

ANSWERS

1. a. Cu(TPP) is active in UV-Vis AND why? EXPLAIN YOUR REASON.

If you replace Cu²⁺ with Zn²⁺ and you have Zn(TPP), what will happen to the UV-vis spectra? EXPLAIN your answer

Ans. a. Molecules comprising n-electrons, which are both bonding and non-bonding electrons, can absorb energy in the form of ultraviolet-visible light to excite these electrons to higher anti-bonding molecular orbitals. The lower the energy gap between the highest occupied molecular orbital and the lowest occupied molecular orbital, the more easily are the electrons excited, absorbing a longer wavelength of light.

UV-Vis is used to determine the optical absorption in the visible light region. The UV-Vis spectrum shows the transition of electrons as a consequence of UV-Vis light interactions with chemical bonds.

Reasons for Cu(TPP) showing activity in UV-Vis:

- the metallation increases the symmetry that results in less Q bands.
- the presence of conjugated compounds.
- the presence of the porphyrin section in the catalyst sample
- the large absorbance shows transition from free base porphyrin to confirm metallation.
- pi to pi* transitions between bonding and antibonding molecular orbital.

However, when we replace Cu²⁺ with Zn²⁺, the differences in the central transition metal ions resulted in changes in the energy of electron transitions which caused changes in UV-vis spectra.

Due to this, there is a massive shift in spectra from wider wavelengths at peak intensities in CuTPP to sharp, prominent peaks at shorter and lower wavelengths in ZnTPP.

SUMMARIZED EXPLANATION

CuTPP is active, as it shows peaks in the Ultraviolet-Visible range. As CuTPP has a Tetraphenylporphyrin ligand, Tetraphenylporphyrin(TPP) ligand has an extended conjugated structure, due to these extended conjugations, its HUMO-LUMO gap falls in lower energy, such that Q falls in 300-800 nm region. This complex causes Ultraviolet-Visible radiation to be absorbed, therefore making it UV-Vis active. Moreover, due to this, its appearance is violet to deep purple colored.

The wavelength observed by bands is in peak, which is in the range of 380-800nm. In the Ultraviolet-Visible spectrum of CuTPP, we observe solet bands at 427 nm and Q bands around 538 nm and 620 nm. These are the characteristics of metalloporphyrin, confirming metallation and solet at 427 nm, indicating the presence of porphyrin moiety.

On replacing Cu^{+2} with Zn^{+2} , we get ZnTPP. For ZnTPP, the solet bands are at 418 nm and Q bands are at 547 nm and 584 nm. ZnTPP contains closed-shell(complete) metal ions(d^{10}); in Zn^{2+} , $d\pi$ (d_{xz} , d_{yz}) metal-based orbitals are relatively lower in energy in comparison with ligand π system. So, they have very little effect on the porphyrin π - π^* energy gap.

b. Is Wilkinson`s catalyst $[\text{RhCl}(\text{PPh}_3)_3]$ active in UV-Vis AND why? EXPLAIN YOUR REASON.

Where the UV-vis spectra of the Wilkinson`s catalyst $[\text{RhCl}(\text{PPh}_3)_3]$ will be shifted if you replace Cl- with SCN in its crystal structure?

b. Yes, it is active. The peaks in the visible zone correspond to electronic transitions between ground and excited states for the species. They are linked to the bonds amongst Rh and three triphenylphosphine ligands arranged in a square planar geometry which can be interpreted through the Angular Overlap Model. Due to their presence and specific positions, the red-violet color of the Wilkinson complex is observed.

The Rh atom is free enough to get involved in favorable interactions through its highest occupied molecular orbital and lowest occupied molecular orbital molecular orbitals. The highest occupied molecular orbital can provide electron density to the dihydrogen anti-bonding orbital, facilitating the cleavage of H-H bond and, according to the proposed mechanism for Wilkinson complex catalytic action, leading to the formation of hydride complexes; however, the lowest occupied molecular orbital orbital can receive electron density from the π bonds of the alkyne, rendering both carbon atoms available for C-H bond formation. If Cl is replaced with SCN, due to the presence of the M-SCN bond and interaction between Metal and sulfur of the SCN group, UV-Visible activity is shifted at larger wavenumber.

SUMMARIZED EXPLANATION

Yes, the Wilkinson catalyst is active in Ultraviolet-Visible Spectrum between 300-450 nm. As they are linked to the bonds amongst Rh and three triphenylphosphine ligands arranged in a square planar geometry which can be interpreted through the Angular Overlap Model. Their presence and positions justified the red-violet color of the Wilkinson's complex.

If we replace the chloride with SCN^- , then there would be a blue shifting the UV-vis spectra. As SCN^- is a weak field ligand when compare to Cl^- it would undergo a lesser splitting of d-orbital. This means SCN^- complex would need more energy for excitation. As energy is inversely proportional to wavelength, there would be a decrease in wavelength. So the blue shift will occur.

2. Identify the weakest coordinating ligand in the following complexes. Clearly explain your reasoning.



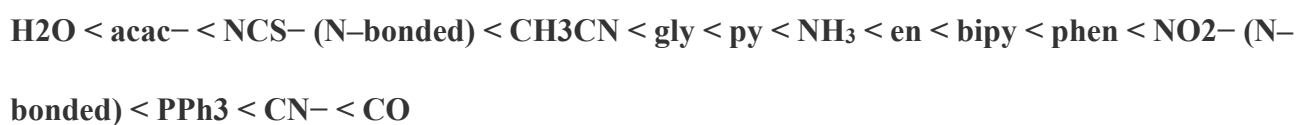
The weakest one is the Wilkinson's catalyst $[\text{RhCl}(\text{PPh}_3)_3]$.

Strong field ligands are those ligands which have higher crystal field stabilization energy value.

Here, C and N are donor atoms. Example: In CO and NH_3 , C and N are donor atoms, respectively.

Similarly, weak field ligand are those ligands which have lower crystal field stabilization energy value. Examples: Cl, PMe_3 , PPh_3 , etc.

Spectrochemical series for the strength of ligand is given below.



Weak field ligands: H_2O , F^- , Cl^- , OH^-

Strong field ligands: CO, CN^- , NH_3 , PPh_3

SUMMARIZED EXPLANATION (For each complex in question)

Ligands in which donor atoms are halogen, oxygen, and sulfur are weak ligands. On the other hand,

Ligands in which donor atoms are carbon, phosphorus, and nitrogen are strong ligands.

Stronger field ligands will have lesser electronegative donor atoms and have higher crystal field stabilization energy value. However, Weak field ligands have lower crystal field stabilization energy value.

Ligands present in each of the complexes and the weakest coordinating ligands on the basis of spectrochemical series are:

A) $\text{HRh}(\text{CO})(\text{PMe}_3)_3$ — ligands are CO, PMe_3

Weakest - PMe_3

B) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ — ligands are NH_3 , Cl^-

Weakest - Cl^- (sigma-donor pi donor tendency)

C) Wilkinson's catalyst $[\text{RhCl}(\text{PPh}_3)_3]$ — ligands are Cl^- , PPh_3

Weakest - Cl^- (donating tendency through sigma and pi)

Here, PPh_3 is strong pi acceptor ligand.

D) Vaska's Complex, $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$ — ligands are $\text{P}(\text{C}_6\text{H}_5)_3$, Cl^-

Weakest - Cl^-

Here, except Cl , all other are good pi acceptor.

The weakest among all of them is Wilkinson's catalyst, as Cl^- has donating tendency through sigma and pi and PPh_3 being a strong pi acceptor ligand.