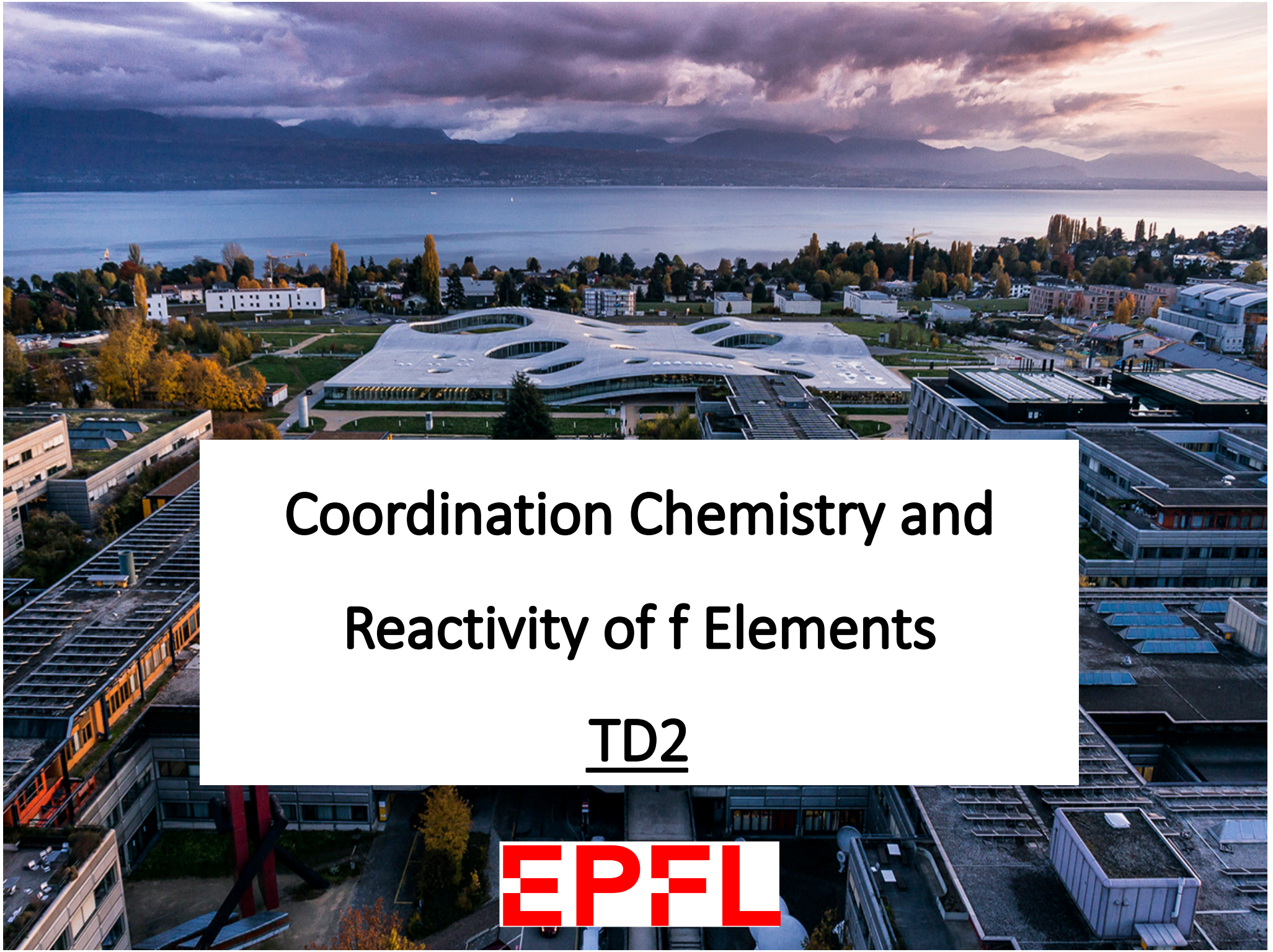


Coordination Chemistry and Reactivity of f Elements

TD2

EPFL

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+}

Question 2

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 3

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

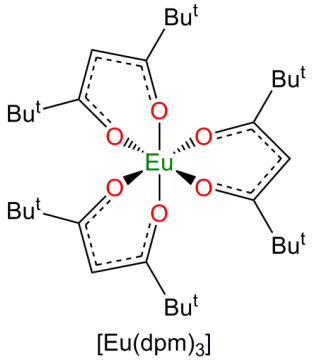
2) What are the applications NMR « Shift reagents »?

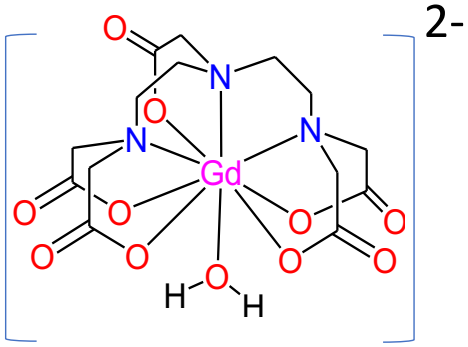
Question 4

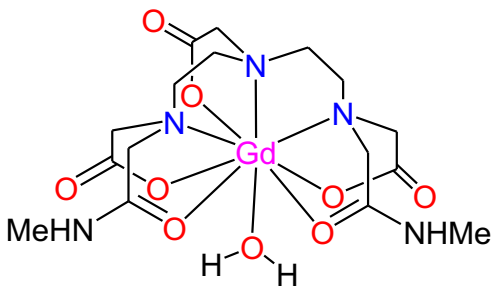
1) Indicate how for the following complexes the thermodynamic stability vary and why.

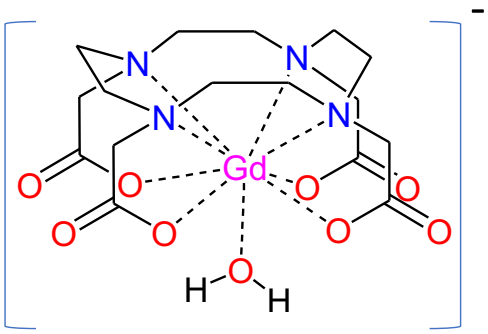
2) Indicate which complex has the highest kinetic stability and why.

3) Indicate how these complexes can be synthesised.



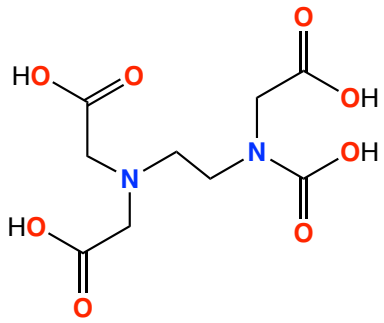




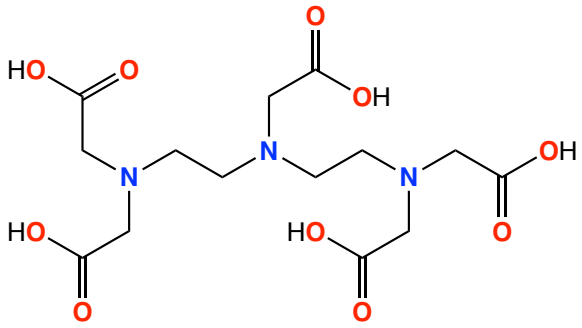


Question 5

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

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?

Question 7

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

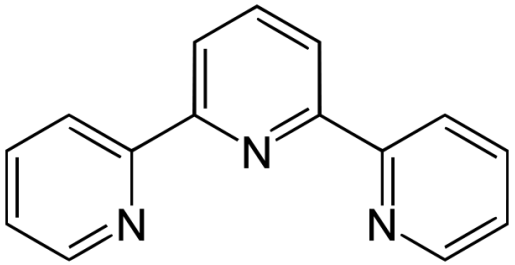
2) Identify the advantages and disadvantages of luminescent complexes of lanthanides compared to lanthanide inorganic materials.

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

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