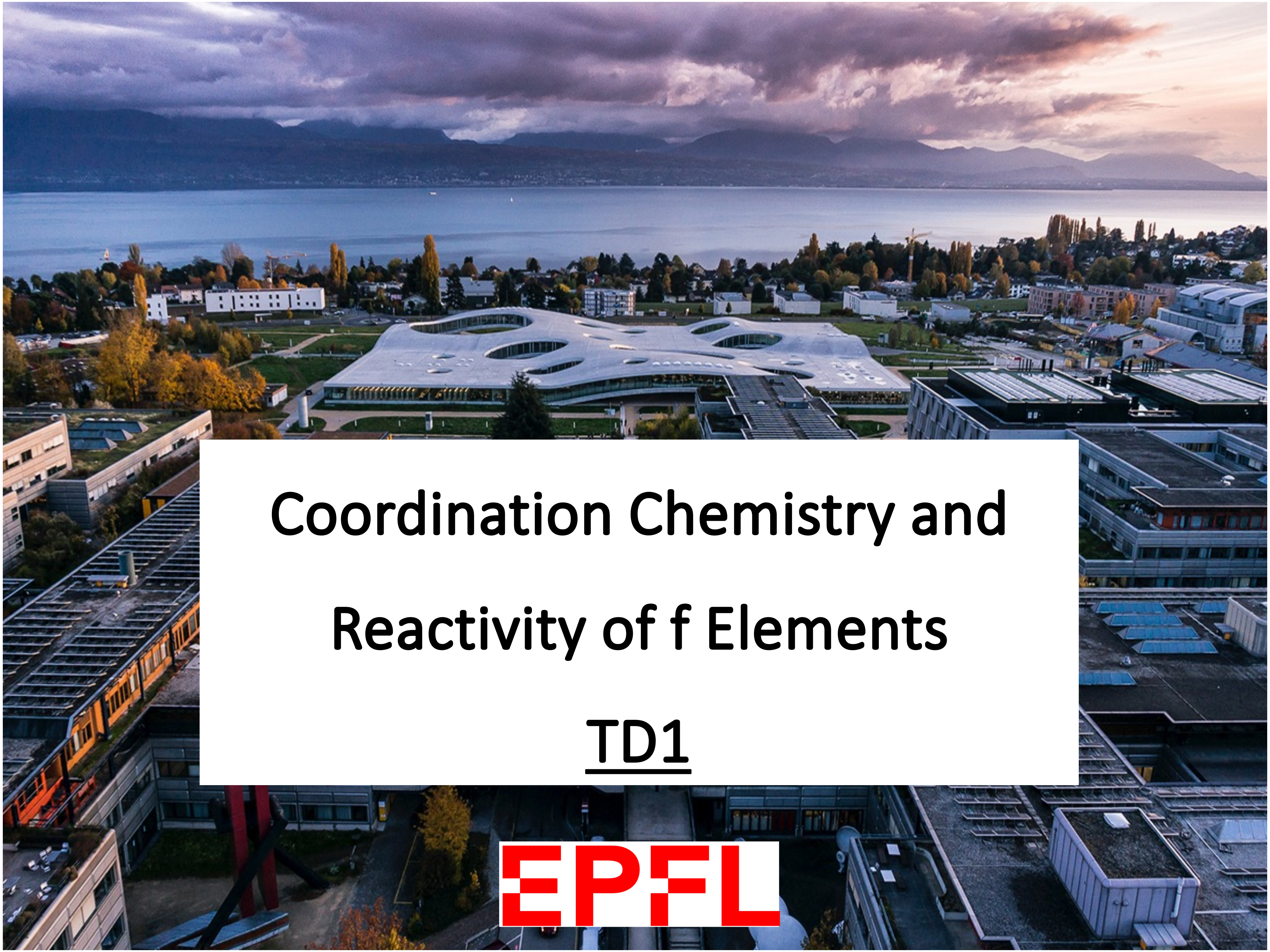
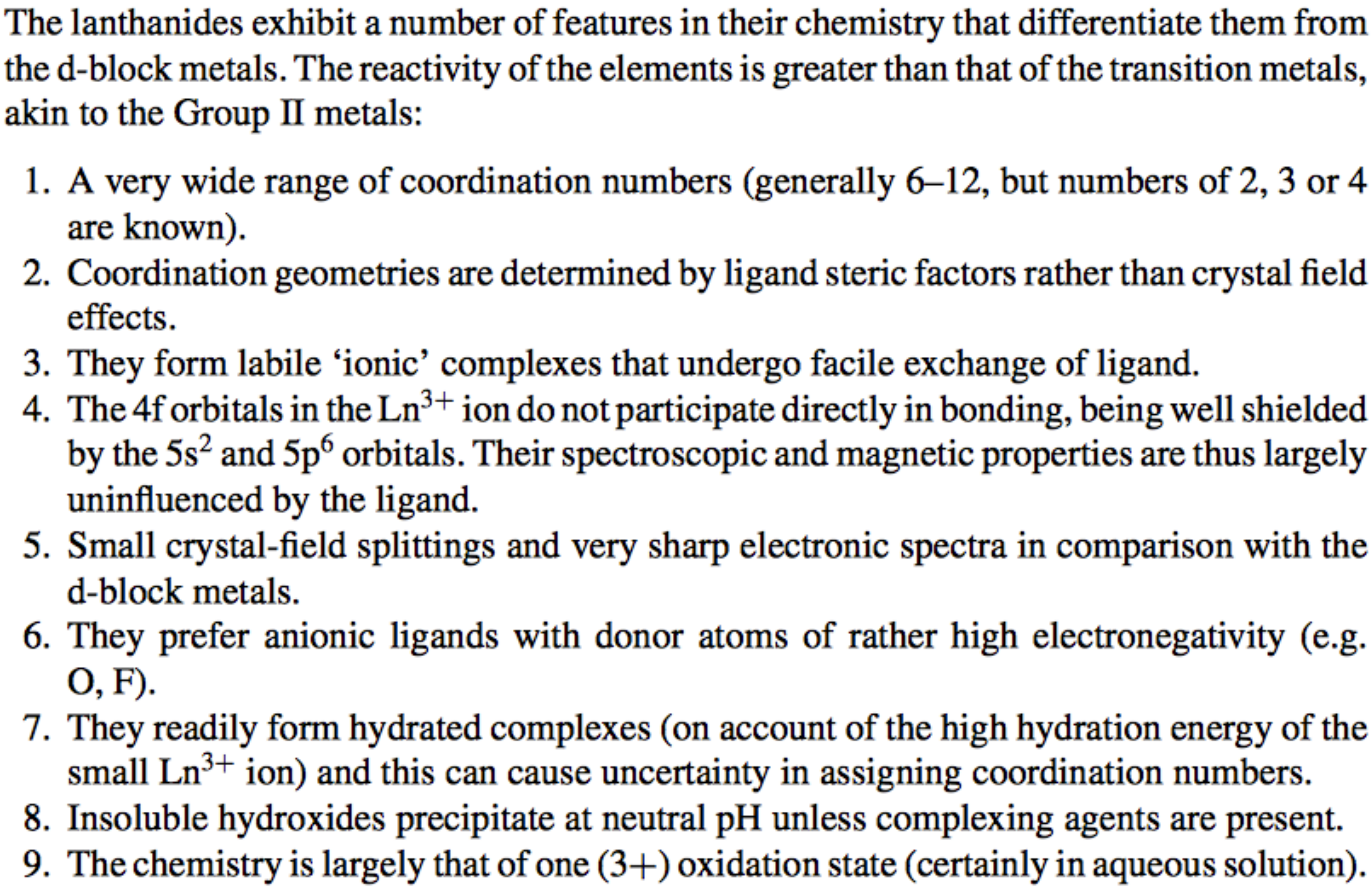


Coordination Chemistry and Reactivity of f Elements

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 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 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).

Simon Cotton

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		

Answers 1:

	4f	3d
Electron configuration of ions	Variable	Variable
Stable oxidation states	+3	Variable
Coordination numbers in complexes	8-12	Mostly 6
Trends in coordination numbers	Decrease along the period	Mainly Constant
Donor atoms in complexes	Hard	Hard and soft
Hydration energy	High	Moderate
Ligand exchange reactions	Fast	Fast and slow
Magnetic properties of ions	Independent of ligands	Dependent of ligand field
Electronic spectra of ions	Sharp lines	Broad lines
Crystal field effects in complexes	Weak	Strong
Organometallic compounds	Ionic	Covalent
Multiply bonded atoms in complexes	Very rare	Common

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.

Answers 2:

4) 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.

Ln: - Ln luminescence used in LEDS, displays
- Diesel oxidation catalysts (DOC) takes advantage of the two available oxidation states of Ce: Ce^{3+} and Ce^{4+}
- MRI agent (gadolinium) due to the presence of 7 unpaired electrons (paramagnetism)

Reduction catalysts in organic chemistry (high reducing power of Ln^{2}+)

An: - The radioactivity of uranium and thorium is used in nuclear energy production
- military applications and as fuel in space voyage

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?

Answers 3:

1) Why Lanthanide(III) ions form only electrostatic interactions?

The 4f orbitals are not diffuse. Because of this they cannot overlap with ligand orbitals and therefore do not participate in bonding. As a result crystal-field effects are very small and they form mainly electrostatic interaction

2) What type of ligands lead to stable Ln(III) complexes

Ln ions prefer to bind to **hard donors** such as negative oxygen and fluorides rather than soft such as P and S containing molecules. Moreover **multidentate ligands and bulky ligands** leads to higher stability

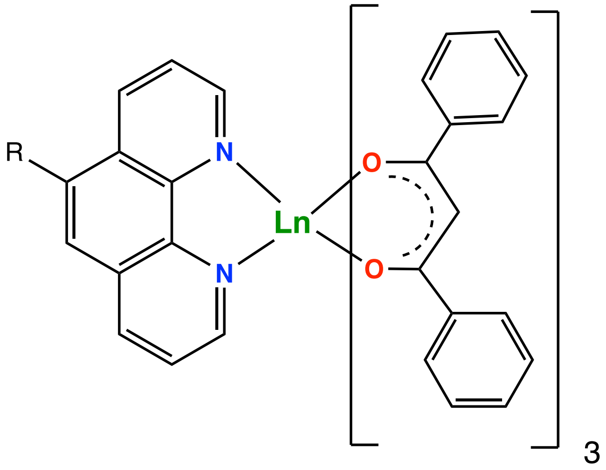
Answers 3:

3) What are the consequences of a mainly electrostatic interaction on coordination numbers and geometries? Can square planar geometries be found?

f-orbitals are ‘inner’ orbitals and therefore not able to participate in directional bonding; there are none of the ligand-field effects found in transition metal chemistry with the concomitant preference for octahedral, tetrahedral coordination or square planar. In summary, the **coordination number (CN) adopted by a particular complex is determined by how many ligands can be packed around the central metal ion**; coordination numbers between 2 and 12 are known in lanthanide complexes. Geometries are those corresponding to the simple polyhedra that would be predicted from electron- pair repulsion models; tetrahedral (CN 4), trigonal bipyramidal (CN 5), octahedral (CN 6); though with coordination numbers 2 and 3 deviations from simple linear and trigonal planar geometries in the solid state often occur (and are probably due to agostic interactions).
Square planar geometry is not found in f elements (beside extremely rare exceptions)
Because is not sterically favoured.

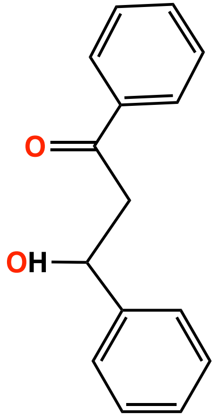
Question 4:

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



[(Phen)(DBM)$_3$Ln]

DBMH =



Answers 4:

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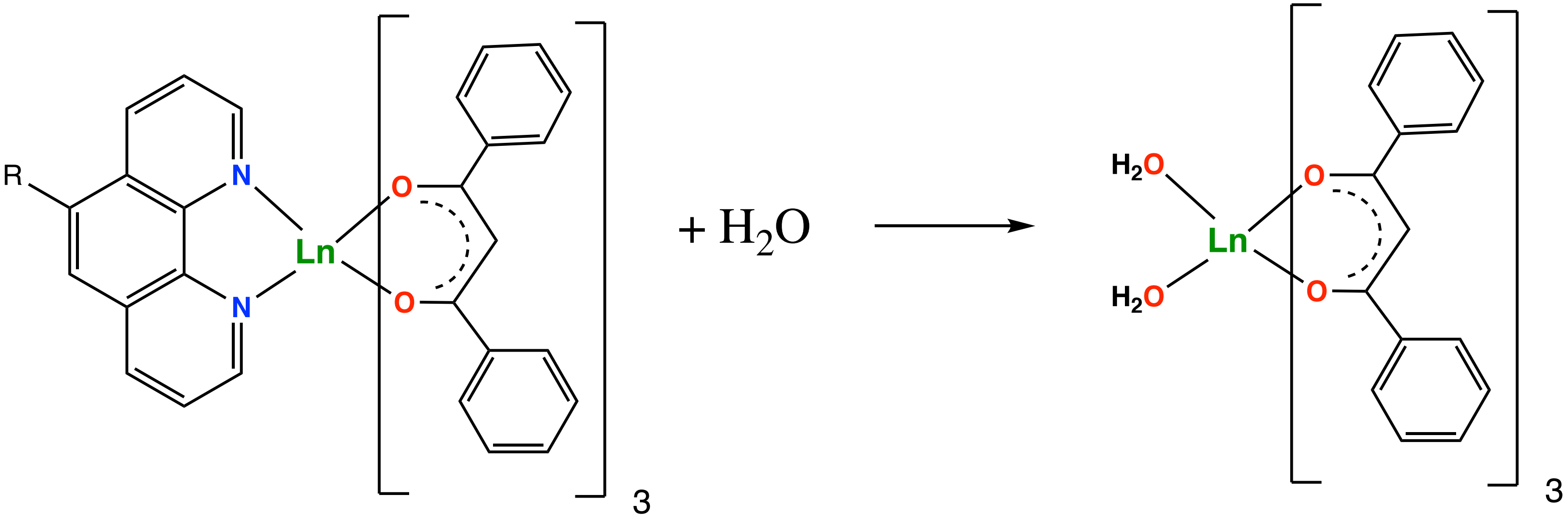


The Ln^{3+} ions are hard ions and form strong interactions with anionic ligands such as DBM^-

The bond with neutral N-donors such as phenanthroline (Phen) are weaker and while relatively stable after some time the water present in air can displace the phenanthroline ligand.

Question 5:

1) Explain why the electronic spectra of Pr^{3+} consist of a number of weak lines, whereas those in the spectrum of 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 (SCN^- can be S-bonded or N-bonded) will bind to Ln(III). And explain why.

3) Explain why Ln-X (X=N, O, P) multiple bond is not common in Ln chemistry.

Answers 5:

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

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

Both d–d and f–f transitions are parity-forbidden according to the Laporte rule.

d-orbitals extend out → **vibronic coupling** possible, which lowers symmetry and makes **d/p mixing** possible

→ d–d transitions to some extent "allowed" so $\boldsymbol{\varepsilon \sim 100\ M^{-1} \cdot cm^{-1}}$

→ excitation to vibrationally excited states gives **broad absorption** (different crystal fields)

4f orbitals are contracted → **f/p mixing and vibronic coupling limited**

→ f–f transitions less "allowed" so $\boldsymbol{\varepsilon < 10\ M^{-1} \cdot cm^{-1}}$

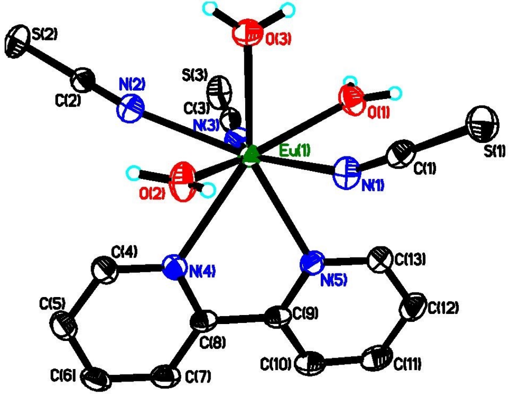
→ no excitation to vibrationally excited states gives **narrow lines**

Answers 5:

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

Thiocyanate will bind with the nitrogen atom. Ln^{3+} ions are ‘hard’ acids, which prefer to bind ‘hard’ bases. Sulfur is a ‘softer’ base than nitrogen.

Hard = smaller and higher charge
Soft = bigger and lower charge



Dobrokhotova, et al. *Inorg. Chim.* **2017**, *456*, 76–85.

3) Explain why Ln-X (X=N, O, P) multiple bond is not common in Ln chemistry.

Multiple bonds require covalent bonds, but f-orbitals are not available for covalent bonds and 5d are too high in energy.

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 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?

Answers 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.

Sm^{2+}, Eu^{2+}, Yb^{2+}, because they have high third ionization energies (half or fully filled f shell or adjacent to half full).
Ce^{4+}, has a low fourth ionization energy.

2) How do complexes of tetravalent and divalent lanthanides react with water ?

Ln^{2+} reduces water to hydrogen:

$$2Ln^{2+}_{(aq)} + 2H^{+}_{(aq)} \rightarrow 2Ln^{3+}_{(aq)} + H_{2(g)}$$

Ln^{4+} oxidizes water to oxygen:

$$4Ln^{4+}_{(aq)} + 2H_2O_{(l)} \mapsto 4Ln^{3+}_{(aq)} + O_{2(g)} + 4H^{+}_{(aq)}$$

3) Only for one lanthanide ion water stable complexes of Ln^{2+} can be obtained. Which one and why?

Eu^{2+} because it has a very low $Ln^{3+} \rightarrow Ln^{2+}$ reduction potential

Answers question 6:

4) What are the possible electron configuration of divalent lanthanide(II) ions?

$4f^{N}$ and $4f^{N-1}5d^{1}$

5) What spectroscopic characterization can you use to distinguish between these two types of configurations?

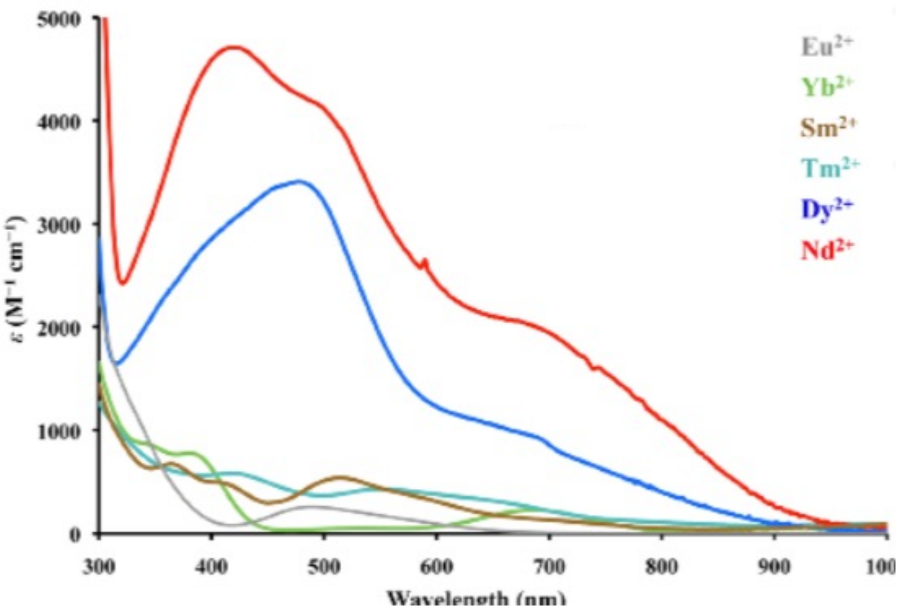
Magnetic moments and UV-Vis spectroscopy → different due to d–d transitions

Question 7:

1) Ln(II) $[(^{\mathrm{SiMe3}}\mathrm{Cp}_3\mathrm{Ln}]\,[(18\text{-crown-}6)\mathrm{K}]$ complexes have been prepared. Explain how they were prepared and why they are relatively stable.

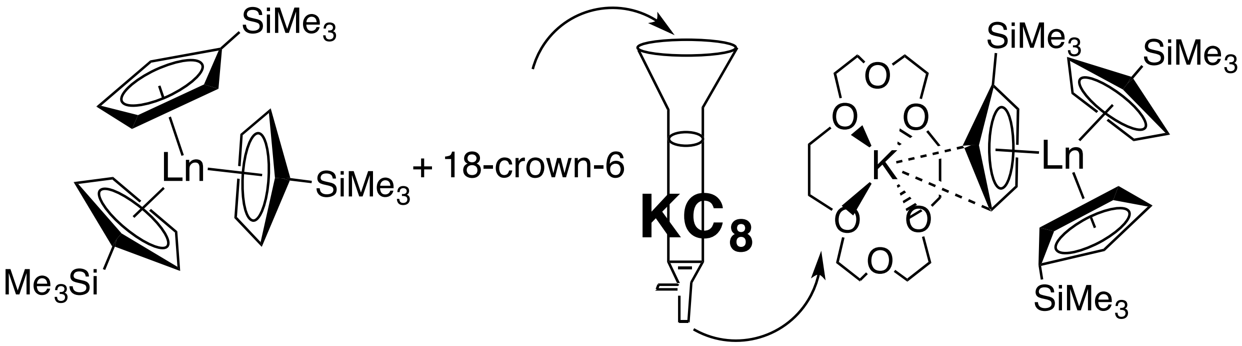
2) Why is the UV-Vis spectra showing higher ε for Dy^{2+} and Nd^{2+} compare to Eu^{2+}, Yb^{2+}, Sm^{2+} and Tm^{2+} in $[(^{\mathrm{SiMe3}}\mathrm{Cp}_3\mathrm{Ln}]\,[(18\text{-crown-}6)\mathrm{K}]$ complexes.

3) What other spectroscopic techniques could be used to confirm the observation obtained from the UV-Vis spectra.



Answers 7:

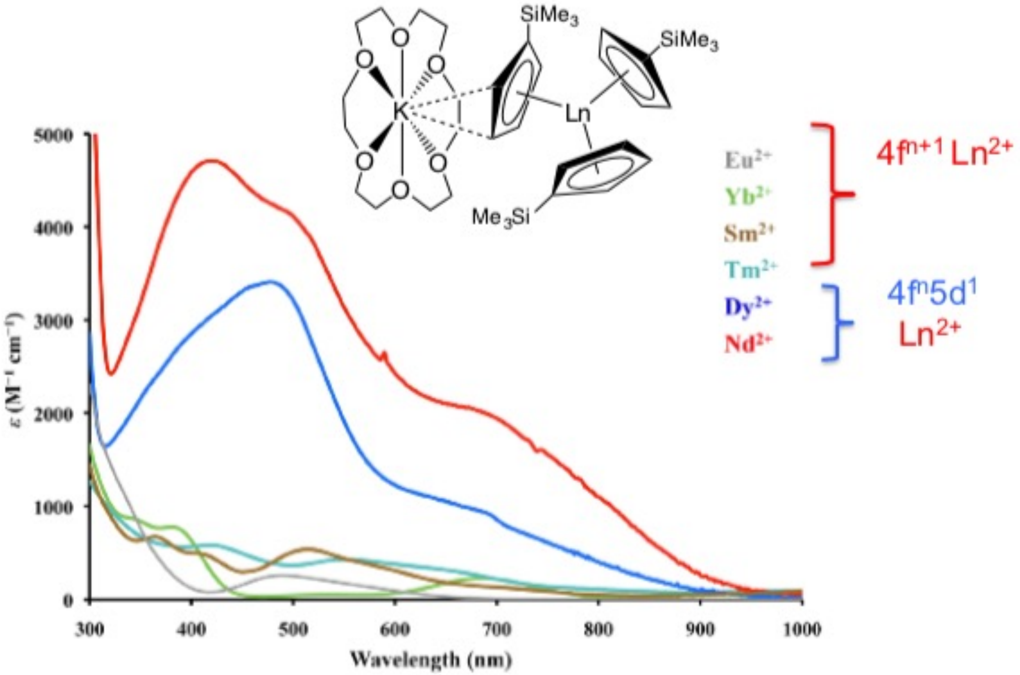
1) Ln(II) [(^{SiMe3}Cp$_3$Ln] [(18-crown-6)K] complexes have been prepared. Explain how they were prepared and why they are relatively stable.



Solution filtered over KC$_8$ so it doesn't oxidize back.
Electron-withdrawing substituents on Cp rings help to stabilize the +2 oxidation state.

Answers 7:

2) Why is the UV-Vis spectra showing higher ε for Dy^{2+} and Nd^{2+} compare to Eu^{2+}, Yb^{2+}, Sm^{2+} and Tm^{2+} in $[(^{SiMe3}Cp_3Ln]\ [(18\text{-crown-}6)K]$ complexes.



For Dy and Nd, higher ε due to d-orbital allowing metal-ligand mixing

For the others, absorbance is due to Laporte allowed 4f-5d transitions

➔ Different electronic configuration

3) What other spectroscopic techniques could be used to confirm the observation obtained from the UV-Vis spectra.

Magnetism

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?

Answers 8:

1) Explain what the term « Lanthanide contraction » means

The lanthanide contraction is the important decrease in the ionic radii along the lanthanide series going from La to Lu (increasing atomic number)(0.14 Å for 8-coordinated Ln^{3+})..

2) Explain why such contraction occurs in lanthanide ions and not in d metals

Such contraction is due to the fact that 4f orbitals do not shield efficiently the nuclear charge.

This poor shielding draws the 6s electrons towards the nucleus resulting in a smaller than expected ionic radii.

This effect does not occur in transition metals because the d orbitals shield more effectively the added protons than the 4f orbitals.

Answers 8:

3) What is the effect of lanthanide ions contraction in their acidic behavior (formation of hydroxides) and Lewis acid character?

The lanthanide contraction leads to an increased charge density increases along the series in a more-then-expected fashion.

The high charge density leads to a higher acidity of the protons of lanthanide bound water molecules
According to the following equilibrium

$$\text{Ln-OH}_2 \overset{\text{pKa}}{\leftrightarrows} \text{Ln-OH} + \text{H+}$$

The lewis acidity increases along the series due to the increased charge/size ratio.

Question 9

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.

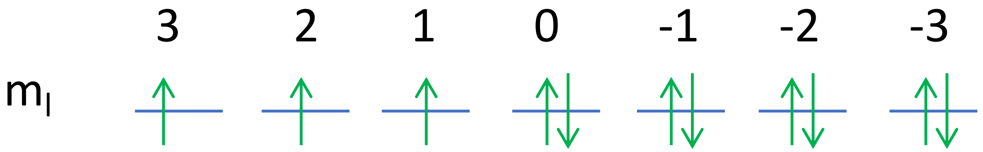
Which one fits better the measured value of the magnetic moment (9.58 μB) and why ?

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

Answer 9

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 9

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 10

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 10

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

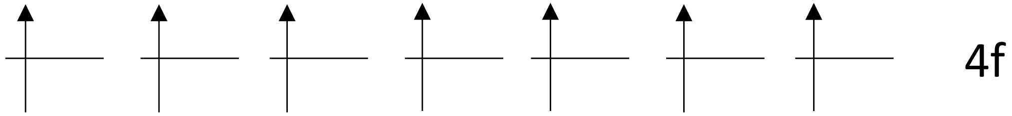
It will be shifted and broad because we have **unpaired electrons,** which will affect the magnetic moment applied and in consequence affect the shift of the protons surrounding the **paramagnetic nucleus**. It will be still visible because of the **short electron relaxation time**.

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] $\mathbf{4f^7}$

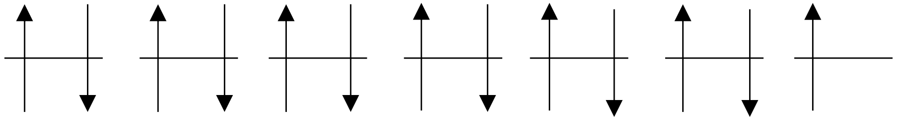
S=7/2



Answer 10

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

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

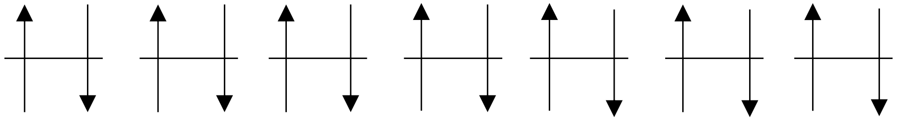


1 unpaired electron S=1/2

The ^{1}H 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] $4f^{14}$



0 unpaired electrons S=0 → diamagnetic

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

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 »?

Answer 11

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