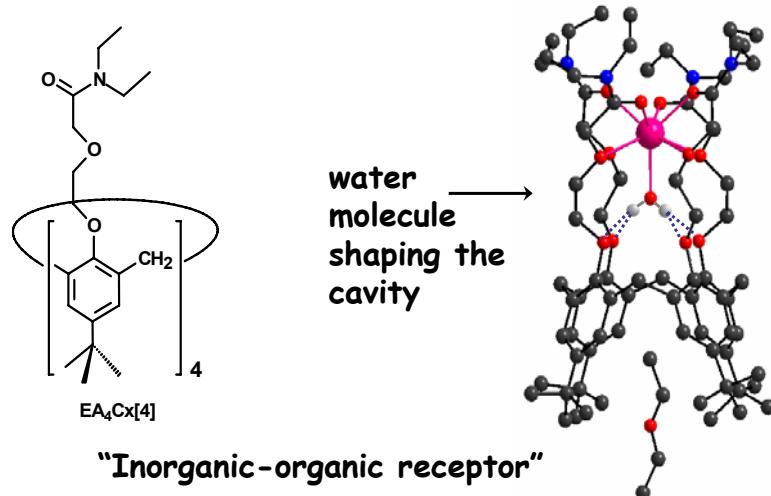
## ES-MS spectra



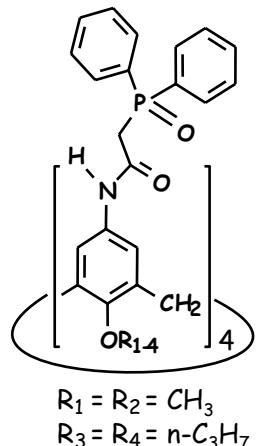
### Temperature, pressure dependence of electronic spectra



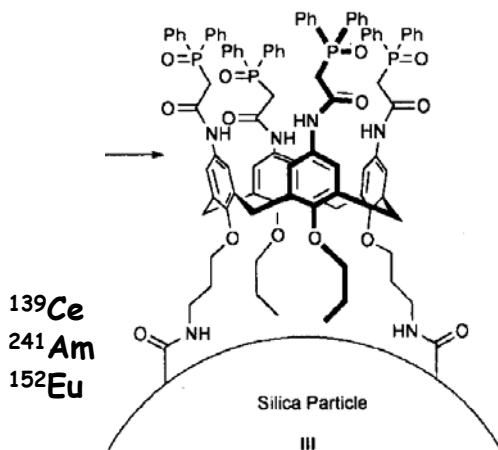
### Derivatized calixarene for An/Ln separation



Chapter 3 Coordination chemistry



**Cx4(CMPO)**



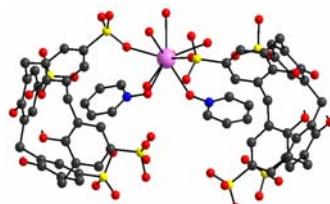
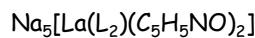
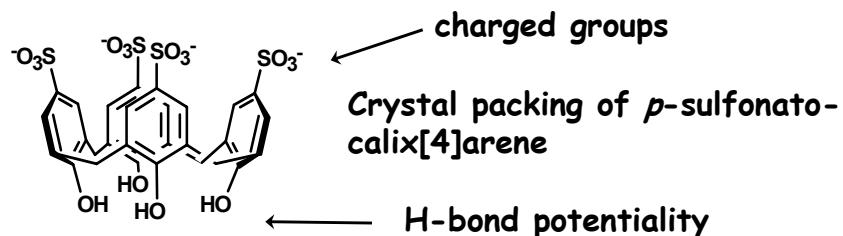
S.E. Matthews et al., *Chem. Commun.*, 2001, 417



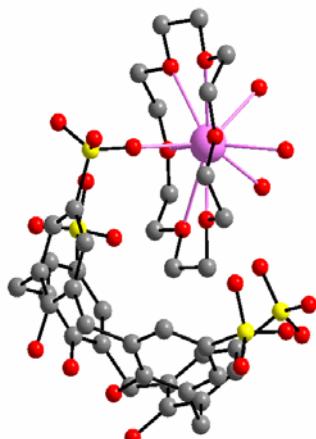
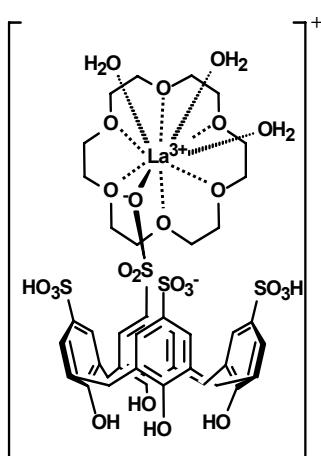
Chapter 3 Coordination chemistry

• Extended systems

Taking advantage of the cone conformation and of strong intermolecular interactions:

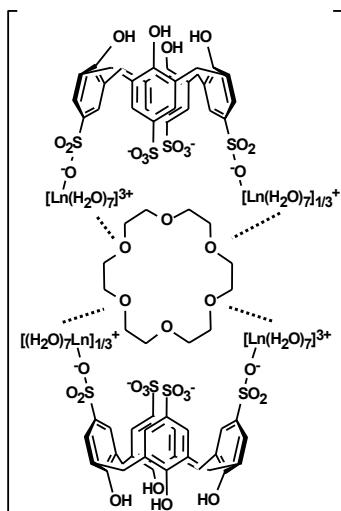


Chapter 3 Coordination chemistry



A. Drlička et al., *Chem. Commun.*  
1999, 1135

Chapter 3 Coordination chemistry

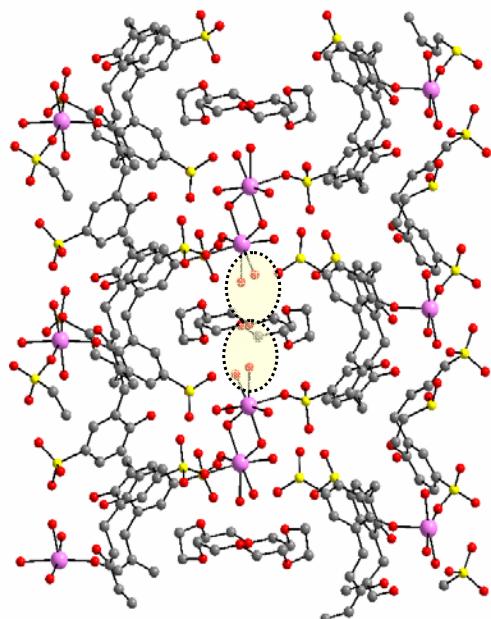


**Micelle-like edifices can be generated:**

**Here crown-6-ether is maintained in the cavity through H-bonds with water molecules bound to  $\text{Ln}^{3+}$**

M. J. Hardie, *Chem. Commun.*  
2000, 849

Chapter 3 Coordination chemistry

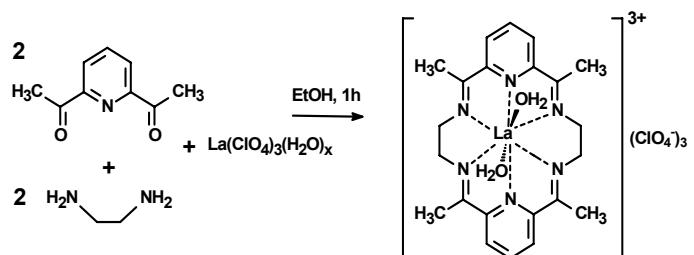


MSc: f-Elements, Prof. J.-C. Bünzli, 2006

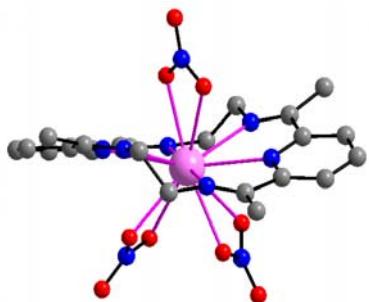
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C. The template effect



Radecka-Parizek 1980



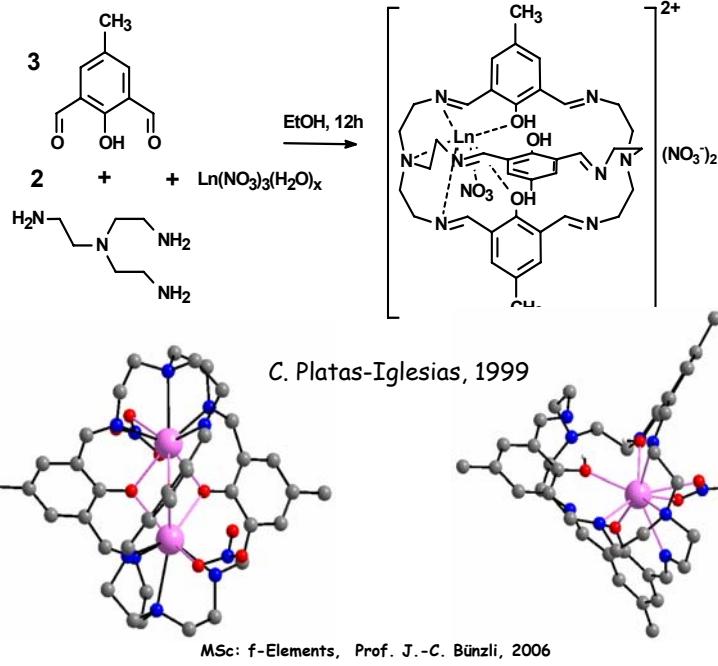
Backer-Dirks, 1979  
[La(NO<sub>3</sub>)<sub>3</sub>L]



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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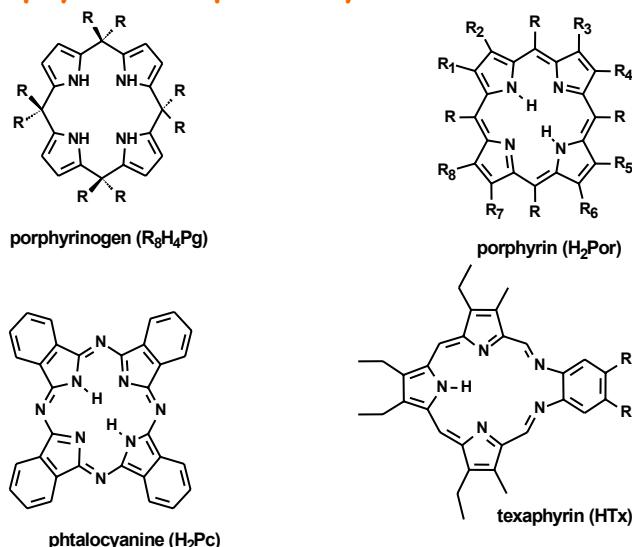
**Chapter 3 Coordination chemistry**



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**Chapter 3 Coordination chemistry**

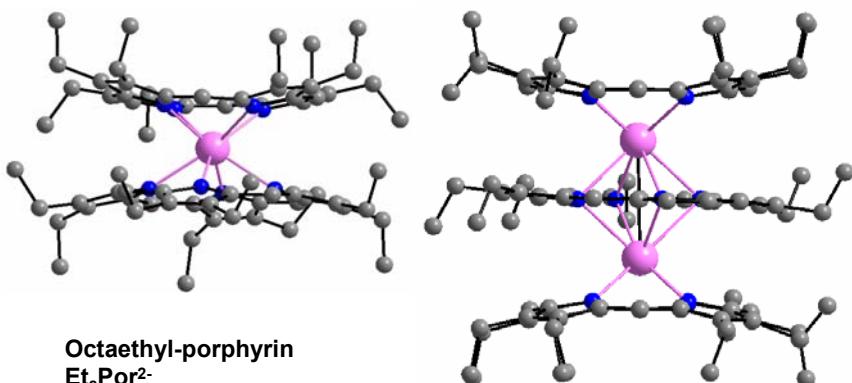
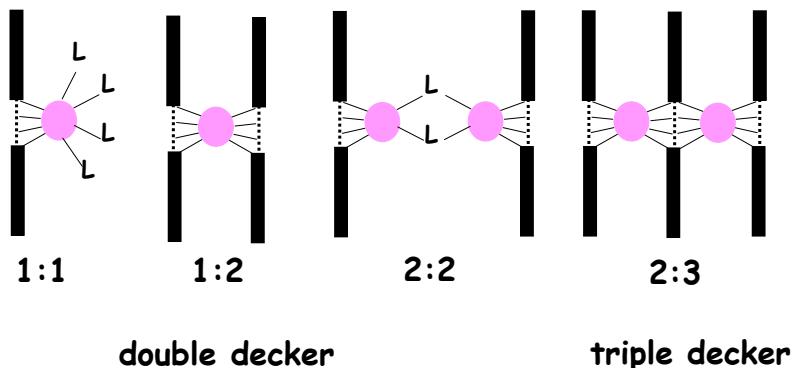
**D. Porphyrins and phthalocyanines**



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

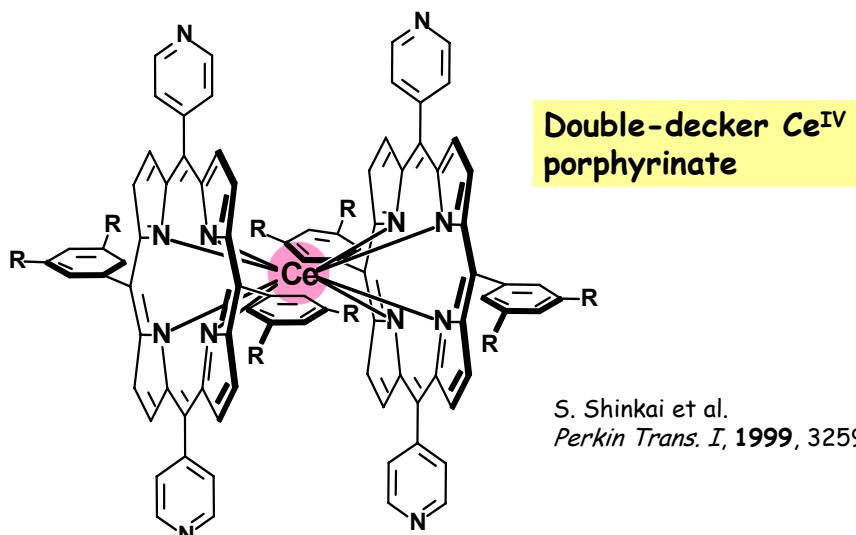
182

## Stoichiometries evidenced for Ln complexes:



J. W. Buchler, 1986

Chirality transcription (memory effect)

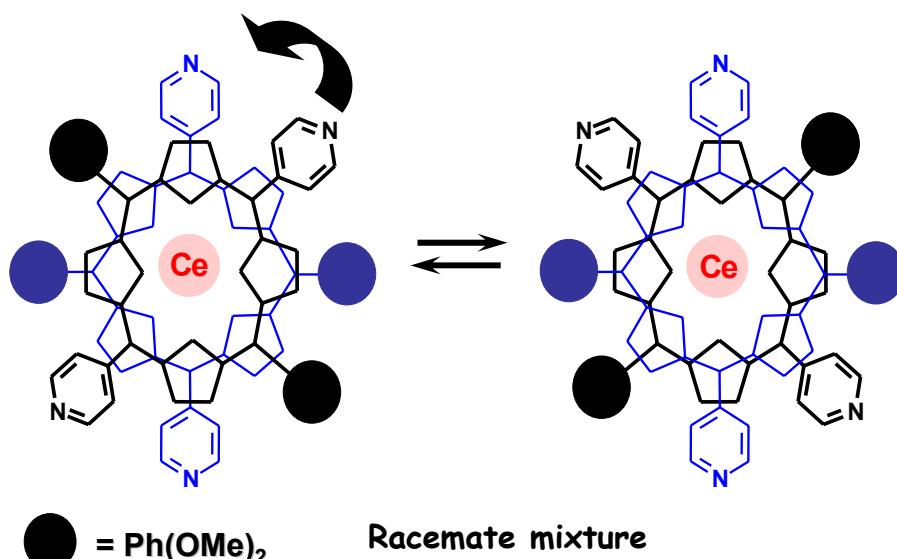


S. Shinkai et al.  
*Perkin Trans. I*, **1999**, 3259



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

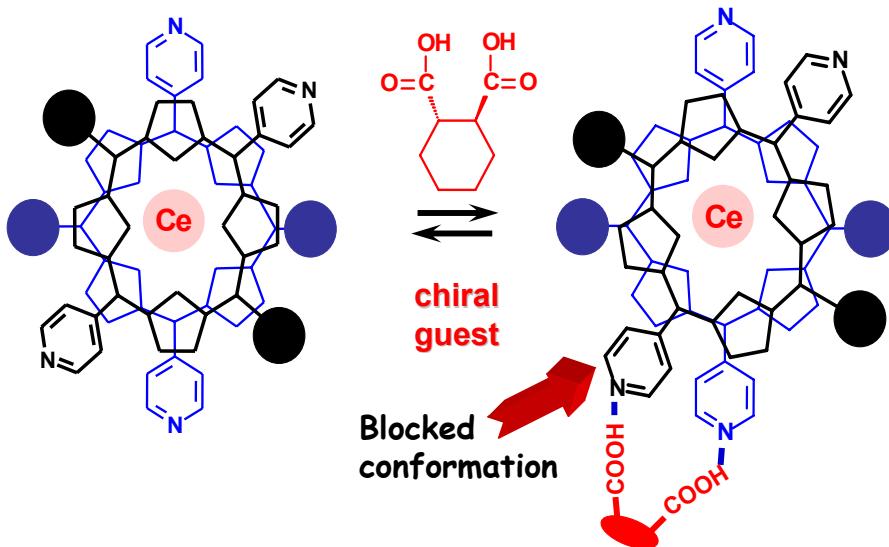
185



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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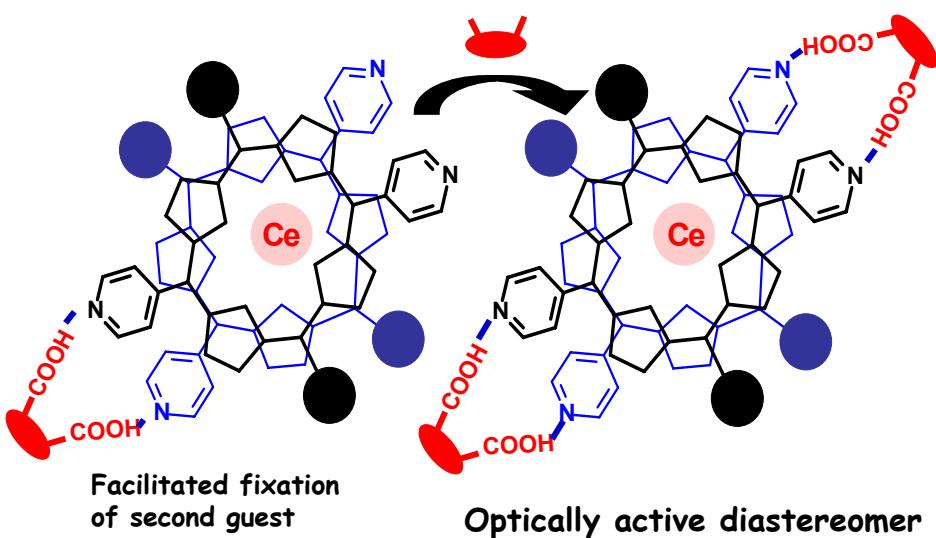
Chapter 3 Coordination chemistry



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

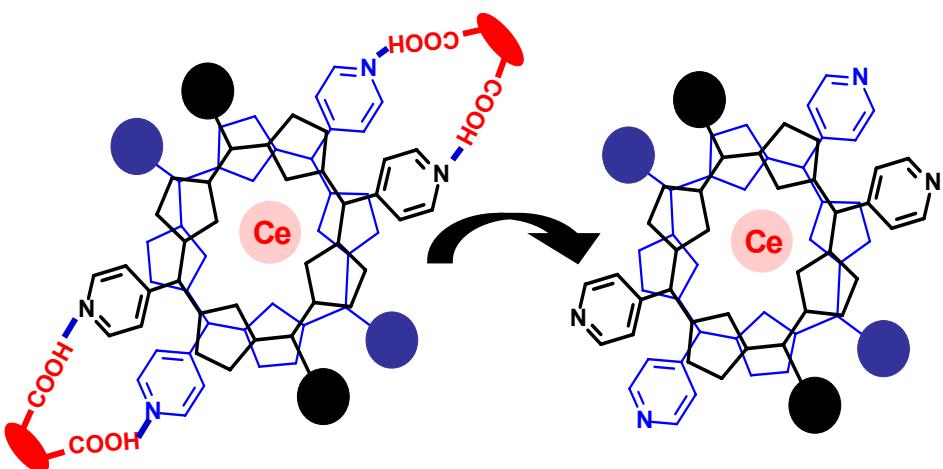
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Chapter 3 Coordination chemistry



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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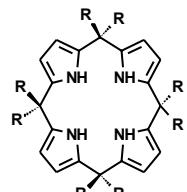


Guest removal : residual enantiomeric excess (3 h at RT  
1 year at -37 °C)

### Activation of small molecules

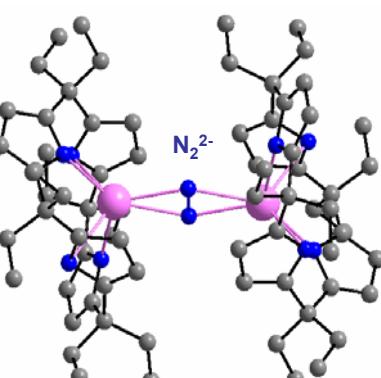
#### Dinitrogen activation

E. Campazzi et al. 1998



porphyrinogen ( $R_8H_4Pg$ )

#### Octaethylporphyrinogen

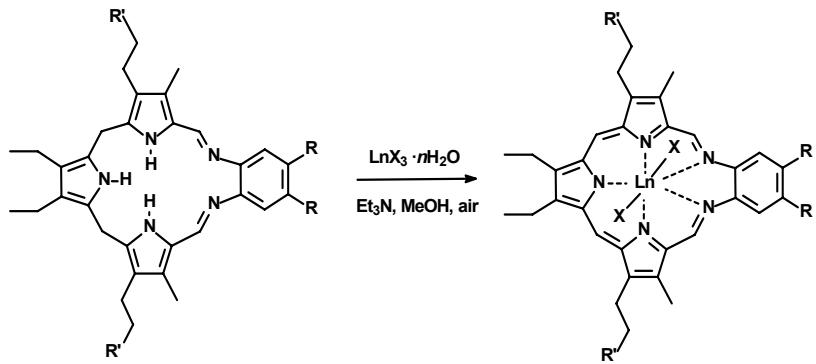


$N-N = 1.234(8) \text{ \AA}$

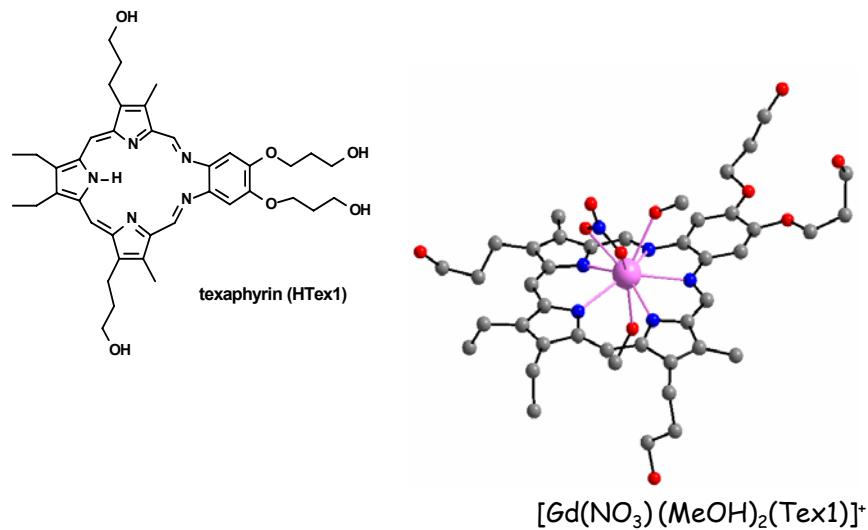
Works also with  $C_2H_4$  and  $C_2H_2$

No loss of  $N_2$  under vacuum

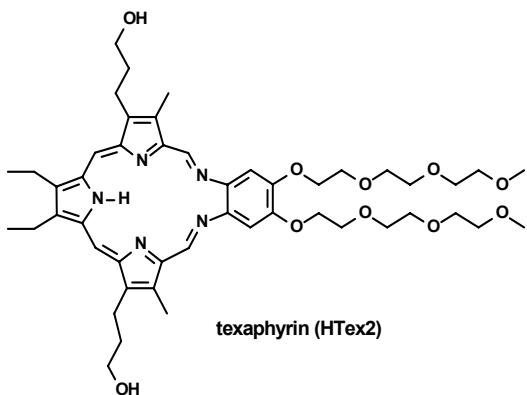
Medical applications: Texaphyrins



John Sessler, Texas A&M University, 1993



**Chapter 3   Coordination chemistry**



J. L. Sessler et al.  
Prog. Inorg. Chem. 2001,  
49, 551.

*GdTex2:* enhancing agent for radiotherapy  
sizeable relaxivity: non-invasive localization in tissues

*LuTex2:* photodynamic therapy (Cancer therapy, photoangioplasty,  
age-related macular degeneration)



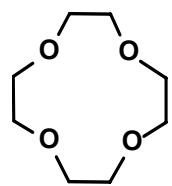
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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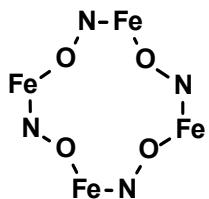
**Chapter 3   Coordination chemistry**

### E. Metallacycles

Exclusive use of hetero-atoms to generate the receptor

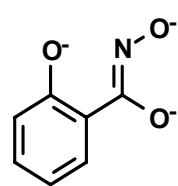


12-crown-4



12-MC<sub>Fe</sub>N<sub>shi</sub>-4

$D = 1.20 \text{ \AA}$



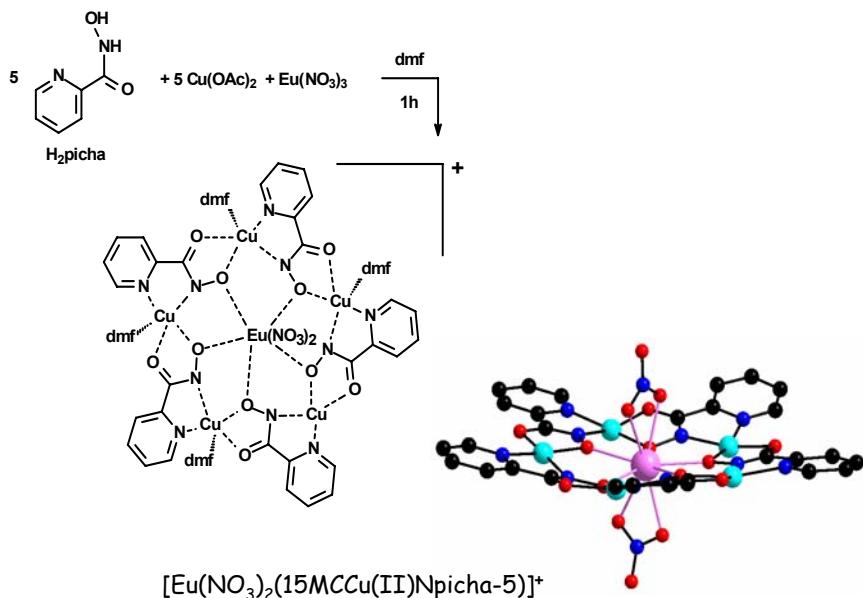
shi<sup>3-</sup>



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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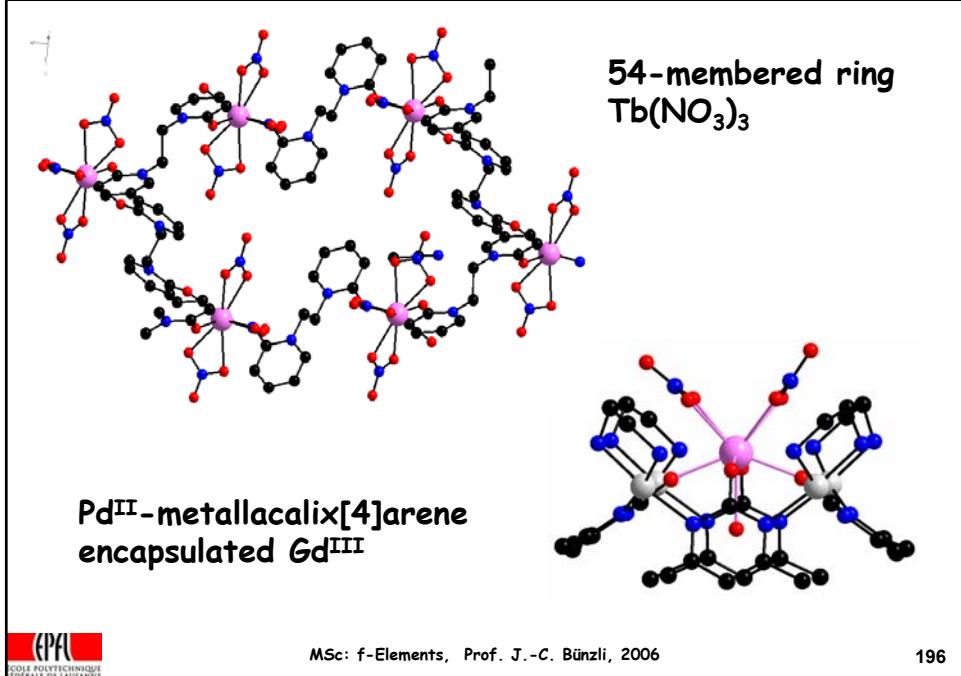
**Chapter 3 Coordination chemistry**



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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**Chapter 3 Coordination chemistry**



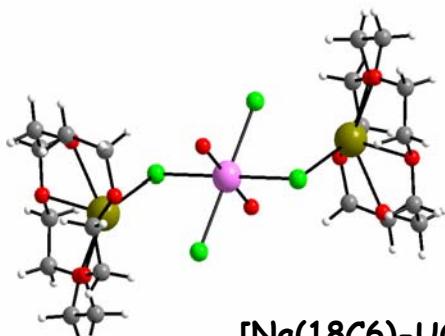
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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### 3.4.3 Some 5f complexes

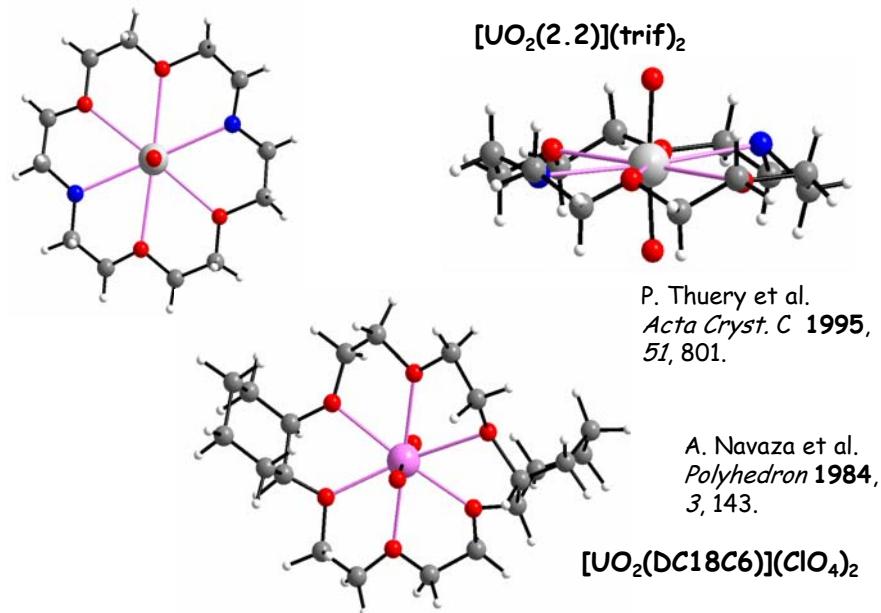
#### a) Crown ethers

Most of the complexes show the receptor being not coordinated if coordinating anions are used.



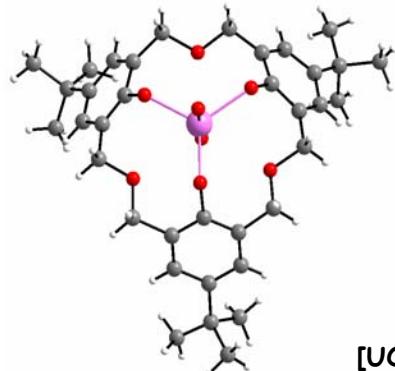
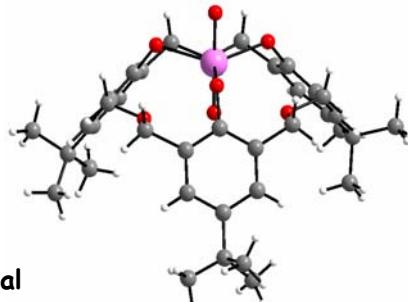
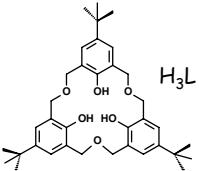
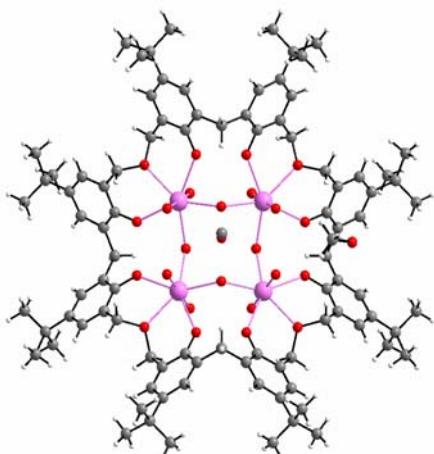
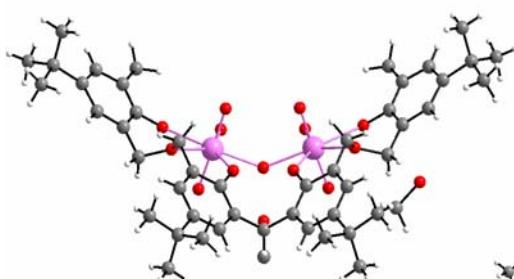
Here  $\text{Na}^+$  binds  $18\text{C}6$  better than  $\text{UO}_2^{2+}$

J.A. Danis et al., *Inorg. Chem.* 2001, 40, 3389

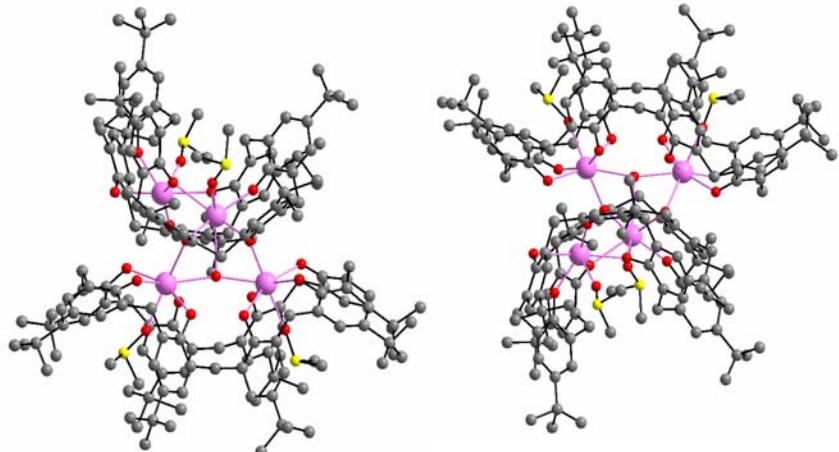


**b) Calixarenes**

Uranium forms very often polymetallic species, except with very small calixarenes.

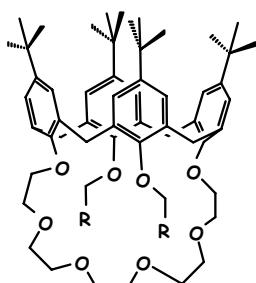
[ $\text{UO}_2\text{L}$ ]  
pseudo trigonal**Homocalix[8]arene,  $\text{HL}_8$**  **$D_{2d}$  symmetry**[( $\text{UO}_2$ )<sub>4</sub>O<sub>4</sub>( $\text{H}_8\text{L}$ )](solv)

P. Thuéry et al., *Polyhedron*  
2003, 22, 3499

*p*-*tert*-butylcalix[8]arene

J. M. Harrowfield et al.,  
*J.C.S. Dalton Trans.* **1991**, 2025

## c) Calix-crowns for selective extraction



% extraction ( $\text{H}_2\text{O}$  to  $\text{CHCl}_3$   
at pH 8.9, 298 K)

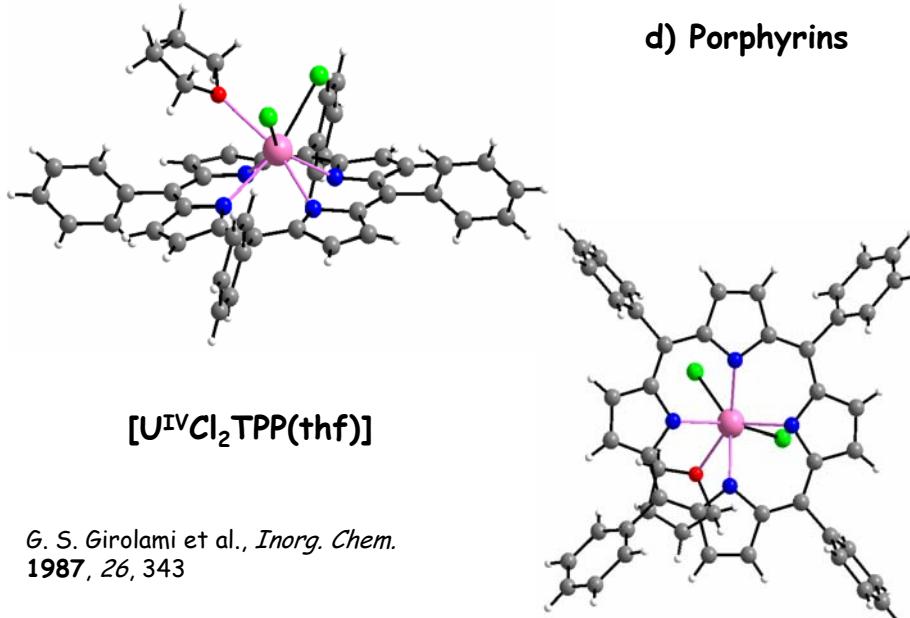
	Mg	Ca	Sr	Ba	Ra
	<0.1	16	73	99	>99.9

$\text{R} = \text{CO}_2\text{H}$

High selectivity for  $\text{Ra}^{2+}$  over the lighter alkaline-earth metal ions.  
High kinetic stability of the  $\text{Ra}^{2+}$  complex.

X. Chen et al., *Inorg. Chem.*  
1999, 38, 5449

d) Porphyrins

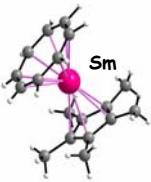


G. S. Girolami et al., *Inorg. Chem.*  
1987, 26, 343

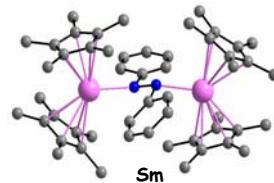
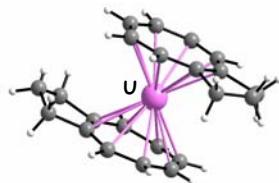
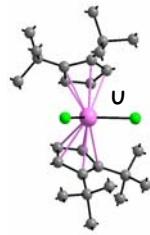
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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## Chapter 4 Organometallics



- 4.1 The first compounds
- 4.2 Alkyl derivatives
- 4.3 Cyclopentadienyl derivatives
- 4.4 Carbonyl and related complexes
- 4.5 Arene complexes
- 4.6 Cyclooctatetraene derivatives
- 4.7 Divalent lanthanide chemistry



## Chapter 4 Organometallics

### 4.1 The first compounds



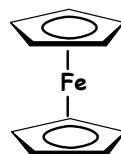
cyclopentadienyl  $Cp^-$



cyclooctatetraenyl  $Cot^{2-}$

pentamethylcyclopentadienyl  $Cp^*$

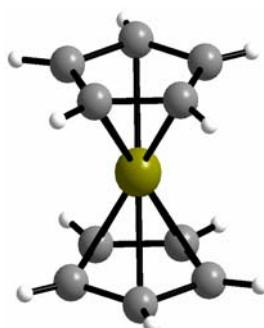
Ferrocene:



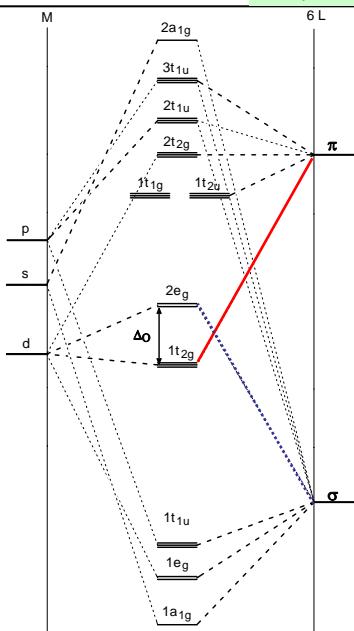
$[Fe(\eta^5-C_5H_5)_2]$

1952

$\eta^5$  points to the binding of the 5 carbon atoms



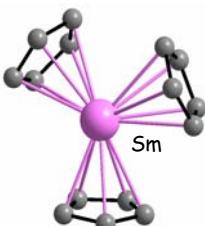
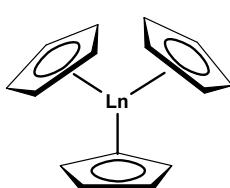
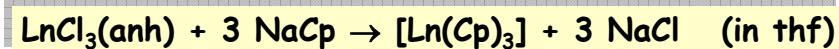
## Chapter 4 Organometallics



**d-Transition metals:**  
18-electron rule  
points to stable  
compounds.

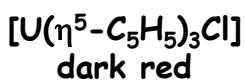
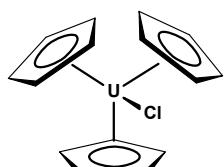
What about f-elements?  
Much energy is needed  
to "transform" f-elements  
into d-elements: cf.  
the energies of the  
[Xe]4f<sup>N-1</sup>5d<sup>1</sup>6s<sup>2</sup> configura-  
tion (Ch. 1) versus  
[Xe]4f<sup>N</sup>6s<sup>2</sup>.

## Chapter 4 Organometallics

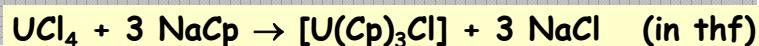


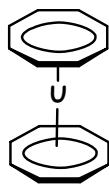
J.M. Birmingham, G. Wilkinson,  
J. Am. Chem. Soc. **1954**,  
76, 6210

Ce, Sm: orange  
Pr: pale green  
Nd: pale blue

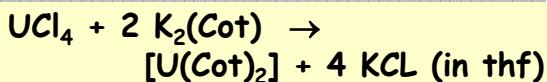


L. T. Reynolds, G. Wilkinson,  
J. Inorg. Nucl. Chem. **1956**,  
2, 246





1968



A. Streitwieser Jr. et al.  
*J. Am. Chem. Soc.* 1968, 90, 7368

D and f organometallic compounds are particularly sensitive to oxygen and water and this problem is more important for f-elements in view of their larger ionic radii and their lower propensity to form covalent bonds.

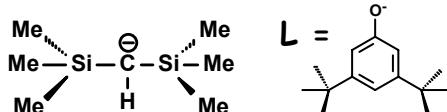
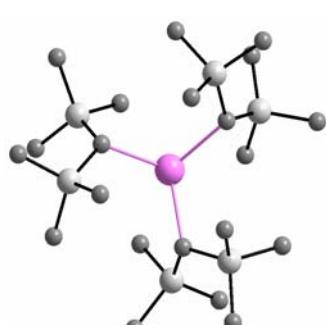
For f-elements, relativistic effects (see Ch. 1) increase the complexity of theoretical models aiming at explaining the chemical bonds in organometallic compounds.



## 4.2 Alkyl derivatives ( $\sigma$ -bonds)

Most difficult to synthesize. Bulky ligands should be used.  
Two main paths:

a) With the help of bis(trimethylsilyl)methyl ligand



$C_3$ -symmetry  
U-C: 2.48 Å  
C-U-C: 107.7°



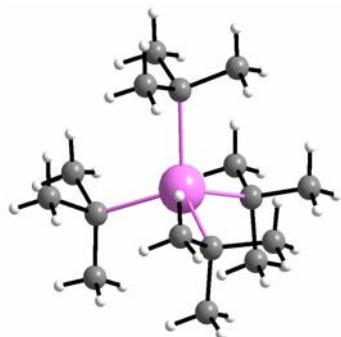
Chapter 4 Organometallics

b) Smaller alkyl groups may also be used, often leading to negatively charged species

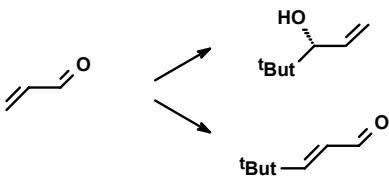


H. Schumann et al., *J. Organomet. Chem.* 1986, 306, 215

$C_S$  symmetry  
 Lu-C 2.32-2.43 Å  
 C-Lu-C 107-109 °



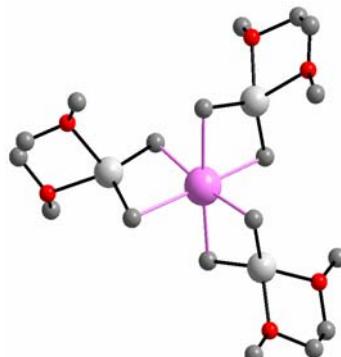
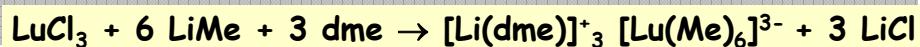
Allows alkylation reactions:



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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The compounds are extremely air- and water-sensitive.  
 They were obtained with several Ln.  
 The structure of  $[\text{Er(Me)}_6]^{3-}$  is also known, with  $[\text{Li}(\text{Me}_2\text{N(CH}_2)_2\text{NMe}_2]^+$  as counterion

Lu-C 2.48-2.57 Å  
 C-Lu-C 86-96 °  
 C-Lu-C eq 176 °

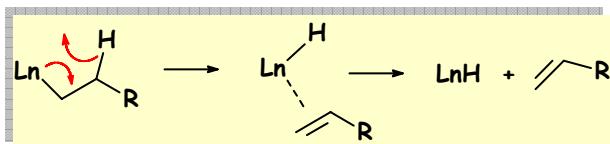
H. Schumann et al., *J. Organomet. Chem.* 1984, 263, 29.



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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## Decomposition of alkyl complexes via $\beta$ -elimination



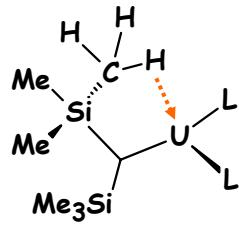
f-elements do not form strong  $\pi$  bonds with alkene, so that the decomposition proceeds easily

Conditions for  $\beta$ -elimination:

- the  $\beta$ -carbon must bear a H atom
- the Ln-C-C-H fragment must be able to take a planar conformation
- the metal ion must have an appropriate empty orbital for binding the H-atom

f-Elements have a large number of empty orbitals, so that they are extremely susceptible to  $\beta$ -elimination. The strategy for producing alkyl derivatives with low coordination numbers therefore involves bulky ligands for which  $\beta$ -elimination is not possible, such as  $\text{CH}(\text{SiMe}_3)_2$ .

### Agostic interaction



U-H-C bridges are formed with H-atoms in  $\gamma$  position with respect to U: this is called a  $\gamma$ -agostic interaction.

Therefore, the coordination number is larger than 3 in this compound and this is often the case for low-CN organometallic compounds

### 4.3 Cyclopentadienyl derivatives ( $\pi$ -bonds)

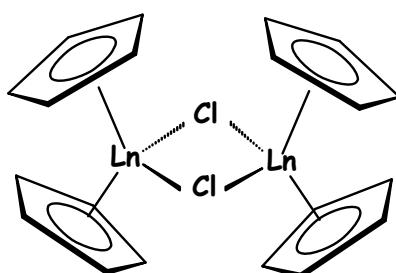
Cp and its derivatives are among the most popular ligands in organometallic chemistry of d- and f-transition metals.

Cp forms both covalent and ionic complexes with 1-5 C-atoms coordinated. The  $\eta^5$ -mode is usually considered to occupy 3 coordination sites (this is somewhat arbitrary).

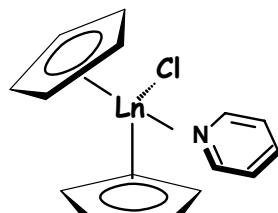
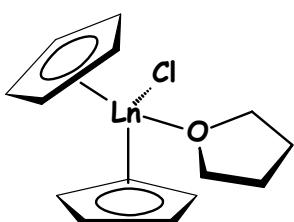
#### Simple $\text{LnCp}_3$ cyclopentadienyls

- $\text{LnCp}_3$  features polar Ln-Cp bonds as shown by:  

$$2 \text{LnCp}_3 + 3 \text{FeCl}_2 \rightarrow 3 \text{FeCp}_2 + 2 \text{LnCl}_3$$
- Rapid exchange of Cp ligands occur
- $\text{LnClCp}_2$  compounds can be isolated as dimers or as Lewis acid adducts

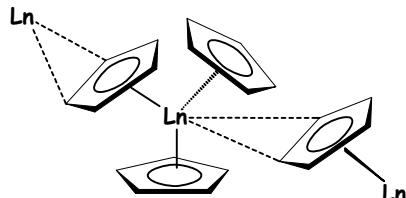
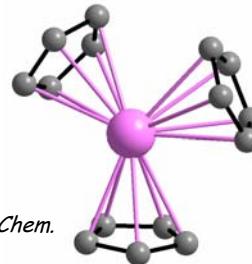


Most dimers feature  $\text{Cl}^-$  as bridging ligands



**Structural changes along the series****La-Pr**

"11-coordinate"  $[\text{Ln}(\eta^5\text{Cp})_3(\eta^2\text{Cp})]$   
(under the form of a coordination polymer)

**Y, Sm-Yb "9-coordinate"  $[\text{LnCp}_3]$** **Sm-C 2.75 Å**

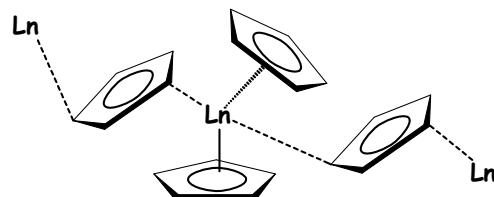
G.Laubereau & J.H. Burns *Inorg.Chem.*  
1970, 9, 1091,

MSc: f-Elements, Prof. J.-C. Bünzli, 2006

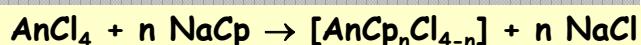
217

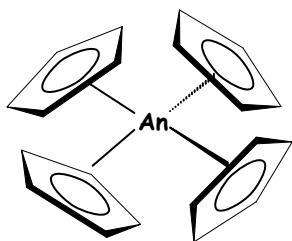
**Sc, Lu**

"8-coordinate"  $[\text{Lu}(\eta^5\text{-Cp})_2(\eta^1\text{-Cp})_2]$   
(coordination polymer)

**Simple  $\text{AnCp}_n$  cyclopentadienyls**

$\text{AnCp}_3$  compounds behave similarly to  $\text{LnCp}_3$ . Most of the Cp chemistry of Th, U, Pa and Np elements however involves +4 oxidation state:

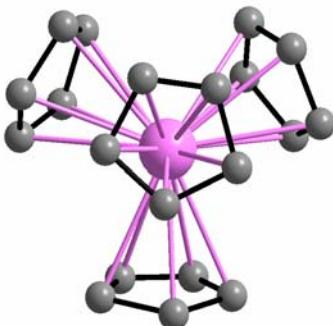




$[An(Cp)_4]$  are the only complexes with four  $\eta^5$ -Cp coordinated in a **tetrahedral** fashion.  
As a comparison, the  $Zr^{IV}$  analogue is  $[Zr(\eta^5\text{-Cp})_3(\eta^1\text{-Cp})]$

Th-C	2.87 Å
Th-Cp	2.61 Å
U-Cp	2.59 Å

R. Maier et al., *J. Alloys & Compounds*  
1993, 190, 269.

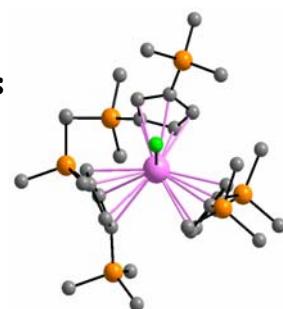


indicating a more covalent U-Cp bond than in the analogue Ln compounds. On the other hand, the Cl ligand in  $[AnCp_3Cl]$  can easily be substituted, making these complexes important synthons in An organometallic chemistry.

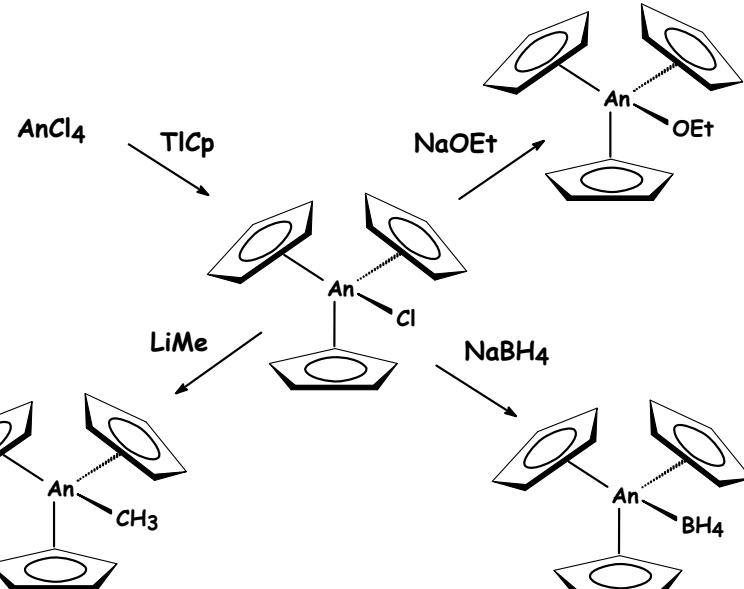
Substituted Cp's are also used, as in this  $Th^{IV}$  derivative:



R. C. Blake et al., *J. Organomet. Chem.* 1998, 551, 261.



Chapter 4 Organometallics

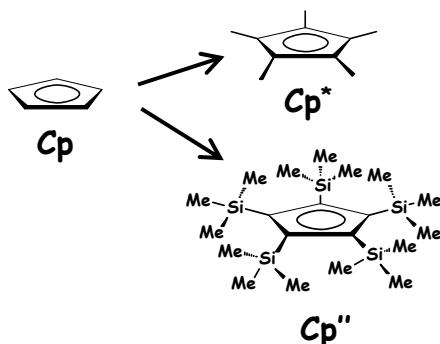


MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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Chapter 4 Organometallics

**Substituted cyclopentadienyls**



The substitution gives more stable, more soluble compounds which are easier to crystallize.

However,  $\text{Ln}(\text{Cp}^*)_3$  and  $\text{An}(\text{Cp}^*)_3$  are not very stable, because the ligand is too bulky.

On the other hand,  $[\text{Ln}(\text{Cp}^*)_2\text{Cl}]$ ,  $[\text{An}(\text{Cp}^*)_2\text{Cl}]$  and  $[\text{An}(\text{Cp}^*)_2\text{Cl}_2]$  are versatile and have an extensive chemistry.



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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Chapter 4 Organometallics

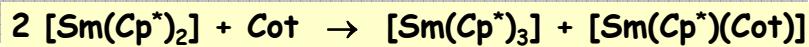


Sm-C  $2.82 \text{ \AA}$

Cp\*-Sm-Cp\*  $120^\circ$

Trigonal co-ordination

W. J. Evans et al., *J. Am. Chem. Soc.*  
1991, 113, 7423



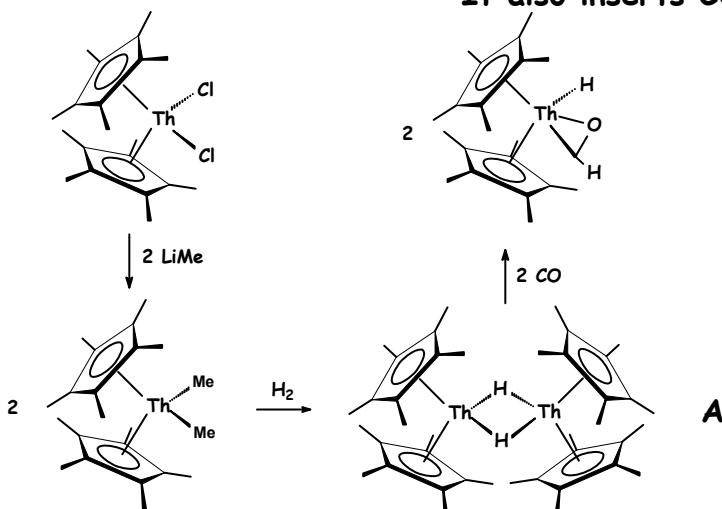
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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Chapter 4 Organometallics

An active Th catalyst (A) for ethene polymerization:

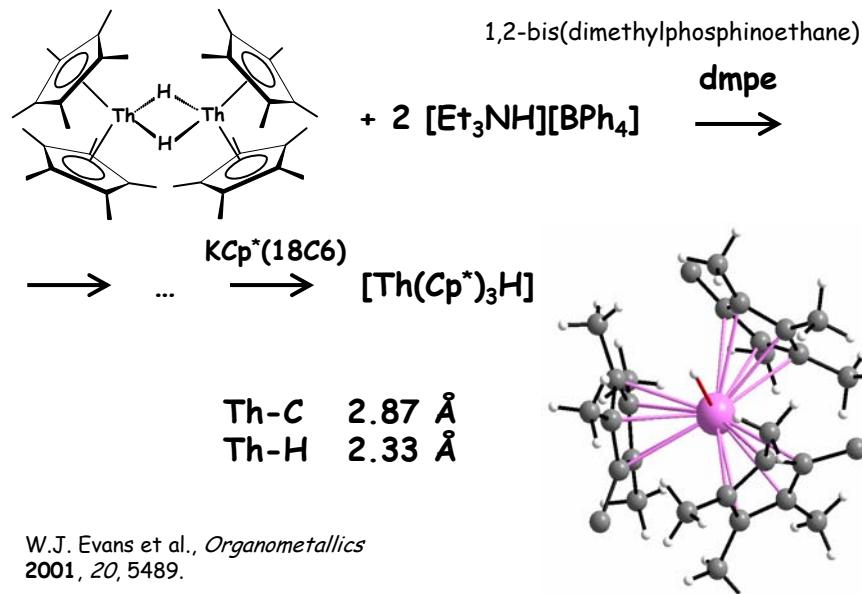
It also inserts CO:



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

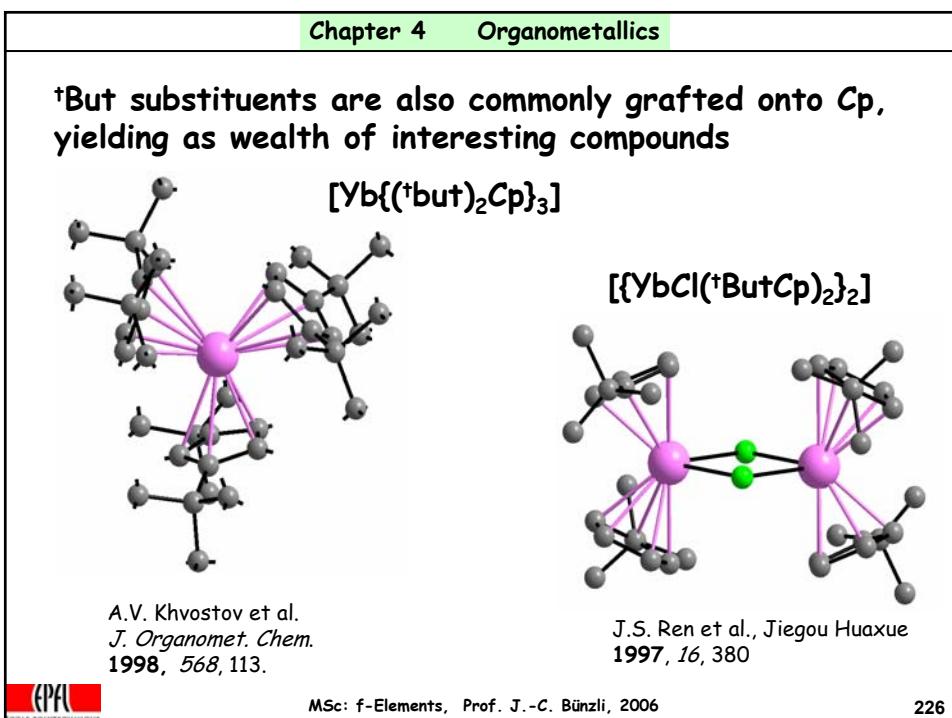
224

Chapter 4 Organometallics



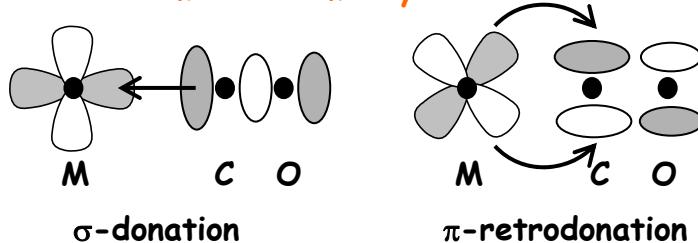
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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#### 4.4 Carbonyl and related complexes

d-Transition metal chemistry:

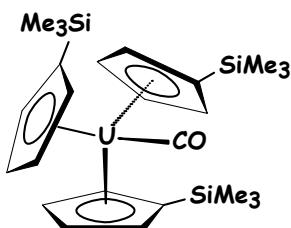


4f-Transition elements: the filled metal orbitals are not outside orbitals so that  $\pi$ -overlap is not effective.

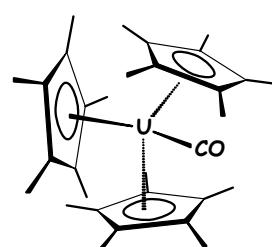
$\text{Ln}(g) + n \text{ CO (g)} \rightarrow \text{Ln}(\text{CO})_n(g)$ ,  $n = 1-6$ , in Ar at  $< 40 \text{ K}$   
Identified by IR spectra. Decompose upon increasing  $T$ .

#### 5f-Transition elements

More covalent so that  $\text{AnCp}_3\text{CO}$  complexes are known



$$\nu(\text{CO}) = 1976 \text{ cm}^{-1}$$



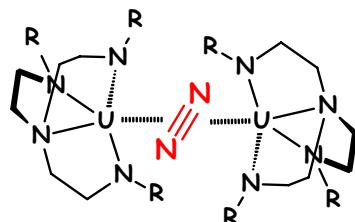
$$\nu(\text{CO}) = 1900 \text{ cm}^{-1}$$

Since  $\nu(\text{CO}) = 2146 \text{ cm}^{-1}$  for free CO, these values point to a significant amount of  $\pi$  back bonding.

**Dinitrogen, isocyanide, alkene, and alkyne compounds**

**Dinitrogen** is isoelectronic with  $\text{CO}$ , but less efficient for  $\pi$ -bond formation.

In the case of f-elements, it forms complexes only with the low oxidation states, e.g.  $\text{Sm}^{\text{II}}$ ,  $\text{Yb}^{\text{II}}$ ,  $\text{U}^{\text{III}}$ .

**Isocyanides  $\text{CN-R}$ :**

$[\text{LnCp}_3(\text{CN-Et})]$  have  $\nu(\text{CN})$  values higher than in free  $\text{CN-R}$  pointing to negligible  $\pi$  back-bonding

**Alkene and alkyne complexes** are also very difficult to make and only occur with low oxidation states

**4.5 Arene complexes**

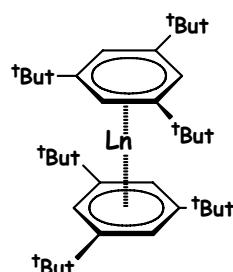
$\eta^6$ -arene ligands (such as benzene) are  $\pi$ -acceptors and  $\delta$ -donors.

Note  $\sigma$ ,  $\pi$ ,  $\delta$ , and  $\phi$  refer to the symmetry of the bonding interaction with respect to the metal-ligand axis: they correspond to 0, 1, 2, and 3 nodal planes.

Arene ligands usually form complexes when the metal is in a low oxidation state.



0-valent compounds sublime in vacuo at 100 °C

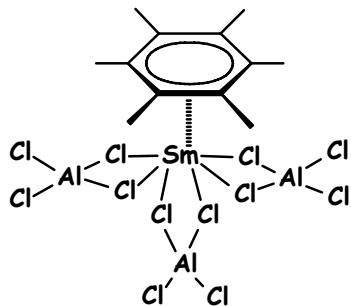


$\text{Ln} = \text{Pr, Nd, Gd, Tb, Dy, Ho, Er, Sc, Y}$

The 0-valent compounds form only for Ln for which the promotion energy  $[Xe]4f^N6s^2 \rightarrow [Xe]4f^{N-1}5d^16s^2$  is relatively small (cf. Ch. 1).

Therefore, involvement of the 5d electron is holding the bis(arene)  $\text{Ln}^0$  compounds together.

A  $\text{Sm}^{\text{III}}$  compound is also known:



#### 4.6 Cyclooctatetraene complexes

$\text{Cot}^{2-}$  is ideally suited for f-element organometallic chemistry because it has a high valency and is sterically bulky (as much as  $\text{Cp}^*$ ).

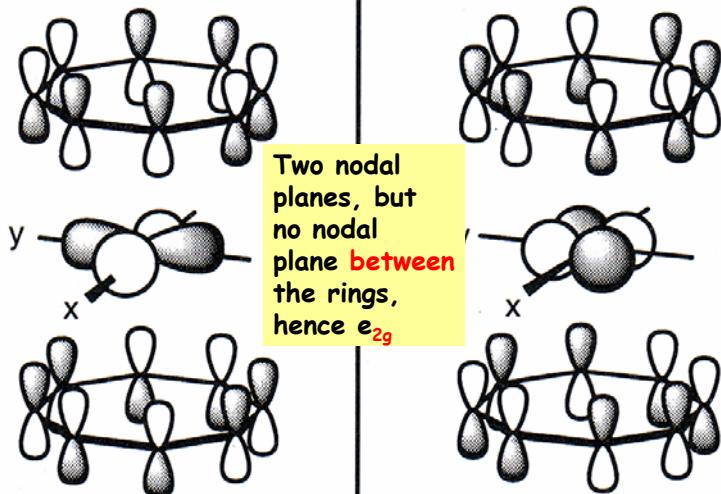
##### Uranocene, $D_{8h}$ symmetry

The two rings are eclipsed in conformation, therefore the  $D_{8h}$  symmetry

The major source of binding is the interaction between the ring  $e_{2g}$  orbitals and the U(6d) orbitals ( $\delta$ -bonds).

The second source of binding is between the ring  $e_{2u}$  orbitals and the U(5f) orbitals ( $\phi$ -bonds). These are only available with f-elements.

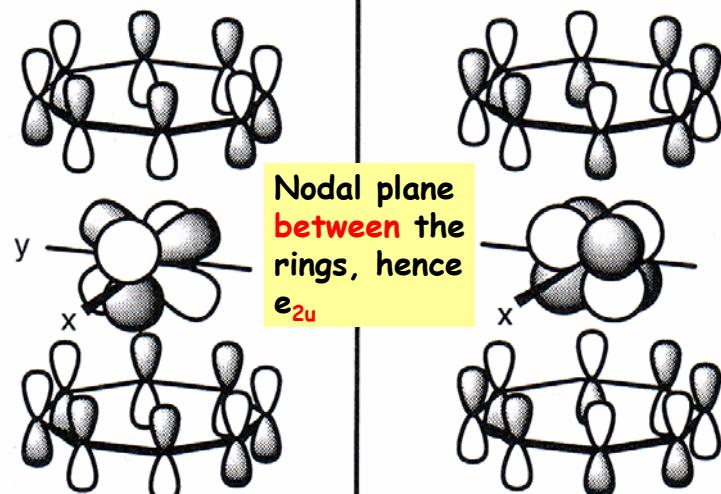
$\delta$ -bonds



(a)  $e_{2g}/d_{x^2-y^2}$

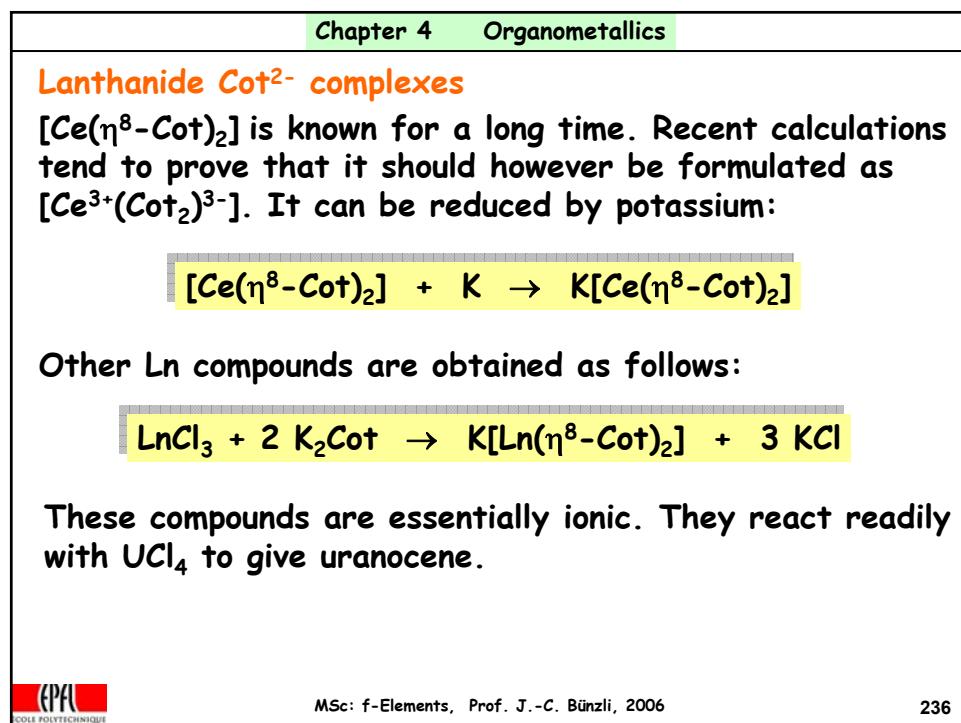
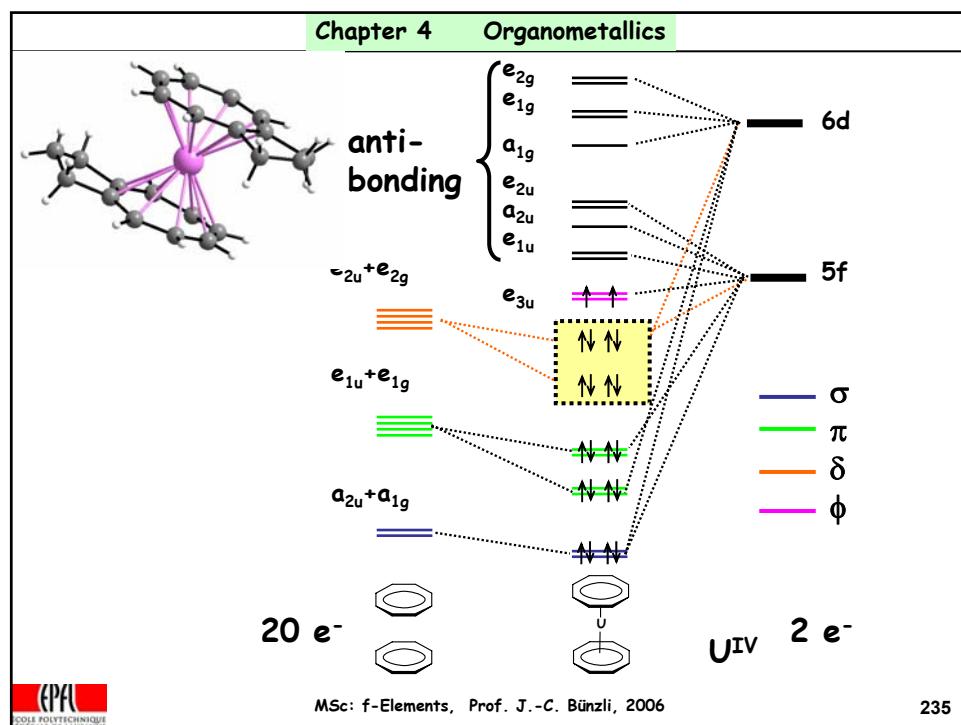
(b)  $e_{2g}/d_{xy}$

$\delta$ -bonds

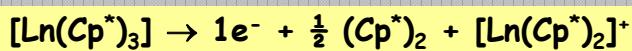


(c)  $e_{2u}/f_{z(x^2-y^2)}$

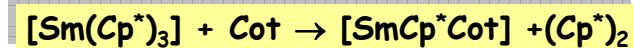
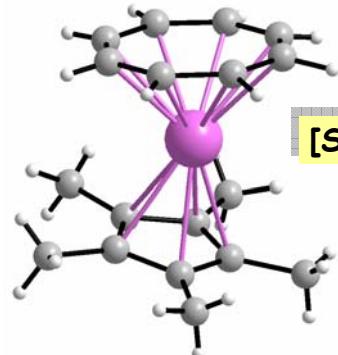
(d)  $e_{2u}/f_{xyz}$



In sterically crowded complexes such as  $[\text{Ln}(\text{Cp}^*)_3]$ ,  $(\text{Cp}^*)$ -functions as one-electron reductive species.



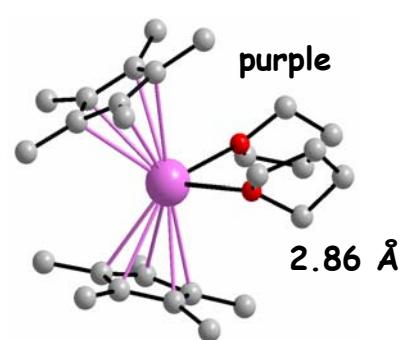
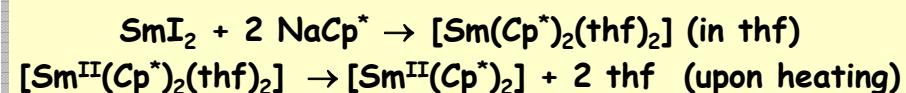
Example: synthesis of the mixed species  $[\text{Sm}(\text{Cp}^*)(\text{Cot})]$



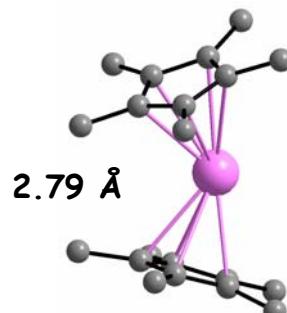
W. J. Evans et al., *Dalton Trans.* 2000, 1609

#### 4.7 Divalent lanthanide chemistry

Initial studies involved  $\text{Sm}^{\text{II}}$ ,  $\text{Eu}^{\text{II}}$ ,  $\text{Yb}^{\text{II}}$

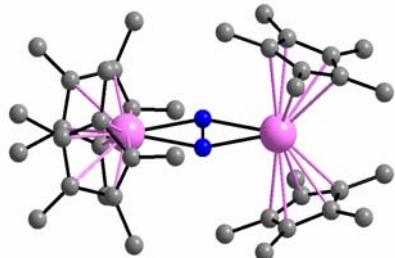
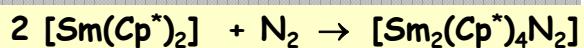


Sm-C:



W. J. Evans et al., *J. Am. Chem. Soc.*, 1981, 103, 6507 and 1984, 106, 4270

These species are highly reactive and generate interesting redox chemistry. For instance, they can add dinitrogen upon crystallization:

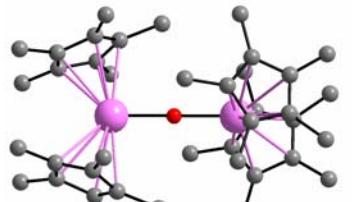
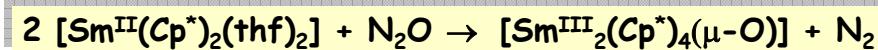


First  $\text{N}_2^{2-}$  complex of a  
Ln ion

Sm-C      2.73 Å  
Sm-N      2.36 Å  
N-N      1.09 Å  
similar to  $\text{N}_2$  ?

W. J. Evans et al., *J. Am. Chem. Soc.*  
1988, 110, 6877

An  $\text{O}^{2-}$  bridging ligand:  $[\text{Sm}^{\text{III}}(\text{Cp}^*)_2-\text{O}-\text{Sm}^{\text{III}}(\text{Cp}^*)_2]$



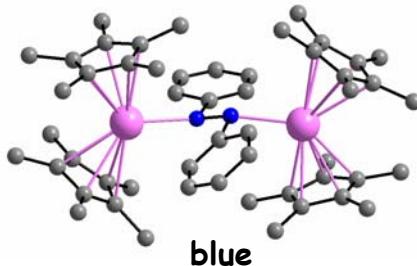
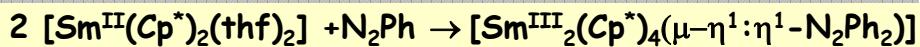
Sm-O  
Sm-C

2.09 Å  
2.74 Å



In fact, many O-containing substrates produce this compound (NO, thf, a.s.o)

W. J. Evans et al., *J. Am. Chem. Soc.* 1985, 107, 405

Insertion of trans-azobenzene:  $[Sm^{II}_2(Cp^*)_4N_2Ph_2]$ 

Magnetic data indicate the presence of  $Sm^{III}$  (1.9 M.B.)

$Sm\text{-H}$  distances (ortho position) are close to agostic interaction

$Sm\text{-C}$  2.74 Å

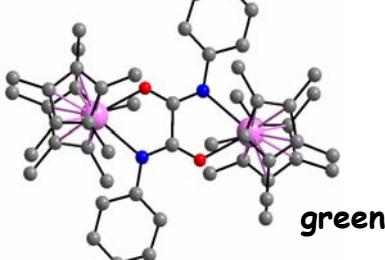
$Sm\text{-N}$  2.40 Å

**N-N** 1.25 Å, identical to neutral  $N_2Ph_2$   
expected distance: 1.44 Å

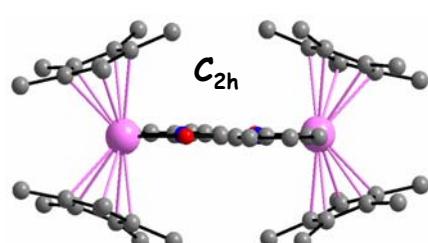
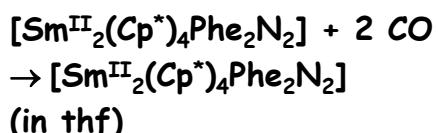
W. J. Evans et al., *J. Am. Chem. Soc.* 1988, 110, 4983

MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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Insertion of CO:

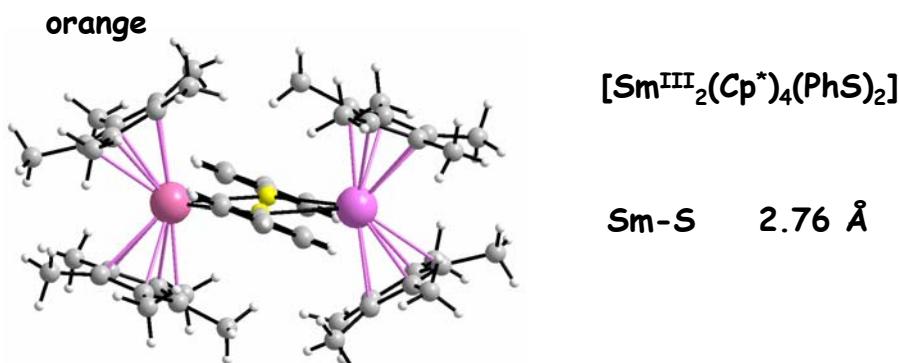
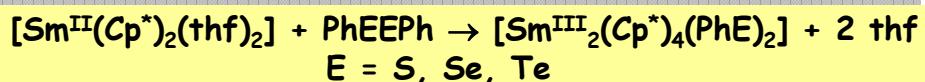


W. J. Evans et al., *J. Am. Chem. Soc.* 1988, 110, 4983

MSc: f-Elements, Prof. J.-C. Bünzli, 2006

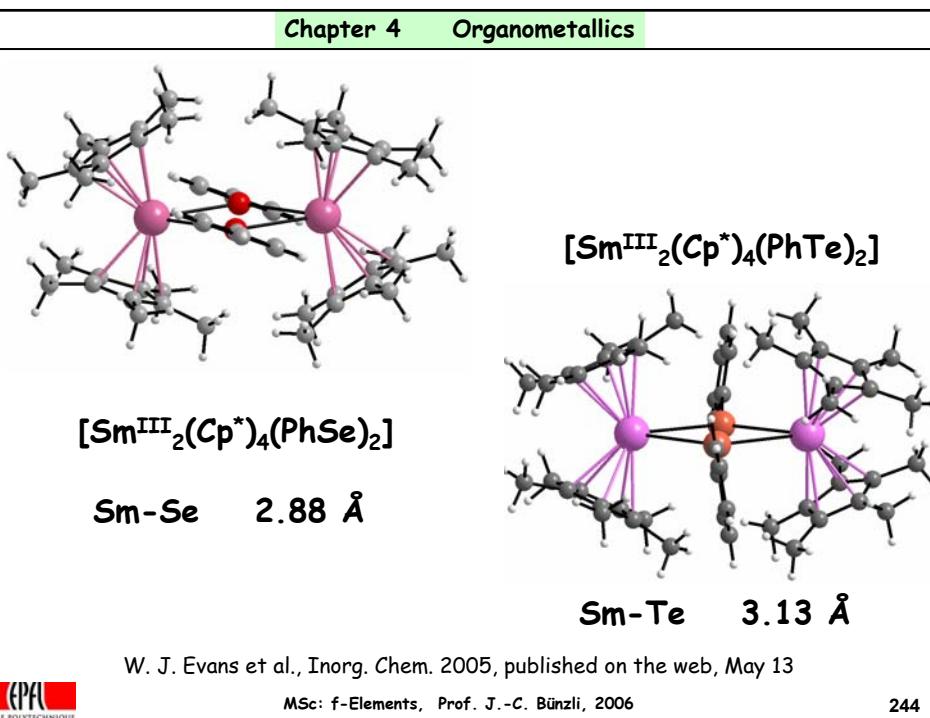
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## Chalcogenolate complexes:

W.J. Evans et al., *Inorg. Chem.* 2005, Published on the web, May 13

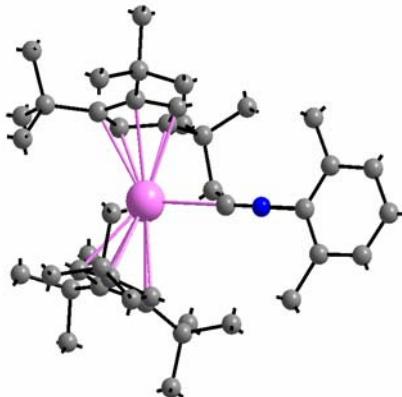
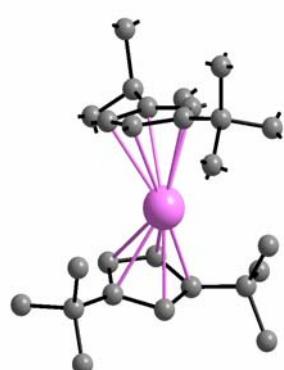
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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W. J. Evans et al., *Inorg. Chem.* 2005, published on the web, May 13

MSc: f-Elements, Prof. J.-C. Bünzli, 2006

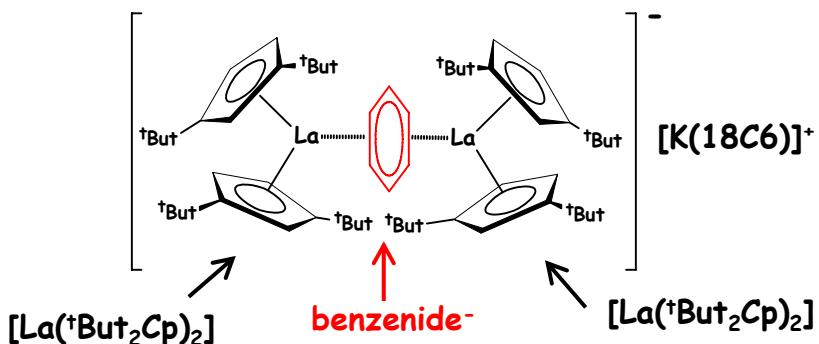
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Examples of  $\text{Yb}^{\text{II}}$  chemistry

## Perspectives

A divalent  $\text{Tm}^{\text{II}}$  precursor,  $[\text{Tm}^{\text{II}}\text{I}_2(\text{dme})_2]$ , is available.

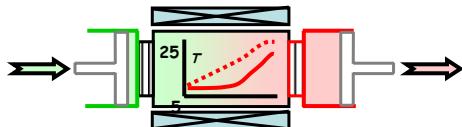
Evidence for divalent complexes of  $\text{La}^{\text{II}}$ ,  $\text{Ce}^{\text{II}}$ ,  $\text{Pr}^{\text{II}}$ ,  $\text{Nd}^{\text{II}}$  is also at hand.



M.F. Lappert et al., *J. Am. Chem. Soc.* 1998, 120, 12958

## Chapter 5 Selected applications of 4f-elements

- 5.1 Magnetocaloric effect and refrigeration
- 5.2 Catalysts for DNA and RNA cutting
- 5.3 Lighting applications
- 5.4 Luminescent chemical sensors
- 5.5 Luminescent biochemical sensors
- 5.6 Tracing biomolecular interactions
- 5.7 Another application of luminescence
- 5.8 Magnetic resonance medical imaging



### 5.1 Magnetocaloric effect (MCE) and refrigeration

#### Definition

Magnetothermodynamic or magnetocaloric effect, or adiabatic temperature change = heating or cooling of a magnetic materials due to varying magnetic field.

Discovered for iron by Marburg in 1881.

The MCE is intrinsic to all magnetic materials and is due to the coupling of the magnetic sublattice with the magnetic field, which changes the magnetic part of the entropy.

Analogy with gases:

- Isothermal magnetizing of a paramagnet reduces the entropy, just as adiabatic compression of a gas does.
- The process is reversible and de-magnetizing restore the initial entropy, similarly to expansion for a gas.

Thermodynamics of the MCE near the Curie temperature (magnetic ordering temperature):

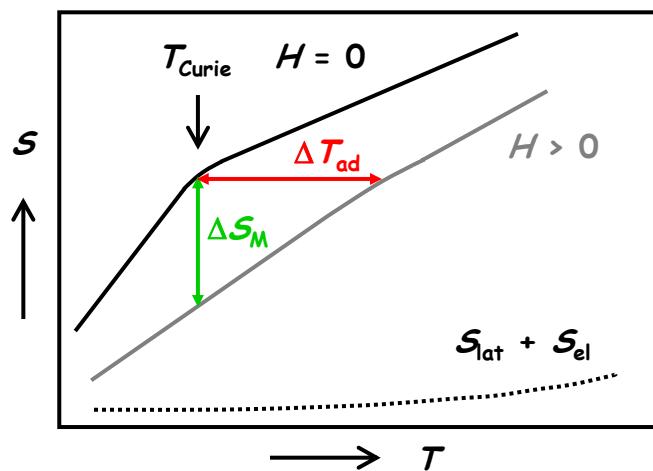
$$S(T, H) = S_M(T, H) + S_{\text{lat}}(T) + S_{\text{el}}(T)$$

magnetic      lattice      electronic

↓

large variation with  $T$

small, and small variation with  $T$



$\Delta S_M$  = isothermal magnetic entropy change =  $f(T_0)$   
 $\Delta T_{ad}$  = isentropic temperature change =  $f(T_0)$

Maximum at  $T_{\text{Curie}}$

**Paramagnetic and ferromagnetic materials:**

increasing  $H$  increases the magnetic order  
and decreases  $S$  and

$$\Delta T_{ad}(T, \Delta H) > 0 \quad (\text{the magnetic solid heats up})$$

$$\Delta S_M(T, \Delta H) < 0$$

decreasing  $H$  decreases the magnetic order  
and increases  $S$  and

$$\Delta T_{ad}(T, \Delta H) < 0 \quad (\text{the magnetic solid cools down})$$

$$\Delta S_M(T, \Delta H) > 0$$

**Basic equations (Maxwell)** $M$  = magnetization $C$  = heat capacity at constant pressure $H$  = magnetic field

$$\left( \frac{\partial S(T, H)}{\partial H} \right)_T = \left( \frac{\partial M(T, H)}{\partial T} \right)_H$$

**For an isothermal and isobaric process:**

$$\Delta S_M(T, \Delta H) = \int_{H_1}^{H_2} \left( \frac{\partial M(T, H)}{\partial T} \right)_H dH$$

That is, the magnetic entropy change is proportional to the derivative of magnetization with respect to  $T$ , at constant field. The infinitesimal adiabatic  $T$  rise for a reversible adiabatic-isobaric process is:

$$dT = - \left( \frac{T}{C(T, H)} \right)_H \cdot \left( \frac{\partial M(T, H)}{\partial T} \right)_H dH$$



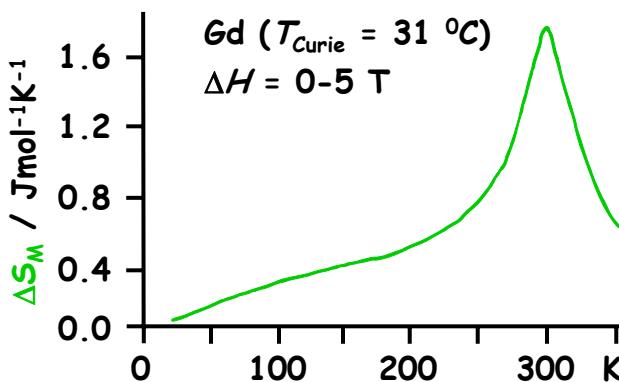
Integrating the latter equation yields:

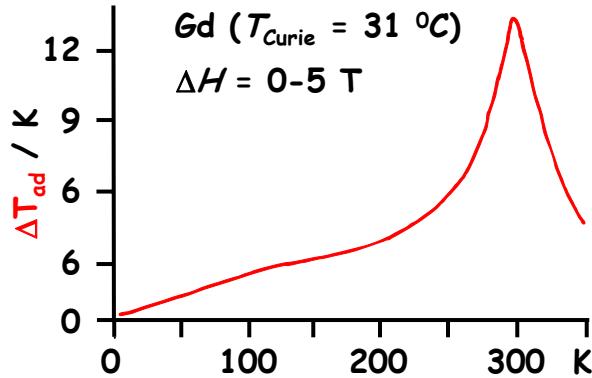
$$\Delta T_{ad}(T, \Delta H) = - \int_H^{H_2} \left( \frac{T}{C(T, H)} \right)_H \cdot \left( \frac{\partial M(T, H)}{\partial T} \right)_H \cdot dH$$

- Paramagnets and ferromagnets heat up when  $H$  increases.
- The largest effect occurs for  $T_{\text{Curie}}$ .
- For a given  $\Delta S_M$ ,  $\Delta T_{ad}$  is larger at higher  $T$ , but also when **C is small**. Therefore, paramagnets only display sizeable MCE effect at  $T$  close to 0 K.
- Potential applications:
  - liquefaction of helium and hydrogen
  - reaching ultra low temperatures
  - air conditioning and refrigeration

Magnetic ordering upon lowering  $T$  is a cooperative phenomenon generating large changes in bulk magnetization, over a small  $T$  range around  $T_{\text{Curie}}$  (or  $T_{\text{Néel}}$ ).

4f metals, alloys and compounds have a larger magnetic entropy than 3d elements and are ideally suited for these applications.





- Field dependence is 3 K / T in low magnetic fields and 2 K / T in higher magnetic fields
- All other compounds with  $T_{Curie} > 290 \text{ K}$  have lower MCE effect

### Giant magnetocaloric effect (gMCE)

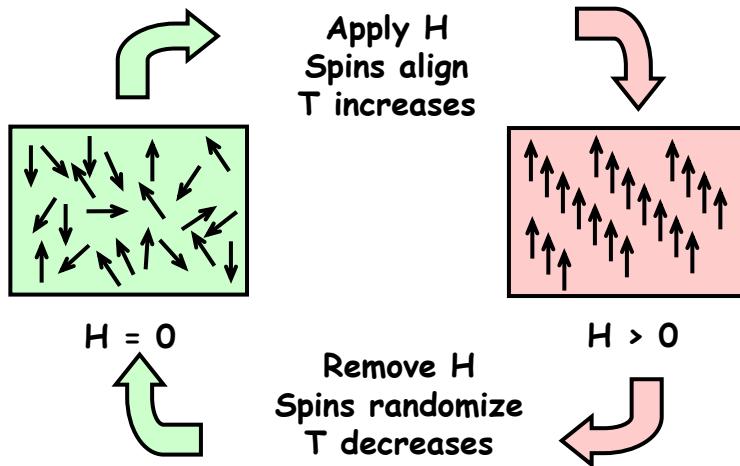
Looking for first-order transitions: they theoretically occur at constant T and therefore  $(\partial M / \partial T)_H$  can reach large values (in theory, infinity)

$\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4 \quad (0 < x < 0.5)$  Pecharsky & Gschneidner, 1997

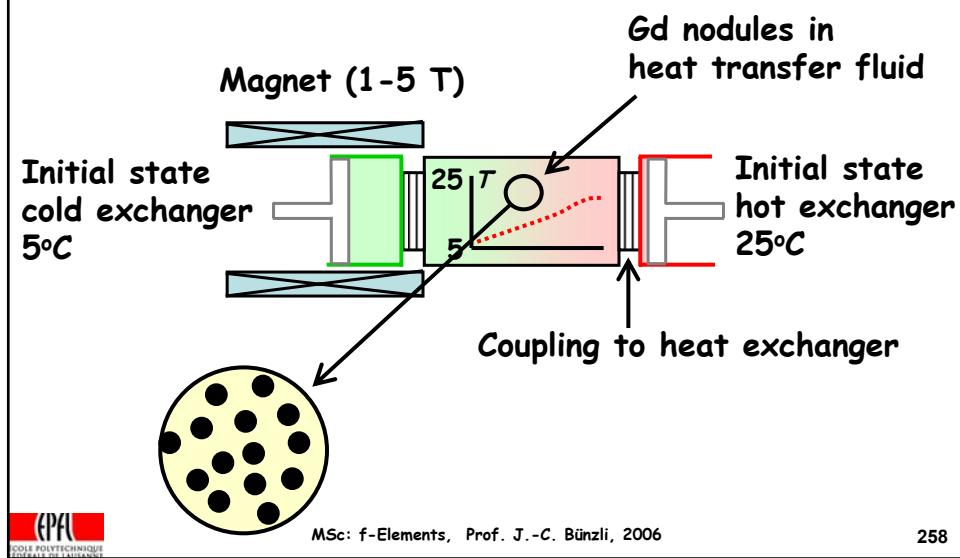
- $\Delta S_M$  twice as large as Gd
- Curie temperature can be tuned from 20 to 305 K by varying  $x$  and by introducing small amounts of Ga
- the effect is reversible

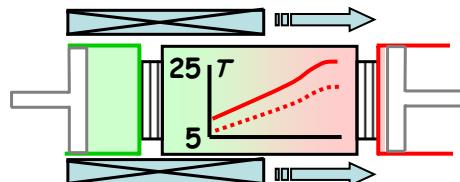
Main application: continuous magnetic refrigeration

## Principle of the magnetic refrigerator



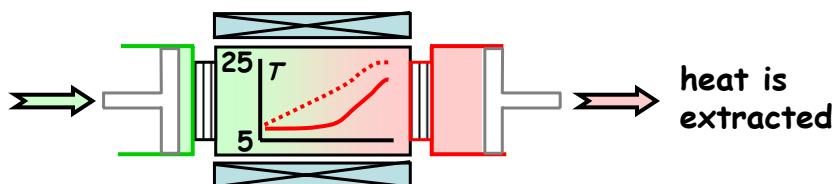
## Principle of the magnetic refrigerator





**Step 1:**  
The magnetic field is switched on, heating the bed

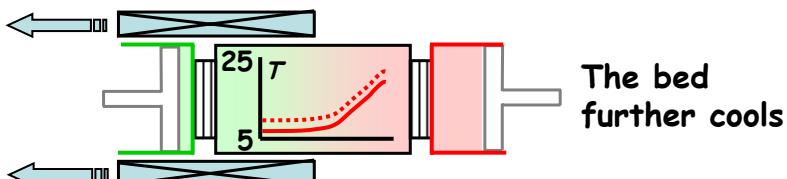
**Step 2: The flow of the cooling fluid is then switched on**



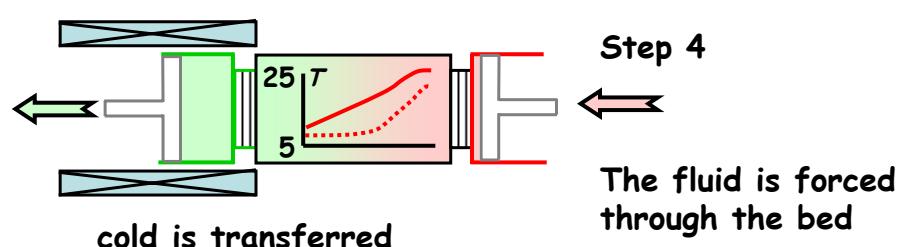
The Gd bed is cooled by the cooling fluid

**Step 3**

The flow of cooling fluid is stopped and the magnetic field switched off



The bed further cools

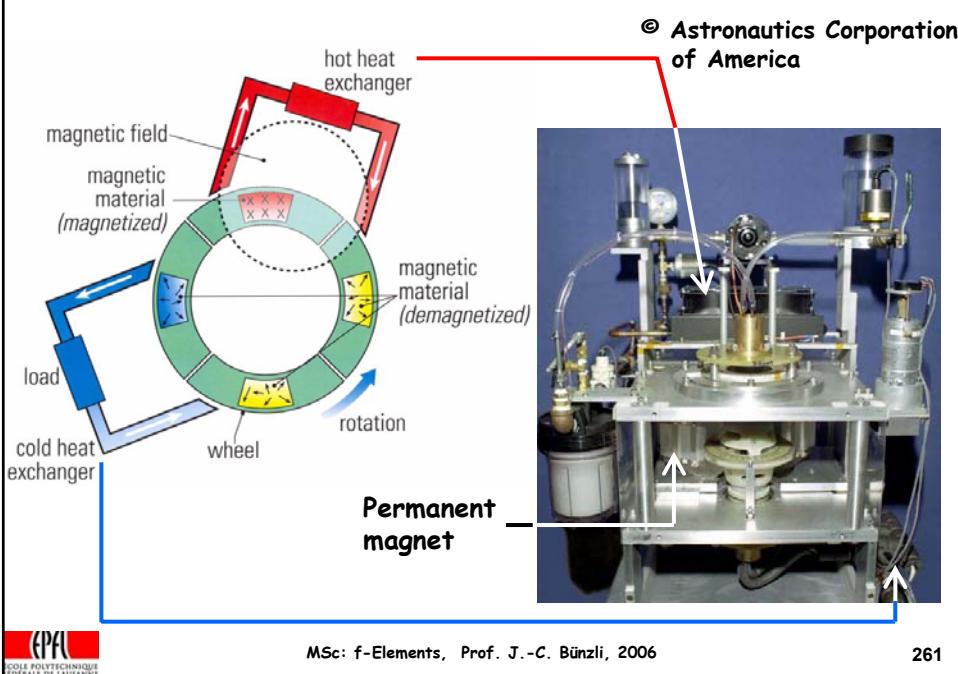


cold is transferred

**Step 4**

The fluid is forced through the bed

**Chapter 5 Selected applications**

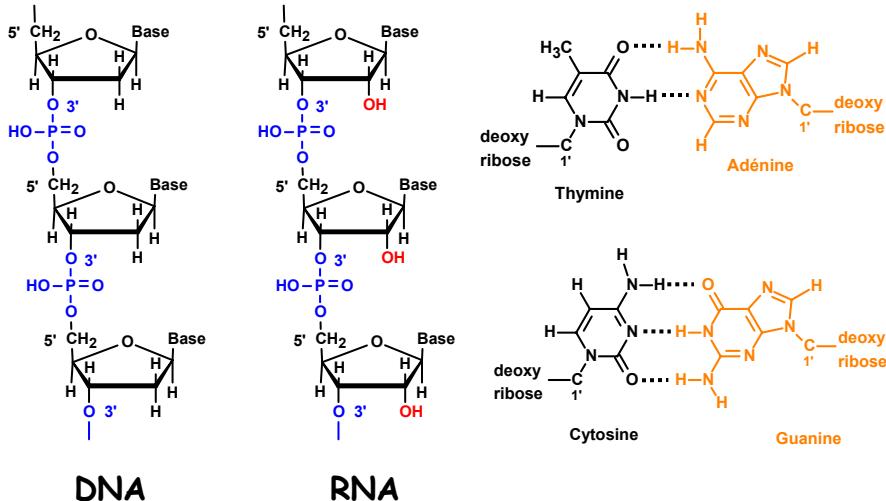


MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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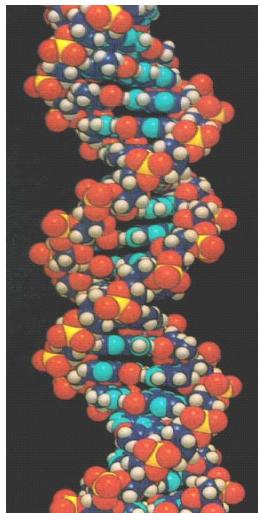
Chapter 5 Selected applications

## 5.2 Catalysts for DNA and RNA cutting



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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**DNA/RNA cleavage:**

- biotechnology
- therapy
- artificial enzymes

**Cleavage at phosphodiester bridges**

**Lifetimes:**

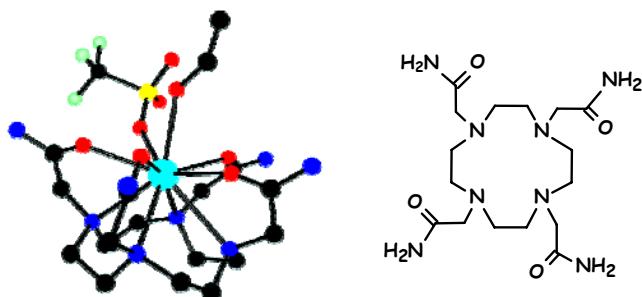
- DNA alone	$2 \times 10^8$ years
- catalyst	few hours
- RNA alone	$10^3$ years
- catalyst	few minutes

1992

Komiyama et al. demonstrate that  $\text{Ln}^{\text{III}}$  chlorides are active catalysts, especially  $\text{CeCl}_3$

1994

Komiyama demonstrates that  $\text{Ce}^{\text{IV}}$  is better  
J. Morrow proves the same effect with  
a cyclen derivative,  $[\text{La}(\text{trif})(\text{tcmc})]^{2+}$

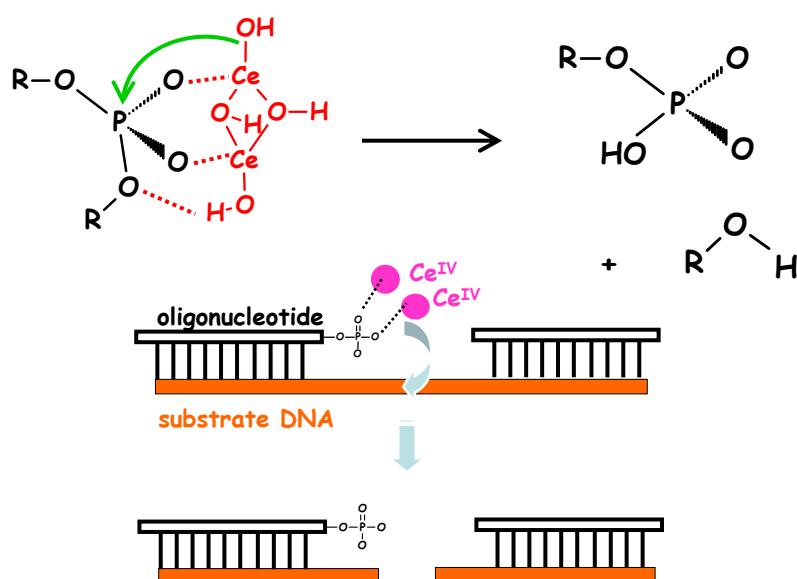
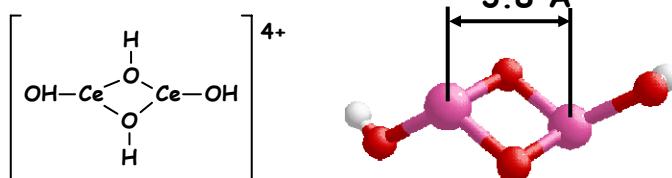


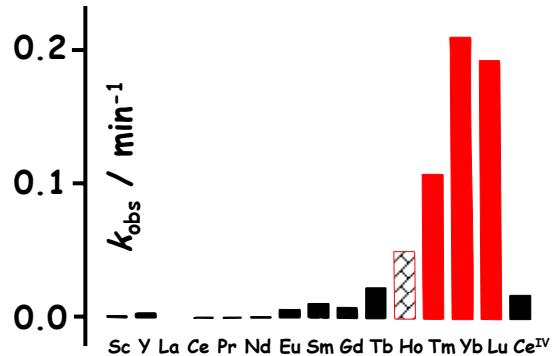
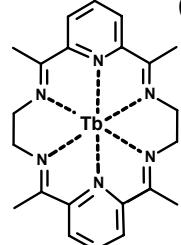
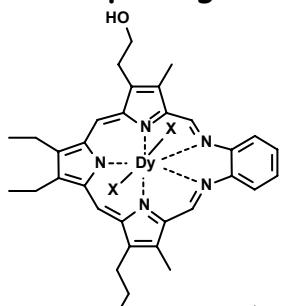
### Present status

$\text{Ce}^{\text{IV}}$  is the best catalyst for DNA cutting  
 $\text{Tm}^{\text{III}}$ ,  $\text{Yb}^{\text{III}}$ ,  $\text{Lu}^{\text{III}}$  are best catalysts for RNA cleavage

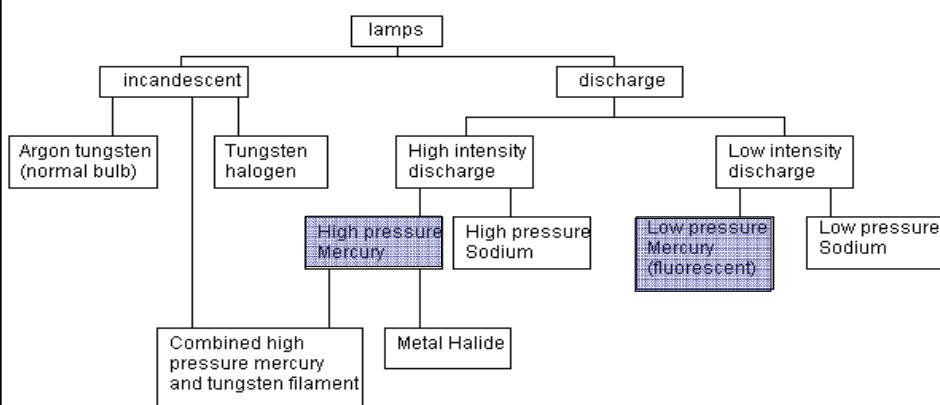
### Proposed mechanism for DNA cleavage

In fact, the active species seems to be an hydrolyzed species containing  $\text{Ce}^{\text{IV}}$ . At pH 7.4, the following species are present in solution:

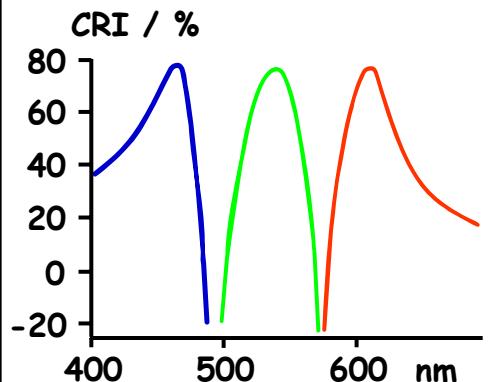


**RNA splitting**

M. Komiyama in Handbook on the Physics and Chemistry of Rare Earths, Vol. 34, Ch. 222, 2005.

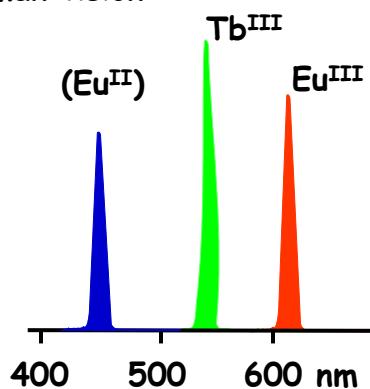
**5.3 Lighting applications**

### Producing white light: trichromatic stimuli

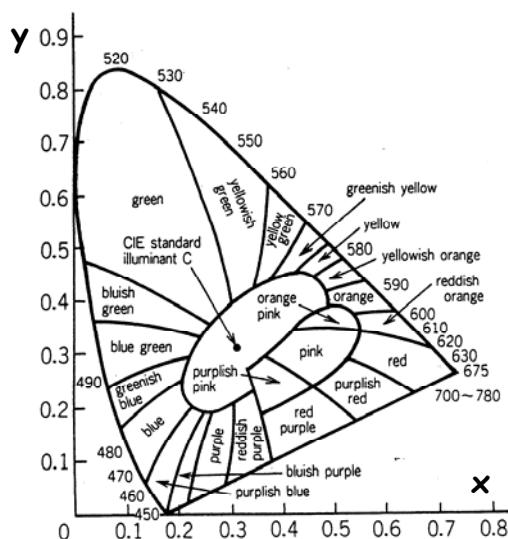


Color rendering index obtained by mixing the three prime colors

There are three "prime" colors corresponding to the three spectral responses of human vision



### Trichromatic diagram



$$X = \frac{1}{K} \int_{380}^{780} P(\lambda) \cdot p(\lambda) \cdot \bar{x}(\lambda) \cdot d\lambda$$

$$Y = \frac{1}{K} \int_{380}^{780} P(\lambda) \cdot p(\lambda) \cdot \bar{y}(\lambda) \cdot d\lambda$$

$$Z = \frac{1}{K} \int_{380}^{780} P(\lambda) \cdot p(\lambda) \cdot \bar{z}(\lambda) \cdot d\lambda$$

$$K = \int_{380}^{780} P(\lambda) \cdot p(\lambda) \cdot \bar{y}(\lambda) \cdot d\lambda$$

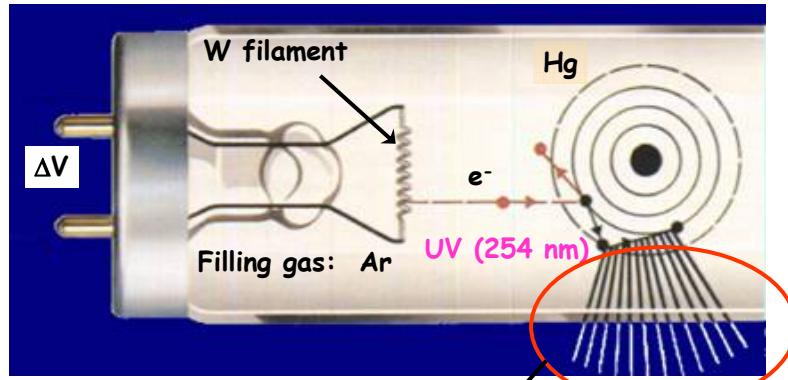
Emission  
Reflectance  
Trichromatic stimuli

$$x = \frac{X}{X + Y + Z}$$

$$y = \frac{Y}{X + Y + Z}$$



## Chapter 5 Selected applications



**UV photons excite phosphor-containing coating leading to a white emission thanks to an appropriate blend of phosphors**

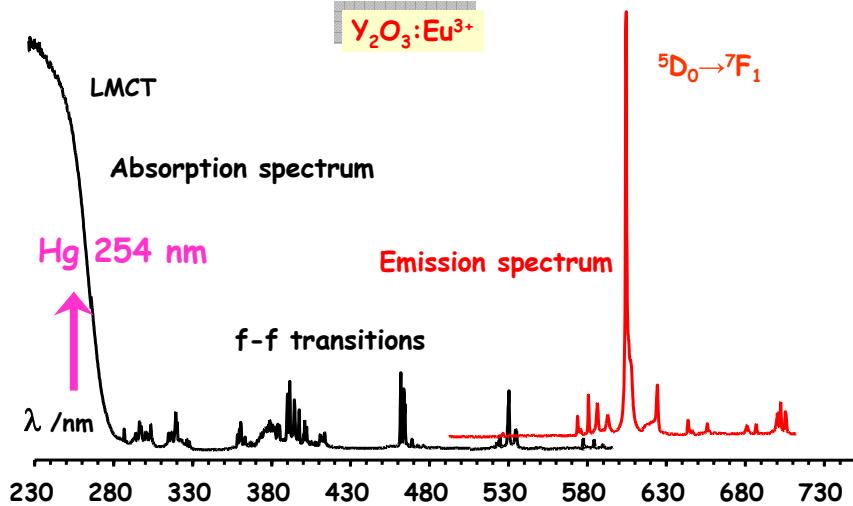
(Courtesy of P. Ceintrey, Rhodia Electronics & Catalysis)

## Chapter 5 Selected applications

### Major phosphors used by lighting industry

Year	Phosphor		
1960	$\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Sb}^{3+}, \text{Mn}^{2+}$ (white)		
1974	$\text{BaMg}_2\text{Al}_{16}\text{O}_{27}:\text{Eu}^{2+}$	$\text{CeMgAl}_{10}\text{O}_{19}:\text{Tb}^{3+}$	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$
1990	$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ $(\text{Sr}, \text{Ca})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$	$(\text{La}, \text{Ce})\text{PO}_4:\text{Tb}^{3+}$ $\text{CeMgAl}_{10}\text{O}_{19}:\text{Tb}^{3+}$ $(\text{Gd}, \text{Ce})\text{MgB}_5\text{O}_{10}:\text{Tb}^{3+}$	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$
2005	$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$	$(\text{La}, \text{Ce})\text{PO}_4:\text{Tb}^{3+}$	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$

Chapter 5 Selected applications



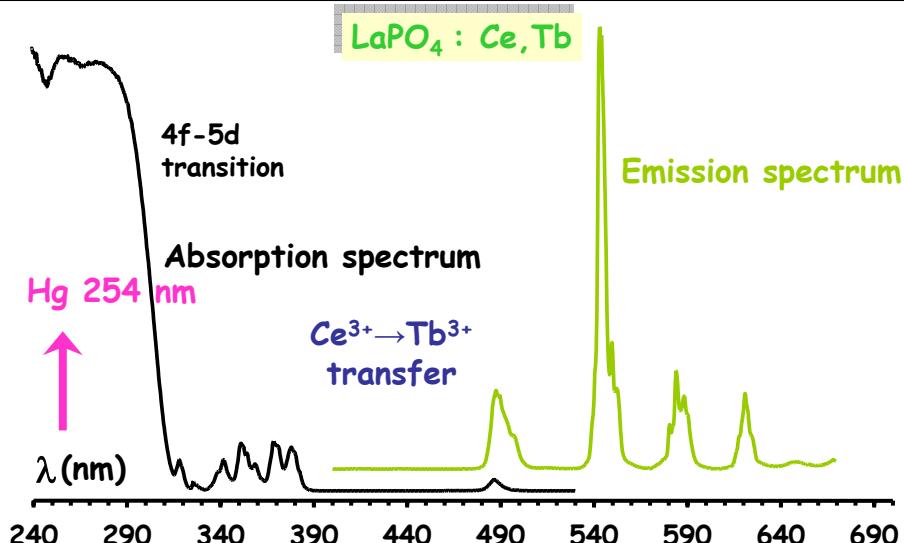
Y<sub>2</sub>O<sub>3</sub> features metal ion sites with O<sub>h</sub> symmetry, e.d. transitions are therefore forbidden



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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Chapter 5 Selected applications



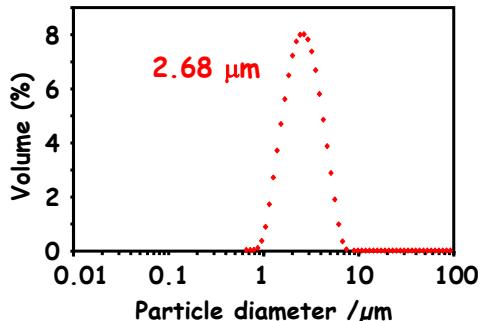
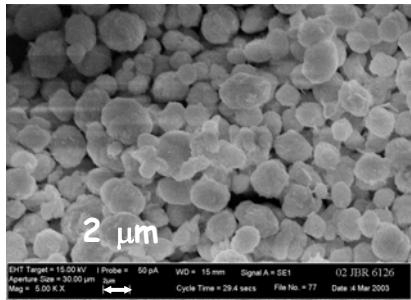
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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**Synthesis**

Main difficulty is to reach adequate particle size

Example: **red phosphor**



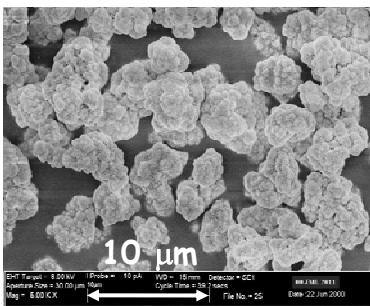
(Courtesy of P. Ceintrey, Rhodia Electronics & Catalysis)



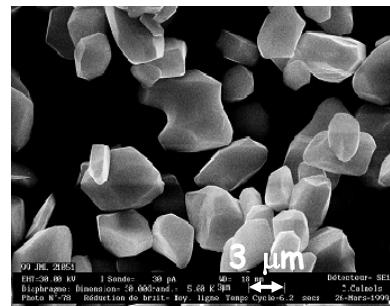
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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**Green phosphor** is obtained by co-precipitation leading to incorporation of  $Ce^{3+}$  and  $Tb^{3+}$  in the  $LaPO_4$  lattice; allows control of morphology, particle size and oxidation state of Ce and Tb.



Precursor



After flux addition

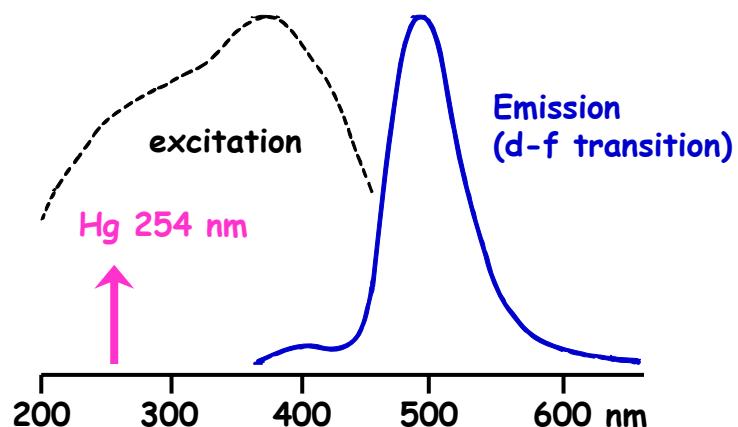
(Courtesy of P. Ceintrey, Rhodia Electronics & Catalysis)



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

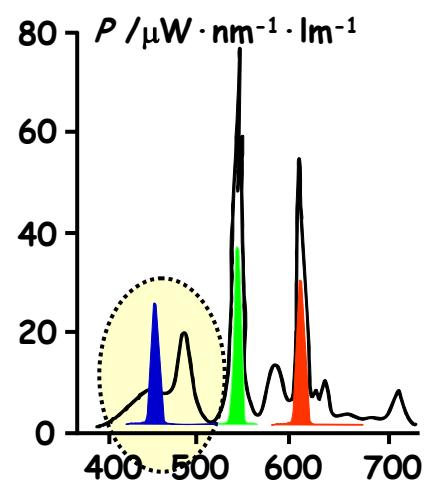
276

**Blue phosphor**  
 $\text{Sr}_4\text{Al}_4\text{O}_{25}:\text{Eu}^{\text{II}}$

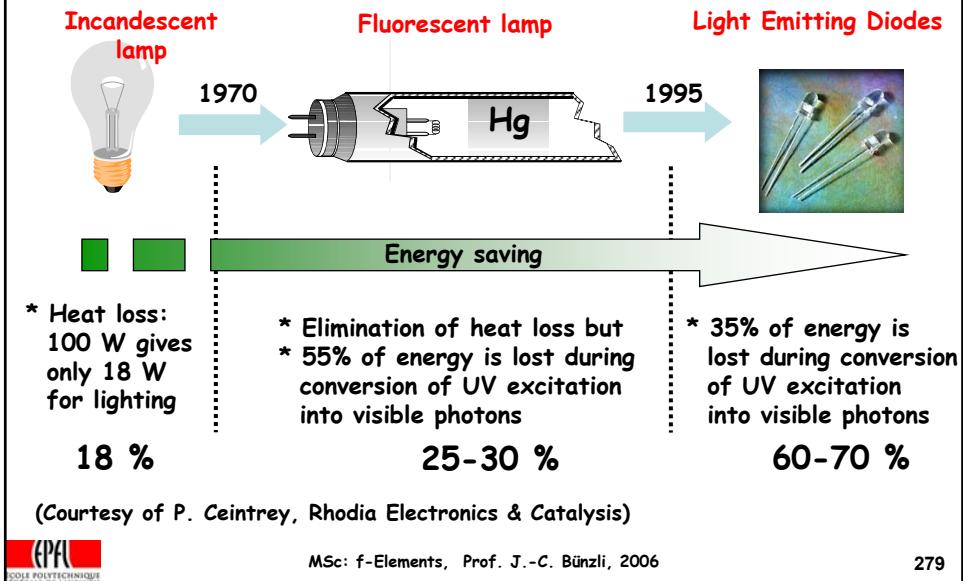


Spectral distribution  
of a luminescent lamp  
with the following  
phosphors:

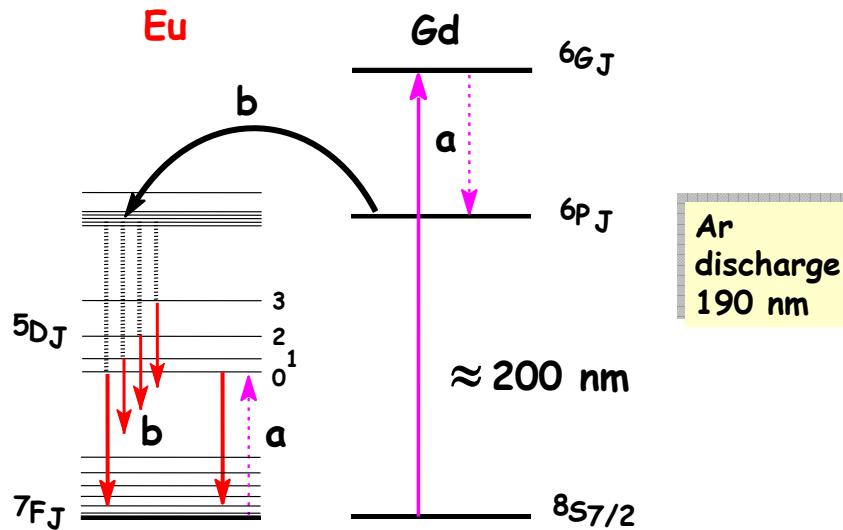
$\text{BaMg}_2\text{Al}_{16}\text{O}_{27}:\text{Eu}^{\text{II}}$   
 $\text{CeMgAl}_{11}\text{O}_{19}:\text{Tb}^{\text{III}}$   
 $\text{Y}_2\text{O}_3:\text{Eu}^{\text{III}}$



## The future of lighting



## Eliminating mercury from lamps: quantum cutting



## 5.4 Luminescent chemical sensors

The specific spectroscopic properties of  $\text{Ln}^{\text{III}}$  ions make them ideal luminescent probes:

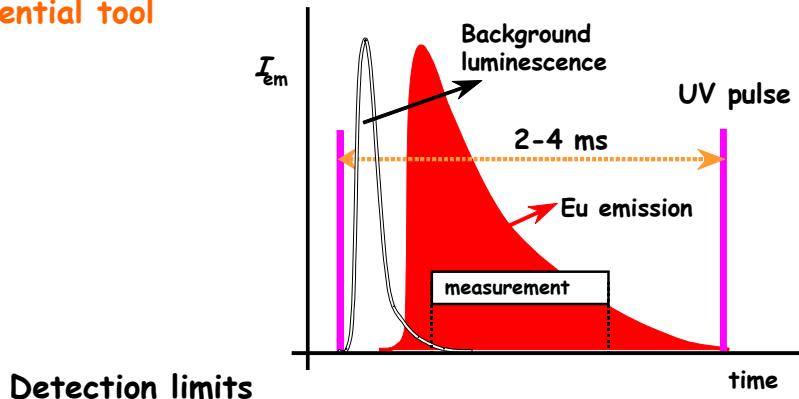
- easily recognizable line-like spectra
- long lifetimes of excited states
- large Stokes' shift upon ligand excitation

Time-resolved luminescence allows high signal-to-noise ratios, henceforth high sensitivity

Lanthanide-containing luminescent probes can be used as:

- structural probe (site symmetry)
- analytical probes (mainly for bio-analyses)
- imaging probe for medical diagnosis (tumor imaging)

### Time-resolved luminescence: an essential tool

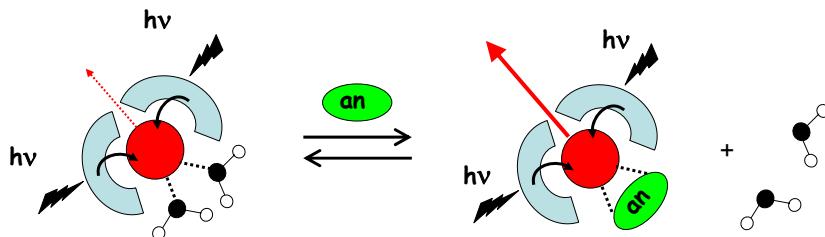


Detection limits

Ion	$I_{\text{exc}}$	$\varepsilon/10^3$	$I_{\text{em}}/\text{nm}$	$\tau/\mu\text{s}$	Q	Det. lim.
Eu	340	36	613	730	0.69	0.05 pM
Sm	340	36	643	50	0.02	3.5 pM

**Ln<sup>III</sup> luminescence as signaling method**

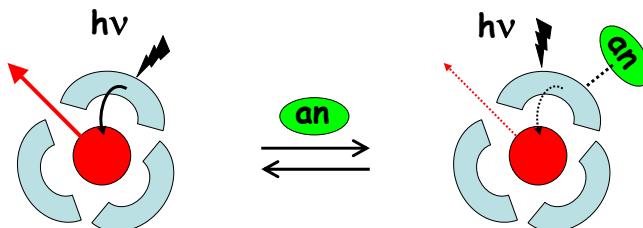
- a) Direct binding of the analyte modifies the Ln<sup>III</sup> inner co-ordination sphere



Here, water molecules are expelled, lifting the luminescence quenching.

J.-C. Bünzli & C. Piguet, Chem. Soc. Rev. 2005, 34, 1048

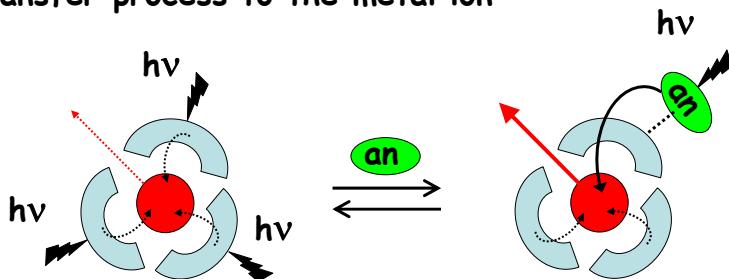
- b) Binding of the analyte to a ligand modifies its energy-transfer properties



Here, binding of the analyte results in a quenching of the metal-centered luminescence.

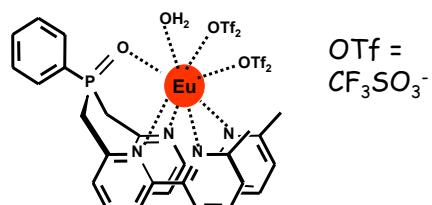
Alternatively, luminescence can be activated by such a binding.

c) Binding of the analyte to a ligand initiates an energy-transfer process to the metal ion



Note: in bio-analyses, specific biochemical reactions are usually used to render the analysis target specific.

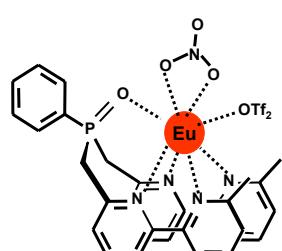
a) Modification of inner coordination sphere: anion analysis



In acetonitrile:

$$Q = 2.6 \%$$

$$\tau = 0.86 \text{ ms}$$



$$Q = 30 \%$$

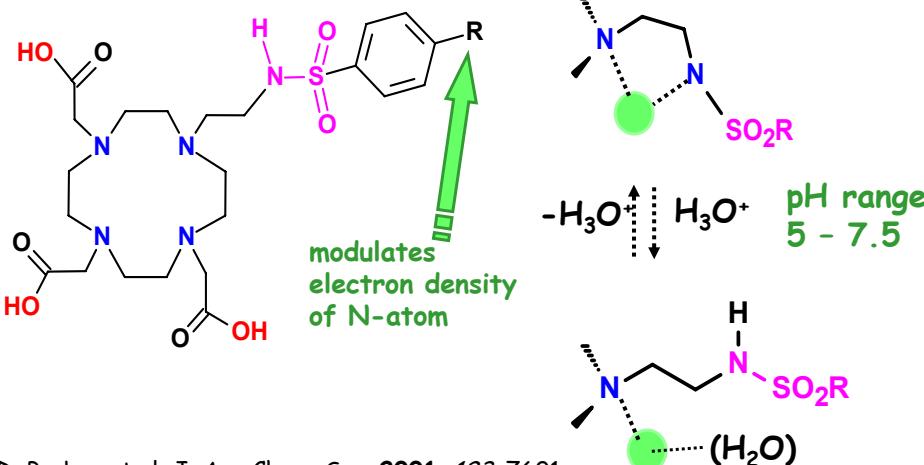
$$\tau = 1.45 \text{ ms}$$

$$K_{\text{assoc}} = 10^6$$

L. J. Charbonnière et al., *J. Am. Chem. Soc.*  
2002, 124, 7779

## Supramolecular pH sensor

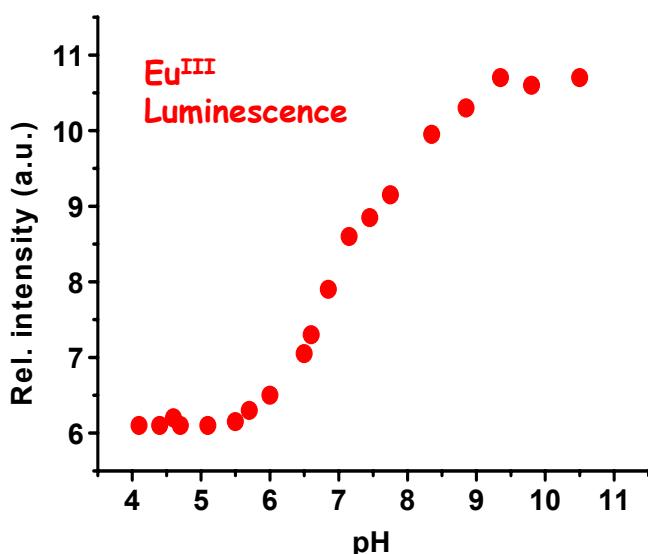
pH sensor



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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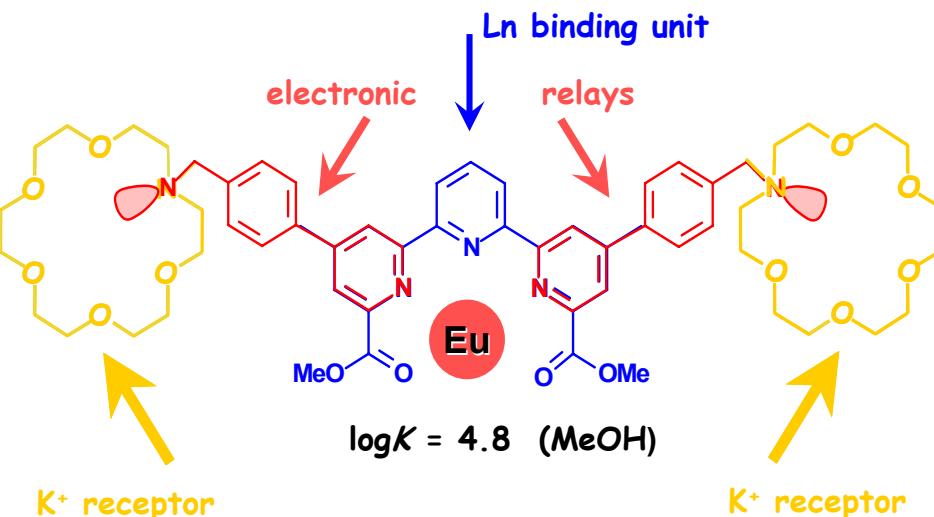
## Supramolecular pH sensor



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

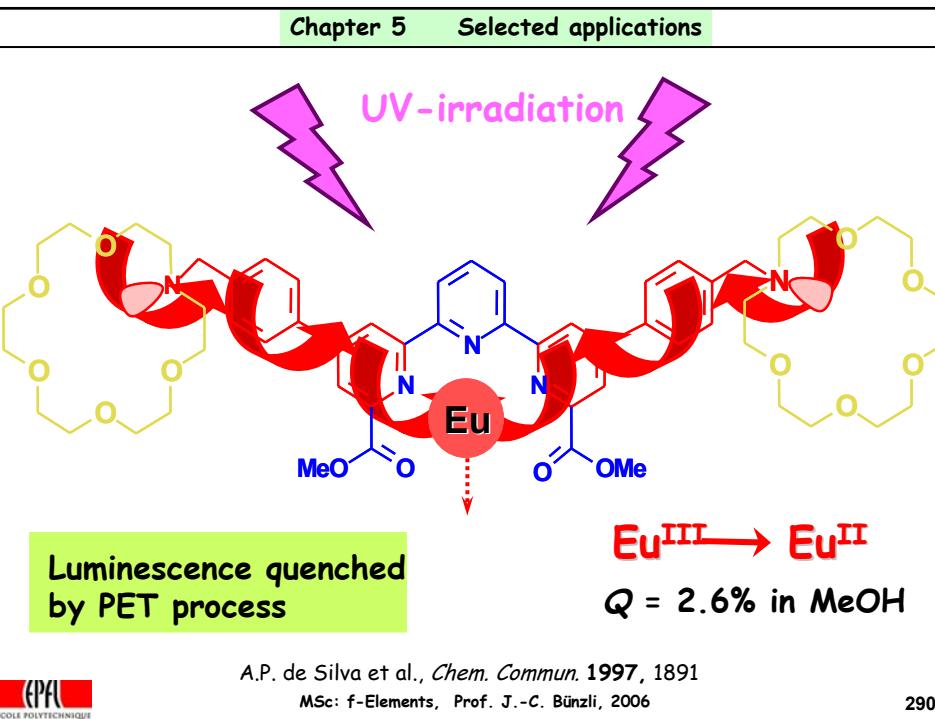
288

## b) Removal of a quenching process

A.P. de Silva et al., *Chem. Commun.* 1997, 1891

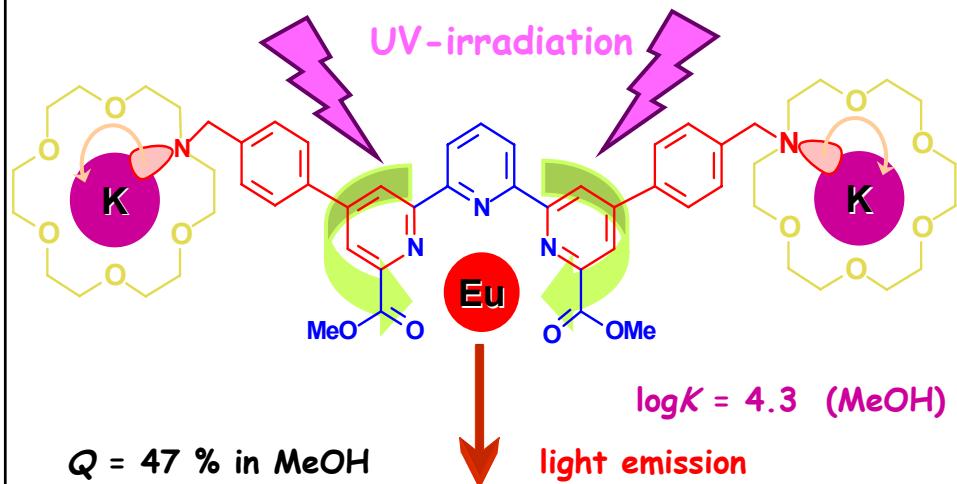
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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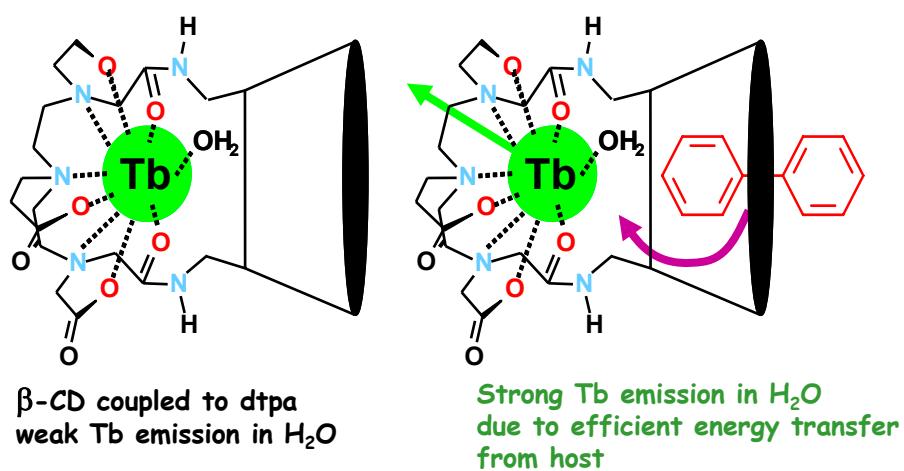
A.P. de Silva et al., *Chem. Commun.* 1997, 1891

MSc: f-Elements, Prof. J.-C. Bünzli, 2006

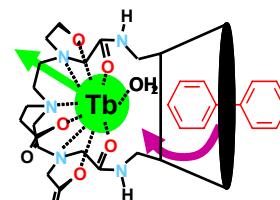
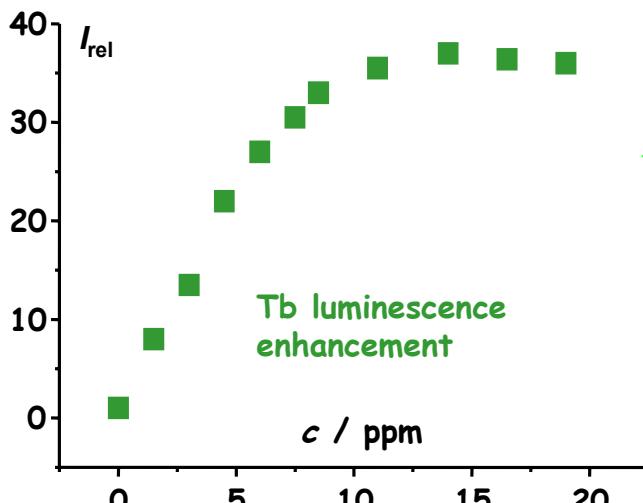
290

A.P. de Silva et al., *Chem. Commun.* 1997, 1891

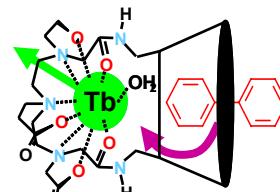
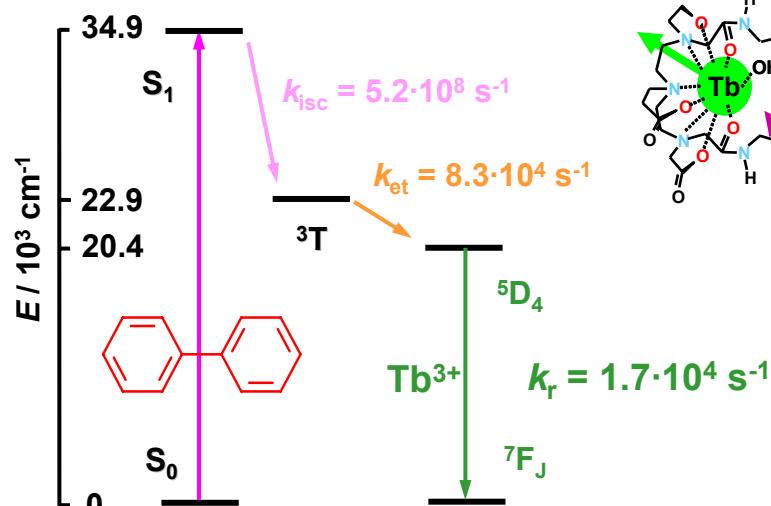
## c) Initiating an energy transfer process

Nocera et al., *Coord. Chem. Rev.* 1998, 171, 115

## Supramolecular PAH sensor



## Supramolecular PAH sensor



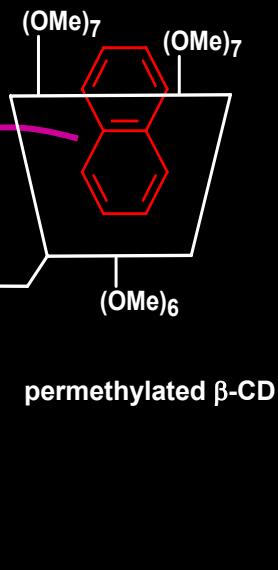
Chapter 5 Selected applications

Supramolecular PAH sensor (2)

Enhancement of the Tb luminescence in de-oxygenated solution by supramolecular fixation of naphtalene

sensitised  $\text{Tb}^{3+}$  emission

Large association constant:  $\log K = 4$



D. Parker et al., J. C. S., Perkin Trans. 2, 2000, 1329

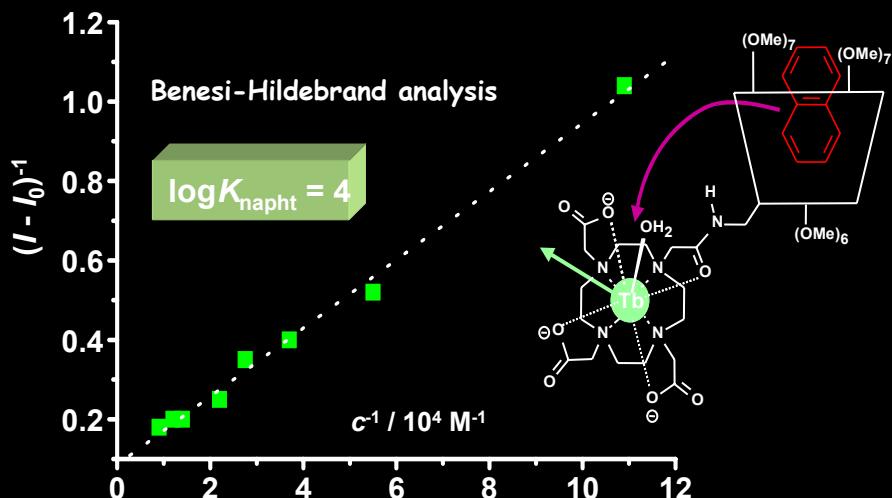


Chapter 5 Selected applications

Supramolecular PAH sensor (2)

Benesi-Hildebrand analysis

$$\log K_{\text{napht}} = 4$$

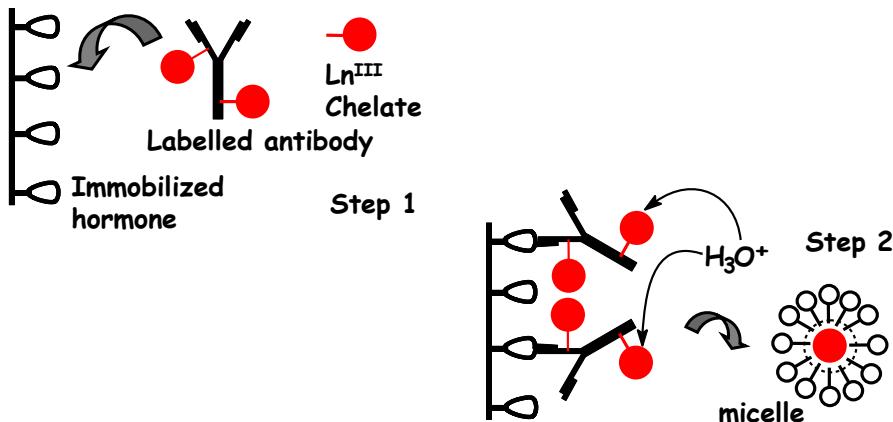


D. Parker et al., J. C. S., Perkin Trans. 2, 2000, 1329



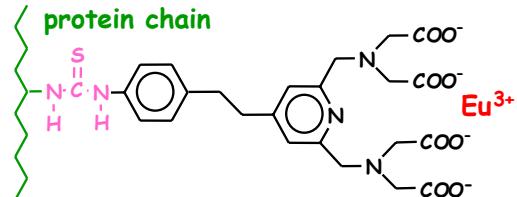
## 5.5 Luminescent biochemical sensors

### Time resolved heterogeneous immunoassays

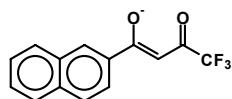


### Delfia® technology

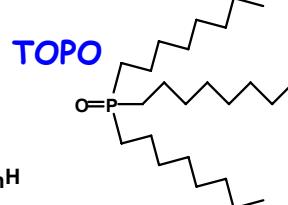
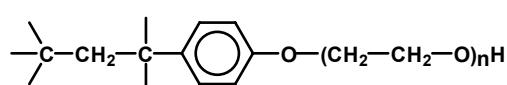
Linking the 1<sup>st</sup> chelate on the protein chain

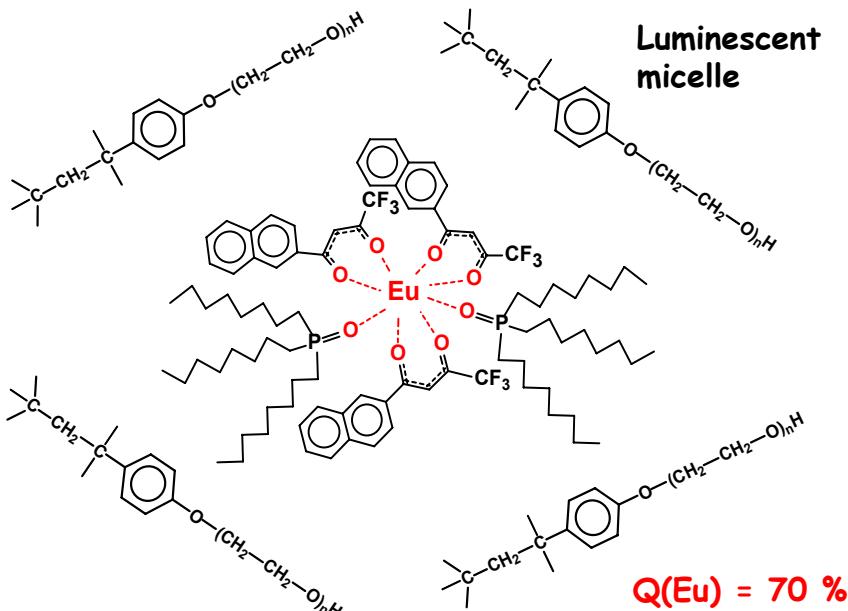


Production of the in situ luminescent chelate:



Triton X-100



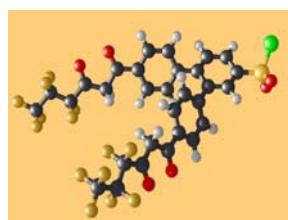
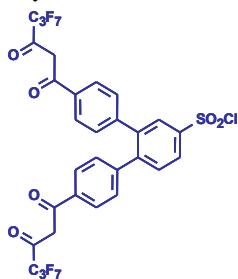


### Time resolved homogeneous immunoassays

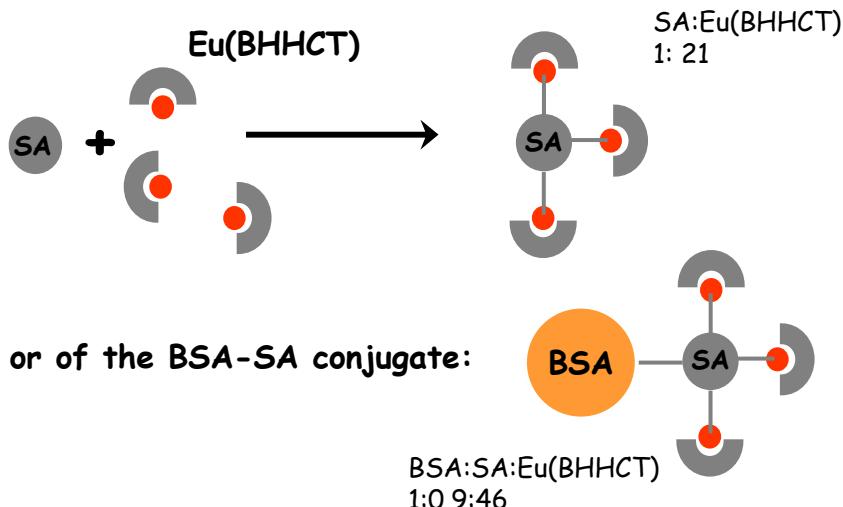
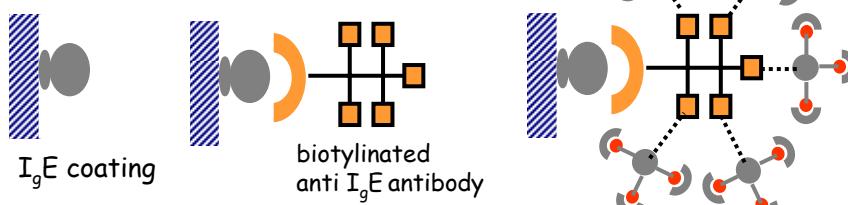
#### Human immunoglobulin IgE

- Related to various allergies
- lowest concentration among the five immunoglobulins
- detection limit for radioimmunoassay: 40-300 pg/ml in 2-5 days

#### Development of an Eu-based luminescent immunoassay:



J. Yuang, G. Wang, H. Kimura, K. Matsumoto  
*Anal. Biochem.* **1997**, 254, 283

**Step 1: Labeling of streptomycin SA****Step 2:****Step 3: TRS measurement**

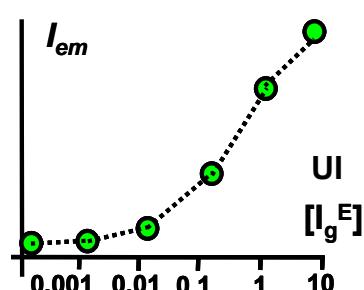
Detection limit:

 $1.5 \times 10^{-3}$  IU/ml

4 pg/ml

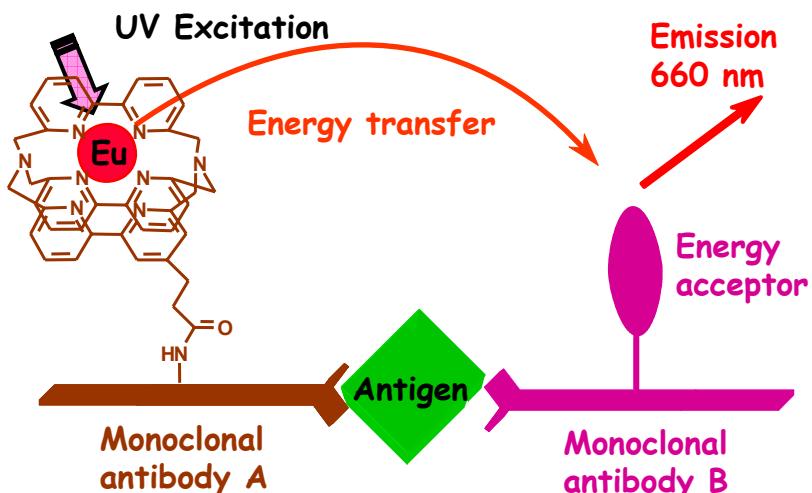
 $10^{-18}$  mol $6 \times 10^5$  molecules

Time: 4-5 hours

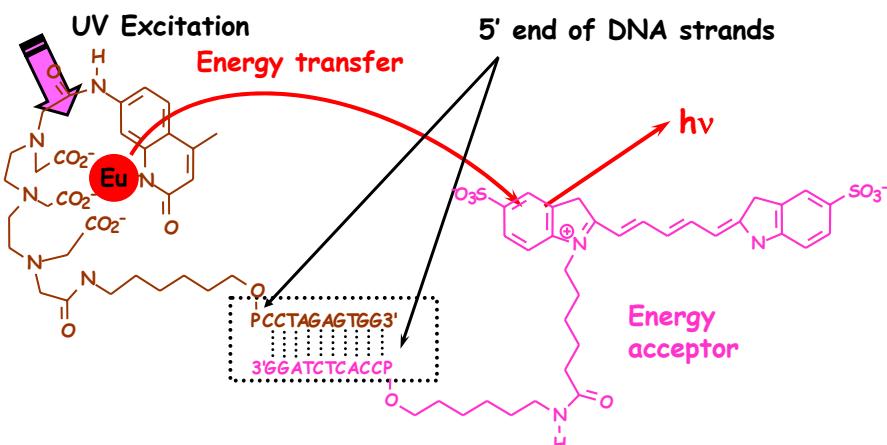


## Time resolved homogeneous immunoassays

## LRET: Luminescent resonance energy transfer



## Hybridization detection



## 5.6 Tracing biomolecular interactions

Molecular interactions between biomolecules are key mechanisms in living cells.

Moreover, high throughput screening strategies are being developed in which pharmaceutical industry is testing as many compounds as possible (from combinatorial chemistry) on molecular targets.

Henceforth the need for developing adequate analytical techniques able to work in the microliter range.

Homogeneous immunoassays based on  $\text{Ln}^{\text{III}}$  luminescence (cf. § 2.7) are ideal in this respect.

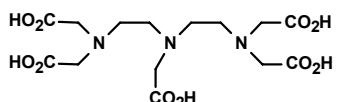
Technically a luminescence resonance energy transfer (LRET) is used.



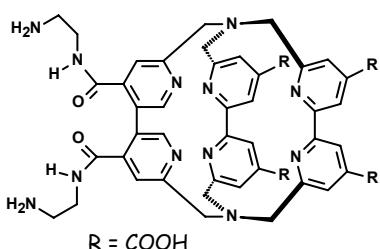
### TRACE® technology (Time Resolved Amplified Cryptate Emission)

#### a) Choosing the right chelate

Key parameters are stability and dissociation kinetics



dtpa  $\log K = 19-23$   
 $\Delta G_{\text{diss}}^{\#} = 10-50 \text{ kJmol}^{-1}$

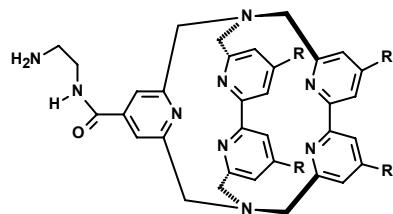


bipyridine cryptand  
 $\Delta G_{\text{diss}}^{\#} = 100-120 \text{ kJmol}^{-1}$

[Eu(tbp)]



The quantum yield is relatively low:  $Q = 2\%$ , mainly because water is co-ordinated in the first co-ordination sphere and because of a PET process. Water can be expelled by fluoride ions:  $Q = 7\%$ . PET process (leading to the reduction into  $\text{Eu}^{\text{II}}$ ) can be minimized by decreasing the cavity size, since the ionic radius of  $\text{Eu}^{\text{II}}$  is larger ( $1.30 \text{ \AA}$ ) compared to  $\text{Eu}^{\text{III}}$  ( $1.12 \text{ \AA}$ , CN = 9).

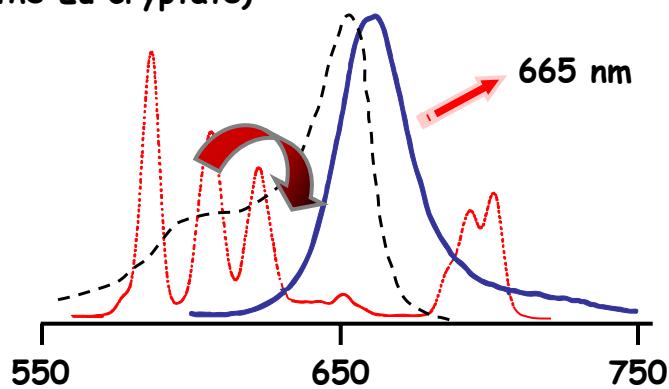


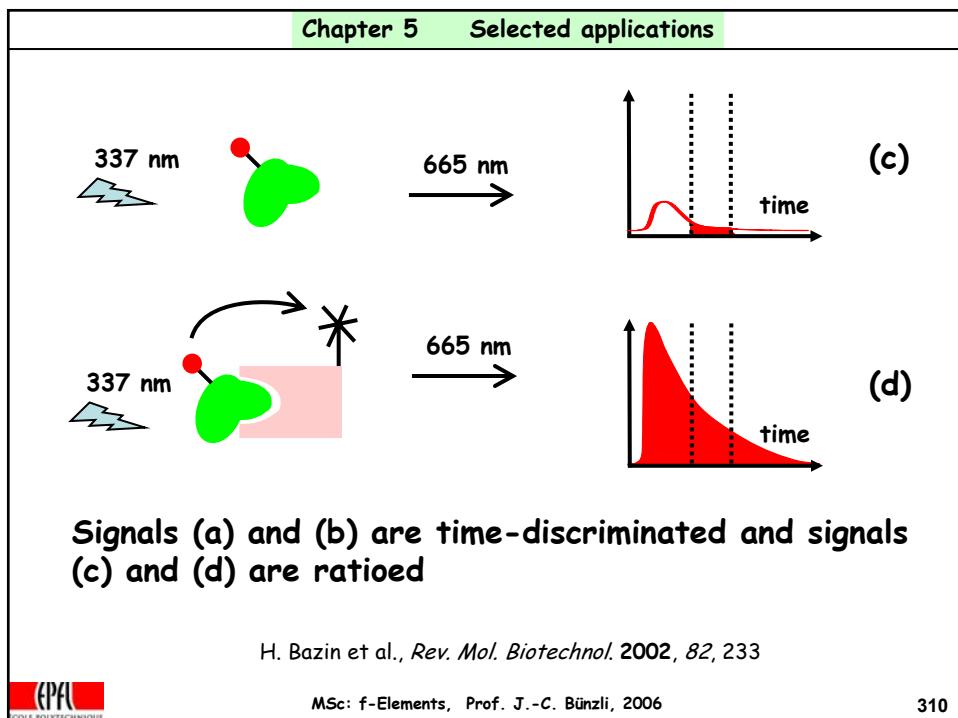
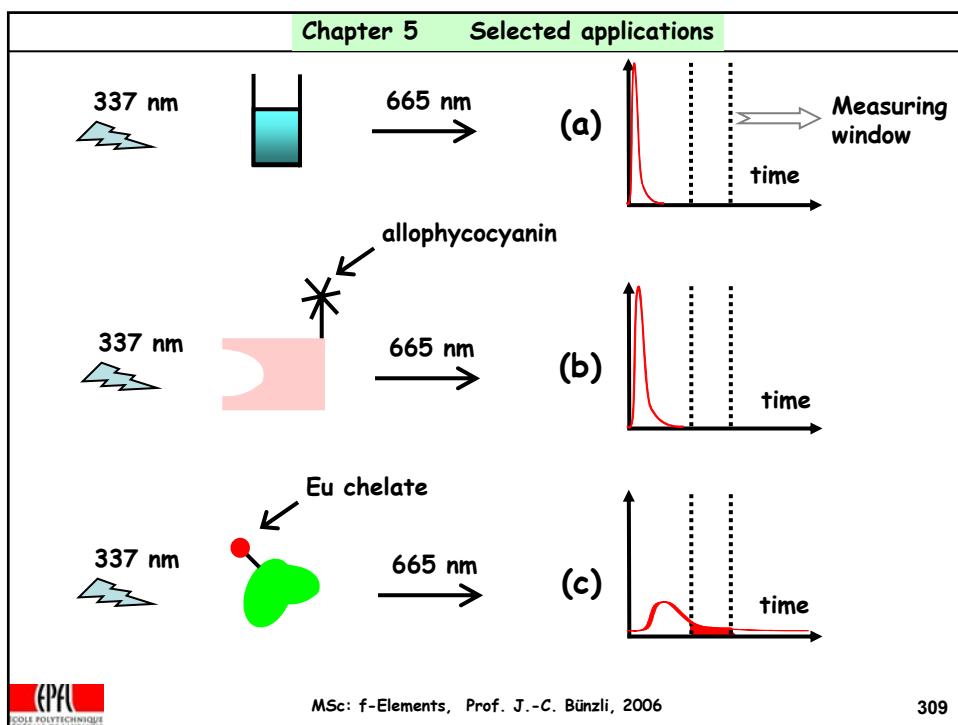
### b) Choosing the energy acceptor

Allophycocyanin (105 kDa phycobiliprotein)

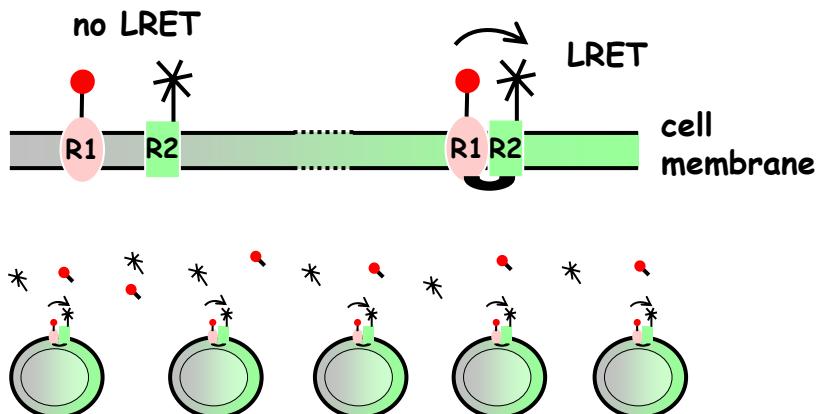
High absorption coefficient,  $Q = 70\%$

$R_0 = 95 \text{ \AA}$  (distance for 50 % energy transfer from the Eu cryptate)

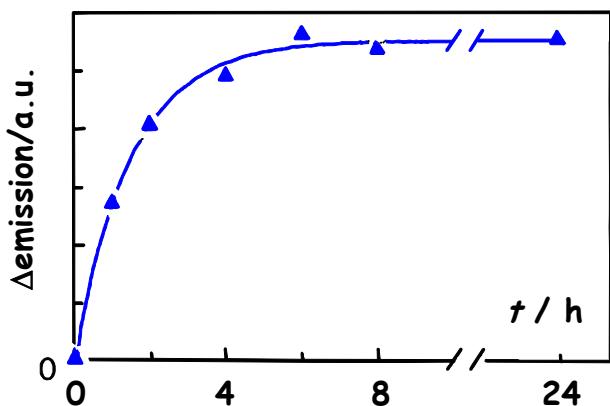




## c) Application: cell surface detection of membrane protein

Idea: prove that the  $GABA_B$  receptor is a heterodimerD. Maurel et al. *Anal. Biochem.* 2004, 329, 253

## Kinetic of association showing the saturation of the binding sites after 8 hours

D. Maurel et al. *Anal. Biochem.* 2004, 329, 253

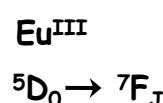
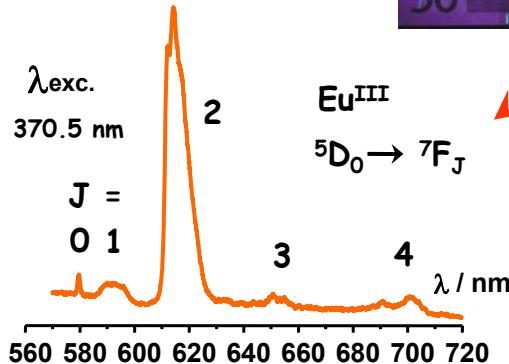
## 5.7 Another application of luminescence

- Security inks

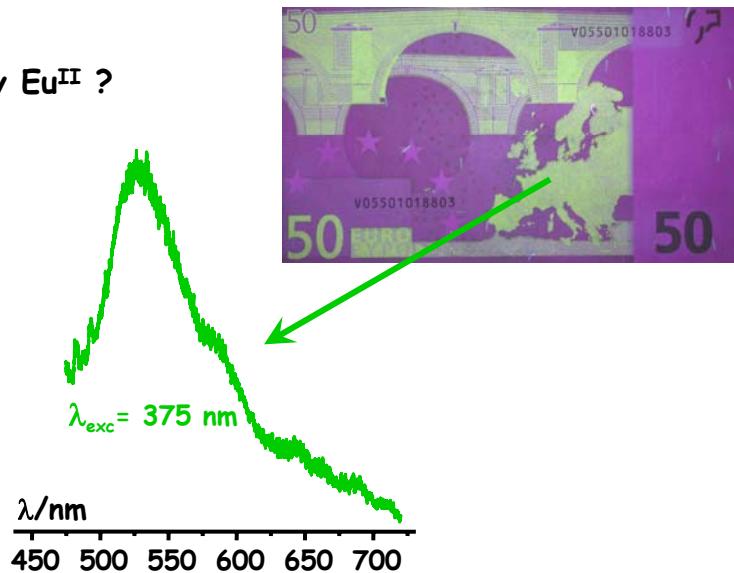
Euro bills



The euro is protected by the luminescence from europium: red from  $\text{Eu}^{\text{III}}$



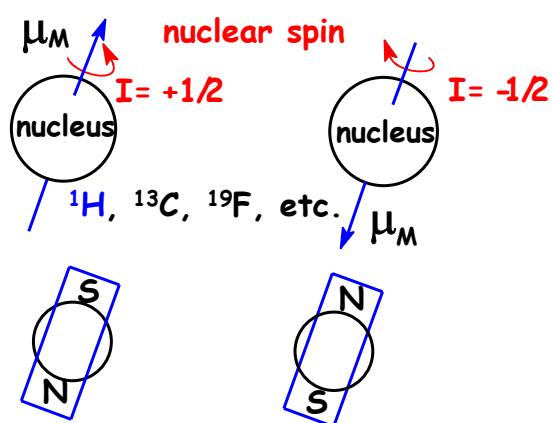
Europium was discovered by Eugène A. Demarçay in 1901 in Paris

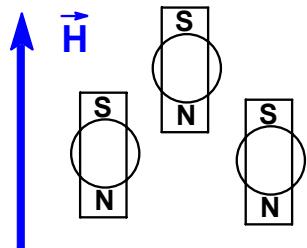
Possibly Eu<sup>II</sup> ?

## 5.8 Magnetic resonance medical imaging (MRI)

### Principle of the NMR experiment

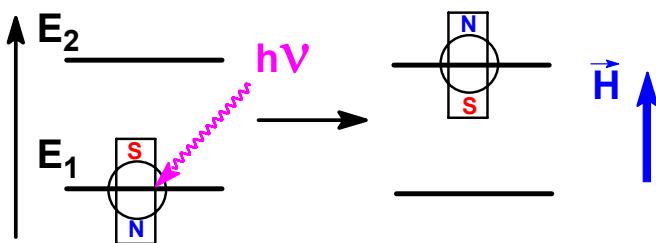
A nucleus behaves like a small magnet





Nuclear magnetic moments align in a magnetic field

Transitions to the upper level can be induced by a radiofrequency field



If  $H \approx 1.4$  tesla,  $\nu \approx 60$  MHz

Upon excitation by a radiofrequency pulse, the nuclei return to the ground state via two simultaneous and exponential relaxation processes:

$$N = N_0 \times e^{-t/T_1} \quad T_1 = \text{longitudinal relaxation time (transfer to surroundings)}$$

$$N = N_0 \times e^{-t/T_2} \quad T_2 = \text{transverse relaxation time (loss of phase)}$$

The total rate of relaxation is proportional to:

$$k_{\text{relax}} = \frac{1}{T_1} + \frac{1}{T_2}$$

Unpaired electrons generate strong fluctuating magnetic fields and if there are located nearby a nucleus, they will stimulate nuclear relaxation.

Potential relaxation agents:

High spin $\text{Fe}^{\text{II}}$	4 unpaired $e^-$	$\mu_{\text{eff}} = 5.5$
$\text{Mn}^{\text{II}}, \text{Fe}^{\text{III}}$	5	5.9
$\text{Eu}^{\text{II}}, \text{Gd}^{\text{III}}$	7	8.6
$\text{Dy}^{\text{III}}$	5	10.6

small iron particles (super-paramagnetism)

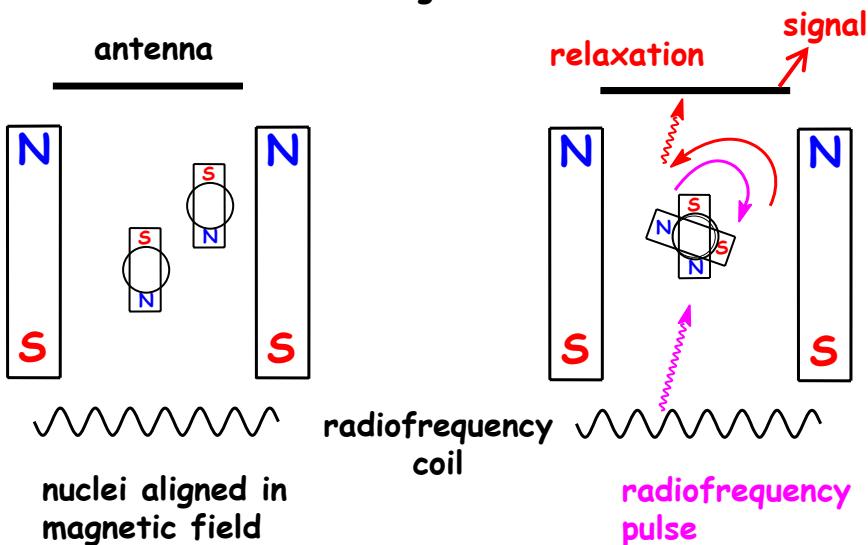
large iron particles (ferromagnetism)

organic radicals (1 unpaired  $e^-$ )

Gadolinium is usually the best and principally reduces  $T_1$



Measurement of transient signal:



## Principle of MRI

Various tissues have different relaxation times

Tissue	$T_1/\text{ms}$	$T_2/\text{ms}$
Fat	150	150
Liver	250	44
Muscle	450	64
White matter	300	133
Grey matter	475	118
Spleen	400	107
Pancreas	275	43

Therefore, differentiation can be made



## Principle of MRI with contrast agent

- Proton relaxation from water molecules is measured
- Water molecules outside the cells are put into contact with the (Gd-containing) contrast agent, so that their relaxation is faster (**10<sup>6</sup>-fold!**) and discrimination can be made with respect to water molecules inside the cell
- The effect of the contrast agent, called **relaxivity** is defined as follows:

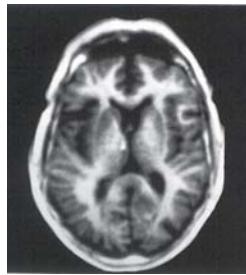
$$r_i = \frac{1}{\Delta T_i \cdot [CA]} \quad i = 1, 2 \quad \text{mmol}^{-1}\text{s}^{-1}$$

$\Delta T_i$  = difference in  $T_i$  without and with CA

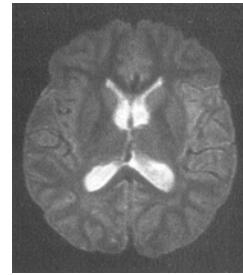
[CA] = concentration of contrast agent



## Chapter 5 Selected applications

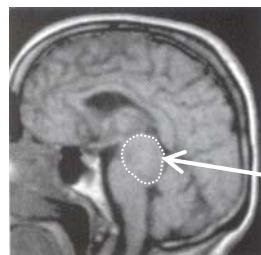


$T_1$ -weighted images



© Guerbet  
SA, Paris

$T_2$ -weighted images



tumor

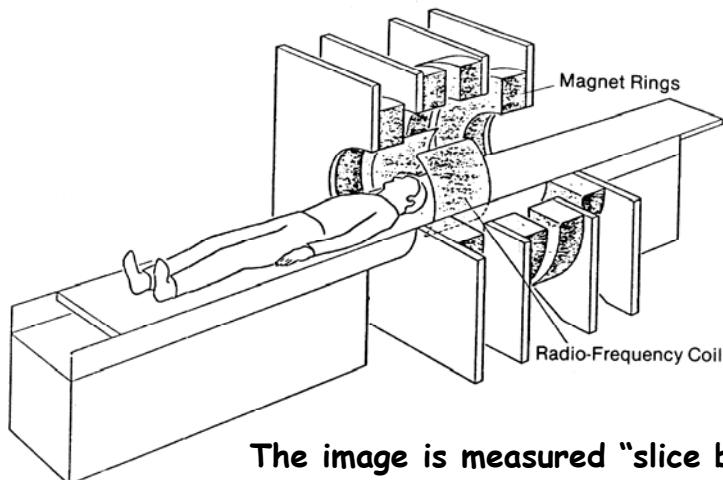


MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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## Chapter 5 Selected applications

### Principle of MRI



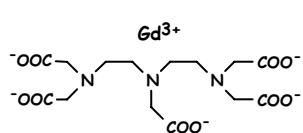
The image is measured "slice by slice  
and reconstructed



MSc: f-Elements, Prof. J.-C. Bünzli, 2006

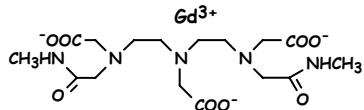
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## First generation contrast agents



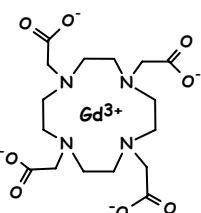
$[\text{Gd}(\text{dtpa})]^{2-}$  Magnevist®

$\log K = 22.1 \quad r_I = 3.7 \text{ mM}^{-1}\text{s}^{-1}$



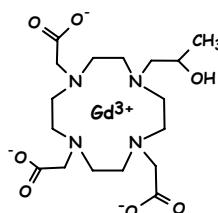
$[\text{Gd}(\text{dtpa-bma})]$  Omniscan®

$\log K = 16.9 \quad r_I = 4.6 \text{ mM}^{-1}\text{s}^{-1}$



$[\text{Gd}(\text{dota})]^-$  Dotarem®

$\log K = 25.8 \quad r_I = 3.4 \text{ mM}^{-1}\text{s}^{-1}$



$[\text{Gd}(\text{HP-DO}_3\text{A})]$  ProHance®

$\log K = 23.8 \quad r_I = 3.7 \text{ mM}^{-1}\text{s}^{-1}$

## The search for high relaxivity

Important parameters are:

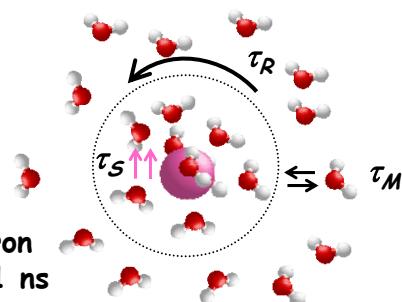
- water exchange rate (both inner and outer sphere)
- rotational correlation time of the molecule  $\tau_R$
- electron spin relaxation time  $\tau_S$

$[\text{Gd}(\text{dota})]^-$ :

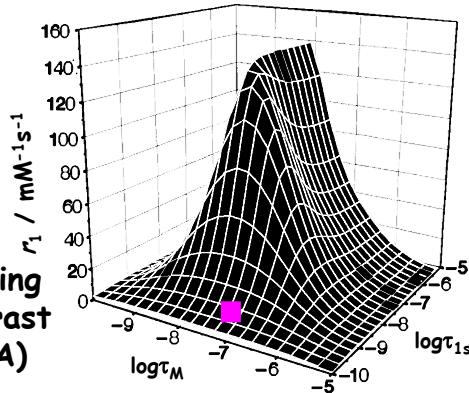
$$\tau_M = 1/k_M = 244 \text{ ns}$$

$\tau_{1s}$  is the longitudinal electron spin relaxation time = 1 ns

$$\tau_R = 80 \text{ ps}$$



Theoretical relaxivity  
for an slowly rotating  
molecule ( $\tau_R > 30$  ns)

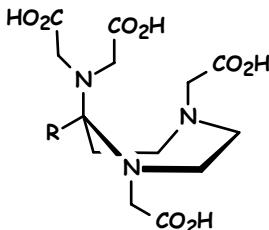


One solution for increasing  
 $\tau_R$  is to couple the contrast  
agent with proteins (BSA)  
or to insert it into high-  
molecular weight compounds  
(such as dendrimers).

[Gd(dota)]<sup>-</sup>

S. Aime et al. *Chem. Soc. Rev.* 1998, 27, 19

Present state: relaxivities up to 90 mM s<sup>-1</sup>

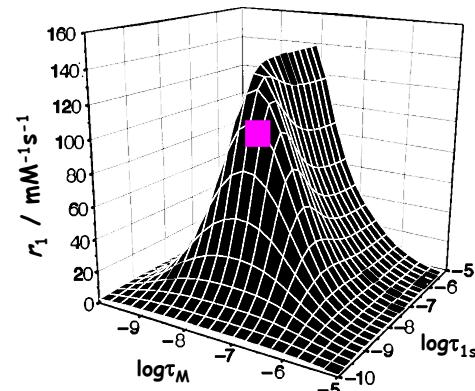


H<sub>4</sub>AAZT

[Gd(AAZT)]<sup>-</sup>       $r = 7.1 \text{ mM s}^{-1}$

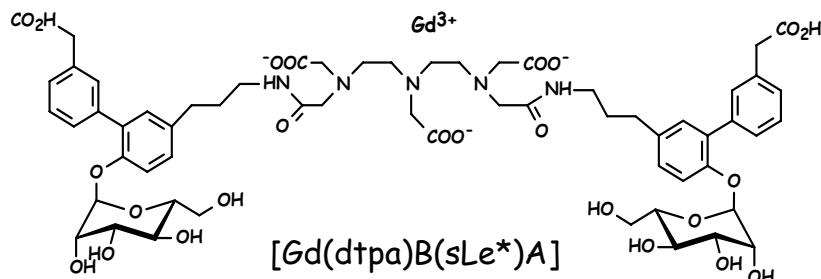
But:

the conjugate with BSA  
[[Gd(AAZT)]<sup>-</sup>-(BSA)]  
has  $r = 90 \text{ mM s}^{-1}$



### Specific contrast agents

Contrast enhancement agent for blood vessels targeted for E-selectin, which is secreted upon inflammation (e.g. in subjects with hepatitis)



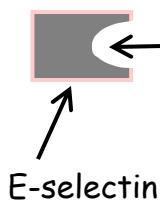
12-step synthesis with overall yield of 5 % ...

D-mannopyranosyl derivative

S. Boutry et al. *Magn. Res. Med.* 2005, 53, 800

MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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$[Gd(dtpa)B(sLe^*)A]$

Prolonged vascular residence: 50 min in hepatitis vs 30 min in healthy subject

healthy



hepatitis

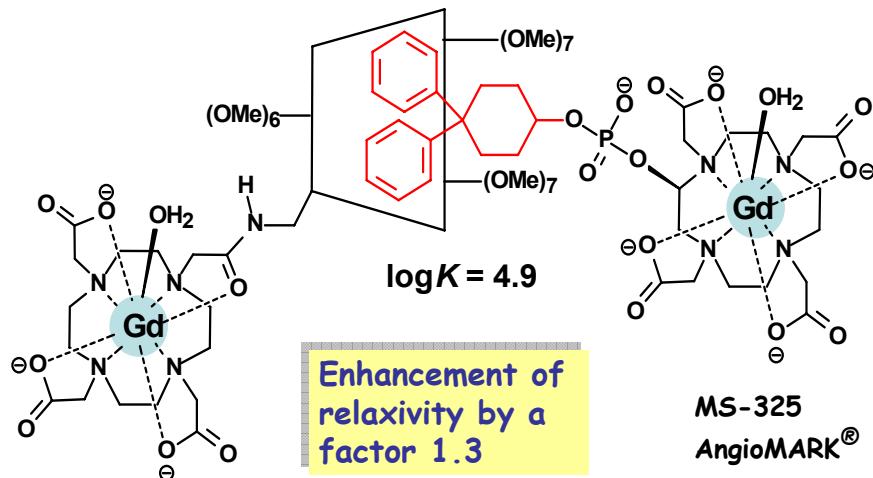


S. Boutry et al. *Magn. Res. Med.* 2005, 53, 800

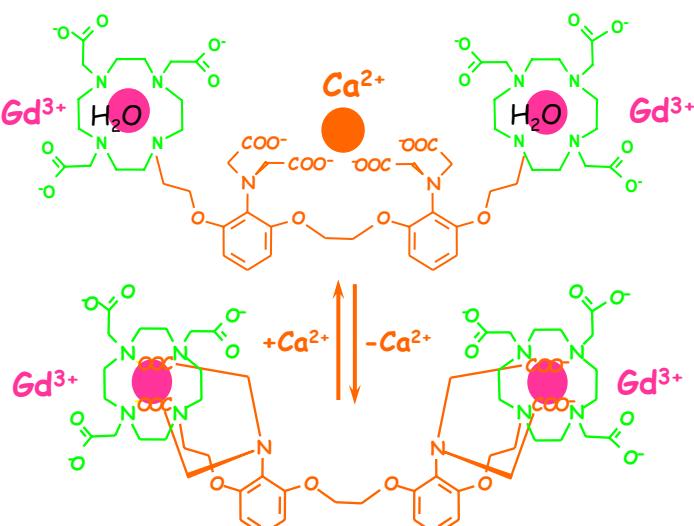
MSc: f-Elements, Prof. J.-C. Bünzli, 2006

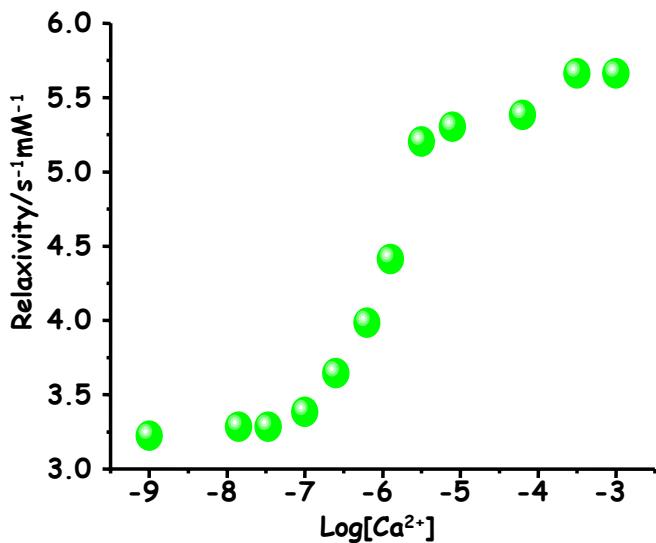
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## Supramolecular chemosensors based on relaxivity



## Calcium sensor



**Calcium sensor based on a contrast agent**W.H. Li, S.E. Fraser, T.J. Meade, *J. Am. Chem. Soc.*, 1999, 121, 1413

MSc: f-Elements, Prof. J.-C. Bünzli, 2006

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