

CH4514 - Advanced Metals Chemistry Tutorial 2

1. The ligand, L (Fig. 1), reacts with Nd^{3+} and Yb^{3+} salts in water to form coordination complexes that display strong infra-red emission when sensitised with visible light. The electronic process that produces this fluorescence in the Yb complex (Fig. 2) involves a transition from the first excited state to the ground state.

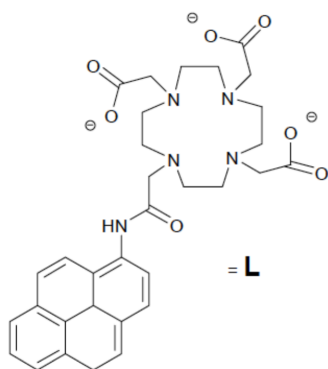


Figure 1

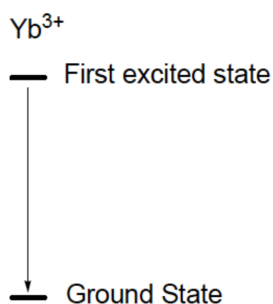


Figure 2

(i) Describe the features of the macrocyclic ligand, which make it suitable for the purpose described.

(ii) State which complex (Nd or Yb) will have the higher stability constant in aqueous solution and explain your reasoning.

(iii) Use Hund's rules to determine the term symbols $^{(2S+1)}L_J$ of the ground and first excited states of the Yb complex.

2. The colour of SmI_2 is intense purple while that of SmI_3 is pale orange. Explain this difference with reference to the appearance of their absorption spectra.

3. Explain why $[\text{WS}_4]^{2-}$ is red while $[\text{WO}_4]^{2-}$ is white.

4. Why are the physical properties of Ln^{3+} species very similar?

5. $[\text{Ru}(\text{bpy})_3]^{2+}$ is a very commonly used photoredox catalyst but $[\text{Fe}(\text{bpy})_3]^{2+}$ is not. Based on the electronic structure of the two complexes rationalize why the latter would not work as well.

Answers

1 (i). The ligand contains hard donor carboxylate oxygen atoms, which bind tightly to the Ln^{3+} hard cations. The ligand is strongly negatively charged and polydentate. Thus, Ln^{3+} binding will be strong as a function of both the chelate and macrocyclic effects. The pyrene substituent present creates an antenna to sensitize the luminescence as the f-f transitions of the lanthanoid metal are Laporte forbidden.

1 (ii). This is based on a HSAB argument. Yb is smaller than Nd and so its charge density is higher and it is thus harder. It will therefore have a higher stability constant in water (hard donor ligand). The reason why Yb is smaller than Nd is a result of an increased Z_{eff} for Yb.

1. (iii). Yb^{3+} is $4f^{13}$
 m_l : +3 +2 +1 0 -1 -2 -3
 $\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow$

Total spin angular momentum, $S = 7(1/2) - 6(1/2) = 1/2$
Multiplicity $(2S + 1) = 2$

$L = (3 + 3 + 2 + 2 + 1 + 1 + 0 - 1 - 1 - 2 - 2 - 3) = 3 \Rightarrow F$ state

J can take values of $(L + S), (L + S) - 1, \dots, (L - S)$
For $>$ half-filled subshell, ground state J is highest $(L+S)$ value, i.e. 3.5 (7/2)

Thus ground state term symbol is ${}^2F_{7/2}$

First excited term is ${}^2F_{5/2}$

2. Colour of Sm^{3+} is due to an f-f transition, which is Laporte forbidden. The 4f orbitals are deep seated/little radial extension – thus Laporte not relaxed by vibronic coupling as does exist for d-block metal complexes. The absorption bands are sharp because energies not affected by molecular vibrations (known as Franck-Condon effects). The Sm^{2+} absorption is due to 4f to 5d transition – completely allowed and broad (1 mark).

3. Given the high oxidation state of W and the strong π -donor nature of the chalcogen ligand the absorption is due to an LMCT transition. As sulfur is less electronegative, the π -system will be higher in energy and therefore the LMCT will be low enough in energy to be in the visible part of the spectrum (around 500 nm to appear red).

4. The chemical properties of an ion are mainly dependent on its size and charge. For the various Ln^{3+} ions, since the charge remains the same and the decrease in size is just marginal, their chemical properties are very similar, making their separation difficult. But, it is this small variation in properties that permits the separation of the lanthanoids by fractional means.

5. Both absorb through a strong MLCT state. However, the splitting of the d-orbitals in $[\text{Fe}(\text{bpy})_3]^{2+}$ is far smaller than in the corresponding $[\text{Ru}(\text{bpy})_3]^{2+}$. Thus, there is a very low lying MC state that dominates the excited state properties, making electron transfer from/to the excited MLCT state of $[\text{Fe}(\text{bpy})_3]^{2+}$ much more unlikely (which is the dominant reaction mode in photoredox catalysis).