Examen

" Coordination Chemistry and Reactivity of f Elements"

Prof. Marinella Mazzanti

Date: 26.06.2024

Nom: _____

Prénom: _____

N° Sciper: _____

Points:_____(sur 50)

1) (5 points)

Complexes of all lanthanide(II) ions have been isolated using the ligand $^{SiMe3}Cp^{-}$.
a)Indicate the formula of the complexes obtained and how these complexes have been prepared. Indicate if the same complexes could be isolated with the ^{CMe3}Cp ligand and justify your answer?. (2.5 points)

b) Indicate the outcome of the following reactions of Ln^{2+} and justify (2.5 points)

(OAr= $C_6H_3{}^tBu_2$-2,6)

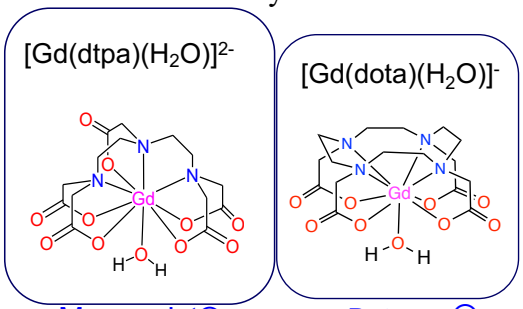
2) (5 points)
a) Using only your periodic table give and justify the electronic configuration of Dy^{3+}
Work out the ground state of Dy^{3+} (2 points)

b) Calculate the magnetic moment of a Dy^{3+} complex using the spin-only formula and the SOC formula. Explain why one fits better with the measured value of the magnetic moment (10.6 mB). (2 points)

c) Explain why none of these two formulas correctly predict the magnetic moment of Sm^{3+} (1 points)

3) (**5 points)**

The complexes $[Gd(dtpa)(H_2O)]^{2-}$ and $[Gd(dota)(H_2O)]^{-}$ (structure below) are used in a clinical medical analysis.



a) Indicate the name of this technique and what is the role of the complexes. (1.5)

b) Identify the one most important property of these complex that has led to their use in humans. Indicate how the property arises from the structure. (1.5)

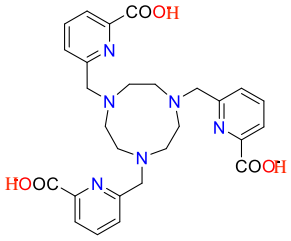
c) Indicate which one you would choose if you had to undergo an analysis and why.(1)

d) Indicate the limitation of these complexes and suggest one possible modification leading to more efficient compounds. (1)

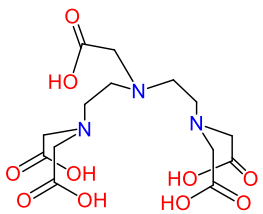
4) (5 points)

a) What are) the emission colors of Eu^{3+} and Tb $^{3+}$? (1 point)

b) Draw the structure of the europium complexes formed by the following ligands L in water after adjustement of the pH at 7.4. (1.5)



H_3tpatcn



H_5dtpa

b)

c) Indicate which one of these complexes is likely to have a higher luminescence quantum yield and explain why. (2.5)

5) (5 points)

Indicate what are the most stable oxidation states for the lanthanide ions and actinide ions. (specify for each ion when needed)(2.5)

Indicate all possible oxidation states accessible for each lanthanide ions (1)

Explain why a larger number of oxidation states are accessible to early actinide ions. (1.5)

6) (6 points)

a) Suggest three possible routes for the synthesis of the complex $[Yb(OR)_3]$ (2)

b) Indicate the advantages and disadvantages for each route. (2)

c) Draw possible structure of these complexes depending on the bulk (very bulky , not bulky) of the R substituent (2)

7) (4 points)

Lanthanide ions in water undergo the following equilibrium:

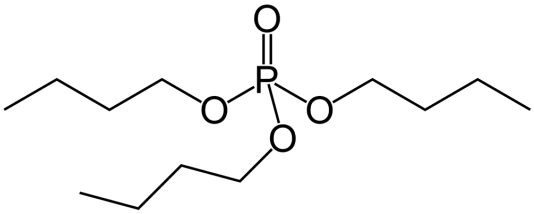
$$m\ [Ln(H_2O)_x]^{3+} \leftrightarrows [Ln_m(OH)_\ell(H_2O)_{(n-\ell)}]^{(3m-\ell)+} + \ell\ H^+$$

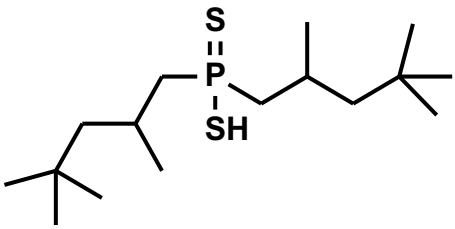
a) Indicate how the value of the associated constant vary along the lanthanide series and why.

b) Indicate what how the presence of polydentate carboxylate ligands binding the lanthanide will shift the equilibrium

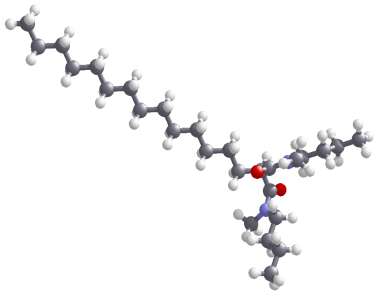
8) (5 points)

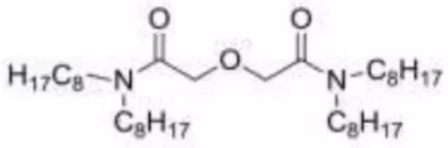
The three molecules indicated below are used at different step of the reprocessing of spent nuclear fuels . Please indicate which elements can be separated by each molecule in the extraction of nuclear fuel after dissolution in nitric acid.





BTP (PUREX) Cyanex



(

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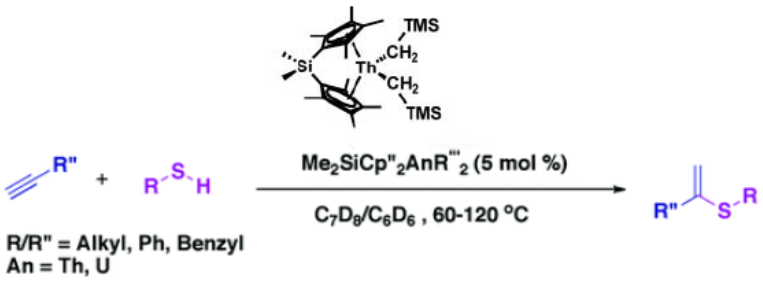
Diamex (long chain amides)

9) (5 points)

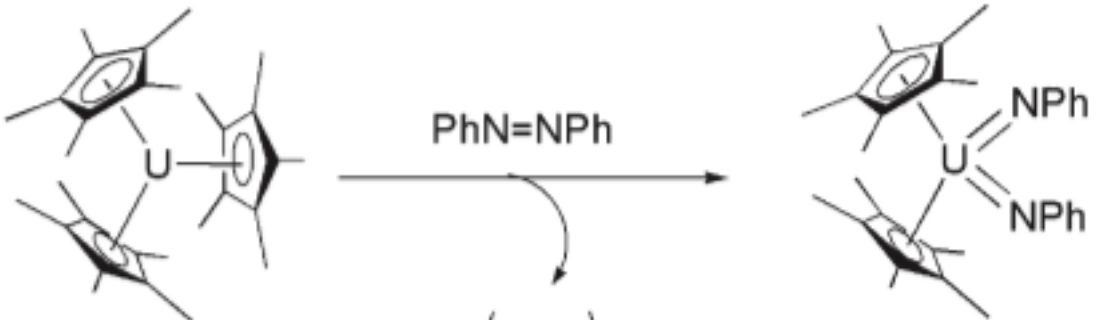
Suggest a mechanism for the following reaction catalyzed by an actinide complex. Indicating the name of the reaction involved in each each step (4 points)



10) 5 points

Assign the oxidation state of the complexes reported below , the possible additional byproducts and the type of reactivity involved (name of reactions, number of electrons involved) in the following reactions:

a) (2.5 points)



b)