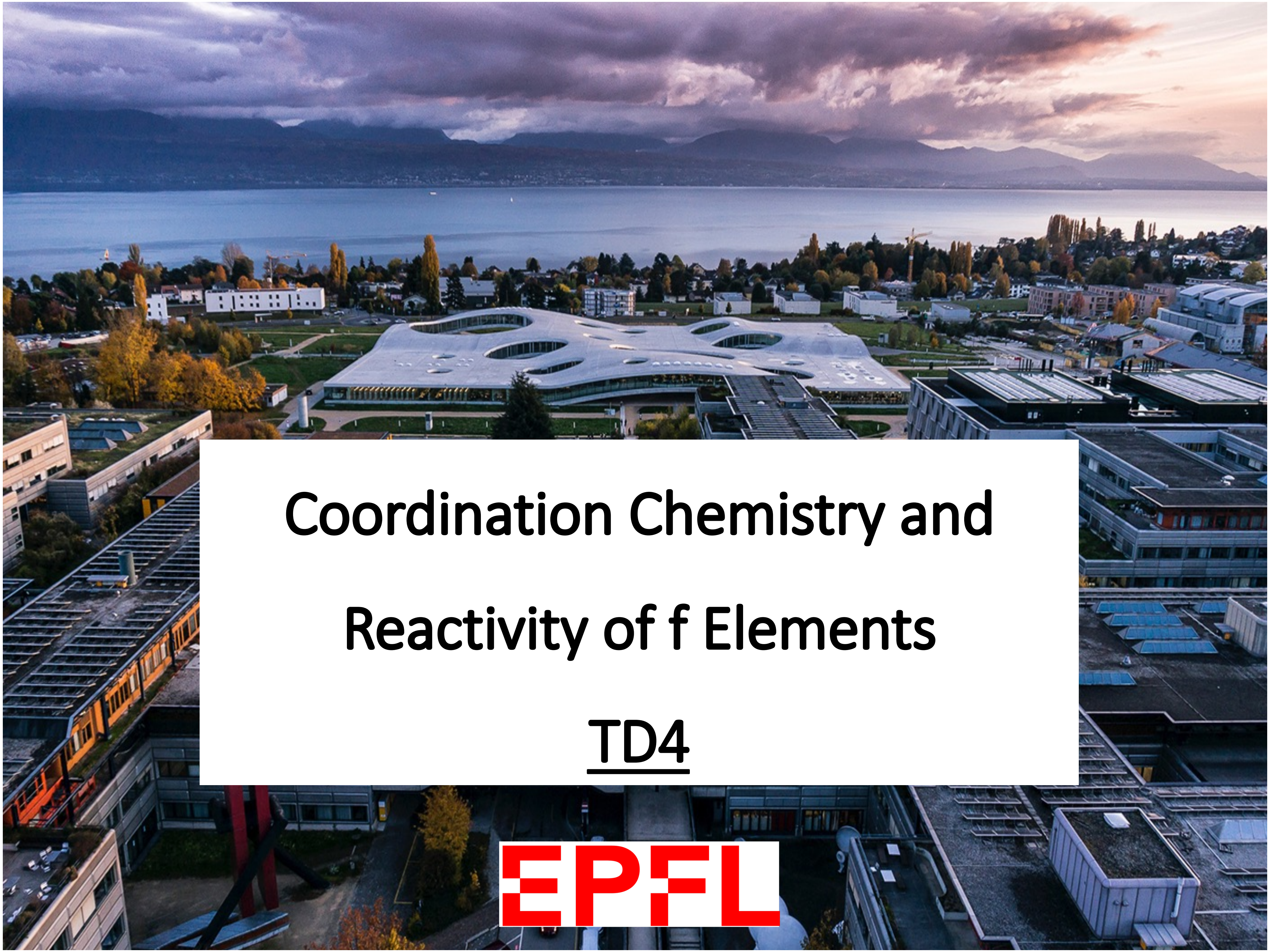

Coordination Chemistry and Reactivity of f Elements

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 ?

Answer 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.

Protonolysis: $Ln(N(SiMe_2)_2)_3 + 3\ HOR \rightarrow [Ln(OR)_3] + 3\ HN(SiMe_2)$

Salt metathesis: $LnX_3 + 3\ KOR \rightarrow [Ln(OR)_3] + 3KX$

Oxidation: $Y + 3\ ROH \rightarrow [Y(OR)_3] + 1.5\ H_2$

EPFL

Answer 1

3) What are the advantages and disadvantages of each ?

	Advantages	Disadvantages
Protonolysis: $Ln(N(SiMe_2)_2)_3$ + 3 HOR → $[Ln(OR)_3]$ + 3 $HN(SiMe_2)$	- No chloride retention - Avoid “ate” complex formation - Soluble starting material	- Silylamide needs to be prepared - Bulky nature of the silylamide, it may be inert to substitution
Salt metathesis: LnX_3 + 3 KOR → $[Ln(OR)_3]$ + 3KX	- LnX_3 commercially available	- Insoluble LnX_3 - Possibility of chloride retention - Can give unwanted mixture with ”ate” complex
Oxidation: Y + 3 ROH → $[Y(OR)_3]$ + 1.5 H_2	- No need to make the ligand salt - Production of a gas	- Metal may need purification - Reaction could need heat or a catalyst - Might result in mixed-valent compounds

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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)

EPFL

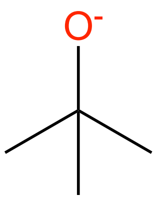
Answer 2:

A) Explain in what case alkoxide ligands tends to form polynuclear or mononuclear complexes.

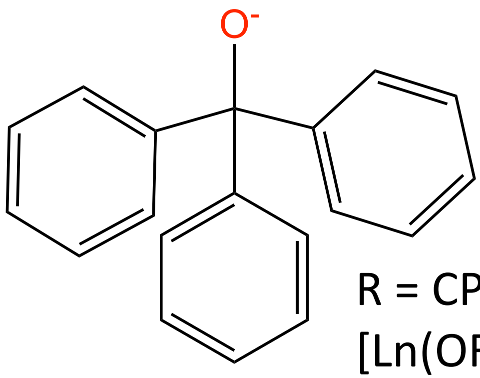
C) Give an example for a mononuclear and a polynuclear alkoxide complex.

<u>Alkoxide</u> = conjugated base of an alcohol = R—O^-

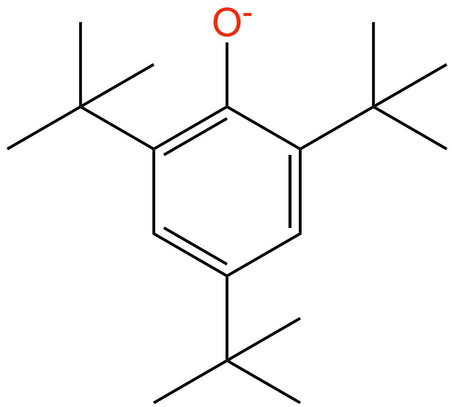
- The size of alkoxide clusters depends upon the size of the R-groups
- Bigger the R-group, smaller the alkoxide cluster
- Very bulky aryloxides can be used to isolate monomeric complexes



R = ^{t}Bu
$[Ln(OR)_3]_3$



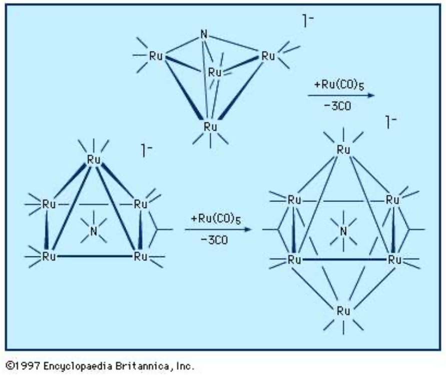
R = CPh_3
$[Ln(OR)_3]_2$



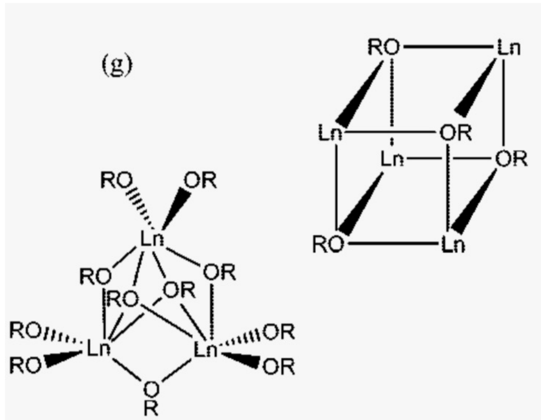
R = $(C_6H_2{}^tBu_3)$
$[Ln(OR)_3]$
Monomer

Answer 2:

B) Transition metal clusters can feature metal-metal bond.
Explain why Ln-Ln bond is not observed in alkoxide clusters of lanthanides.



Ru-Ru bonds



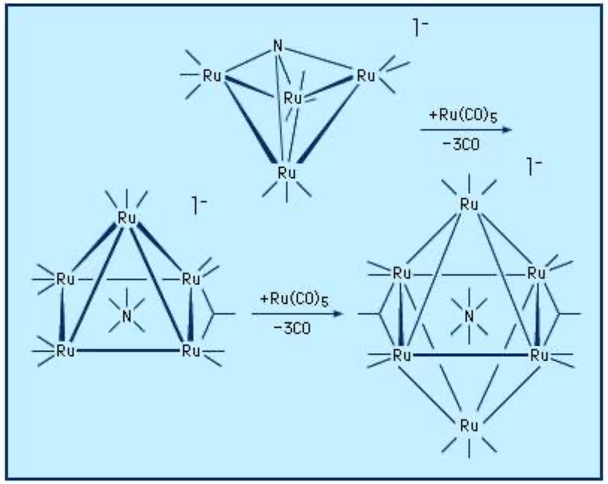
No Ln-Ln bond

- f orbitals are inner core

  They cannot be involved in the orbital overlap required to form M-M bonds

Answer 2:

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



- Transition metal carbonyls from metals in low oxidation states where d orbitals can overlap well with the antibonding orbitals of CO and give back-bonding.
- f orbital involvement in bonding in lanthanide compounds is minimal and the high oxidation state will contract the orbitals even further.
- CO is a rather weak σ -donor, and lanthanides tend to complex only with good σ -donors.

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.

$$SmCl_3 + 3\ KN(SiMe_3)_2 \xrightarrow{THF,\ N_2}$$

$$YbI_2 + 2\ KN(SiMe_3)_2 \xrightarrow{THF,\ N_2}$$

$$NdI_2 + 2\ KN(SiMe_3)_2 \xrightarrow{THF,\ N_2}$$

$$TmI_2 + 2\ KN(SiMe_3)_2 \xrightarrow{THF,\ N_2}$$

$$CeCl_3 + 4\ KOSi(O^tBu)_3 \xrightarrow{THF,\ N_2}$$

$$CeCl_3 + 3\ KOSi(O^tBu)_3 \xrightarrow{THF,\ N_2}$$

$$Ce(N(SiMe_3)_2)_3 + 3\ HOSi(O^tBu)_3 \xrightarrow{THF,\ N_2}$$

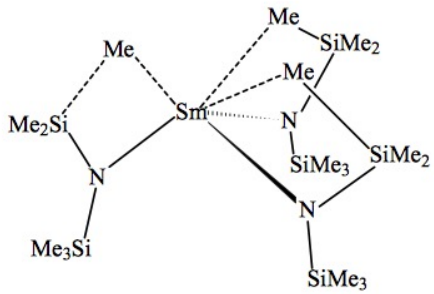
Answer 3

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.

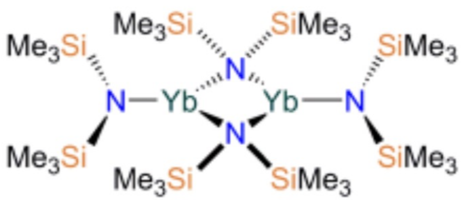
A) $SmCl_3 + 3\ KN(SiMe_3)_2 \xrightarrow{THF,\ N_2} [Sm(N(SiMe_3)_2)_3] + 3\ KCl$



B) Pyramidal geometry due to agostic interaction

C) Salt metathesis → Sm(III)

A) $YbI_2 + 2\ KN(SiMe_3)_2 \xrightarrow{THF,\ N_2} [Yb(N(SiMe_3)_2)_2] + 2\ KI$



B) Bridging mode allows to saturate the large coordination sphere of Yb and Sm

C) Salt metathesis → Yb(II)

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Answer 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.

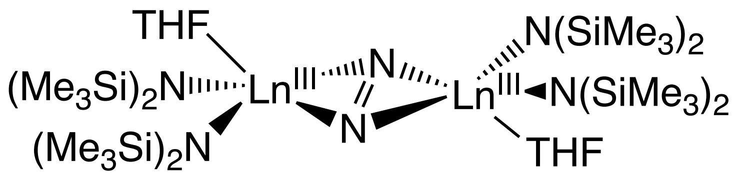
C) Give the name of the reactions and the oxidation state of the metal ions.

A)

$NdI_2 + 2\ KN(SiMe_3)_2$

$TmI_2 + 2\ KN(SiMe_3)_2$

$\xrightarrow{THF,\ N_2}$ $[Ln(N(SiMe_3)_2)_2(N_2)] + 2\ KI$



B) Tm^{2+} and Nd^{2+} are very reducing and their complexes cannot be isolated because they reduce N_2 to N_2^{2-}

C) In situ salt metathesis + redox reaction → Ln(II) to Ln(III)

Answer 3

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

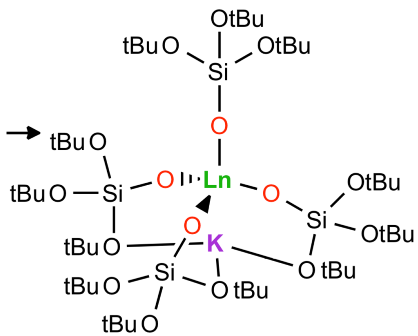
B) Explain the observed differences in the structure of final products and reactivity.

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

A)

$CeCl_3 + 4\ KOSi(O^tBu)_3 \xrightarrow{THF,\ N_2} [KCe(OSi(O^tBu)_3)_4] + 3\ KCl$

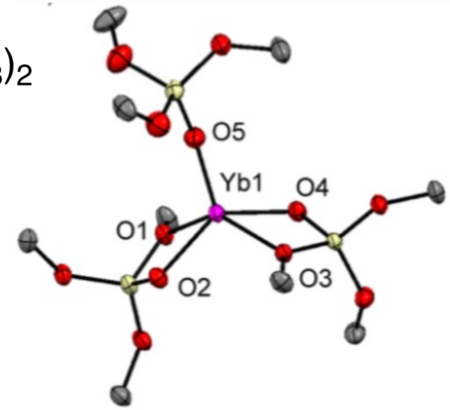
$CeCl_3 + 3\ KOSi(O^tBu)_3 \xrightarrow{THF,\ N_2} x\ [KCe(OSi(O^tBu)_3)_4] + y\ KCl + z\ CeCl_3$

→ 

B) Tetrakis complex is favored when potassium ligand salt is used whatever the stoichiometry

C) Salt metathesis → Ce(III)

A) $Ce(N(SiMe_3)_2)_3 + 3\ HOSi(O^tBu)_3 \xrightarrow{THF,\ N_2} [Ce(OSi(O^tBu)_3)_3] + 3\ HN(SiMe_3)_2$



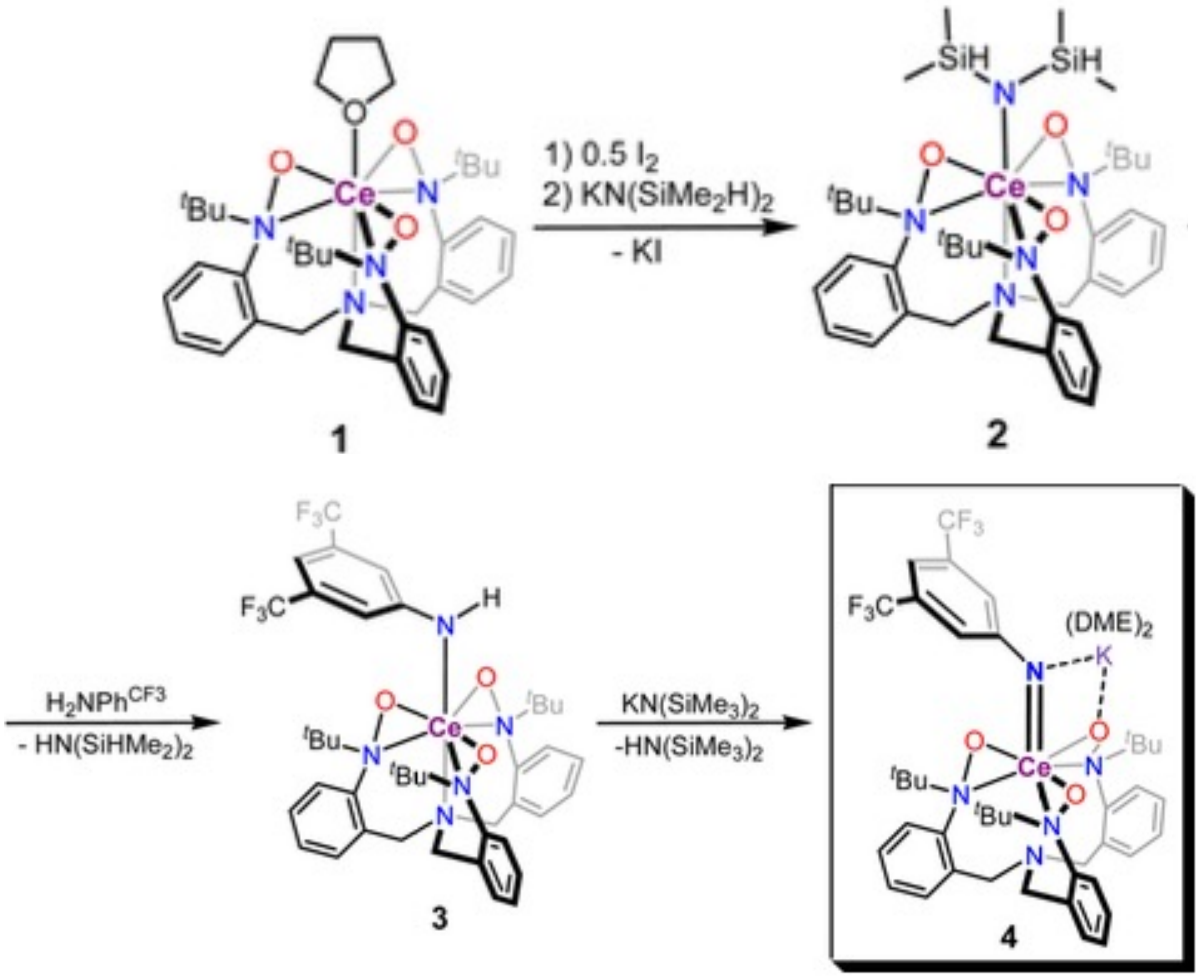
B) Tris ligand complex can be formed when potassium is removed from the reaction mixture.

C) Protonolysis → Ce(III)

Question 4

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

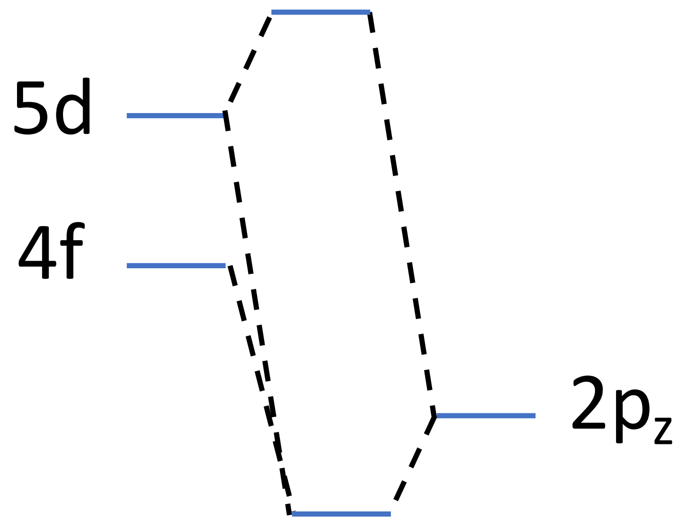
2) Describe the different steps of the following method for the formation of a Ce imide.



Answer 4

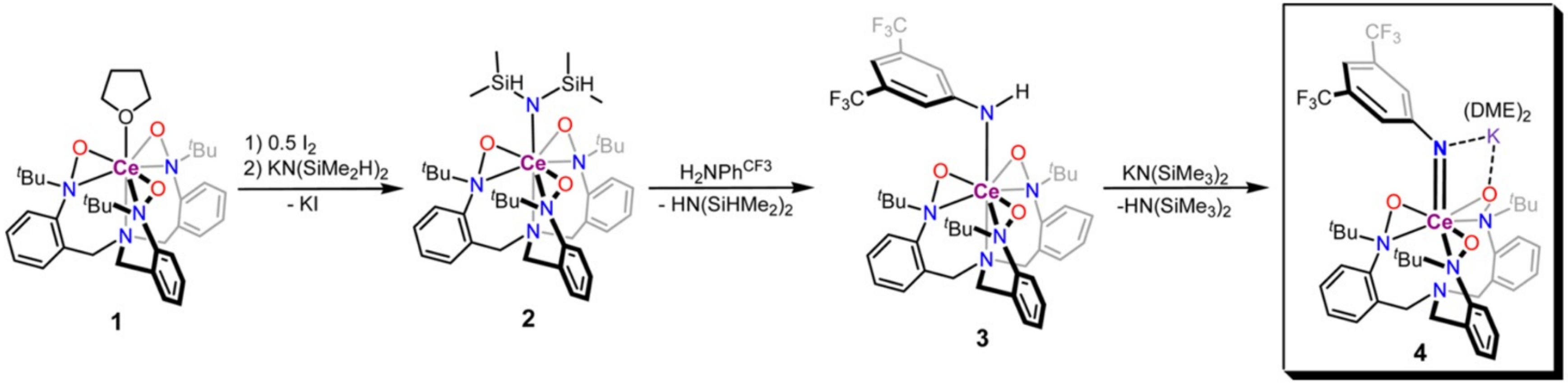
1) Explain why Ln-X (X=N, O, P) multiple bond is not common in Ln chemistry.

f-orbitals are not available for covalent bonds and 5d are too high in energy



Answer 4

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



1→ Oxidation to Ce(IV) with iodine

2→ Salt metathesis to exchange I^- with an amide

3→ Ligand exchange by protonolysis of amide

4→ deprotonation of the NH

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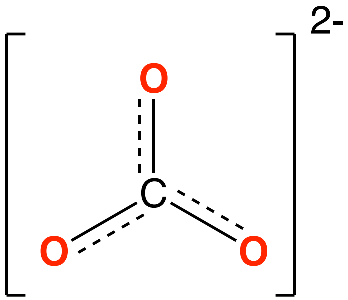
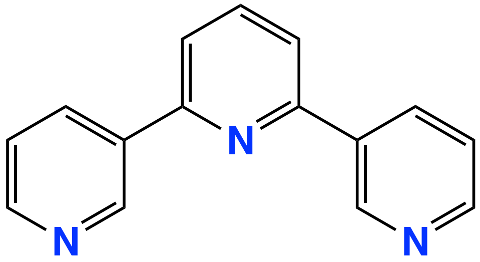
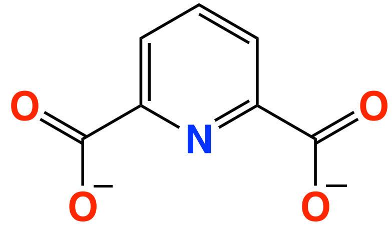
Question 5



carbonate



terpy



dpa^{2-}

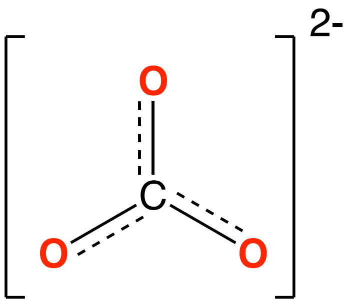
1) Draw the structure of the complexes 1:3 (Ln:L) for the ligands above

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

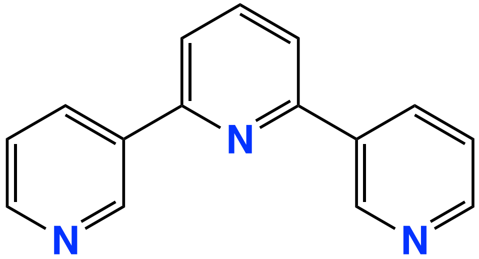
3) Indicate the order of stability in water and the species formed in the decomposition

Answer 5

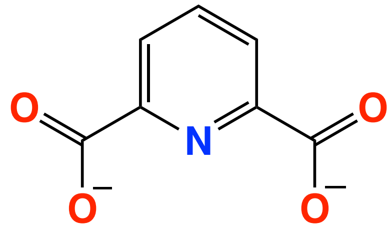
1) Draw the structure of the complexes 1:3 (Ln:L) for the ligands



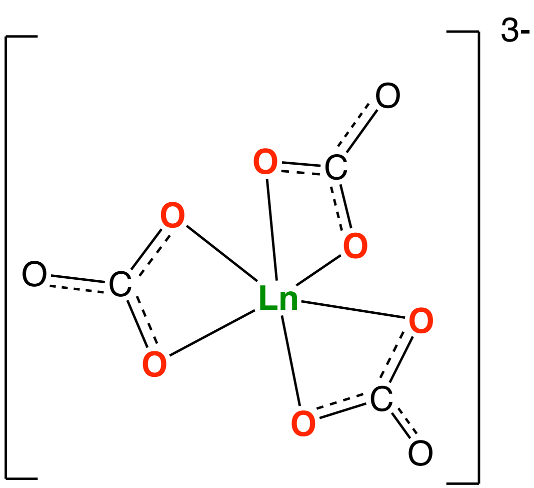
carbonate

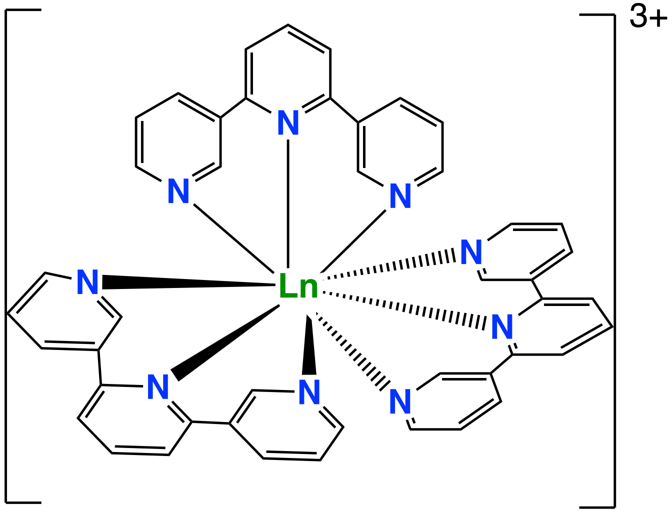


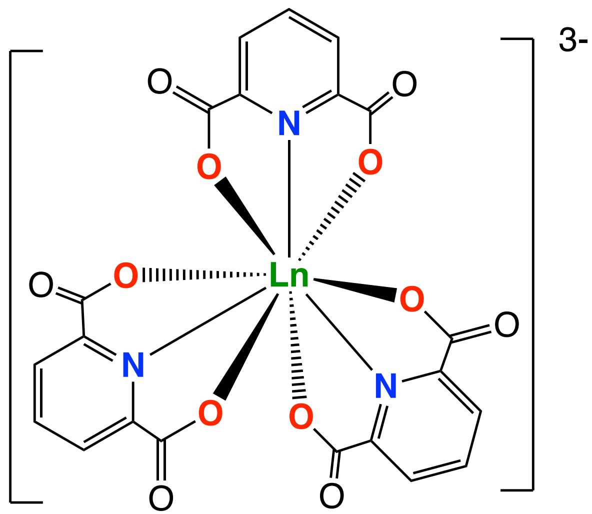
terpy



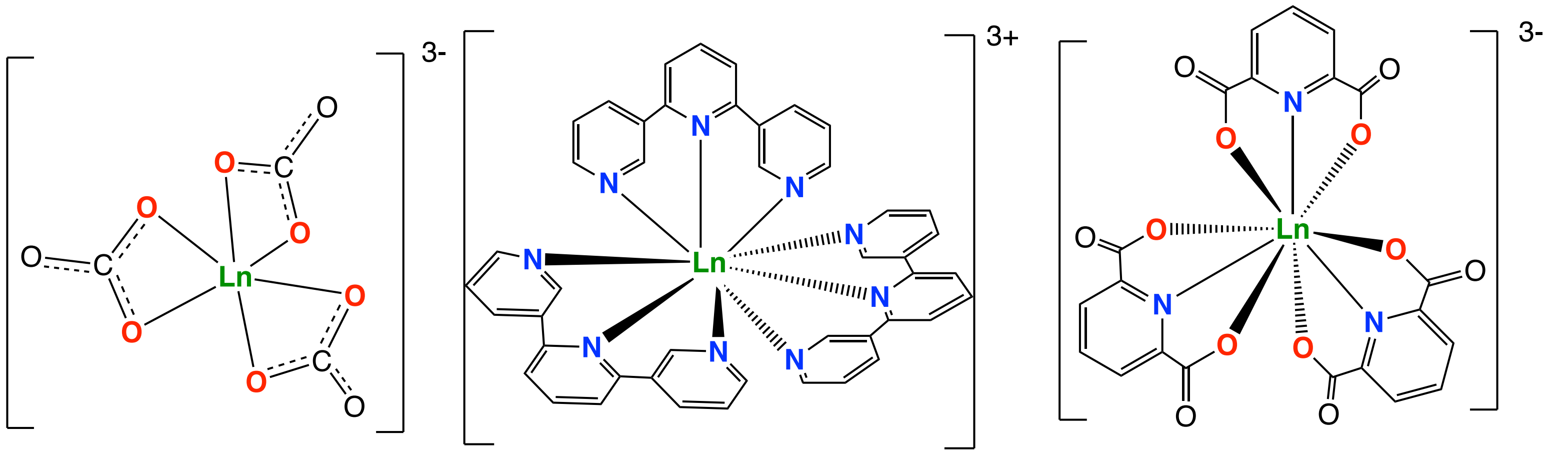
dpa^{2-}







Answer 5



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

$$LnCl_3 + 3\ K_2CO_3 \xrightarrow[\text{(weakly coordinating solvent)}]{\text{thf}} [Ln(CO_3)_3]K_3 + 3\ KCl$$

$$Ln(OTf)_3 + 3\ \text{terpy} \xrightarrow[\text{(polar weakly coordinating solvent)}]{CH_3CN} [Ln(\text{terpy})_3](OTf)_3$$

$$LnCl_3 + 3\ K_2\text{dpa} \xrightarrow[\text{(weakly coordinating solvent)}]{\text{thf}} [Ln(\text{dpa})_3]K_3 + 3\ KCl$$

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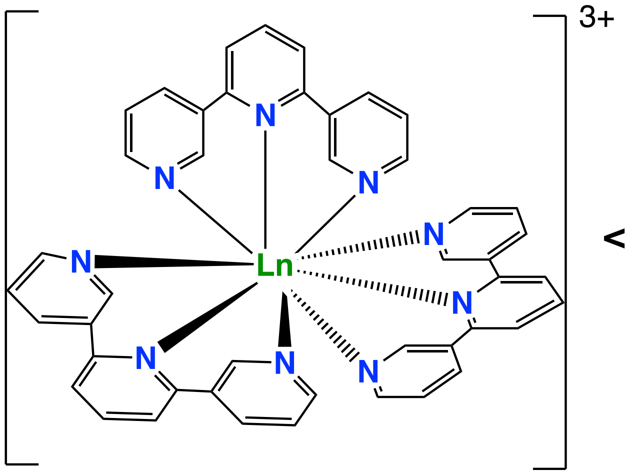
Answer 5

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



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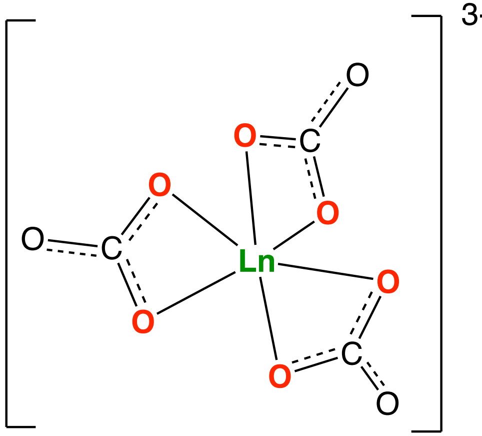

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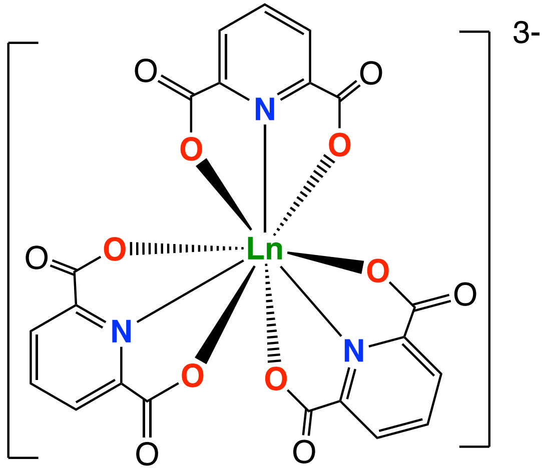
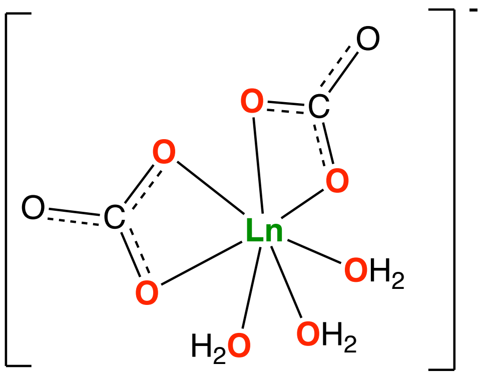
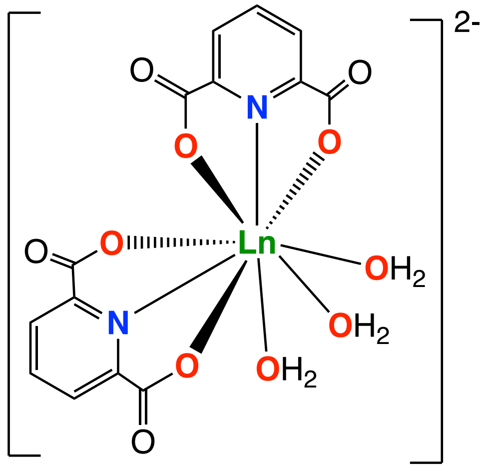


Species formed in water

$[\mathbf{Ln}(H_2O)_9]^{3+}$





Question 6

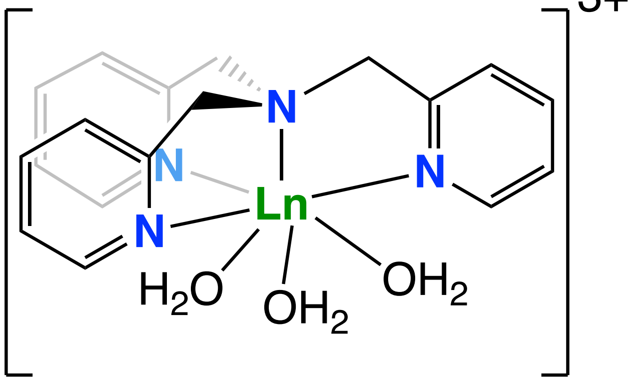
Considering the following reaction of hydrolysis

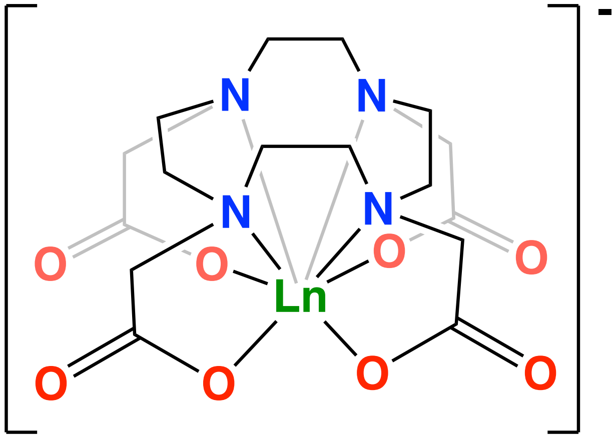
$$m\,[Ln(H_2O)_x]^{3+} \leftrightarrows [Ln_m(OH)_\ell(H_2O)_{(n-\ell)}]^{(3m-\ell)+} + \ell\,H^+$$

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





Answer 6

Considering the following reaction of hydrolysis

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

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

1) The acidity of the lanthanide aquo complex increases along the Ln series, due to the reduction on the ionic radii (lanthanide contraction), which results in a higher charge density on the Ln^{3+}.

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

2) The binding of a polydentate ligand will reduce partially the charge density on the Ln^{3+} ion, resulting in a reduction of the acidity of the complex.

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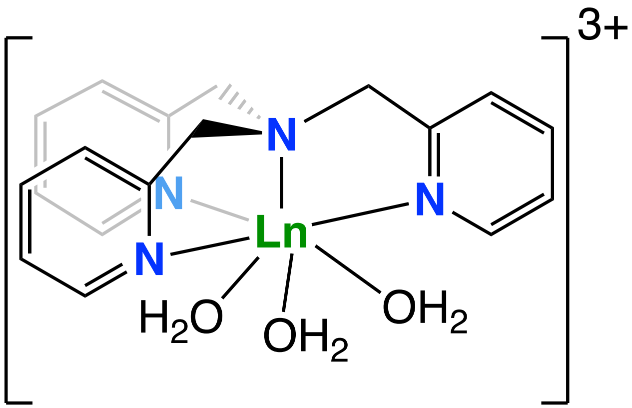
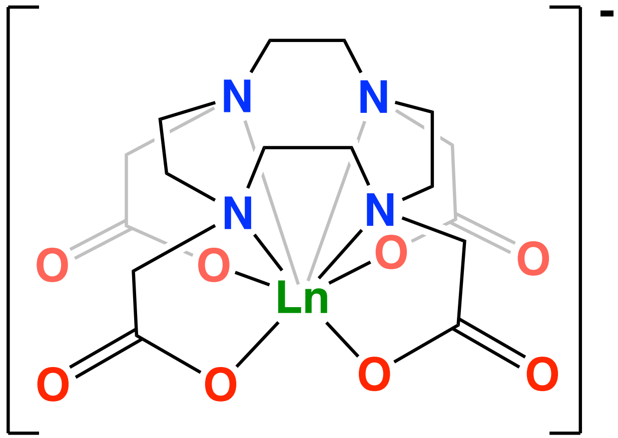
Answer 6

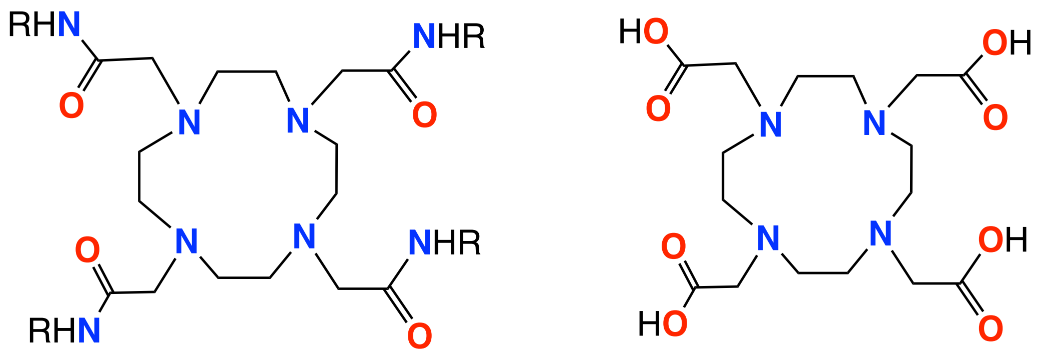
3) Considering the following complexes: Which complex will form more easily hydroxides and why





3) The complex with the neutral ligand (tpa) has a higher charge density on the Ln^{3+} and therefore it will polarize easier the water molecules, liberating H^+ and generating the respective hydroxide.

Question 7



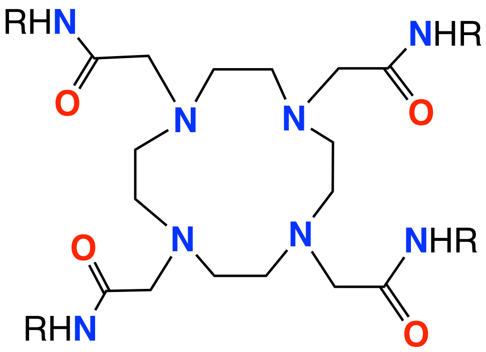
1) Indicate which ligand form the most thermodynamically stable complex

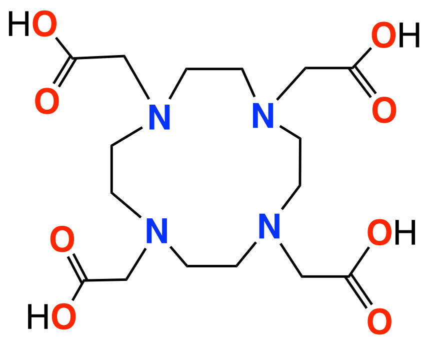
2) Indicate how the kinetic stability of the two complexes vary

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

4) Indicate how their stability in water vary

Answer 7





1) Indicate which ligand form the most thermodynamically stable complex

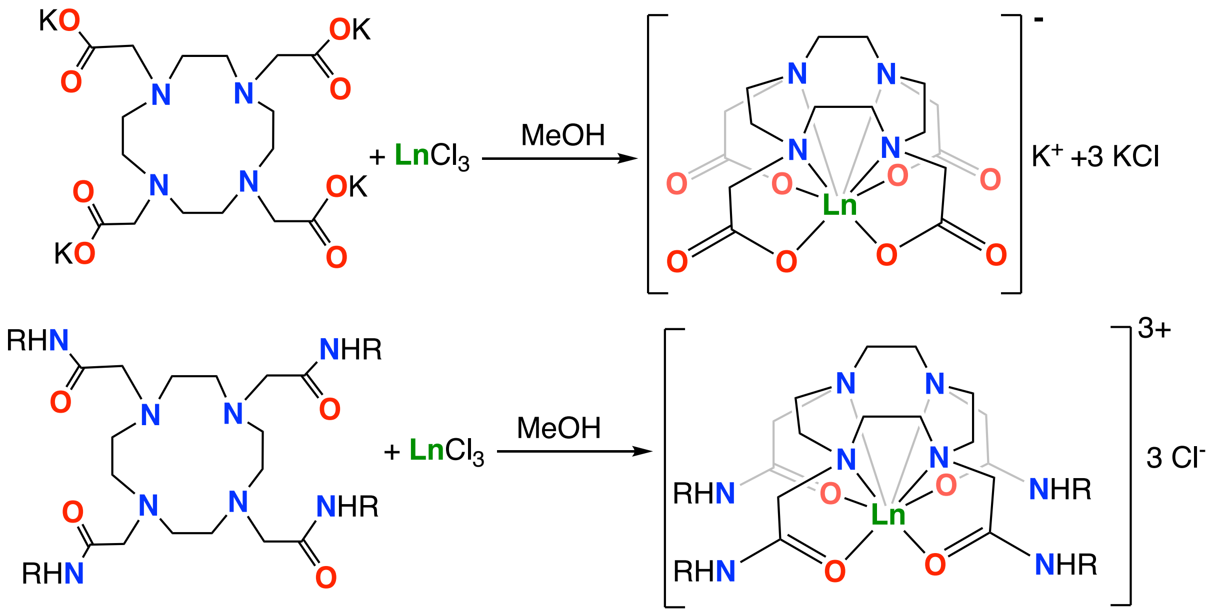
1) The ligand DOTA (on the right) will give the most thermodinamically stable complex, due to the presence of 4 negative O-donor atoms.

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

2)They will exhibit similar kinetic stability

Answer 7

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



4) Indicate how their stability in water vary

4) The DOTA ligand gives very stable complex in water due to the chelate and macrocyclic effects, together with a higher number of negative O-donor atoms

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If you have any questions about these exercises you can send a mail to :

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Arsene: fang-che.hsueh@epfl.ch