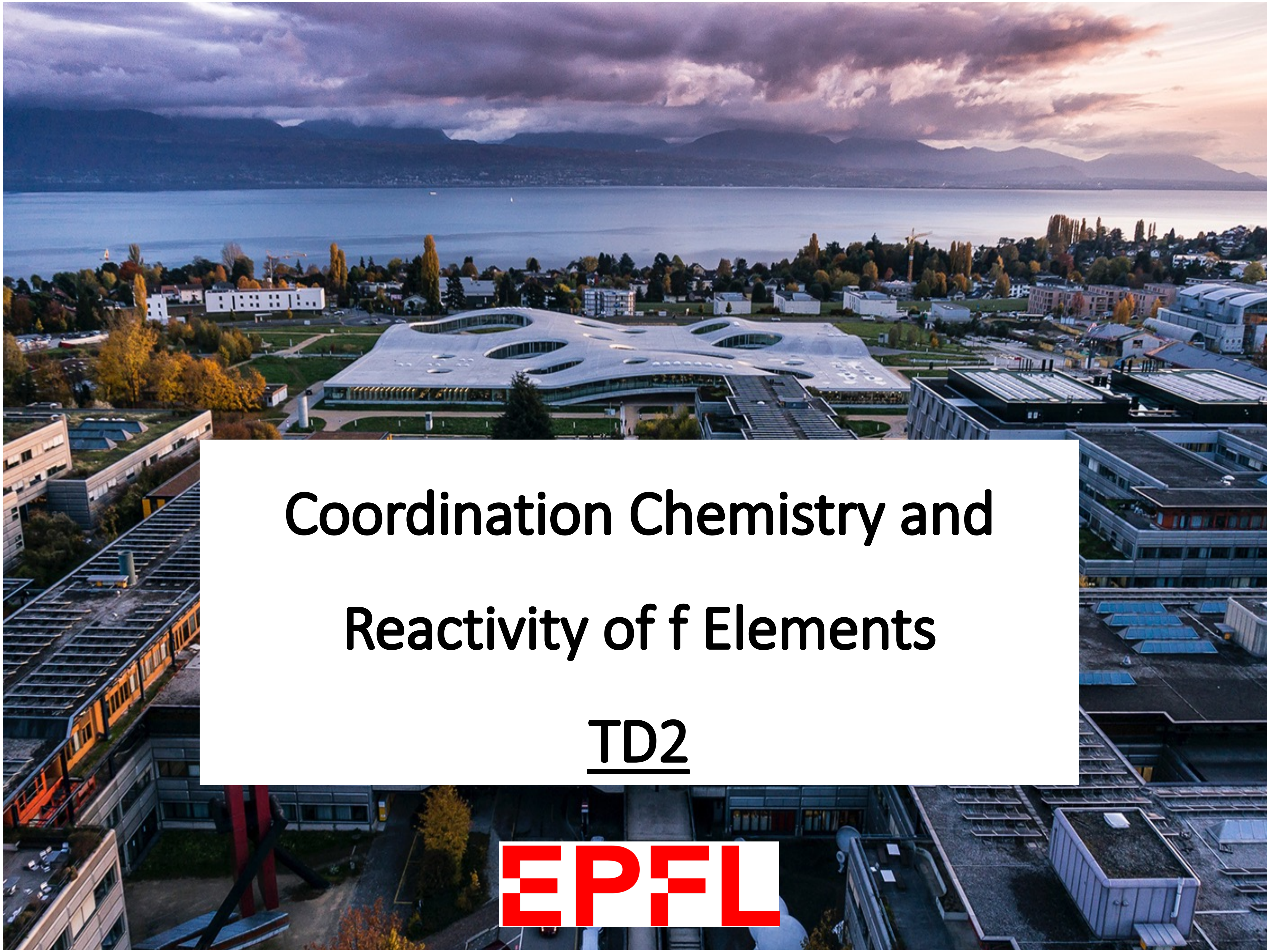


Coordination Chemistry and Reactivity of f Elements

TD2

Question 1

1) Using only your periodic table give and justify the electronic configuration of Er^{3+}

Work out the ground state of Er^{3+}.

2) Calculate the magnetic moment of a Er^{3+} complex using the spin-only formula and the SOC formula.

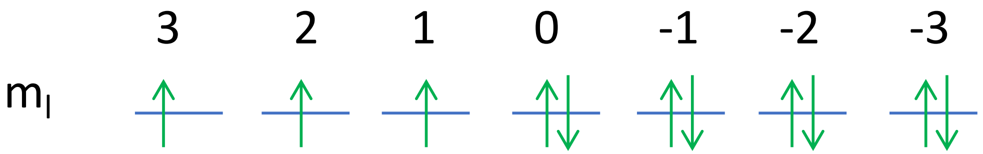
Which one fits better the measured value of the magnetic moment (9.58 μB) and why ?

3) Explain why none of these two formulas correctly predict the magnetic moment of Eu^{3+}

Answer 1

1) Using only your periodic table give and justify the electronic configuration of Er^{3+}
Work out the ground state of Er^{3+}.

$Er: 4f^{12}5d^{0}6s^{2}$ → Er^{3+}: Configuration: $\mathbf{4f^{11}}$



$S = \Sigma m_s = 3/2$
Multiplicity = 2S+1 = 4
$L = \Sigma m_l = 6$

0	1	2	3	4	5	6
S	P	D	F	G	H	I

J = L+ S (more than half filled) = 15/2

Ground state: $^{4}\mathbf{I}_{15/2}$

Answer 1

2) Calculate the magnetic moment of a Er^{3+} complex using the spin-only formula and the SOC formula. Which one does better fit the measured value of the magnetic moment (9.58 μB) and why ?

$$\mu_{\text{spin only}} = \sqrt{n(n+2)} = 3.87$$

$$\mu_{\text{spin-orbit}} = g_J\sqrt{J(J+1)} = 9.58$$

Spin-orbit coupling rules the magnetic properties of lanthanides so the Landè formula is more appropriate.

3) Explain why none of these two formulas correctly predict the magnetic moment of Eu^{3+}

Population of low-lying excited J-states

In the case of Eu and Sm the first excited states are close to the ground state at room T so the experimental magnetic moment is the mix of ground and excited state moments.

Question 2

1) What consequences has the paramagnetism of the lanthanide ions on the proton NMR spectra of their complexes?

2) How would you expect a ^{1}H NMR spectrum of a Gd(III) complex to look like? Why?

3) Indicate how you expect the proton NMR of a Yb(II) and of a Yb(III) complex to look like

Answer 2

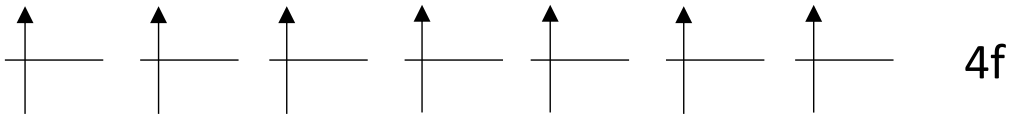
1) What consequences has the paramagnetism of the lanthanide ions on the proton NMR spectra of their complexes.

It will be shifted and broad because we have **unpaired electrons,** which will affect the magnetic moment applied and in consequence affect the shift of the protons surrounding the **paramagnetic nucleus**. It will be still visible because of the **short electron relaxation time**.

2) How would you expect a ^{1}H NMR spectrum of a Gd(III) complex to look like? Why?

No signal because it has the longest spin relaxation time and 7 unpaired electrons.

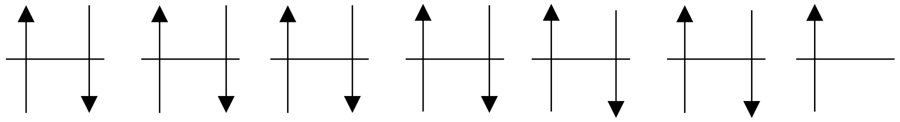
Gd^{3+} : [Xe] $\mathbf{4f^7}$
S=7/2



Answer 2

3) Indicate how you expect the proton NMR of a Yb(II) and of a Yb(III) complex to look like.

Yb^{3+} : [Xe] **$4f^{13}$**



4f

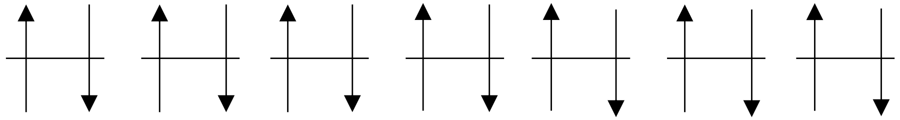
1 unpaired electron

S=1/2

The ^1H NMR spectrum of **Yb(III)** complexes will shift from the diamagnetic region

But will not be silent due to **fast electron relaxation**

Yb^{2+} : [Xe] $4f^{14}$



4f

0 unpaired electrons

S=0 → diamagnetic

The ^1H NMR spectrum of **Yb(II)** complexes will not display any paramagnetic shift of the signals

Question 3

1) Give an example of a Ln based NMR « Shift reagent » and explain its mode of action.

2) What are the applications NMR « Shift reagents »?

Answer 3

1) Give an example of a Ln based NMR « Shift reagent » and explain its mode of action.

Paramagnetic lanthanide complexes such as β-diketonates Ln($R_1COCHCOR_2$)$_3$ produce shifts in the NMR spectra of organic molecules capable of forming adducts with them and are thus often referred to as Lanthanide Shift Reagents (LSRs).

2) What are the applications NMR « Shift reagents »?

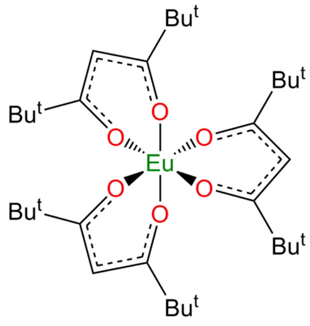
Immense activity in this area in the early 1970s resulted as the use of LSRs enabled simplification of the spectra of organic molecules without the use of high-frequency spectrometers. The spreading-out of the spectrum and differential nature of the shifts removed degeneracies and overlaps, but chiral shift reagents are still used to resolve chiral mixture

Question 4

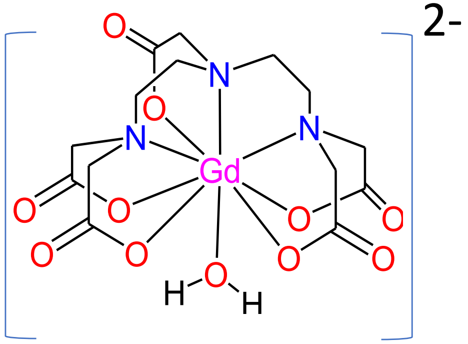
1) Indicate how for the following complexes the thermodynamic stability vary and why.

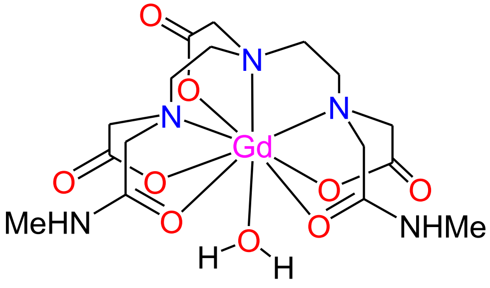
2) Indicate which complex has the highest kinetic stability and why.

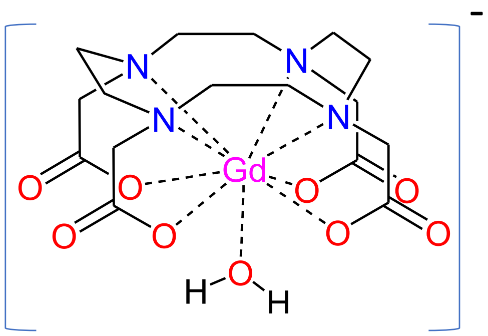
3) Indicate how these complexes can be synthesised.



[Eu(dpm)$_3$]

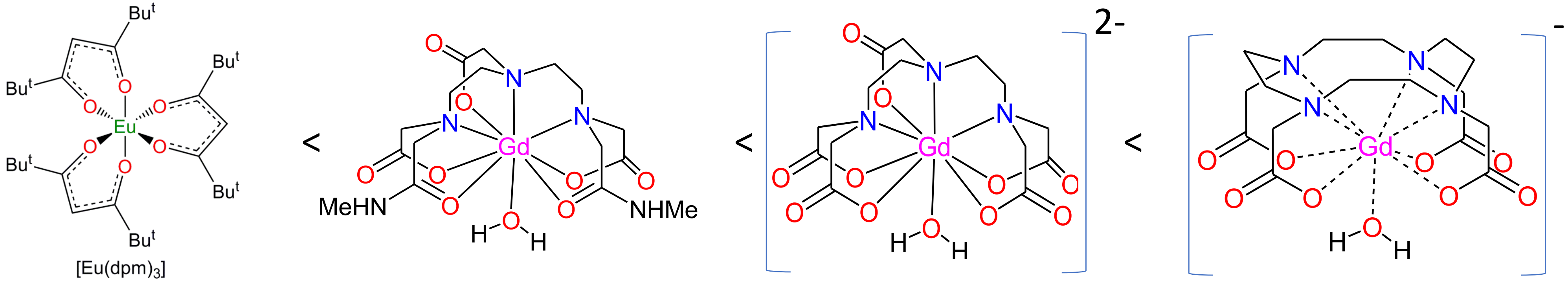






Answer 4

1) Indicate how for the following complexes the thermodynamic stability vary and why.



The Eu complex is the least stable due to the **low denticity** of the diketonate ligand (lower stabilization by **chelate effect**).

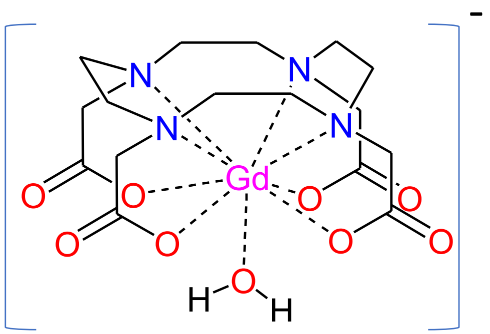
In the remaining complexes we have the same denticity (8 donor atoms) but the **charge of the ligand** and the **nature of the donor atoms** change :

Only 3 negative oxygen in the second ligand, 5 negative oxygen in DTPA .

In dota we have increased **ligand preorganization**.

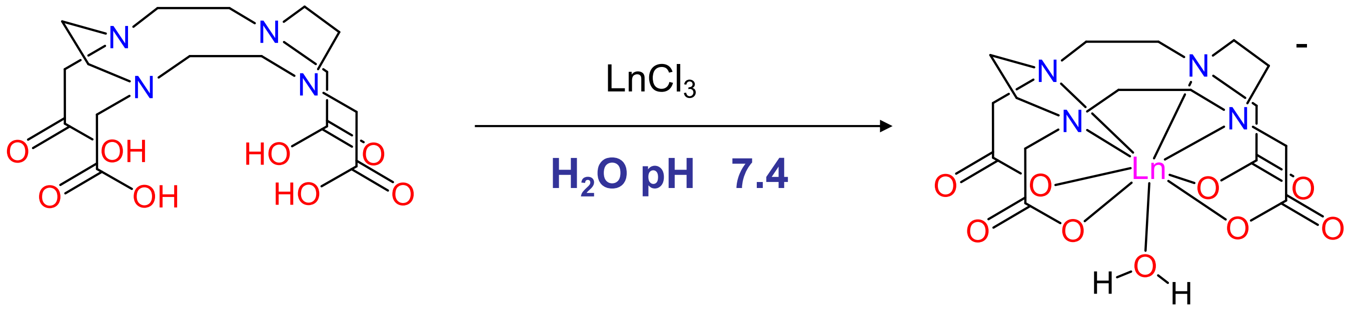
Answer 4

2) Indicate which complex has the highest kinetic stability and why.



Complex with the highest kinetic stability because of the **macrocycle effect**

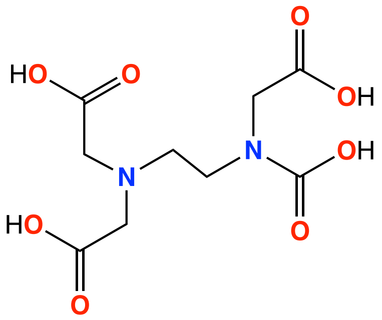
3) Indicate how these complexes can be synthesised.



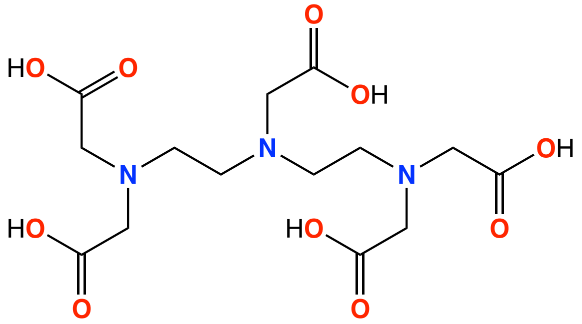
Reaction with lanthanide salt and pH adjustement with KOH

Question 5

1) Draw the structure of Ln(III) complexes with, $EDTA^{4-}$, $DTPA^{5-}$ indicating a synthetic scheme and the CN of complexes.



H_4EDTA = Ethylenediaminetetracetic acid



H_5DTPA = Diethylenetriaminepentaacetic acid

2) Explain how and why the stability constant varies along the Ln series for all ligands.

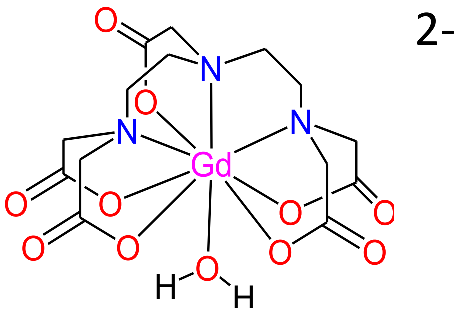
3) Explain the difference in stability for the complexes of the different ligands.

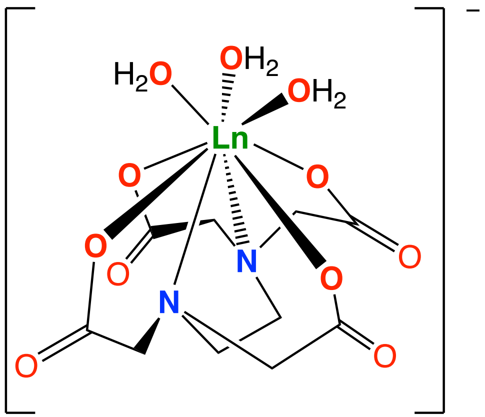
Table 4.2 Aqueous stability constants (log β_1) for lanthanide (3+) ions with fluoride, EDTA, and DTPA

Ligand	Y^{3+}	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
F^-	3.60	2.67	2.87	3.01	3.09	3.16	3.12	3.19	3.31	3.42	3.46	3.52	3.54	3.56	3.58	3.61
$EDTA^{4-}$	18.08	15.46	15.94	16.36	16.56		17.10	17.32	17.35	17.92	18.28	18.60	18.83	19.30	19.48	19.80
$DTPA^{5-}$	22.05	19.48	20.33	21.07	21.60		22.34	22.39	22.46	22.71	22.82	22.78	22.74	22.72	22.62	22.44

Answer 5

1) Draw the structure of Ln(III) complexes with, EDTA^{4-}, DTPA^{5-} indicating a synthetic scheme and the CN of complexes.





In general: $M^{n+} + L^{y-} \Leftrightarrow ML^{(n-y)+}$

For EDTA: $[La(OH_2)_9]^{3+}(aq) + EDTA^{4-}(aq) \rightarrow [La(EDTA)(OH_2)_3]^{-}(aq) + 6\ H_2O(l)$ NC = 9

For DTPA: $[La(OH_2)_9]^{3+}(aq) + DTPA^{5-}(aq) \rightarrow [La(DTPA)(OH_2)]^{2-}(aq) + 8\ H_2O(l)$ NC = 9

Answer 5

2) Explain how and why the stability constant varies along the Ln series for all ligands.

The values for Lu^{3+} are greater than those for La^{3+} as the smaller Lu^{3+} ion has a **greater charge density** and stronger electrostatic interaction with a ligand.

3) Explain the difference in stability for the complexes of the different ligands.

DTPA complexes are more stable than EDTA ones because of the **greater chelate effect** and **increased number of negative donor atoms**.

Question 6

1) Explain how a Gadolinium complex leads to an increase of contrast in a MRI image?

2) What is the property that describes the efficiency of a MRI contrast agent?

3) What parameters influence this property?

4) How can the efficiency of a contrast agent be increased? What possible drawbacks exist?

Answer 6

1) Explain how a Gadolinium complex leads to an increase of contrast in a MRI image

The signal intensity (water protons) depends upon the relaxation times of the protons. In order to enhance the contrast to differentiate between healthy and diseased tissue, **paramagnetic agents** are used to decrease the relaxation time of water protons.

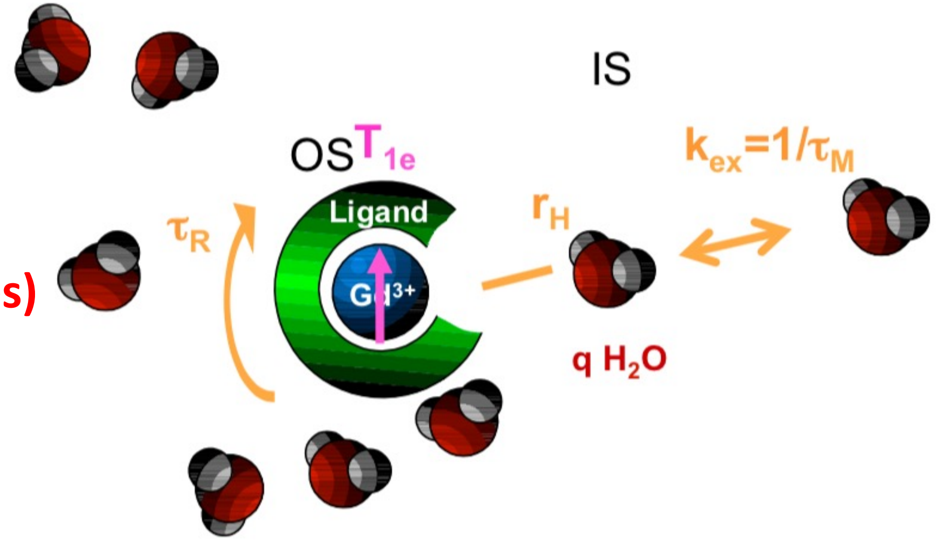
Gd^{3+} has a **large number of unpaired electrons** and has a **long electron-spin relaxation time** that leads to a lower relaxation rate

2) What is the property that describes the efficiency of a MRI contrast agent

Efficiency is described by relaxivity **r** that measures the ability of magnetic compounds to increase the relaxation rates of the surrounding water proton spins.

Answer 6

3) What parameters influence this property?



Parameters:

- **q (number of coordinated water molecules)**
- **$k_{ex}=1/\tau_M$**: water exchange rate

  fast water exchange (high k_{ex})
- **τ_R**: time needed for reorientation of the water bound gadolinium complex usually related to increase in molecular weight if there are no internal motions
- **T_{1e}**: longitudinal and transverse electronic relaxation times (i= 1, 2)

Answer 6

4) How can the efficiency of a contrast agent be increased? What possible drawbacks exist?

Increase : - τ_R: rotational time at medium magnetic field → Increase molecular weight of ligands - connect to larger molecules (proteins , nanoparticles)

- **k_{ex}**: water exchange rate by steric compression
- **q**: number of coordinated molecules at all fields, by decrease of ligand denticity

q > 1 higher efficiency

Drawbacks : - lower stability

- competition with carboxylates (anions, proteins)

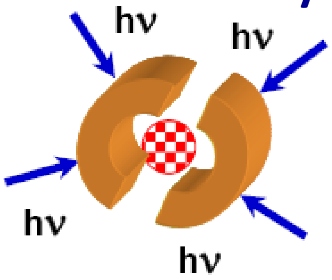
Question 7

1) Explain the principle of the « antenna » effect.

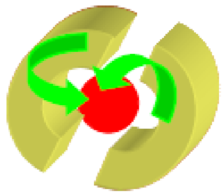
2) Identify the advantages and disadvantages of luminescent complexes of lanthanides compared to lanthanide inorganic materials.

3) Indicate the most important applications of luminescent lanthanide complexes and lanthanide inorganic materials.

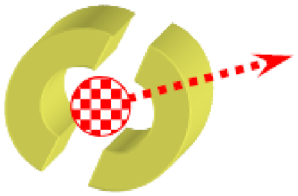
Answer 7



light harvesting



Energy transfer



light emision

1) Explain the principle of the « antenna » effect

Indirect excitation of the lanthanide trough the excited state of the bound ligand.

- The ligand triplet state plays a major role in **the energy transfer process to the emitting state of the lanthanide** because the energy needs to be compatible.

- To prevent back transfer the ligand triplet state needs to be higher in energy than the Ln emitting state.
- Water or solvent molecules disactivate the luminescence
- Leads to large Stokes Shift and excitation can be done at lower energy

Answer 7

2) Identify the advantages and disadvantages of luminescent complexes of lanthanides compared to lanthanide inorganic materials.

Ln complexes → can be excited with **lower energy** than Ln materials

→Large Stokes Shifts

→ but tend to have **lower quantum yields** due to the binding of solvent

3) Indicate the most important applications of luminescent lanthanide complexes and lanthanide inorganic materials

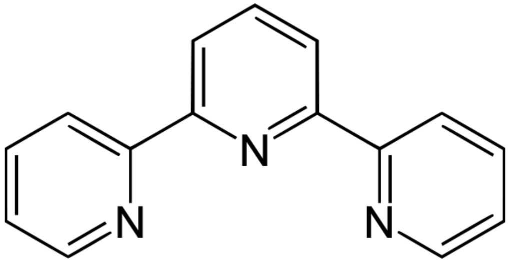
Ln complexes → biological assays

Ln materials → lighting devices, displays light converter and optical fibers

Question 8

1) Explain why $Eu(NO_3)_{3.}x\ H_2O$ reacts (in methanol) with the ligand terpy to form $[Eu(terpy)(NO_3)_3(H_2O)]$ and $Eu(ClO_4)_{3.}x\ H_2O$ reacts with terpy to form $[Eu(terpy)_3].(ClO_4)_3$

2) Draw the structure of the two complexes and give the CN and geometry.



terpy

Answer 8

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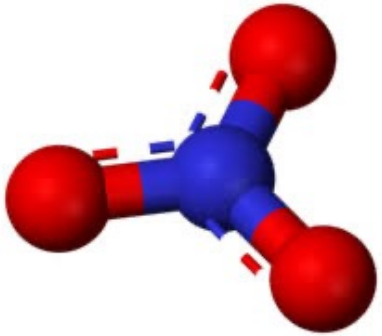
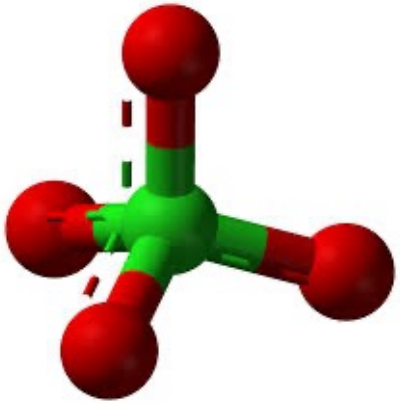


NO_3^-

- Reasonably strong coordinating properties
- Usually as a bidentate ligand
- Competes with terpy.
- Nitrate groups remain bound

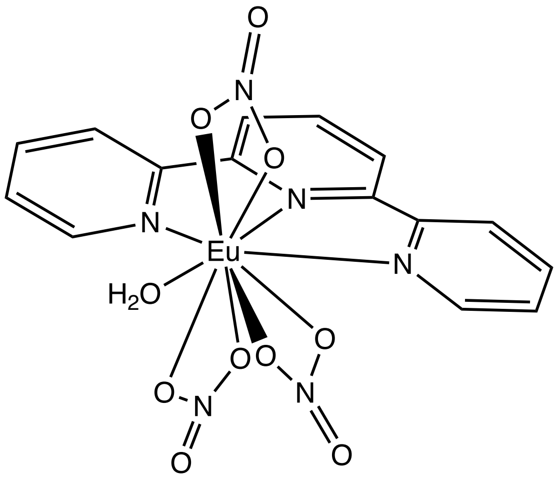


ClO_4^-

- Weakly coordinating anion
- Does not compete with terpy
- Full displacement of the perchlorate

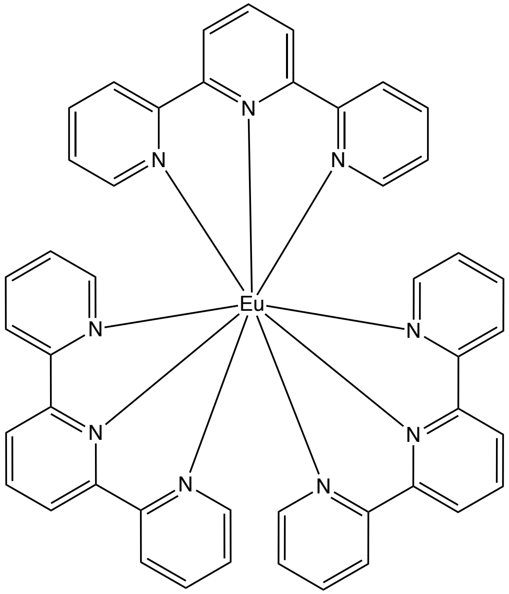
Answer 8

2) Draw the structure of the two complexes and give the CN and geometry.



[Eu**(terpy)(NO$_3$)$_3$**(H$_2$O)]

CN = 10



[Eu**(terpy)$_3$**].**(ClO$_4$)$_3$**

CN = 9