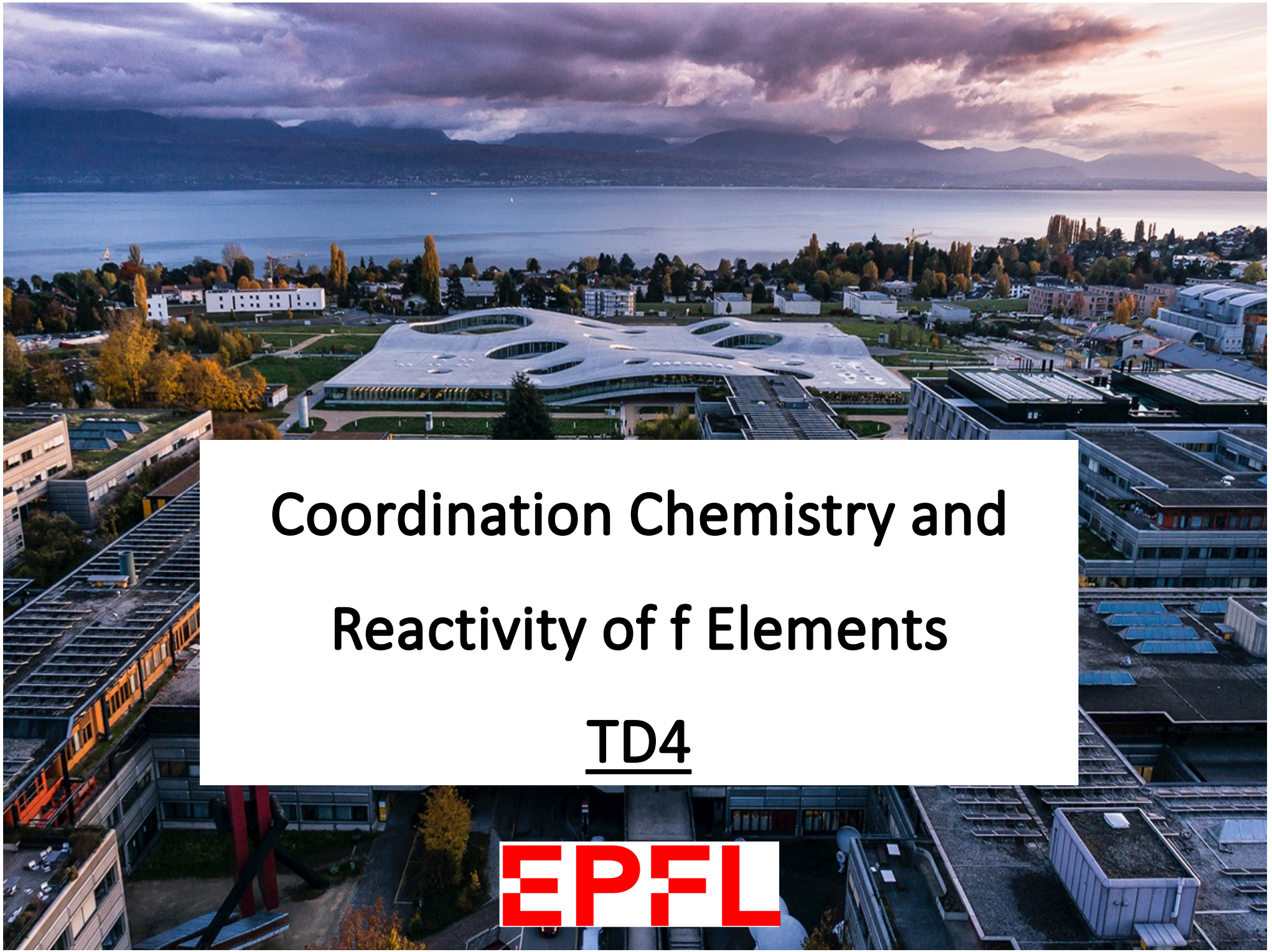


Coordination Chemistry and Reactivity of f Elements

TD4

EPFL

Question 1

1) Indicate the three possible routes for the synthesis of neutral lanthanide alkoxides ([$Ln(OR)_3$].

2) Draw the reaction schemes for each case.

3) What are the advantages and disadvantages of each ?

Question 2:

a) Explain in what case alkoxide ligands tend to form polynuclear complexes drawing some examples

b) In alkoxide clusters of TM metal-metal bond can be present. Explain why metal-metal bond formation is not observed in alkoxide clusters of lanthanides.

c) Give an example for a mononuclear and a polynuclear alkoxide complex.

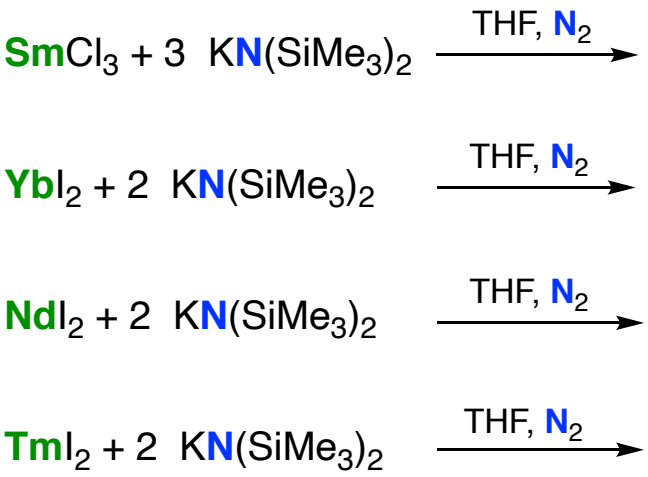
d) Explain why complexes Ln(III) complexes of CO are not known (in contrast to TM)

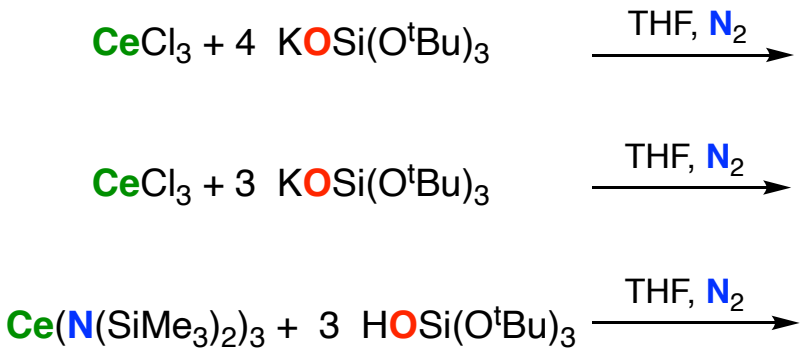
Question 3

A) Complete the following reaction scheme giving the structure of the final products.

B) Explain the observed differences in the structure of final products and reactivity.

C) Give the name of the reactions and the oxidation state of the metal ions.

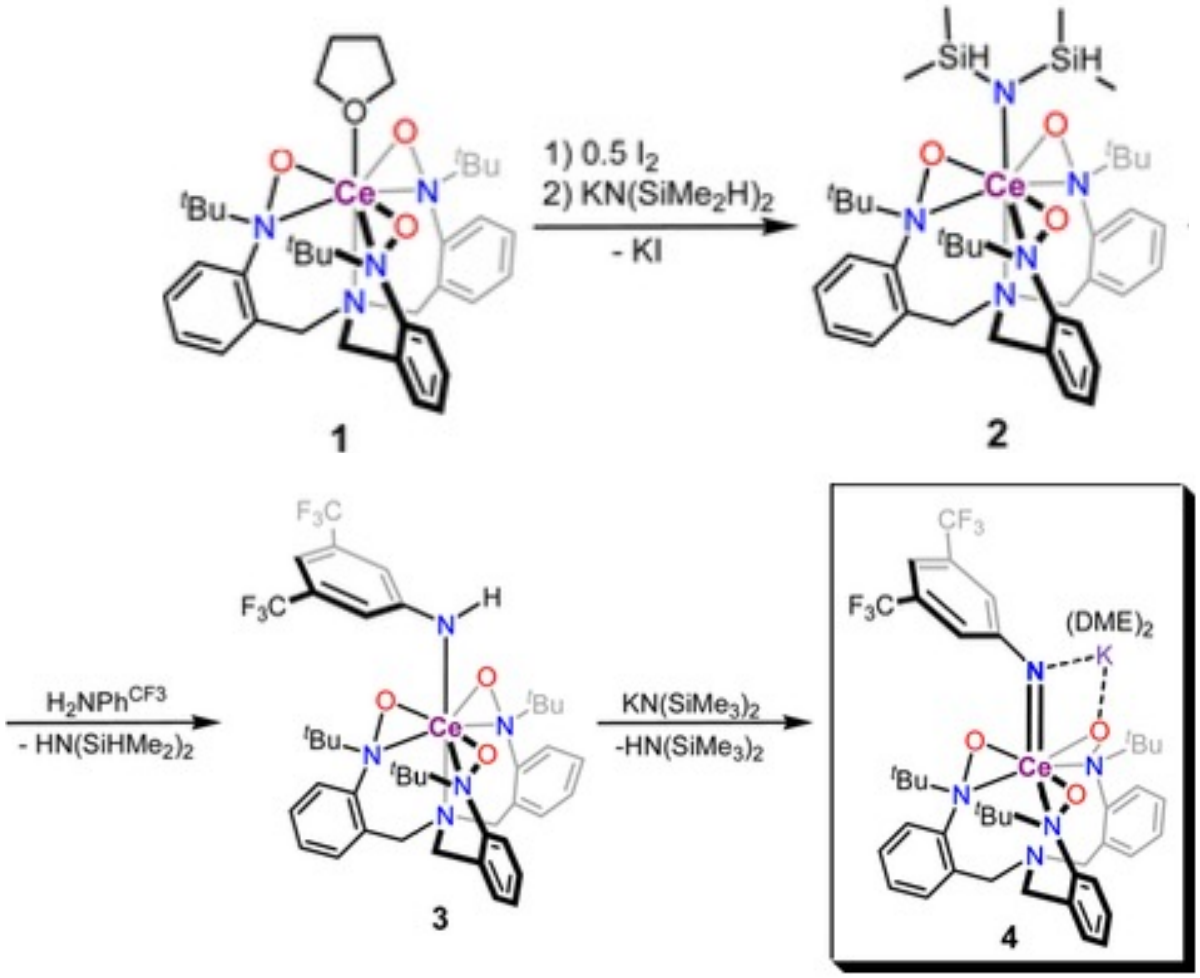




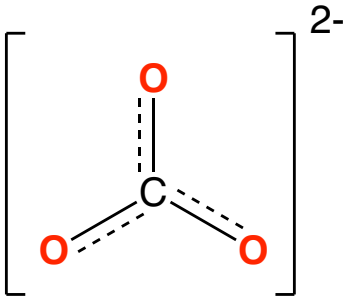
Question 4

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

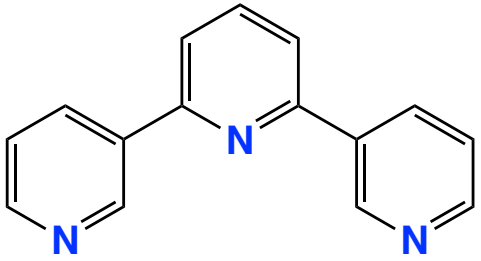
2) Describe the different steps of the following method for the formation of a Ce imide.



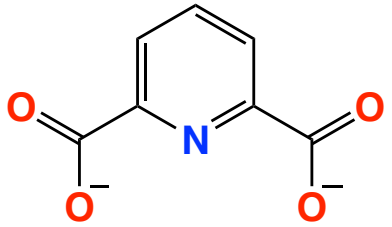
Question 5



carbonate



terpy



dpa^{2-}

1) Draw the structure of the complexes 1:3 (Ln:L) for the ligands above

2) Indicate how you would prepare them (type of Ln salt, solvent)

3) Indicate the order of stability in water and the species formed in the decomposition

Question 6

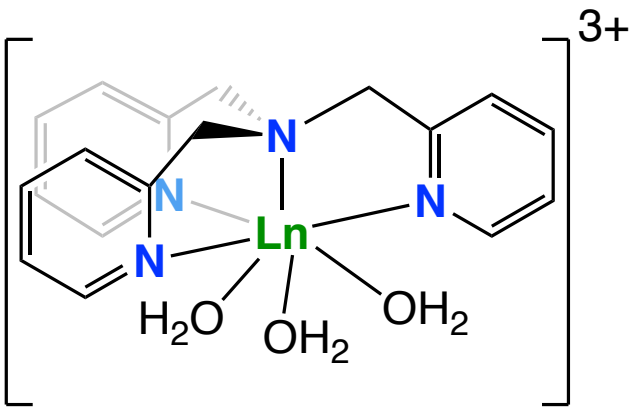
Considering the following reaction of hydrolysis

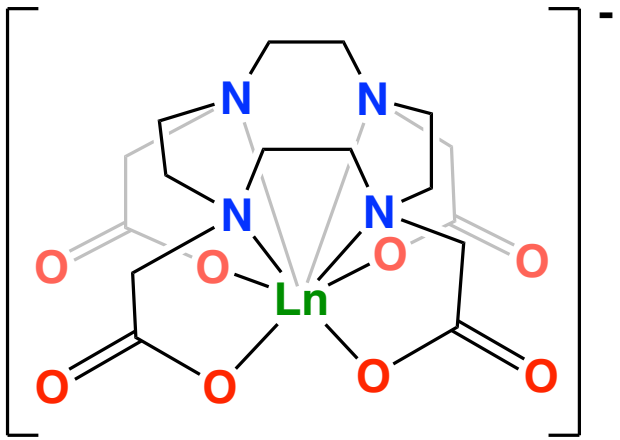
$$m\ [Ln(H_2O)_x]^{3+} \leftrightarrows [Ln_m(OH)_\ell(H_2O)_{(n-\ell)}]^{(3m-\ell)+} + \ell\ H^+$$

1) Indicate how the acidity of the lanthanide aqua complex vary along the series and why

2) Indicate how the binding of a polydentate ligand affects the acidity

3) Considering the following complexes: Which complex will form more easily hydroxides and why





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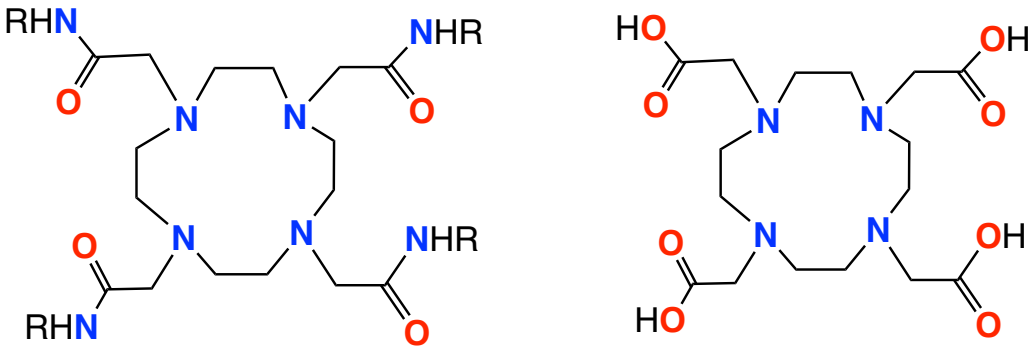
Question 7



1) Indicate which ligand form the most thermodynamically stable complex

2) Indicate how the kinetic stability of the two complexes vary

3) Indicate a possibile route for the synthesis of these two complexes

4) Indicate how their stability in water vary

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