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The Color and Electronic Configurations of Prussian Blue

Read the paper cited below and answer the discussion questions **before class on _____**.

Robin, M.L. The Color and Electronic Configurations of Prussian Blue. *Inorganic Chemistry*, 1, 1962, pp 337-342. DOI: 10.1021/ic50002a028

Discussion Questions:

1. The authors mention that Prussian Blue, $[\text{K}, \text{Fe}^{\text{II}}, \text{Fe}^{\text{III}}](\text{CN})_6$, can be synthesized from either $\text{Fe}^{\text{III}}(\text{ClO}_4)_3$ and $\text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$ or from $\text{Fe}^{\text{II}}(\text{ClO}_4)_2$ and $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$. They also report the results of base hydrolysis of Prussian Blue. What do these two experiments tell us about the structure of the pigment, and why is this significant?
2. Draw the crystal field splitting diagram for high and low spin versions of Fe^{II} and Fe^{III} ions that have an octahedral coordination geometry. The paper states that there are two types of iron ion in the crystal structure of Prussian Blue. What is the difference between them? Which do you expect to have the larger Δ_{oct} , based on what you know about the spectrochemical series?
3. How do the authors use the distinction between allowed and forbidden transitions to confirm the identity of Prussian Blue as ferric ferrocyanide?
4. The authors state in the abstract that "The interpretation of the shift of the high frequency charge transfer bands of $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ on substituting the Fe^{II} with Ru^{II} or Os^{II} then can be used to predict the shifts of the low frequency charge transfer bands of Prussian Blue on substituting $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ with $\text{Ru}^{\text{II}}(\text{CN})_6^{4-}$ or $\text{Os}^{\text{II}}(\text{CN})_6^{4-}$." How do they interpret the shift in the high frequency charge transfer bands, and how does this comparison support or cast doubt on their assignment?
5. How did the authors identify/confirm the location of the electrons in the ground state that give rise to optical absorbance when the molecule is excited?