Problem 11 The Prussian blue

The Prussian blue is a component of black and bluish inks for printing. The precipitate formed upon the dropwise addition of potassium ferrocyanide to the ferric chloride solution contains 34.9% (mass) of iron.
1. Give a formulae of the precipitate and write the chemical equation.
2. Using the crystal field theory show the ***d***-orbital splitting pattern for all Fe atoms in the Prussian blue.
3. What causes the intense color of the pigment?
4. What product initially forms from potassium ferrocyanide and ferric chloride solution in the inverse-mixing-order route? Give the equation.

Solution.

1. Let's write the chemical equation :

$$4\ FeCl_3 + 3\ K_4[Fe(CN)_6] \rightarrow Fe_4[Fe(CN)_6]_3 + 12\ KCl$$

where $Fe_4[Fe(CN)_6]_3$ is the Prussian blue or Berlin blue.
Problem is that adding drops of ferrocyanide to ferric chloride it could appear the precipitate of the form $Fe_4[Fe(CN)_6]_3 . aH_2O$ (a = 14 up to 16) or even $Fe_4[Fe(CN)_{6-x}Cl_x]_3 .a\ H_2O$.
In the first case molecular mass is 859.23 +18a and contains 390.95 g Fe.
So, a = (39095 - 859.23x34.9)/(18x34.9) = 14.5. Not acceptable because **a** is not integer.
For the second case we have molar mass 859.23 +35.5x - 26x + 18a containing 390.95 g Fe.
So, we have 39095- 859.23x34.9 = 34.9 x 9 x (X +2a) where x +2a = 29.
Convenient are x =1 and a =14 or x = 3 and a = 13. Only x =1 and a = 14 are acceptable.
So the formula of precipitate is $Fe_4[Fe(CN)_5Cl] .14\ H_2O$

2. Let us consider the ion $Fe(CN)_6^{-4}$. The electron configuration of Fe^{+2} is $[Ar]d^{+6}$. CN^- is one of the strongest field ligands, so, we shall have 2 electrons in each d_{xy} , d_{yz} , and d_{xz} and none in $d_{x^2-y^2}$ and d_{z^2} being occupied only the orbitals of low spin energy, because the difference of energy between these orbitals is too big.
Fe^{+3} has the configuration $[Ar]d^{+5}$

3. In fact this complex absorbs in visible light , in orange region, between 580 and 650 nm , and we see the complementary color, meaning color blue. Of course this color appears because of this difference of energy between low spin orbitals and high spin orbitals. Cyanide ion is one of the strong field ligand, making the difference of energy between d orbitals xy, xz and yz and x^2-y^2 and z^2.The difference of energy is D = h x ni (frequency) = h x c/lambda(wave lenght).

4. If we add ferric chloride over potassium ferrocyanide, it forms a white precipitate that will become blue. The reaction is :

$$FeCl_3 + K_4[Fe(CN)_6] \rightarrow KFe[Fe(CN)_6] + 3\ KCl$$

and this is normal, because being small quantity of ferric chloride, not all potassium is displaced.

Solution proposed by
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