

An aerial photograph of the EPFL campus in Lausanne, Switzerland. The image shows a large, modern, white building with a unique, organic shape and several circular openings. The building is surrounded by green spaces and other campus buildings. In the background, there is a large body of water (Lake Geneva) and a range of mountains under a dramatic, cloudy sky at sunset or sunrise. The overall scene is a mix of urban architecture and natural beauty.

# Coordination Chemistry and Reactivity of f Elements

TD1

**EPFL**



# Question 1: Using the information below draw a table comparing 4f and d block compounds

The lanthanides exhibit a number of features in their chemistry that differentiate them from the d-block metals. The reactivity of the elements is greater than that of the transition metals, akin to the Group II metals:

1. A very wide range of coordination numbers (generally 6–12, but numbers of 2, 3 or 4 are known).
2. Coordination geometries are determined by ligand steric factors rather than crystal field effects.
3. They form labile ‘ionic’ complexes that undergo facile exchange of ligand.
4. The 4f orbitals in the  $\text{Ln}^{3+}$  ion do not participate directly in bonding, being well shielded by the  $5s^2$  and  $5p^6$  orbitals. Their spectroscopic and magnetic properties are thus largely uninfluenced by the ligand.
5. Small crystal-field splittings and very sharp electronic spectra in comparison with the d-block metals.
6. They prefer anionic ligands with donor atoms of rather high electronegativity (e.g. O, F).
7. They readily form hydrated complexes (on account of the high hydration energy of the small  $\text{Ln}^{3+}$  ion) and this can cause uncertainty in assigning coordination numbers.
8. Insoluble hydroxides precipitate at neutral pH unless complexing agents are present.
9. The chemistry is largely that of one (3+) oxidation state (certainly in aqueous solution).

## Question 1: Table to be filled

	4f	3d
Electron configuration of ions		
Stable oxidation states		
Coordination numbers in complexes		
Trends in coordination numbers		
Donor atoms in complexes		
Hydration energy		
Ligand exchange reactions		
Magnetic properties of ions		
Electronic spectra of ions		
Crystal field effects in complexes		
Organometallic compounds		
Multiply bonded atoms in complexes		

## Question 2:

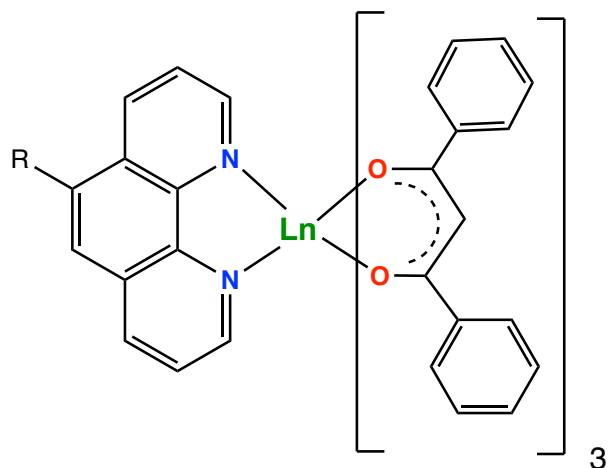
Indicate at least three important applications of lanthanides ions and two of actinide ions and cite the properties of these elements that have led to these specific applications.

## Question 3:

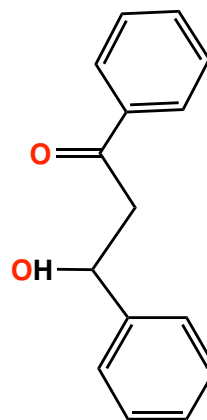
- 1) Why Lanthanide(III) ions form only electrostatic interactions?
- 2) What type of ligands lead to stable Ln(III) complexes
- 3) What are the consequences of a mainly electrostatic interaction on coordination numbers and geometries?

## Question 4:

1) Why are the following complexes not stable? Explain what happens if they are left in air.



DBMH =



## Question 5:

**1)** Explain why the electronic spectra of  $\text{Pr}^{3+}$  consist of a number of weak lines, whereas those in the spectrum of  $\text{V}^{3+}$  are broader and less numerous?

Explain why lanthanide compounds have paler colours compared to transition metal complexes.

**2)** Predict how the ligand thiocyanate ( $\text{SCN}^-$  can be S-bonded or N-bonded) will bind to  $\text{Ln(III)}$ . And explain why.

**3)** Explain why  $\text{Ln-X}$  ( $\text{X}=\text{N}, \text{O}, \text{P}$ ) multiple bond is not common in Ln chemistry.

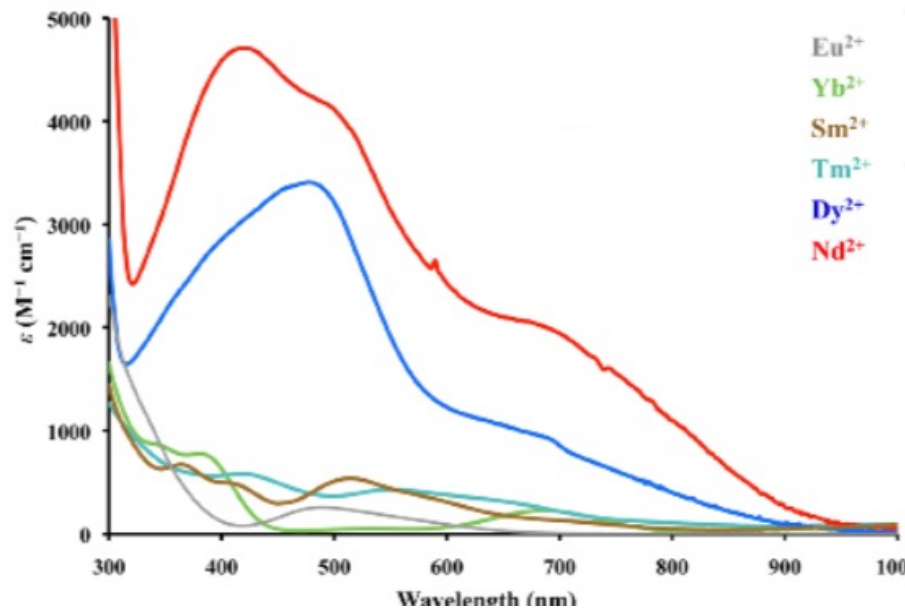
## Question 6:

- 1) Indicate for which lanthanide ions the oxidation state +2 is relatively common and explain why.  
Indicate for which lanthanide the oxidation state +4 is stable.
- 2) How do complexes of tetravalent and divalent lanthanides react with water ?
- 3) Only for one lanthanide ion water stable complexes of  $\text{Ln}^{2+}$  can be obtained. Which one and why?
- 4) What are the possible electron configurations of divalent lanthanide(II) ions?
- 5) What spectroscopic characterization can you use to distinguish between these two types of configurations?



## Question 7:

- 1) Ln(II)  $[(^{\text{SiMe}_3}\text{Cp}_3\text{Ln})[(18\text{-crown-6})\text{K}]$  complexes have been prepared. Explain how they were prepared and why they are relatively stable.
- 2) Why is the UV-Vis spectra showing higher  $\epsilon$  for  $\text{Dy}^{2+}$  and  $\text{Nd}^{2+}$  compare to  $\text{Eu}^{2+}$ ,  $\text{Yb}^{2+}$ ,  $\text{Sm}^{2+}$  and  $\text{Tm}^{2+}$  in  $[(^{\text{SiMe}_3}\text{Cp}_3\text{Ln})[(18\text{-crown-6})\text{K}]$  complexes.
- 3) What other spectroscopic techniques could be used to confirm the observation obtained from the UV-Vis spectra.



## Question 8:

- 1) Explain what the term « Lanthanide contraction » means
- 2) Explain why such contraction occurs in lanthanide ions and not in d metals
- 3) What is the effect of lanthanide ions contraction in their Lewis acid behavior?

## Question 9

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

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

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

Which one fits better the measured value of the magnetic moment ( $9.58 \mu\text{B}$ ) and why ?

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

## Question 10

- 1) What consequences has the paramagnetism of the lanthanide ions on the proton NMR spectra of their complexes
- 2) Indicate how you expect the proton NMR of a gadolinium(III) complex to look like and why
- 3) Indicate how you expect the proton NMR of a Yb(II) and of a Yb(III) complex to look like

# Question 11

- 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 »?