Textbooks:

- S. Cotton, Lanthanide and Actinide Chemistry, Wiley 2006.
- H.C. Aspinall, Chemistry of the f-Block Elements, Gordon and Breach 2001.
- N. Kaltsoyannis, P. Scott, The f elements, Oxford Science 1999.
- Holleman-Wiberg, Inorganic Chemistry, Academic Press 2001.

Other references:

- Handbook on the Physics and Chemistry of Rare Earths, North Holland.
- Modern Aspects of Rare Earths and their Complexes, Elsevier.
- Organoderivatives of Rare Earth Elements, Kluwer.
- Optical Spectroscopy of Lanthanides, CRC.

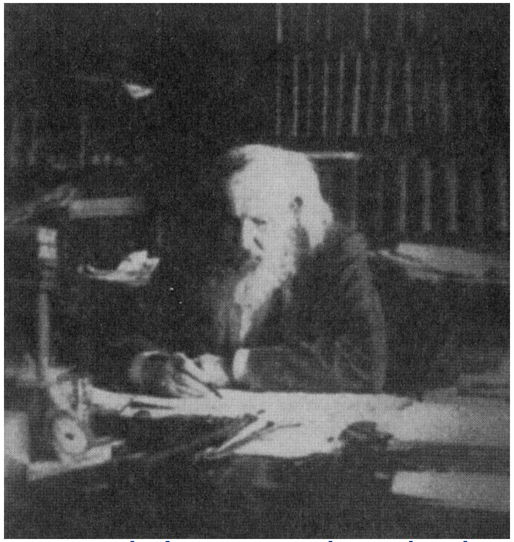
THE LANTHANIDES

Ana de Bettencourt-Dias

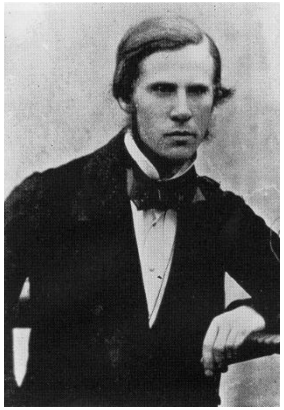
University of Nevada, Reno

CHEMISTRY IN 19TH CENTURY

- *"Lanthanons: These elements perplex us in our researches, baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us; mocking, mystifying and murmuring strange revelations and possibilities."*
  - *Sir William Crookes, Royal Society of Chemistry, 1887.*
- Rare Earths discovered 1838 – 1947, in 1887 all but Eu, Lu and Pm
- Emission spectroscopy
  - Bunsen and Kirchhoff (1859)
- Periodic table
  - Mendeleyev (1869)
- Atomic model/orbitals
  - Bohr (1913)



Mendeleyev at his desk
Mendeleyev's Dream, The Quest for the Elements, P. Strathern, St. Martin's Press.



William Crookes
The fontana history of chemistry, W.H. Brock, Fontana Press.

HISTORY OF LANTHANIDES I

Gadolin
Wikipedia

Mosander
Wikipedia

de Marignac
Wikipedia

- 1787 – Carl Axel Arrhenius (1757-1824, Swedish artillery officer and amateur geologist) discovers new mineral, Ytterbyte (Ytterby, Sweden)
- 1794 – Johan Gadolin (1760-1852) analyzes Ytterbyte and finds it contains new earths (oxides) of unknown elements
- 1797 – Anders Gustav Ekeberg renames mineral Yttria (heavy earth)
- 1803 - Martin Heinrich Klaproth identifies similar mineral, Ceria
- 1830s – Jöns Jakob Berzelius (1779-1848) subjects both earths to extensive studies
- 1838 – Carl Gustaf Mosander (1797-1858) isolates cerium (after Ceres, asteroid, after Roman goddess of crops and wheat)
- 1839 – Mosander isolates lanthanum (greek: lanthanein, to escape notice) and 'didymium' (greek: didumos, twin, as similar properties as lanthanum)
- 1843 – Mosander isolates yttrium, terbium and erbium (after Ytterby)
- 1878 – Jean Charles Galinard de Marignac (1817-1894) isolated ytterbium (after Ytterby)

HISTORY OF LANTHANIDES II

de Boisbaudran
Wikipedia

von Welsbach
Wikipedia

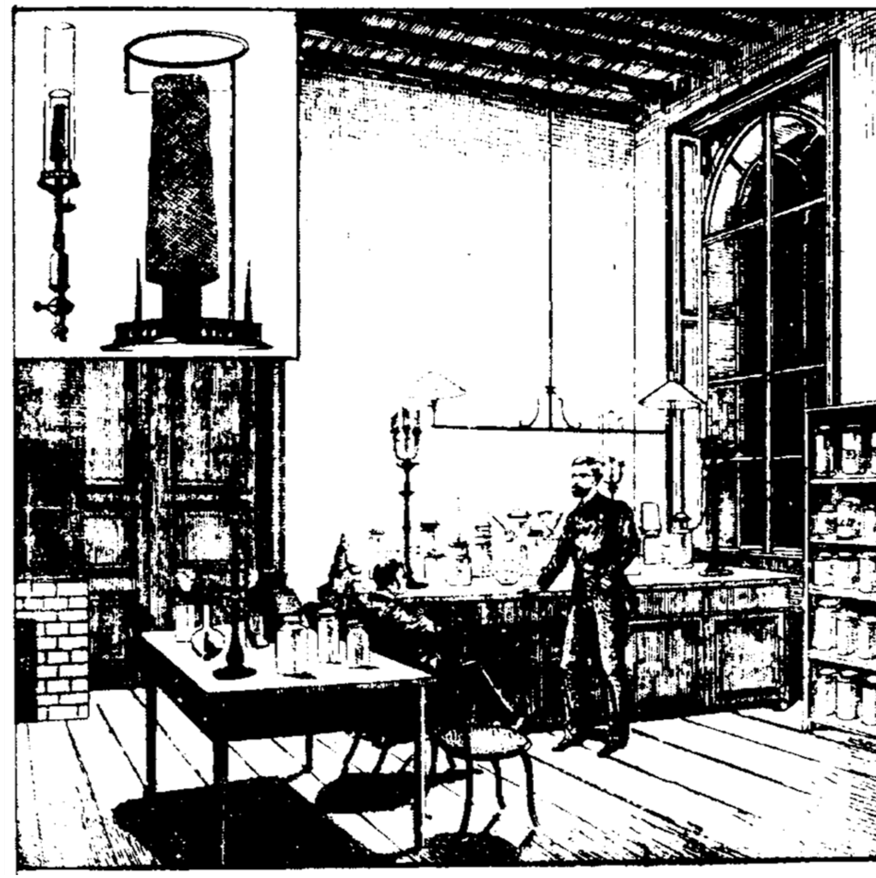
James
ACS

- 1879 – Lars Fredrik Nilson (1840-1899) isolates scandium (after Scandinavia), Per Theodore Cleve (1840-1905) isolates holmium (after Stockholm) and thulium (after Thule, scandinavian for The Most Northerly Land) and Paul Emile François Lecoq de Boisbaudran (1838-1912) isolates samarium (after Samarskite, mineral found in Norway)
- 1880 – Marignac isolated gadolinium (after Johan Gadolin)
- 1885 – Karl Auer Freiherr von Welsbach (1858-1929) separates 'didymium' into praseodymium (green twin, due to its green salts) and neodymium (new twin)
- 1886 – de Boisbaudran isolates dysprosium (greek: dusprositos, hard to get)
- 1901 – Eugéne-Anatole Demarçay (1852-1904) isolates europium (after Europe, after Europa, mortal wife of Greek god Zeus)
- 1907 – Georges Urbain (1872-1938), von Welsbach and Charles James (1880-1928) independently isolate lutetium (after Lutetia, ancient Roman name for Paris)
- 1947 – Jacob A. Marinsky, Lawrence E. Glendenin and Charles D. Coryell isolate promethium (after Prometheus, Greek of of fire and creator of mortals)

FIRST USES OF LANTHANIDES

- Welsbach gas mantles (~1880s)
  - Auer von Welsbach worked in Bunsen's laboratory in Heidelberg and observed that the Bunsen burner flame was increased by the effect of the lanthanides and their oxides
  - 30% thorium oxide, 30% zirconium oxide, 40% lanthanum oxide (cerium oxide also mentioned in patent) initially
  - 99% thorium oxide, 1% cerium oxide after (directly from monazite)
- Ferrocerium (70% cerium, 30% iron)
  - Lighter flints

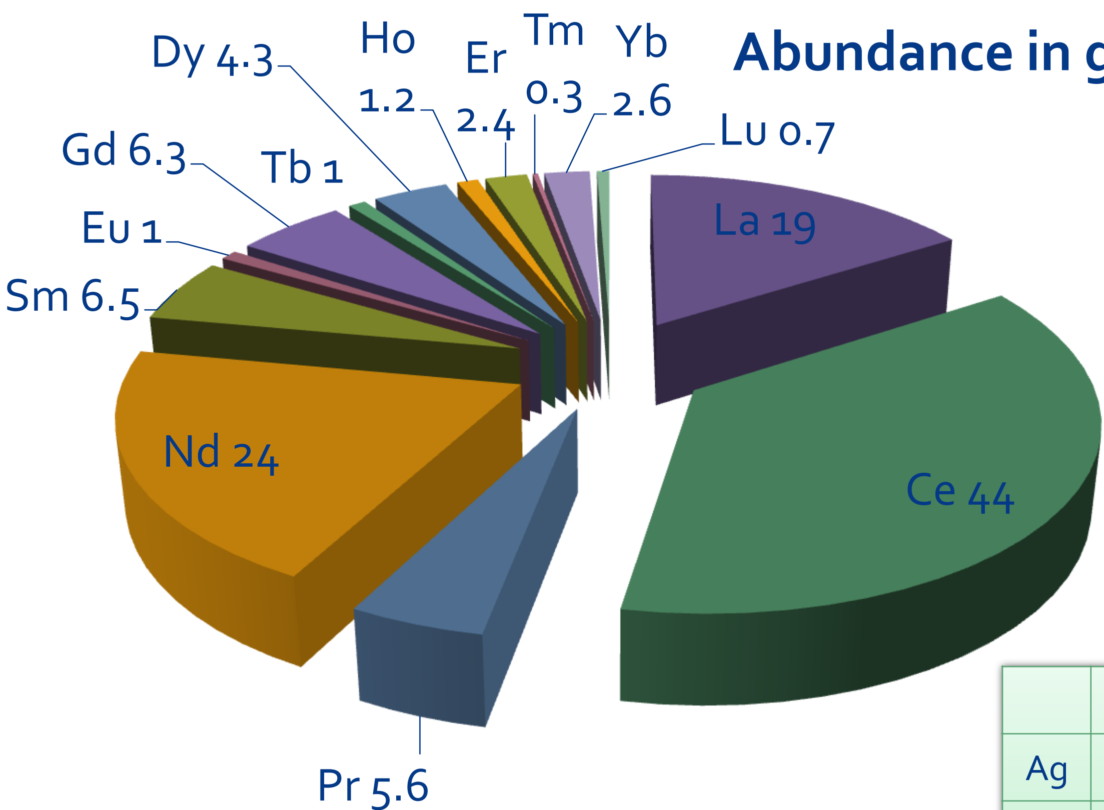
Der Erfinder des „Gasglühlichtes" in seinem Laboratorium.



ABUNDANCE OF LANTHANIDES

	Nat. ab. [g/ton]	Terr. ab. [ppm]
La	19	18
Ce	44	46
Pr	5.6	5.5
Nd	24	24
Sm	6.5	6.5
Eu	1.0	1.0
Gd	6.3	6.4
Tb	1.0	0.9
Dy	4.3	4.5
Ho	1.2	1.2
Er	2.4	2.5
Tm	0.3	0.2
Yb	2.6	2.7
Lu	0.7	0.8

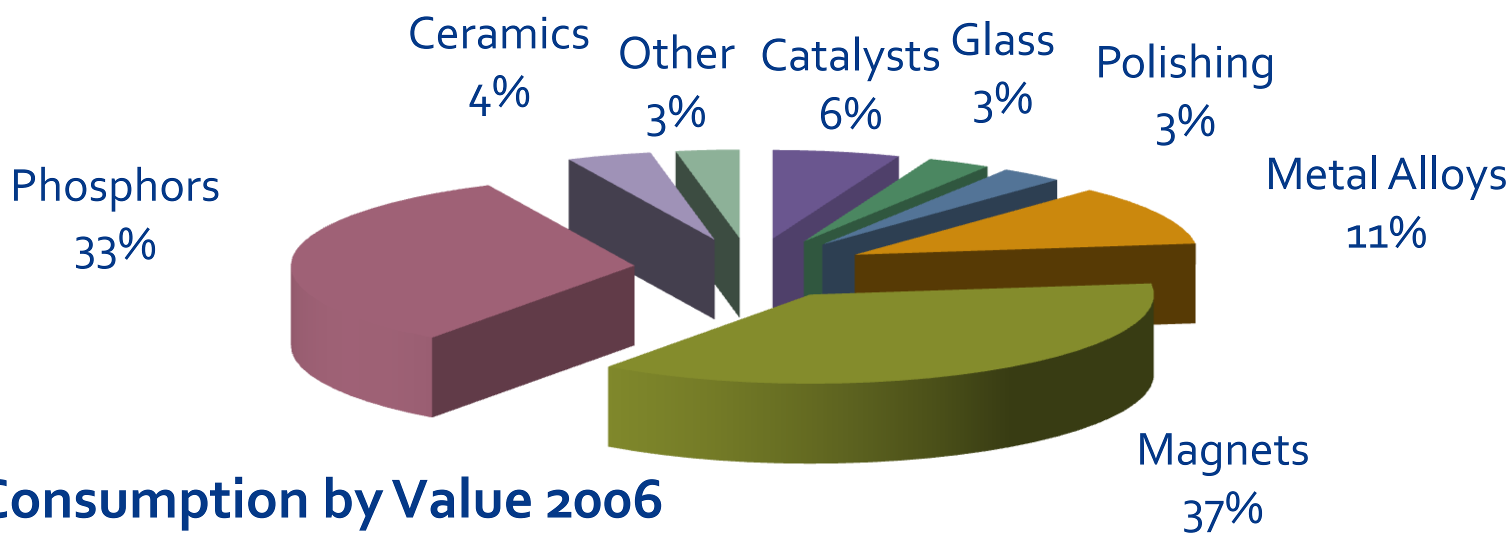
Abundance in g/ton



	[ppm]
Ag	0.07
Pt	0.01
Au	0.004
Ir	0.001

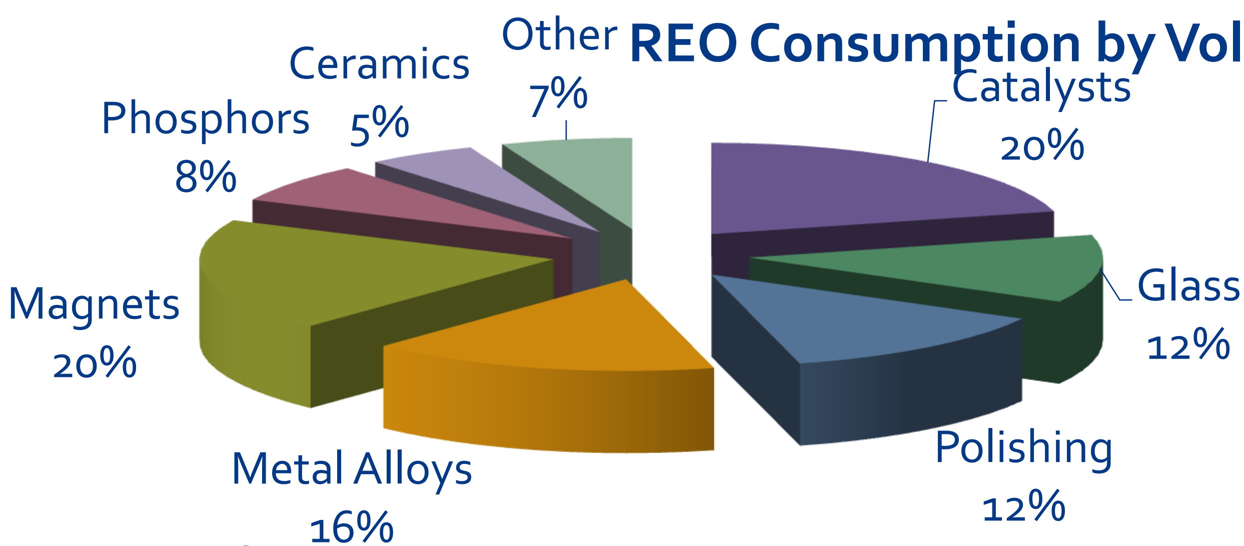
V.M. Goldschmidt, J. Chem. Soc. 655, 1937.
Murty, Gupta in: Sci. & Technol. Rare Earth Materials, Academic Press 1980.
U.S. Geological Survey 2001.

2006 REO CONSUMPTION



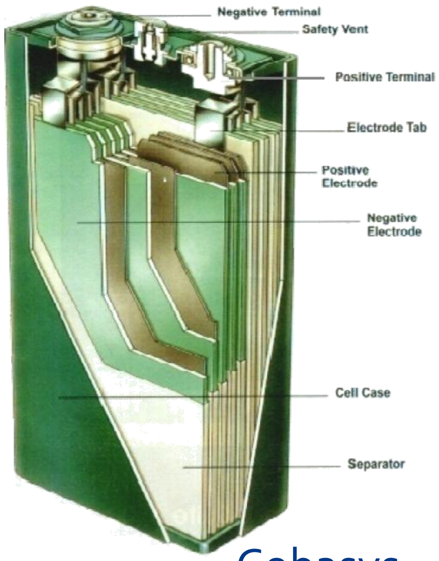
REO Consumption by Value 2006

REO Consumption by Volume 2006



BATTERIES FOR HYBRID VEHICLES

- Toyota committed to produce 1M hybrid vehicles in 2010, considering 2M
- Assume global total of 3M hybrids in 2012
- Typically a NiMH battery for a hybrid vehicle contains 10-12kg rare earths
- If NiMH batteries achieve a 60-70% market share, as a result, additional demand could be 20,000t REO p.a.



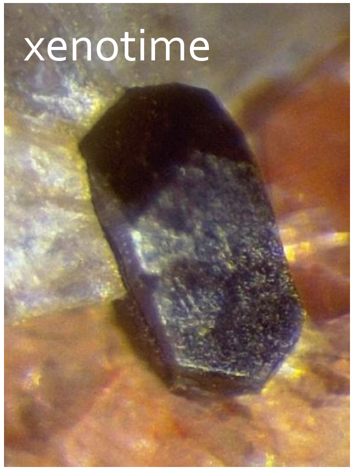
Cobasys

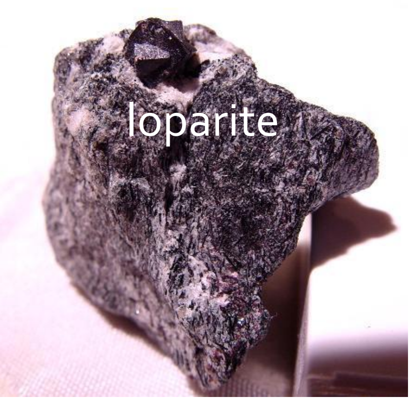
NdFeB MAGNETS

- Demand for rare earth magnet alloys
  - 1990 2,500 tpa
  - 2000 12,000 tpa
  - 2006 22,000 tpa
- 2003/06 growth in demand was 15-25%pa
- Demand for rare earth magnets for voice coils (iPods), for drives of equipment in vehicles and for electronic equipment remains high.
- At current rates of growth, total demand for Nd_2O_3 could be 55,000 tpa in 2012, but price and supply considerations mean it is more likely to be 45-50,000 tpa.

MAJOR ORES

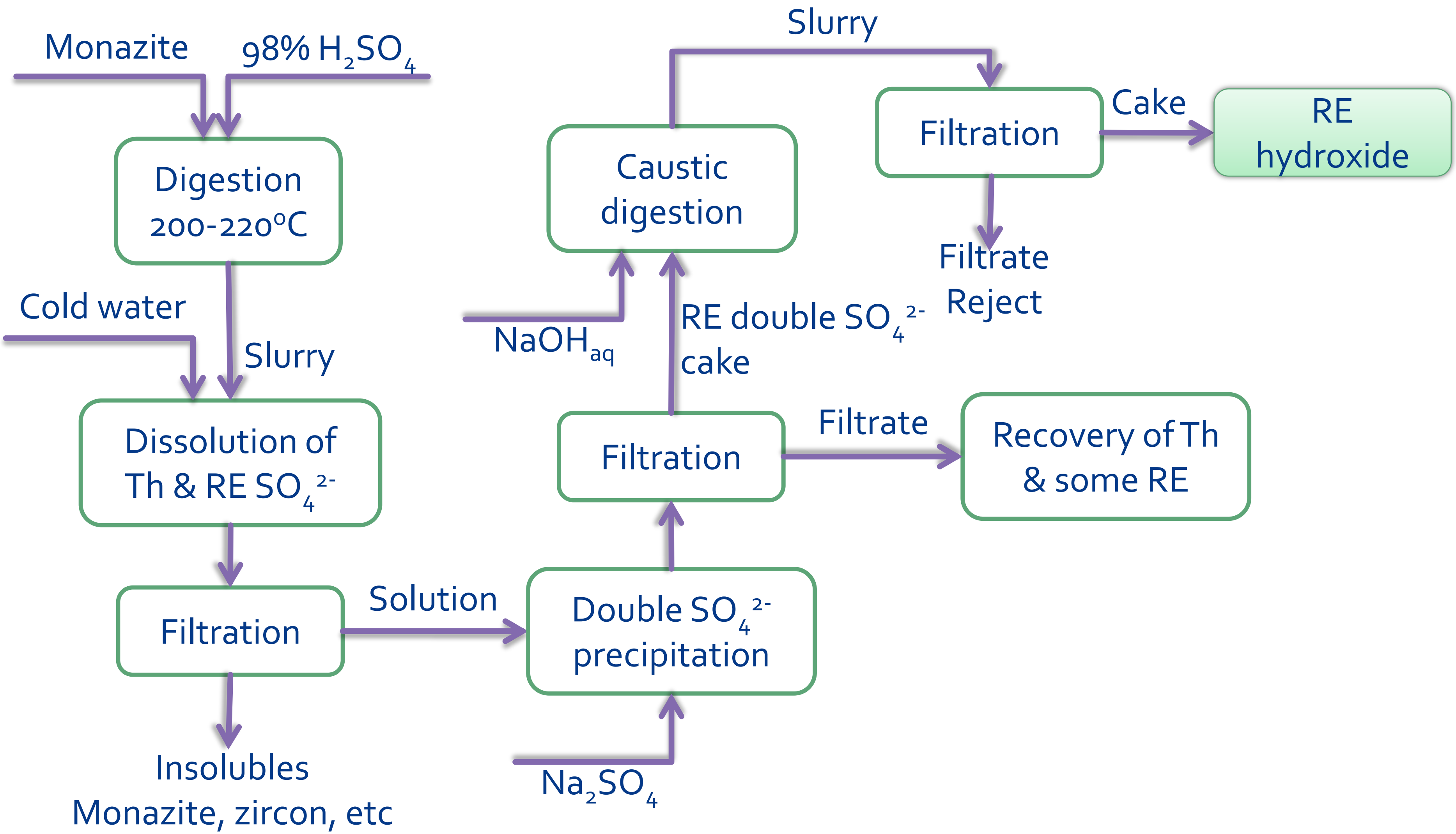
- Bastnasite
  - $(Y,Ce)(CO_3)F$
  - 60% REO
- Monazite
  - $(Ce,La,Y,Th)PO_4$
  - 55-65% REO
- Xenotime
  - YPO_4
  - Concentrated to 40% REO
- Loparite
  - Nb-perovskite
  - Titanate of Ca, Na, Ce with 30% REO
- Iron ore RE
  - RE adsorbed on Fe-Mn ores





webmineral.com

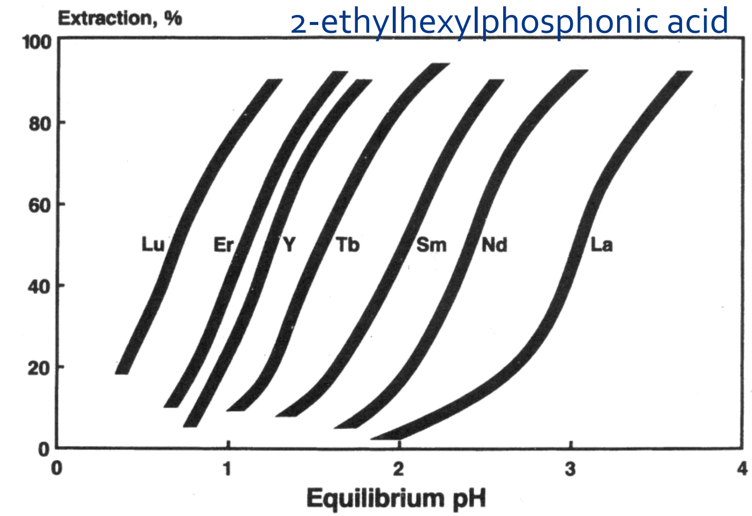
H_2SO_4 PROCESS FOR MONAZITE/RE EXTRACTION



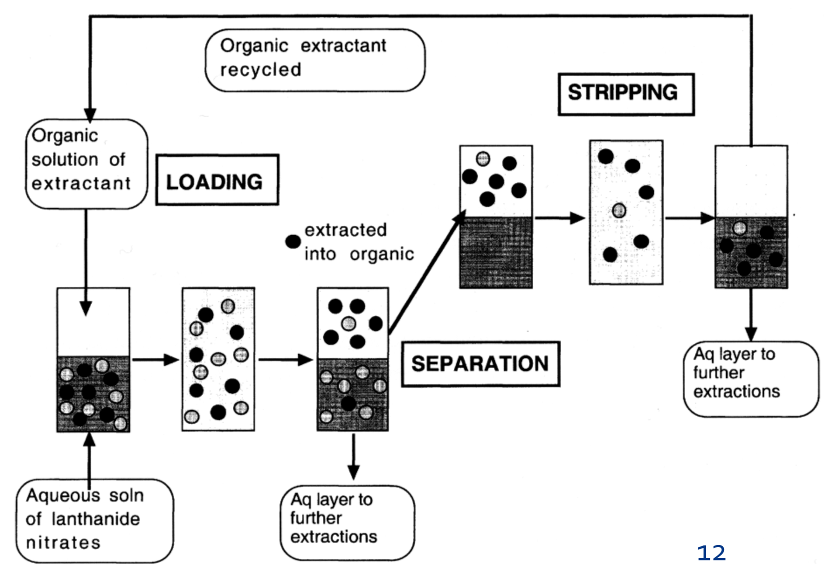
Murty, Gupta in: Sci. & Technol. Rare Earth Materials, Academic Press, 1980.

SEPARATION OF THE INDIVIDUAL Ln

- Fractional crystallization
  - Exploits small differences in solubility
    - Double nitrates, double sulfates, double carbonates, double oxalates
- Fractional precipitation
  - Exploits basicity and solubility differences of hydroxides
    - Double alkali sulfate precipitation
    - Homogeneous precipitation
- Solvent extraction
  - Exploits different complexation abilities with TBP
    - TBP and 14 M HNO_3



2-ethylhexylphosphonic acid



ION EXCHANGE SEPARATION OF Ln

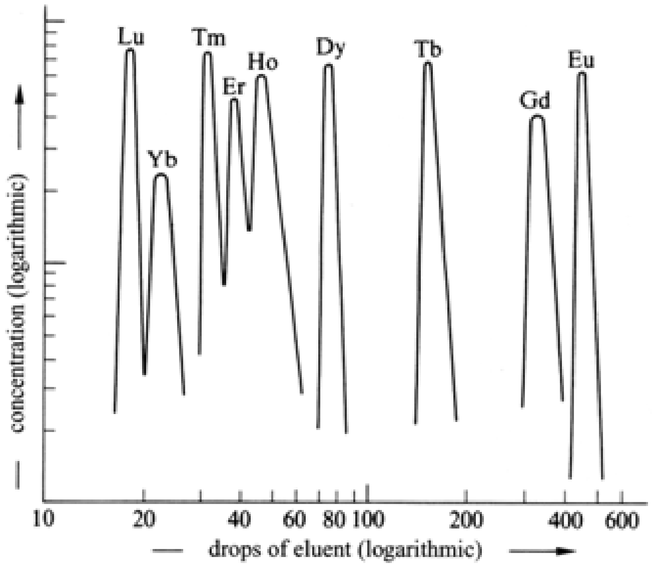


TABLE 1.20
Separation factors for Dowex 1 with 90% MeOH–10% (1 M HNO_3) [10].

Pair	α_z^{z+1}	Pair	α_z^{z+1}	Pair	α_z^{z+1}
Lu–Yb	1.0	Dy–Tb	1.1	Pm–Nd	2.6
Yb–Tm	1.0	Tb–Gd	1.3	Nd–Pr	2.2
Tm–Er	1.0	Gd–Eu	1.6	Pr–Ce	1.7
Er–Ho	1.0	Eu–Sm	1.9	Ce–La	1.7
Ho–Dy	1.0	Sm–Pm	2.3		

TABLE 1.21
Averaged values of individual separation factors for adjacent pairs of lanthanons being eluted with EDTA and its homologues (calculated from 9 sets of stability constant data) [10].

Pair	α_z^{z+1}	Pair	α_z^{z+1}	Pair	α_z^{z+1}
Lu–Yb	1.6	Gd–Eu	1.1	Dy–Y	1.6
Yb–Tm	1.8	Eu–Sm	1.5	Y–Tb	1.5
Tm–Er	2.0	Sm–Pm	(1.8)		
Er–Ho	2.0	Pm–Nd	1.9		
Ho–Dy	2.0	Nd–Pr	2.0		
Dy–Tb	2.7	Pr–Ce	2.4		
Tb–Gd	3.5	Ce–La	3.3		

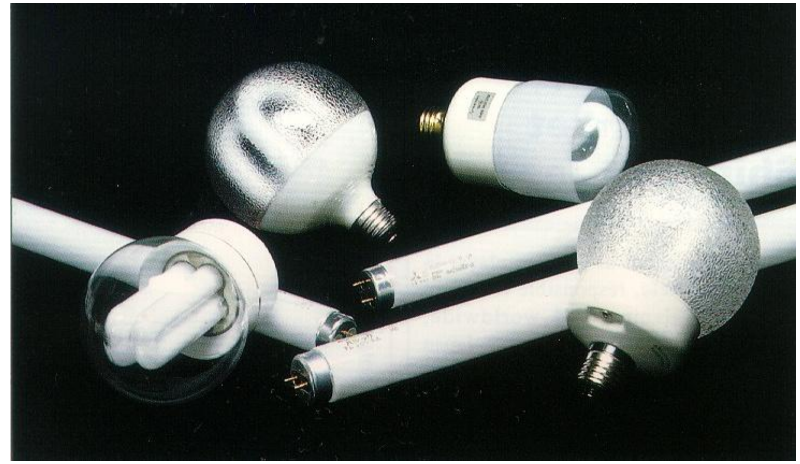
J.E. Powell, in Handbook of Physics and Chemistry of Rare Earths, Ch. 22, Vol 3.

Holleman, Wiberg

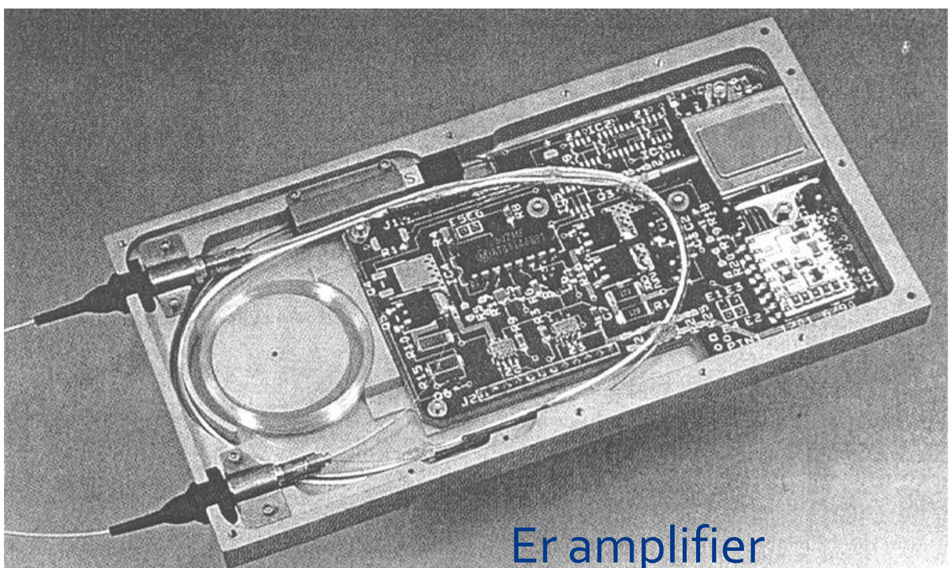
MAJOR APPLICATIONS OF RARE EARTHS

- **Catalysts**
  - Cracking of hydrocarbons
  - Conversion of exhaust gases (gasoline and diesel)
- **Metallurgy**
  - Steel production (removal of O, S)
  - Nodular graphite
  - Hardeners (e.g. in magnesium)
- **Materials**
  - High temperature superconducting ceramics
  - Magnets
  - Neutron moderators in nuclear reactors
  - Hydrogen storage in metal hydrides
- **Science**
  - Shift reagents, luminescent and magnetic probes
  - Catalysts in organic synthesis
- **Optics and lighting**
  - Polishing powders
  - Sun protection (sunglasses)
  - Lasers, particularly NdYAG
  - Phosphors for displays
  - CRT monitors
  - Fluorescent lamps
  - Pigments
  - Optical fiber amplifiers
- **Medicine**
  - Seasickness (Ce oxalate), thromboses (Nd oxalate)
  - X-ray intensifying screens
  - NMR imaging (MRI)
  - Cancer radiotherapy and phototherapy
  - Laser surgery (NdYAG)
  - Luminescent immunoassays

APPLICATIONS I



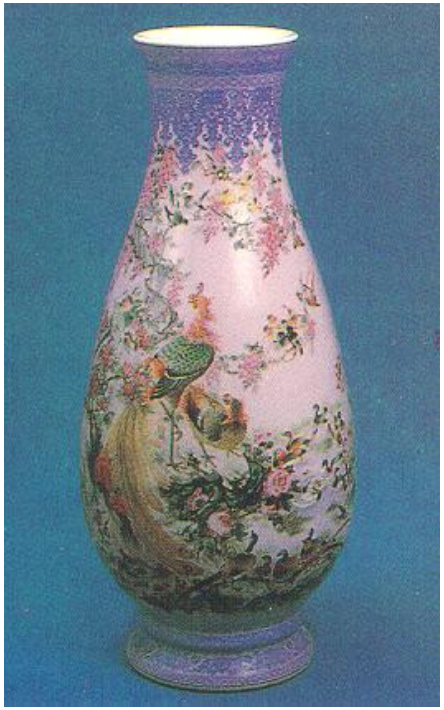
fluorescent lamps



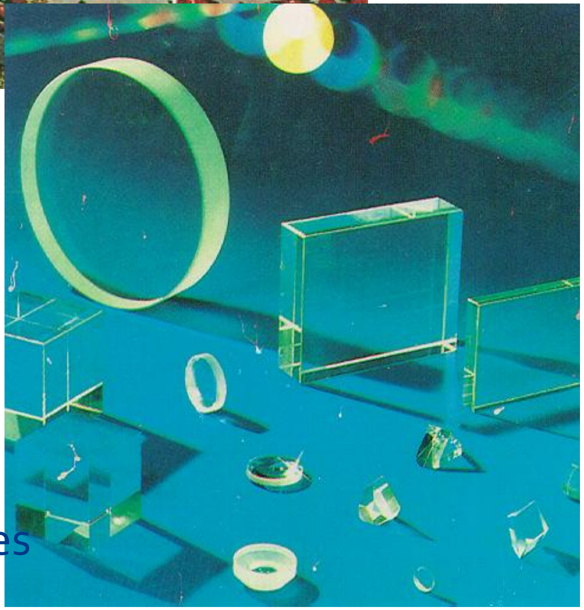
Er amplifier
for optical fibers

rechargeable batteries

APPLICATIONS II

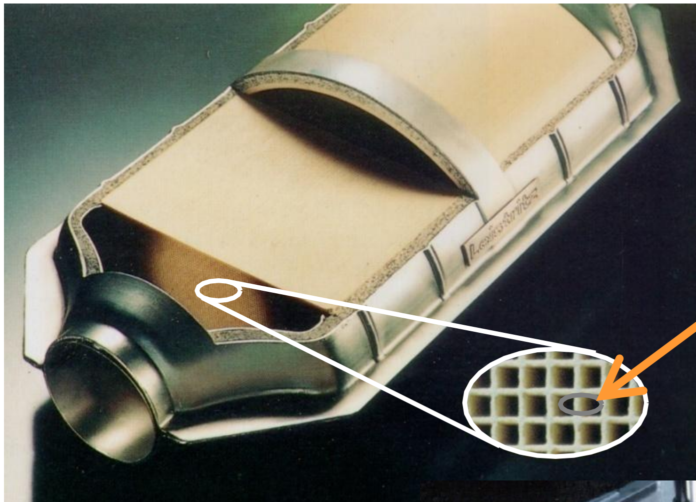


pigments

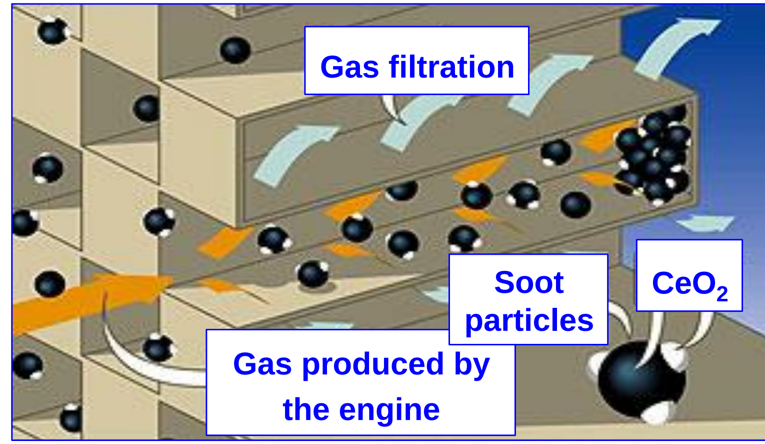


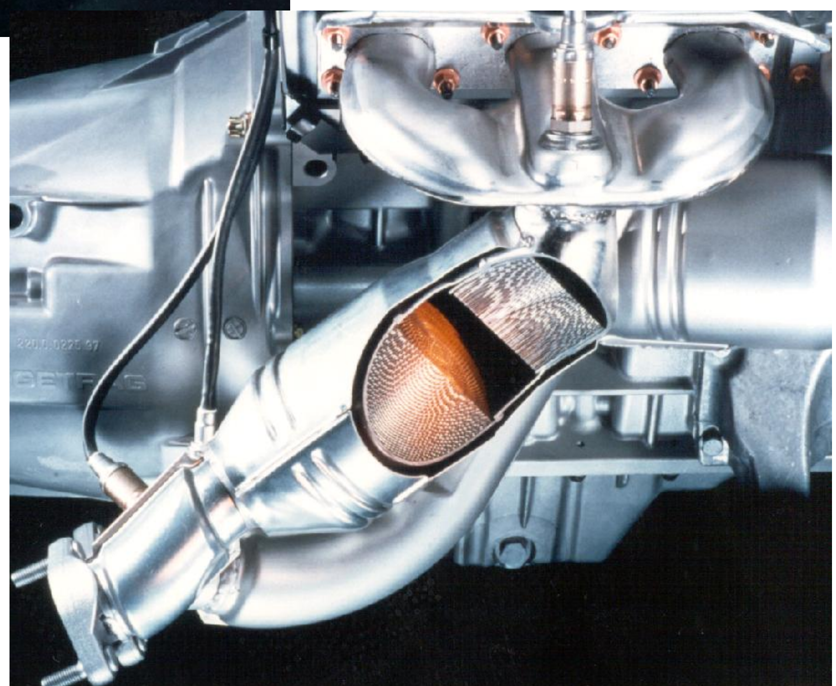
Optical glasses

APPLICATIONS III



CeO_2

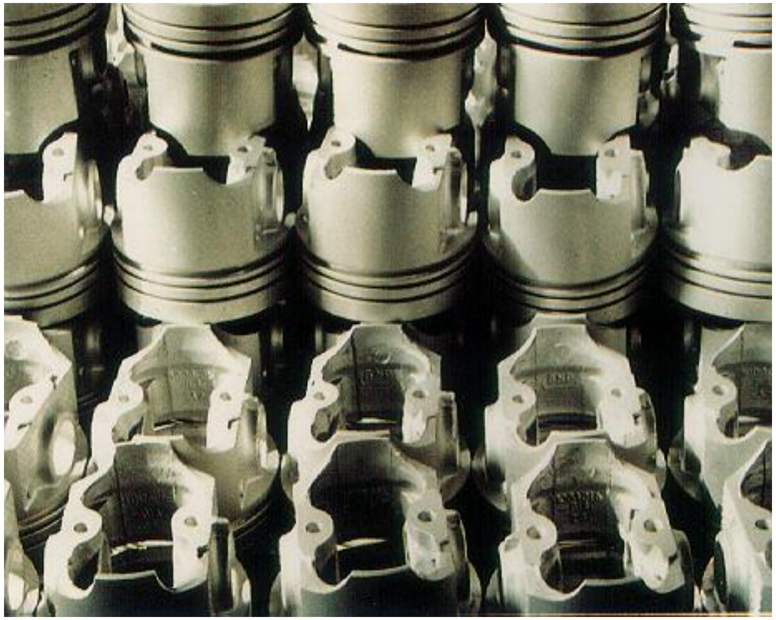




EOLYS®
Soot emission of Diesel engines reduced by 99.9 %

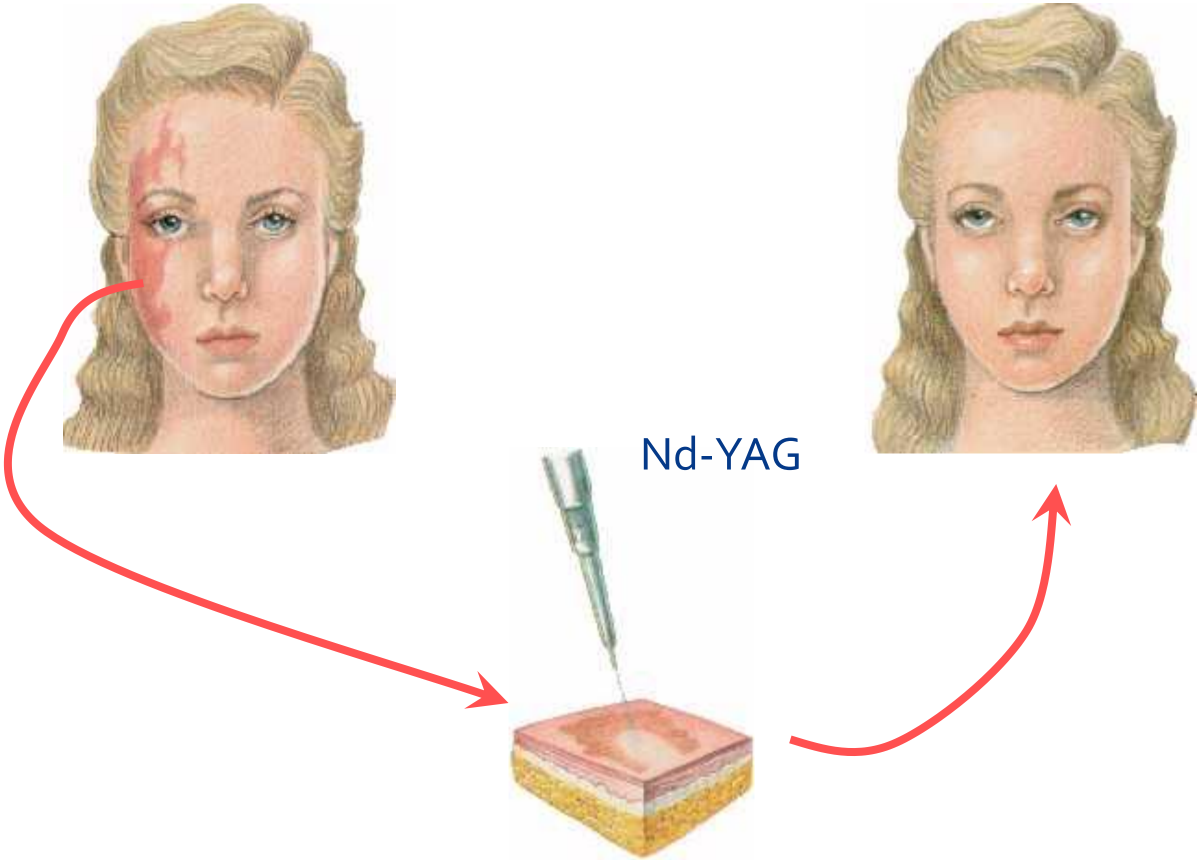
APPLICATIONS IV

crank-shafts



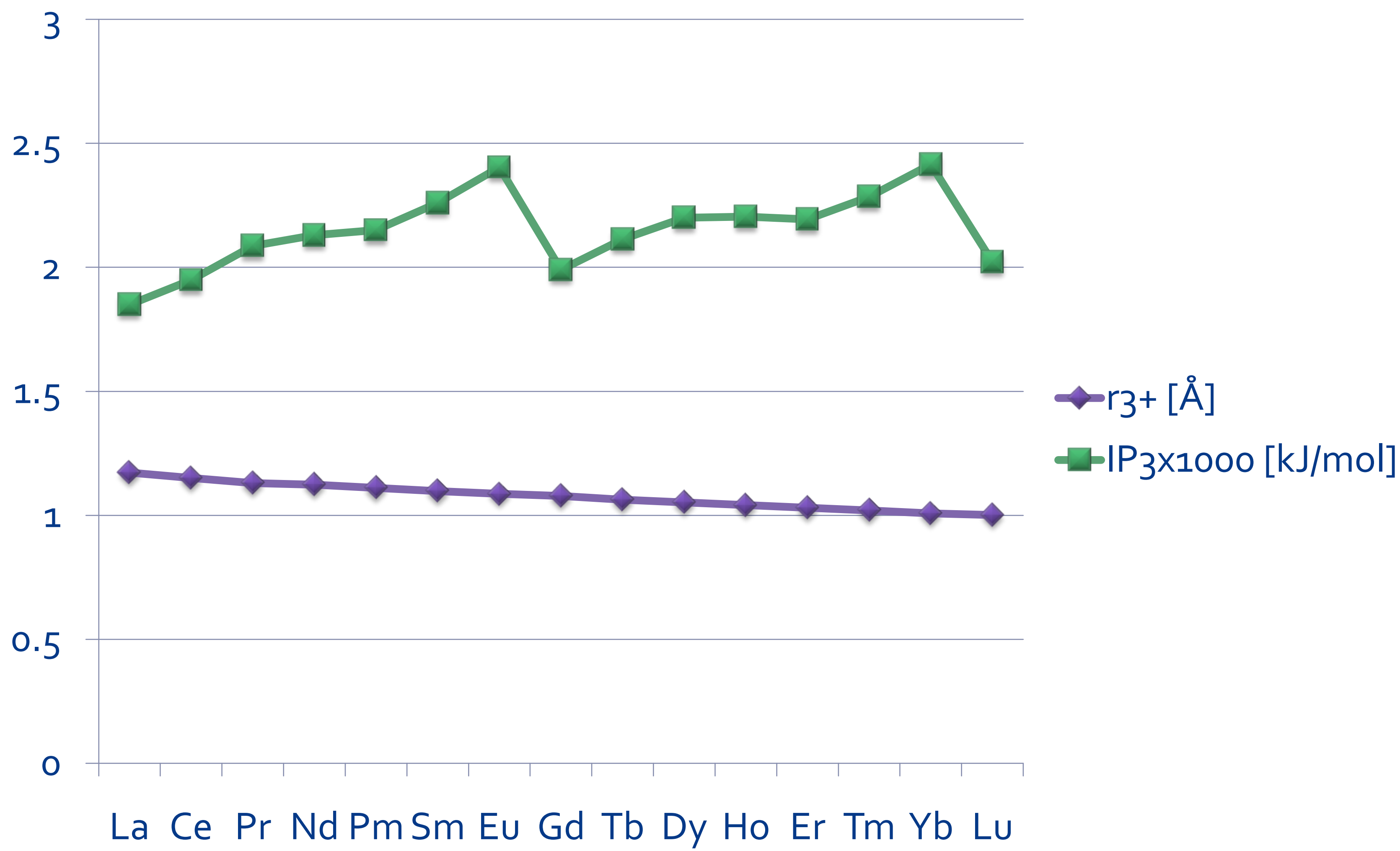
cast aluminum pistons reinforced by rare-earth metals

MEDICAL APPLICATIONS



MRI images

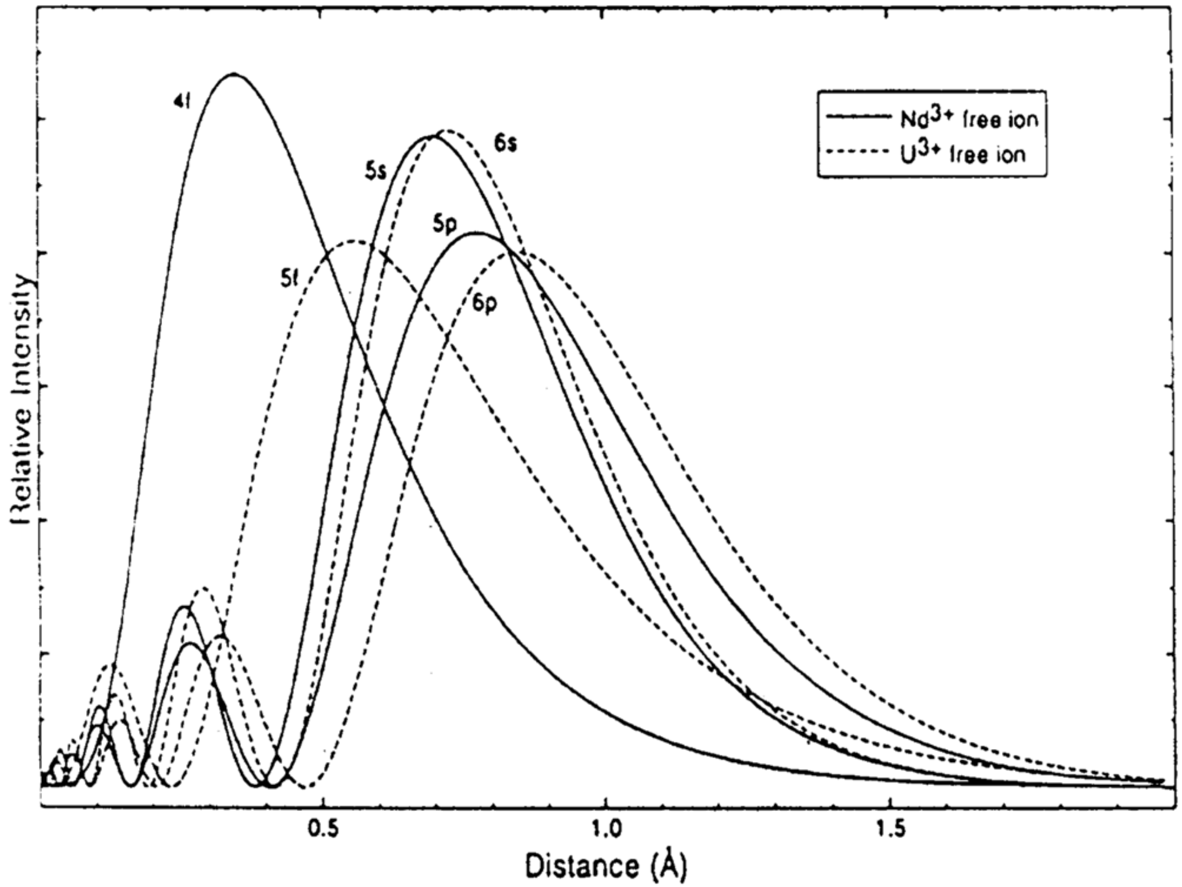
IONIC RADIUS ♦ AND 3RD IONIZATION POTENTIAL ■



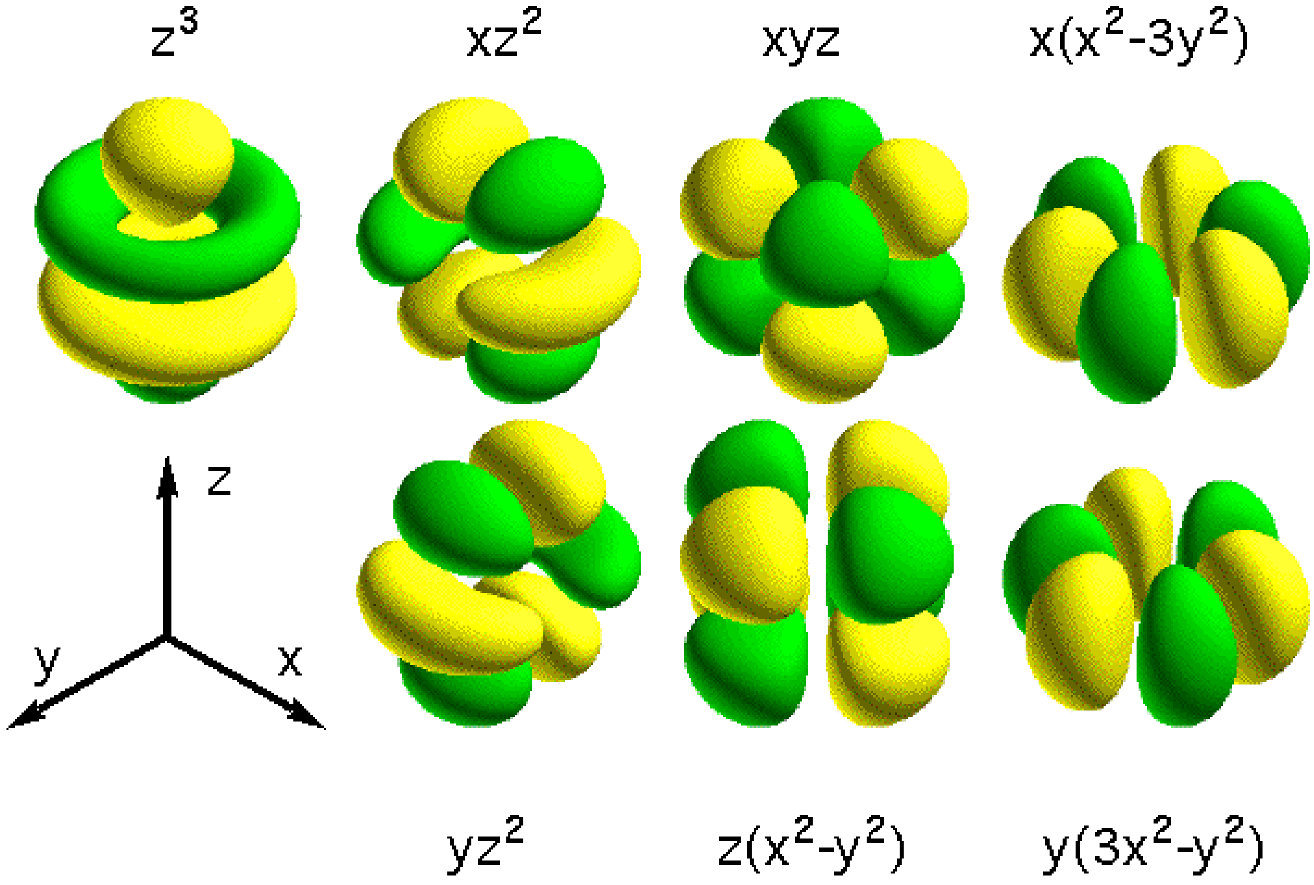
RADIAL PROBABILITY FUNCTION Nd^{3+}, U^{3+}

Relativity

- *s* and *p* contraction
- *d* and *f* expansion



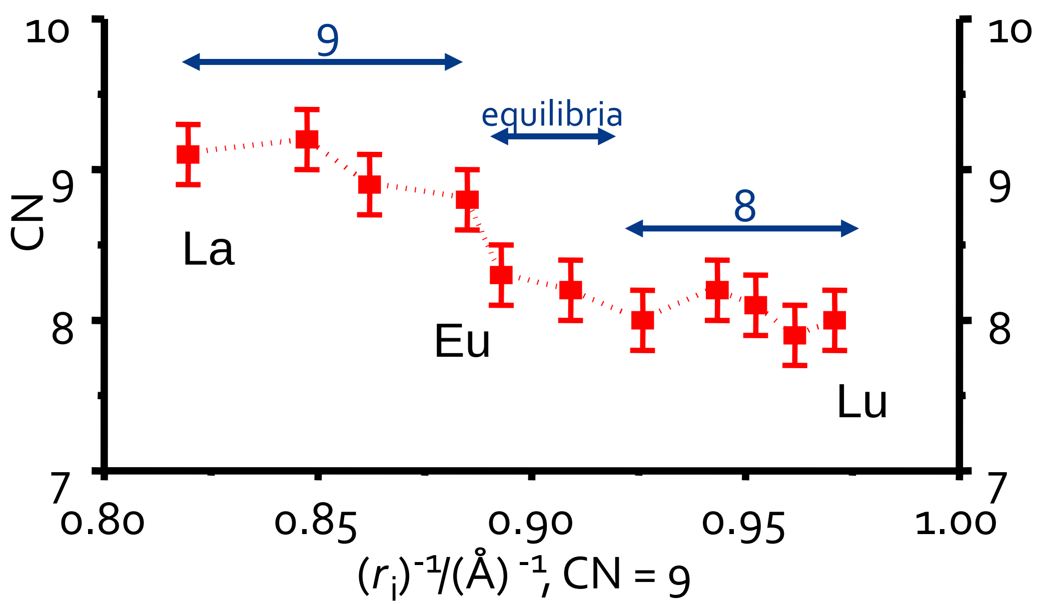
GENERAL SET OF 4f ORBITALS

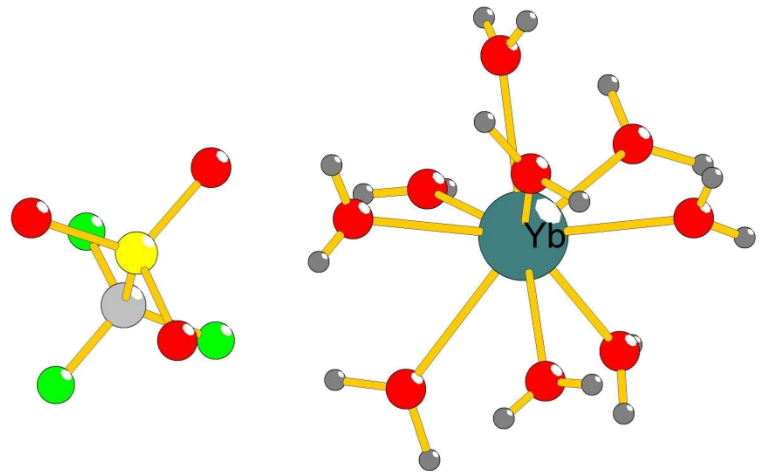


D. L. Cooper
University of Liverpool

COORDINATION NUMBERS WITH WATER

- Solid state, CN = 9 from La-Lu (X-ray structures of bromates and ethylsulfates)
- Solution, CN=8 or 9?
  Change along the series or not?
- Kinetic studies, optical data, NMR data, X-ray and neutron diffraction data





Chem.-Eur.J. (2005), 11, 4065.

Rizkalla & Choppin, Handbook on the Physics and Chemistry of Rare Earths, Vol. 15, Ch. 103 (1991).

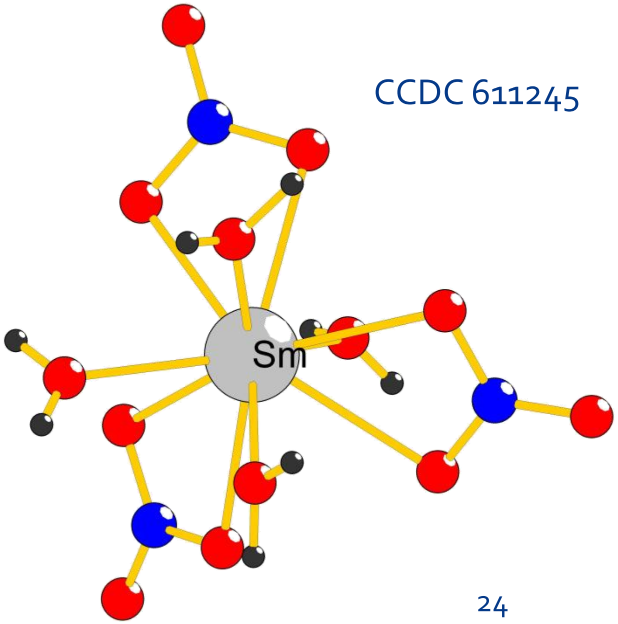
COORDINATION OF SIMPLE ANIONS

- Displacement of coordinated H_2O necessary
- Due to high ΔH_{hydr} difficult – entropy important
- Mechanism
  - Outer sphere complex turns into
  - Inner sphere complex if ligand capable of displacing water

$Ln(NO_3)_3(H_2O)_5$ Ln=La,Ce CN=11
$Ln(NO_3)_3(H_2O)_4$ Ln=Pr-Yb CN=10

$Ln(H_2O)_7(\mu\text{-}X)_2Ln(H_2O)_7$ X=Cl,Br Ln=La,Ce
$[LnCl_2(H_2O)_6]$ Ln=Nd-Lu

Inner sphere complexes: F^-, (Cl^-), ClO_4^-, SO_4^{2-}, OAc^-, (NO_3^-)
Outer sphere complexes: (Cl^-), Br^-, I^-, IO_3^-, ClO_3^-, (NO_3^-)



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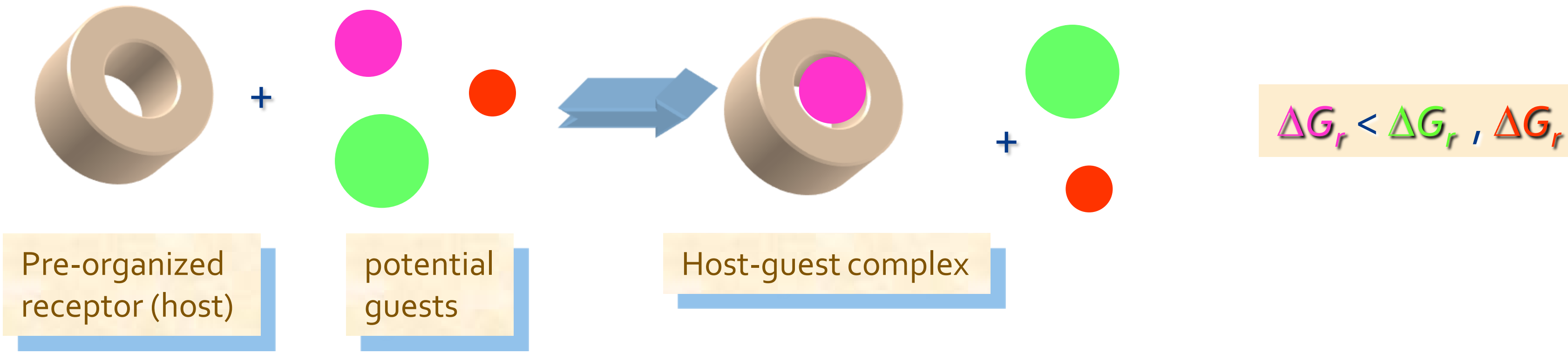
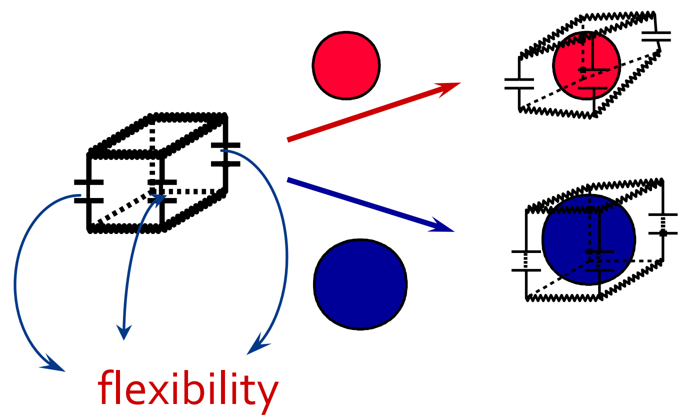
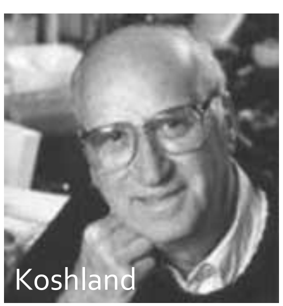
MACROCYCLIC COORDINATION CHEMISTRY OF Ln

- Lock and key principle (E. Fischer, 1894)



- Induced fit concept (Koshland, 1958)
  - Finer recognition
  - Classes of ligands
    - Large flexible macrocycles
    - Macrocycles with pendant arms

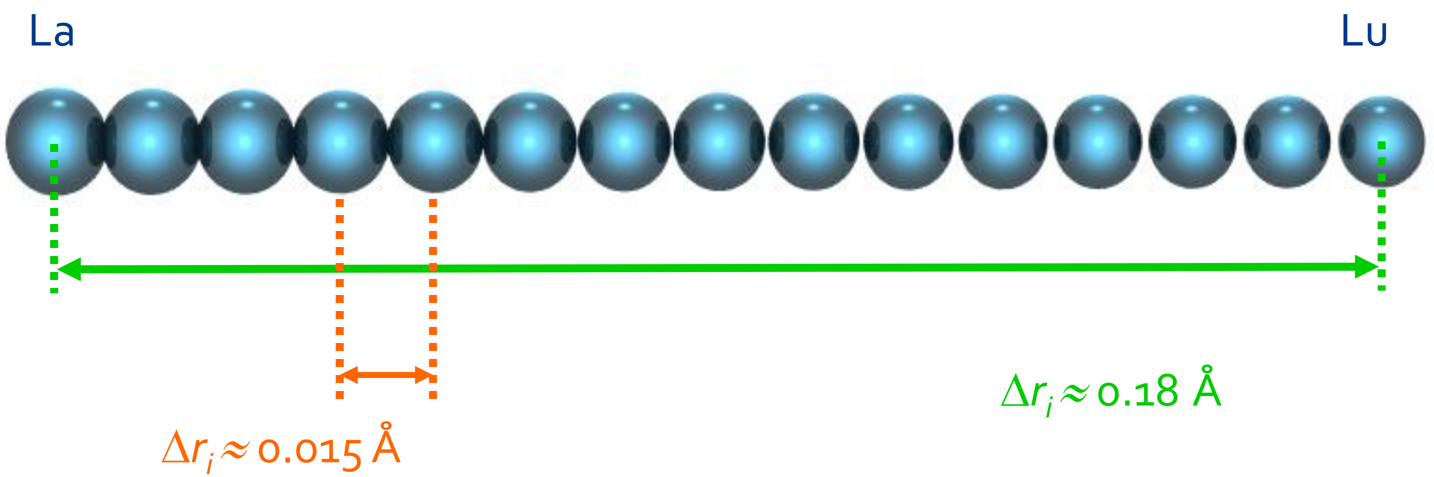




Chem. Soc. Rev. 1999, 28, 347-358.

LOCK AND KEY PRINCIPLE IN 4f COMPLEXES

Principle is difficult to use because Ln(III) are spherical, hard ions with similar properties



Small differences in hardness and size

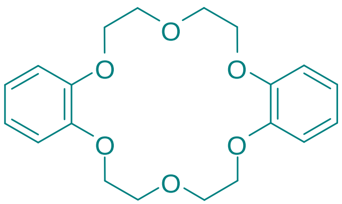
Difficult to match large coordination numbers (8-12)

<u>Receptor design:</u>

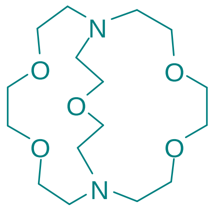
- Steric complementarity
- Interaction matching (HSAB principle)
- Maximizing number of interaction sites
- Maximizing bond strength

MACROCYCLIC COMPLEXES AND NATURAL IONOPHORES

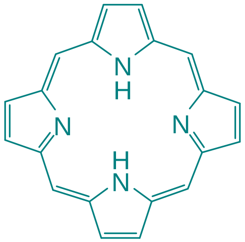
- Ionophores - substances with ability to transfer ion from aqueous phase into hydrophobic phase
- Essential components of transport of alkali cations though biological membranes



$B_2$18C6

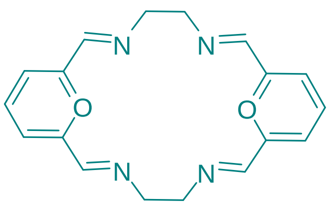


[2.2.1]

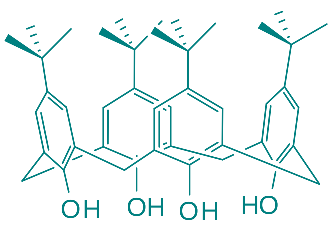


porphyrin

nonactin



[2+2]



calix[4]arene

Hugo Schiff (1915)
Angew. Chem. Int. Ed. 2008, 47, 1016-1020.

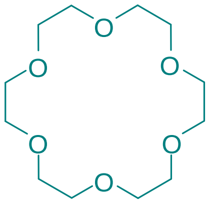
C.J. Pedersen

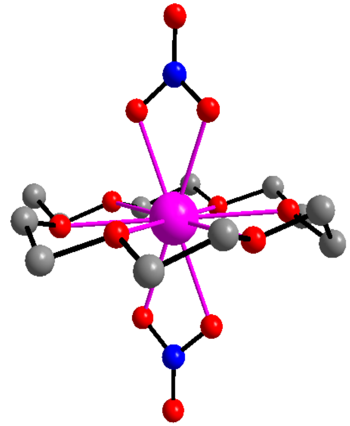
J.-M. Lehn

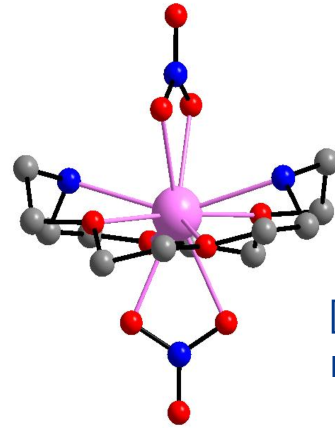
Nobel Prize 1987

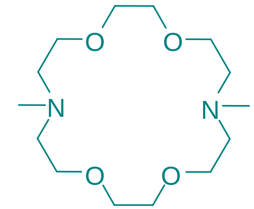
$[Nd(NO_3)_2(18C6)]^+$

Inorg. Chim. Acta 1981, 54, L43.



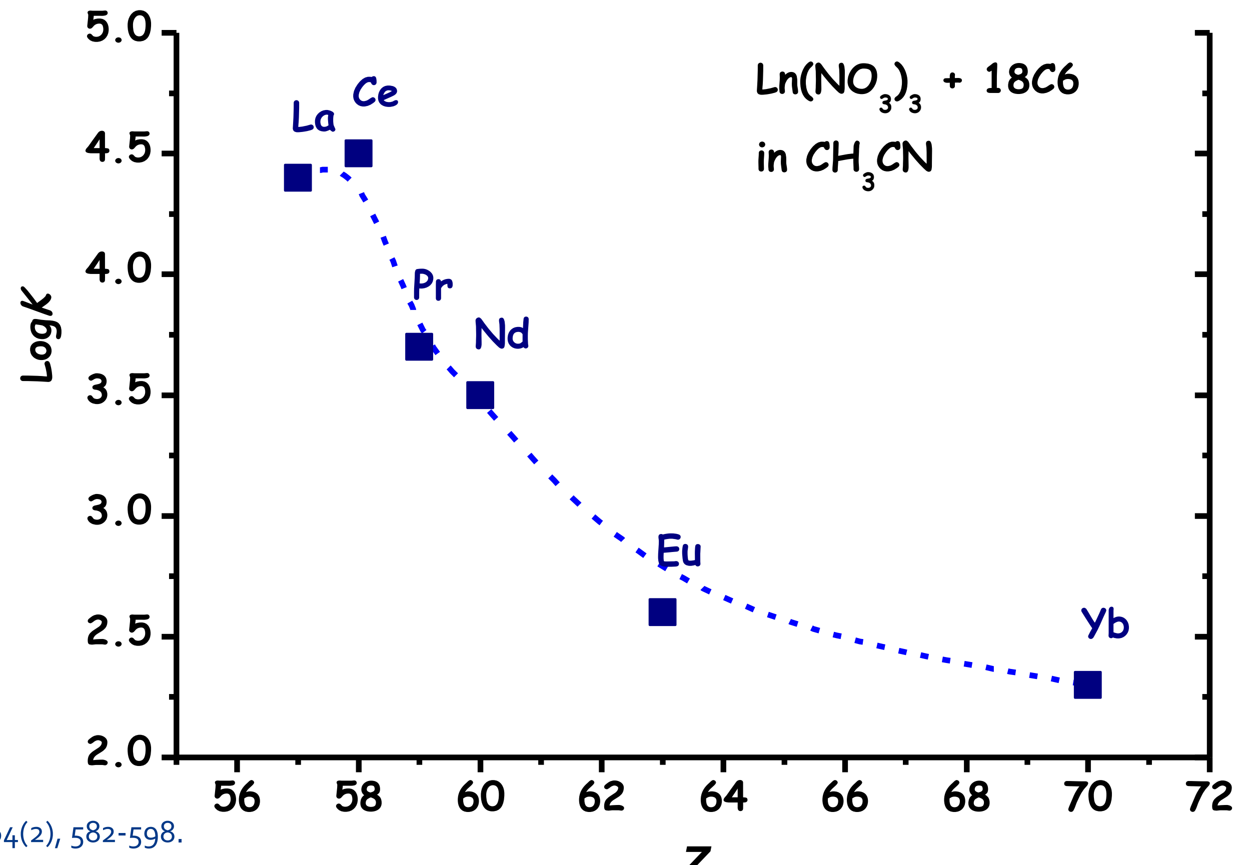






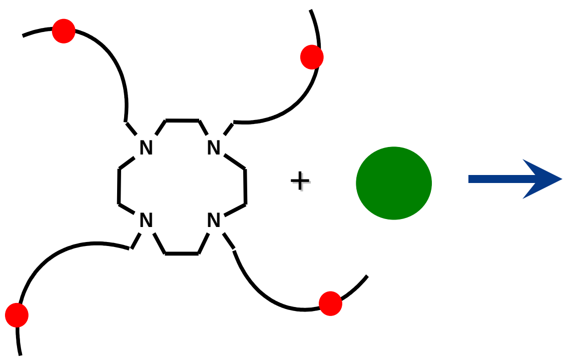
$[Eu(NO_3)_2Me_2(2.2)]^+$

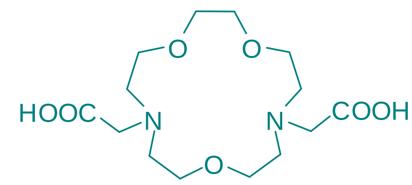
Inorg. Chem. 1988, 27(20), 3518 – 3526.



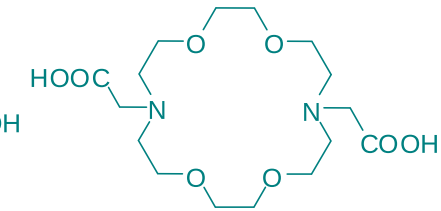
Helv. Chim. Acta 1981, 64(2), 582-598.

LIGANDS WITH PENDANT ARMS

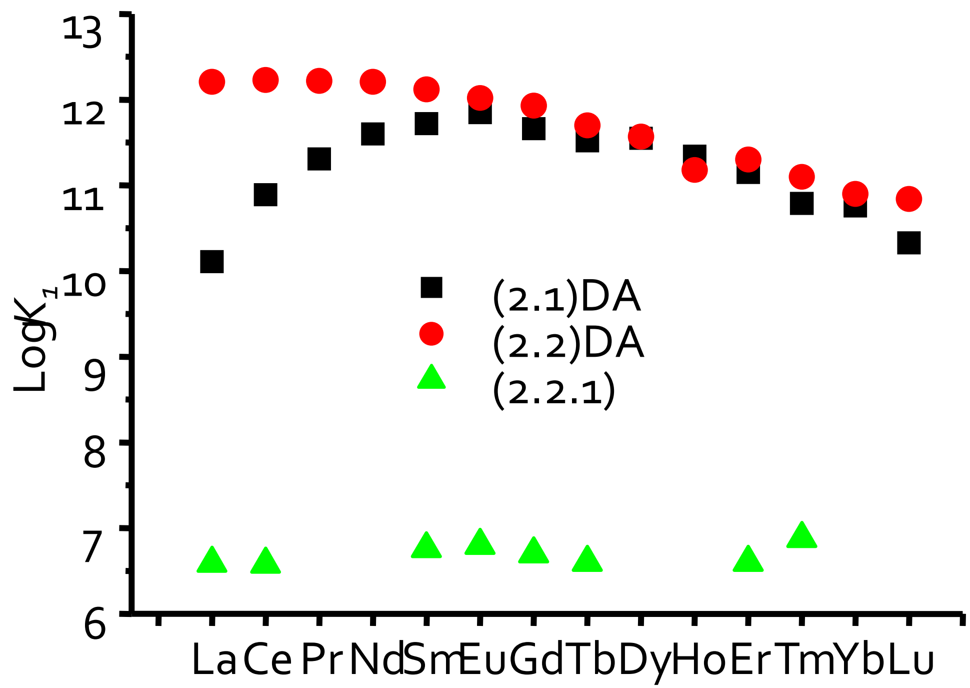




(2.1)DA

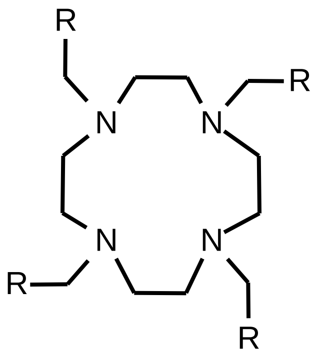


(2.2)DA



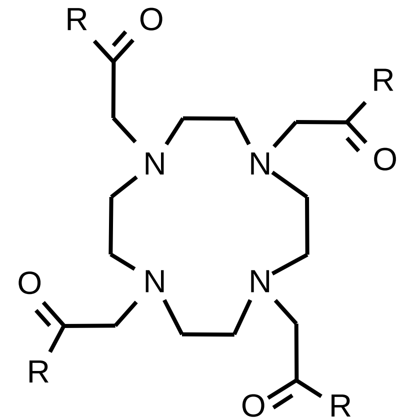
Inorg. Chem. 1986, 25, 355-8; Inorg. Chem. 1983, 22, 3866-9; Inorg. Chem. 1981, 20, 616-9; Doklady Akademii Nauk SSSR, 1984, 278, 379-382.

CYCLEN DERIVATIVES

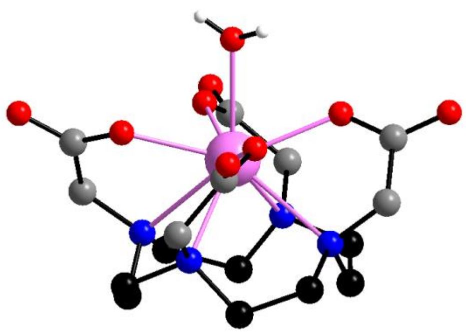


R = H	cyclen
R = CO_2H	H_4dota

H_4dota
Angew. Chem. 1976, 88, 760.

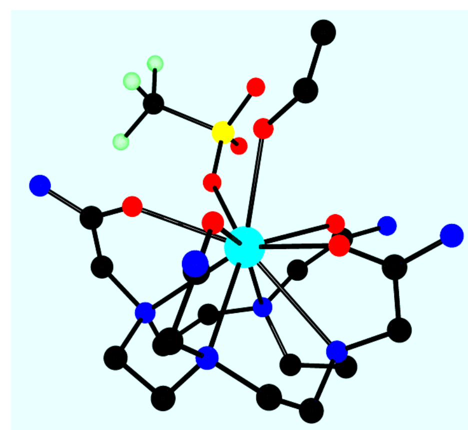


R = NHMe	dtma
NH_2	tcmc



Contrast agent, Guerbet SA 1988

$[Gd(dota)(H_2O)]^-$



$[La(OTf)(EtOH)(tcmc)]^{2+}$
Angew. Chem. Int. Ed. 1994, 33, 773.

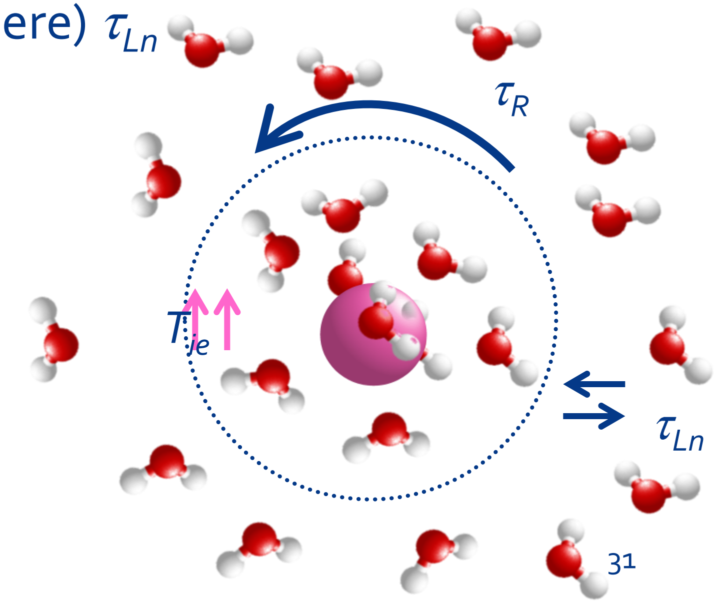
Cleavage of phosphodiester bridges in RNA

MRI WITH CONTRAST AGENTS

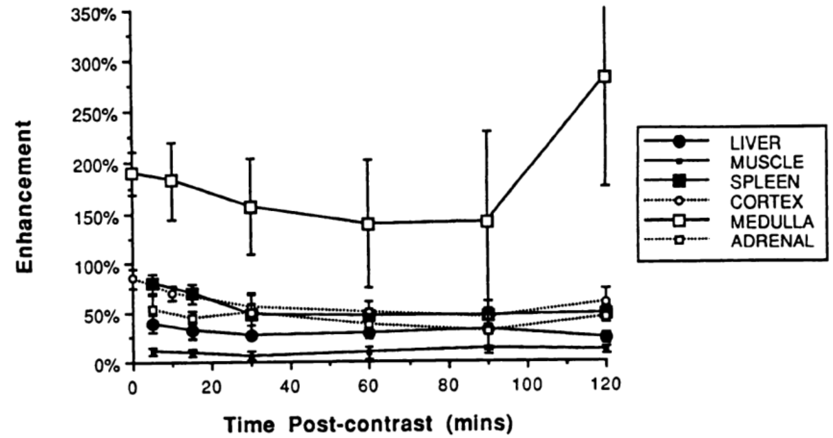
- Proton relaxation from water molecules is measured
- Water molecules outside cells in contact with (Gd-containing) contrast agent $\Rightarrow$ relaxation is faster (10^6-fold!) $\Rightarrow$ discrimination with respect to water molecules inside cell
- Relaxivity
  - effect of contrast agent
  - number of water molecules in coordination sphere q
  - water exchange rate (both inner and outer sphere) τ_{Ln}
  - rotational correlation time of the molecule τ_R
  - electron spin relaxation time T_{1e}

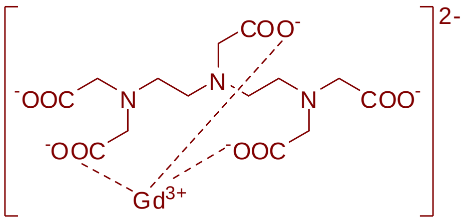
$[Gd(dota)]^-$:

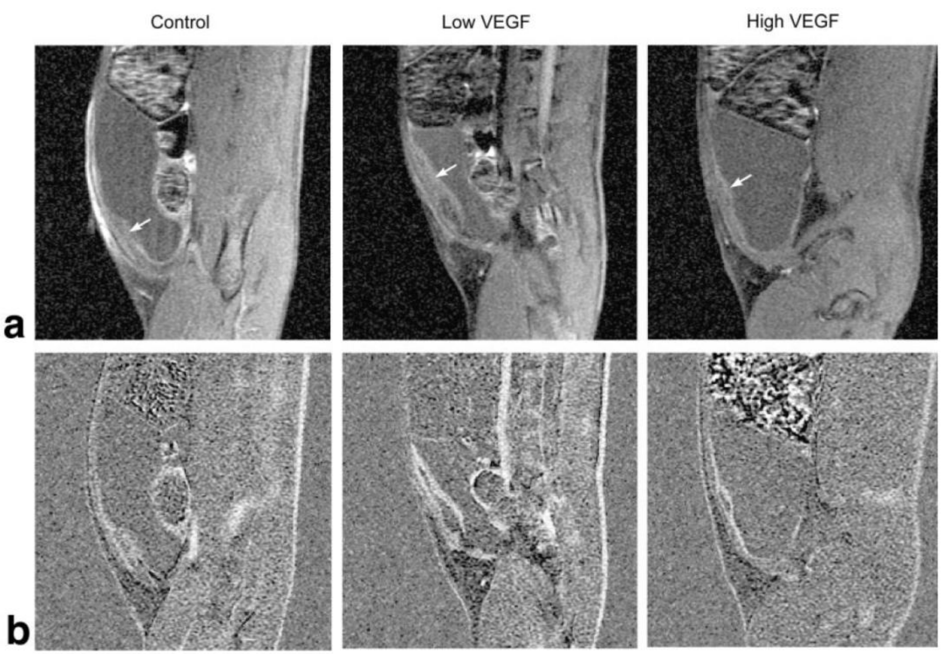
$\tau_{Ln} = 1/k_{Ln} = 244$ ns
$T_{1e} = 1$ ns
$\tau_R = 80$ ps

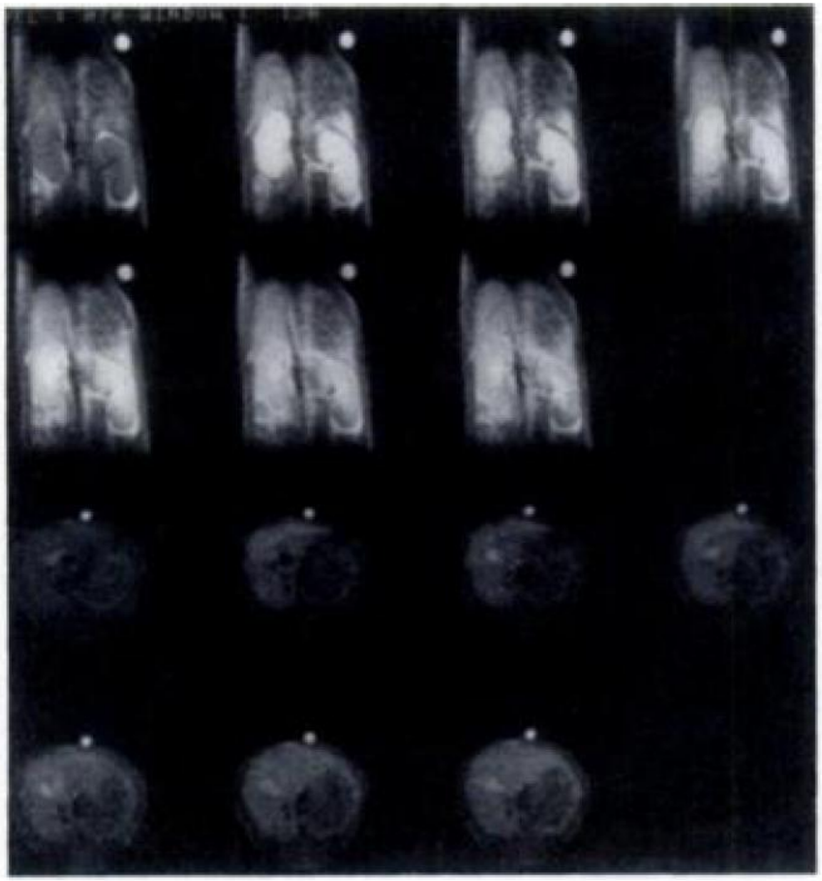


MRI EXAMPLES





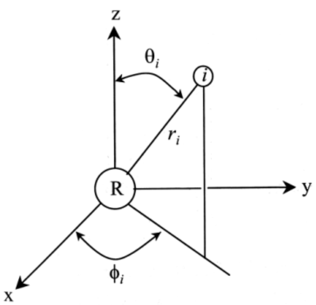


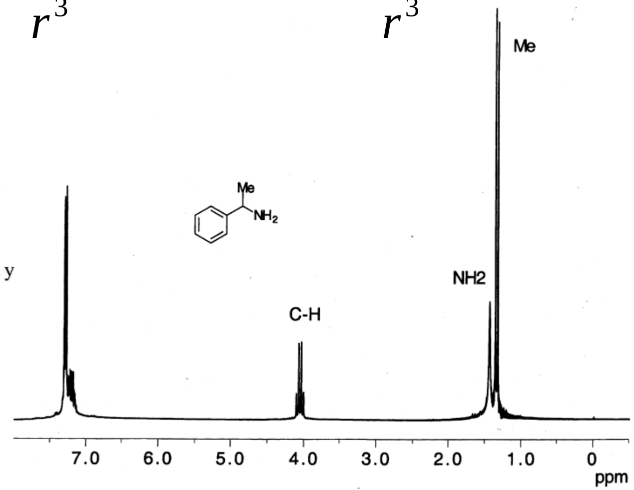


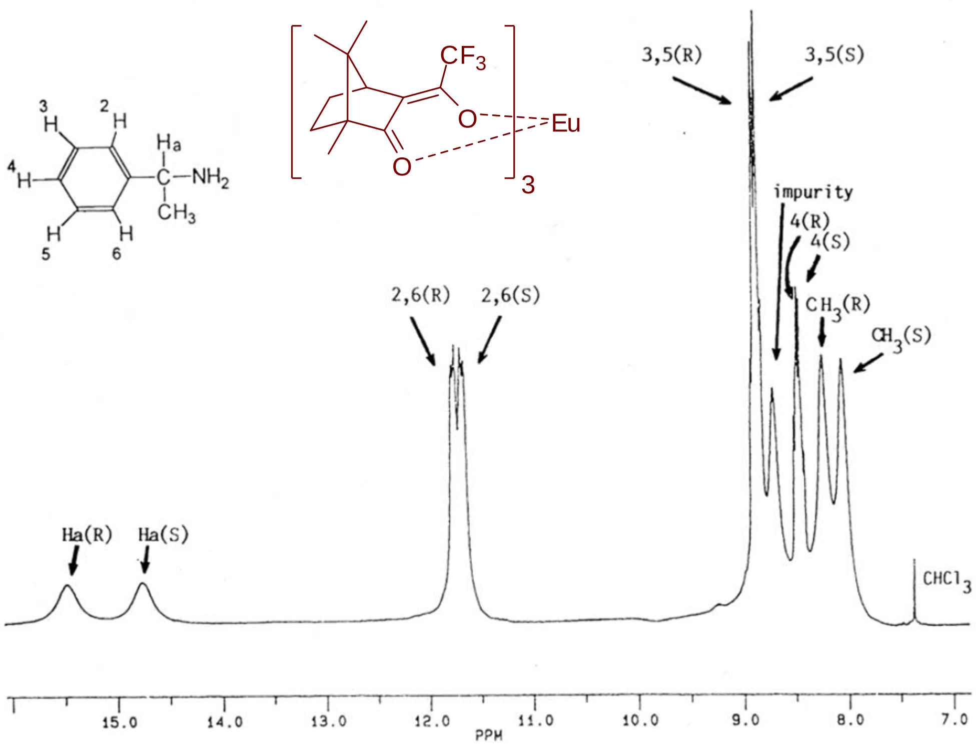
Wang *et al.*, *Radiology* **1990** *175*, 483-488.
Cheng *et al.*, *J. Magn. Res. Imag.* **2005** *21*, 415-423.

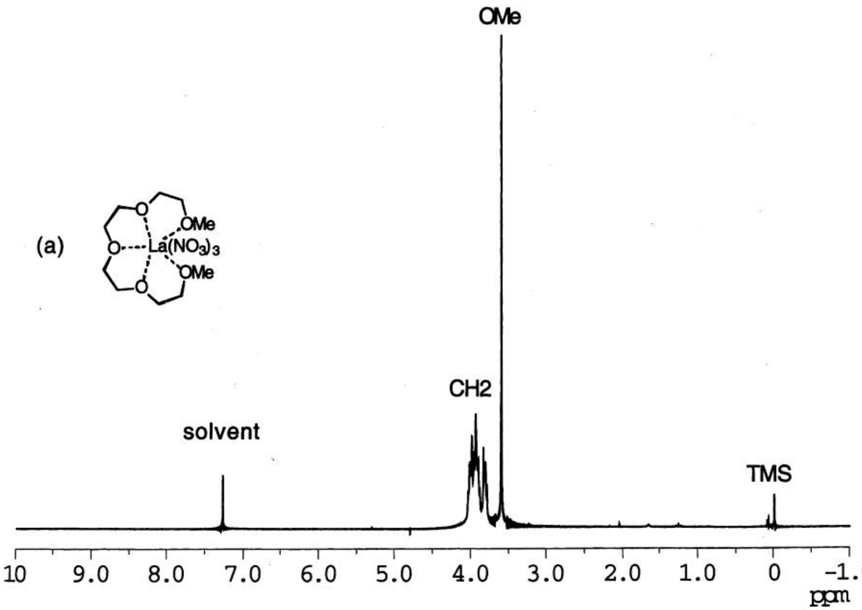
$$\Delta\nu = \frac{D_1(3\cos^2\theta - 1)}{r^3} + \frac{D_2 \sin 2\theta \cos 2\phi}{r^3}$$

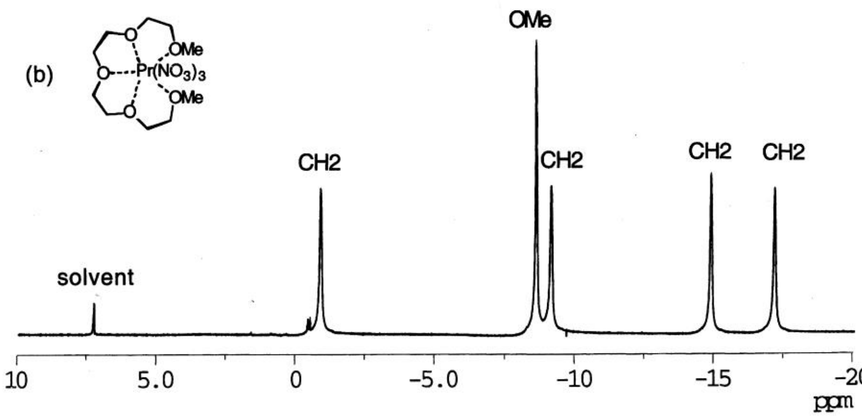
SHIFT REAGENTS



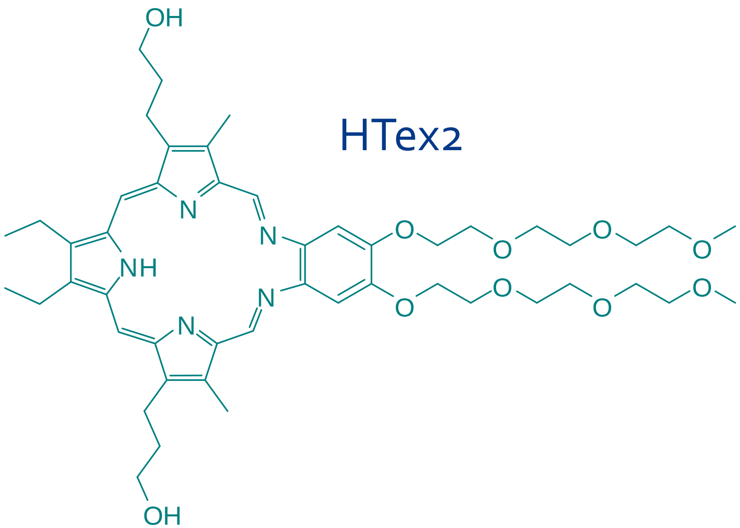




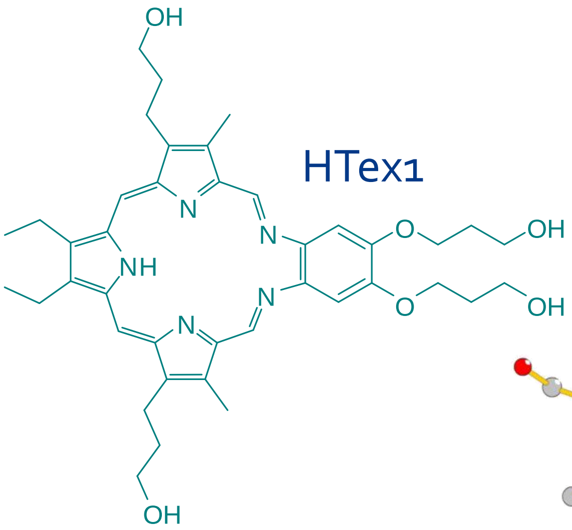




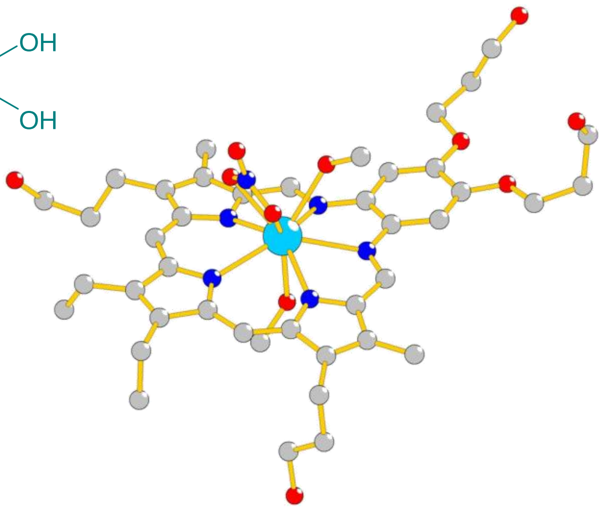
MEDICAL APPLICATIONS: TEXAPHYRINS



HTex2



HTex1



Inorg. Chem. 1993, 32, 3175.

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

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

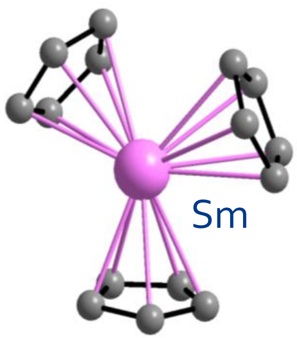
Prog. Inorg. Chem. 2001, 49, 551.
J. Magn. Res. Imag. 1995, 5, 725-9.
Int. J. Rad. Onc., Biol., Phys. 1999, 45, 981-9.
Photochem. Photobiol. 1996, 63, 892-897.

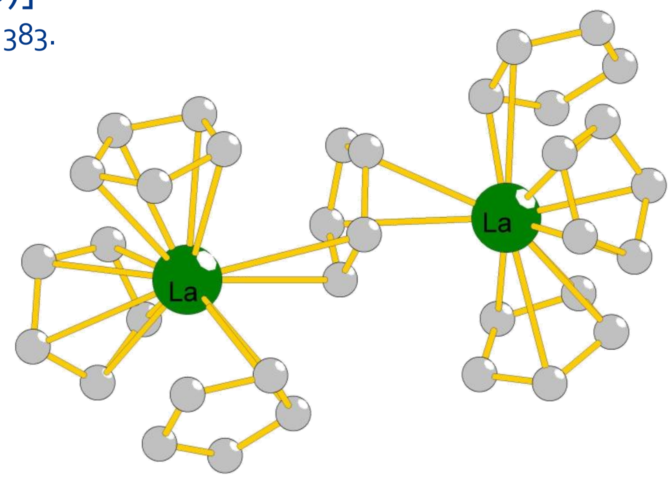
ORGANOMETALLICS – Cp DERIVATIVES

$LnCl_3$(anh) + 3 NaCp → [$Ln(Cp)_3$] + 3 NaCl (in thf)

J. Am. Chem. Soc. 1954, *76*, 6210.
Inorg.Chem. 1970, 9, 1091.

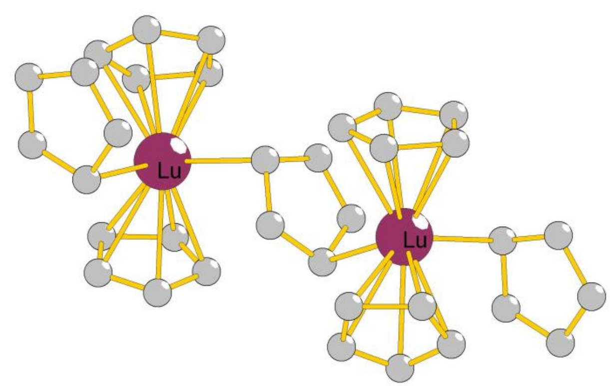
La-Pr "11-coordinate" [$Ln(\eta^5Cp)_2(\eta^2Cp)$]
La analog: Organometallics 1986, 5, 383.





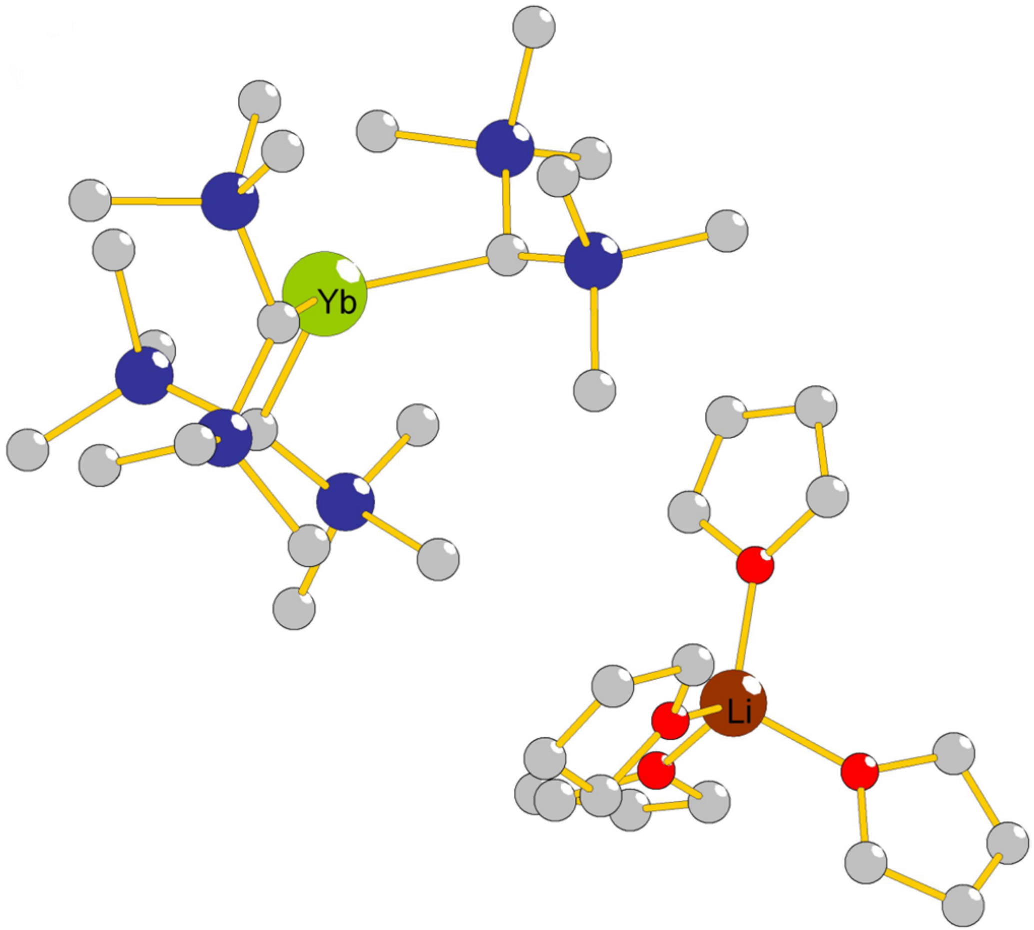
Y, Sm-Yb "9-coordinate" [$LnCp_3$]
Sm analog: Acta Cryst. B 1969, 25, 2580.

Sc, Lu "8-coordinate" [$Lu(\eta^5\text{-}Cp)_2(\eta^1\text{-}Cp)_2$
Lu analog: Angew. Chem. Int. Ed. 1986, 25, 656.



ALKYL DERIVATIVES (σ-BONDS)

$Li[CH(SiMe_3)_2] + YbI_2 \rightarrow [Li(THF)_4][Yb(\{CH(SiMe_3)_2\}_3]$ (in THF)



J. Organomet. Chem. 2002, 663, 263.