

A Gradation in the colour of various Copper Complexes

Arpon Basu

First Year Under-Graduate Student

Indian Institute of Technology, Bombay - 400076

The author states that there is no conflict of interest.

Email ID: arpon.basu@gmail.com

Contact No: 9136550363.

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Abstract

We aim to establish a gradation in the colours of various copper complexes in correspondence to their orders in the spectrochemical series. We also investigated how various complexes may be made/can't be made in a laboratory. We also tried to predict certain properties of copper-fluorine complexes, and presented a mechanism for the complex formation between divalent copper and thiocyanate (S-bonded) based on a reference.

In the end, we concluded that most of the ligands seemed to follow the trend, and included a few actual images and laboratory results for the reader's satisfaction.

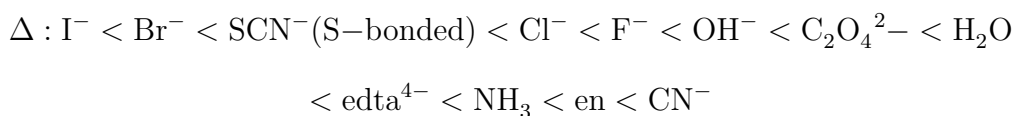
1 Introduction

From time immemorial human beings have been fascinated by the vivid colors of certain chemical compounds. Copper is one of those elements which were discovered early on in human history. At first, humans looked at various copper complexes with awe. With the development of chemistry, gradually humans started to understand the reasons of colors of various complexes.

During our study when we encountered copper compounds we were fascinated with their vivid colors. That prompted and motivated us to try to understand and explain different colors of various copper complexes from a elementary (high-school level) yet theoretical viewpoint. This article is a result of that investigation.

2 Theory

We observe that Cu^{2+} being a d^9 species has exactly one electronic vacancy in its d-orbitals (ie:-exactly one unpaired electron in a subshell having the vacancy, and all other subshells being fully filled up) irrespective of the ligand or the type of splitting. Thus the colour of a Cu(II) complex is directly related to its splitting energy as $\lambda = \frac{hc}{\Delta}$. Thus, based on the spectrochemical series' ordering of the splitting energies of various ligands, we can hope to establish a gradation (from red to blue) of colours of the copper complexes in correspondence to the order of ligands in the spectrochemical series. For our purposes we chose only a part of the spectrochemical series to examine, as given below [1]:

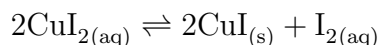


Thus we now begin to investigate the colour of various copper complexes, ligand by ligand.

2.1 I^-

Cu(II)-Iodine complexes are unstable because the equilibrium of the reaction given below lies far to the right[2]: not because $K_{eq} > 1$ (in fact, $K = 1.38 \cdot 10^{-13} \ll 1$), but because CuI is sparingly soluble in water, and if even moderate concentrations of CuI_2 (0.1M) are taken, the large entropic

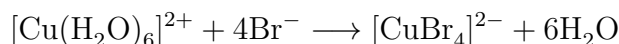
factor generated by the continuous precipitation of CuI drives the reaction to completion by the Le Chatelier's principle.



Thus aqueous copper-iodine complexes are removed from the scope of study.

2.2 Br⁻

Cu(II) forms a complex with bromine on addition of concentrated hydrobromic acid, which has a dark green/olive green colour :

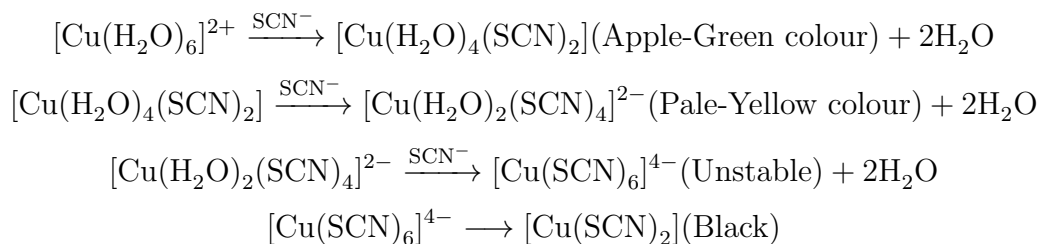


2.3 SCN⁻

We describe a method for the preparation of copper-thiocyanate complex [3]. When we add thiocyanate ions to $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, thiocyanate ions will start to substitute the water molecules in the complex despite SCN^- having a weaker field than H_2O , and this can be explained by Pearson's HSAB theory [4].

Observe that Cu^{2+} is a soft acid (due to more number of d-electrons and low charge density), and SCN^- is a softer base than water (because SCN^- has sulfur as its donating atom, which has lower charge density and electro negativity than oxygen, the donating atom of water), and hence the aforementioned phenomena will take place.

Anyways,



Thus, for proper complex formation between copper and thiocyanate to take place the thiocyanate should be added slowly (dropwise) and the mixture should be continuously stirred, otherwise the reaction may go right up to the black copper thiocyanate salt stage.

2.4 Cl⁻

Here also, as above, the chloride ion substitutes water molecules from hexaaquacopper(II) despite having a weaker field because the chloride ion having an actual negative charge on itself and three lone pairs as opposed to no formal charge and only two lone pairs on the oxygen of the water molecule is more electronically attracted to Cu²⁺ than water is, and hence the substitution is driven forward [5].

Moreover, we use concentrated hydrochloric acid for this reaction, so we can also expect solvolytic effects to play a role.



We also note that apart from [CuCl₄]²⁻, other complexes of copper and chlorine such as [CuCl₃]⁻ [6] (a red coloured complex [7] which exists as its dimer [Cu₂Cl₆]²⁻) [7] and [CuCl₅]³⁻ [6] are also known to exist.

2.5 F⁻

CuF₂, in the presence of fluoride sources such as HF and NaF, primarily forms 3 anionic complexes, namely [CuF₃]⁻, [CuF₄]²⁻ and [CuF₆]⁴⁻ [8].

However, due to lack of resources the colours of these complexes couldn't be determined. Nevertheless, some predictions have been made on the possible colour(s) of these compounds in Section 2.14.

2.6 OH⁻

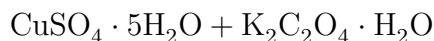
Tetrahydroxycuprate, the complex between Cu(II) ions and hydroxide ions, can be prepared as follows [6]:



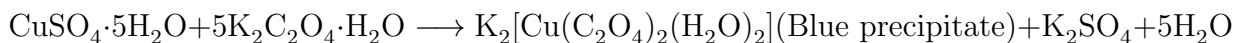
Cu(OH)₂ being an amphoteric compound, dissolves slightly in hot concentrated sodium hydroxide, which on recrystallisation yields the light blue solid sodium tetrahydroxycuprate.

2.7 C₂O₄²⁻

Copper-oxalate complex can be prepared as follows [9]:



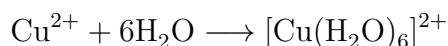
is first warmed to dissolve these salts completely into water, especially, the potassium oxalate into water. They then react to give potassium bis-aquabio-oxalatocuprate(II).



Thus on allowing the reaction mixture to stand crystals of potassium bis-aquabio-oxalatocuprate(II) slowly precipitate out and can be isolated. There is not much difference between the colour of this crystal and that of hydrated copper sulfate crystals.

2.8 H₂O

The complex of Cu²⁺ with water is simply hexaaquacopper, which possesses a well known light blue colour.



2.9 EDTA⁴⁻

EDTA is used to estimate the amount of Cu²⁺, among many other metals also, via complexometric titrations. Adding EDTA to [Cu(H₂O)₆]²⁺ gives rise to a blue coloured complex [10], which is a shade of blue darker than the blue of [Cu(H₂O)₆]²⁺ but lighter than [Cu(en)₂(H₂O)₂]²⁺, which sits well with our predictions from the spectrochemical series.



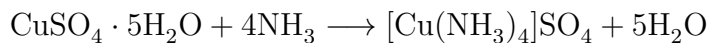
We can make note of an interesting phenomena here [10]:

Note that EDTA⁴⁻ lies below en in the spectrochemical series, but nevertheless the stability constant of [CuEDTA]²⁻ is greater than the stability constant of [Cu(en)₂(H₂O)₂]²⁺, i.e.:- if EDTA is poured into an aqueous solution containing [Cu(en)₂(H₂O)₂]²⁺, EDTA will replace both en and H₂O to form [CuEDTA]²⁻. This once again reaffirms that stability and splitting energy are independent parameters, or rather stability depends on many other factors other than splitting energy.

2.10 NH₃

[Cu(H₂O)₆]²⁺ forms a famous dark blue complex with ammonia, which is incidentally, also a confirmatory test for aqueous Cu(II) ions. Another interesting property of tetraamminecopper is that its formation can't take place in acidic

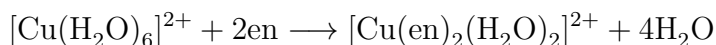
media because adding acid protonates the ammonia, thus rendering its lone pair unavailable for coordination with $\text{Cu}^{2+}(\text{aq})$.



The complex $\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2$, prepared by treating copper hydroxide precipitate with liquid ammonia is a well known reagent known as Schweizer's Reagent [11]. This reagent finds its application in the synthetic fibre industry.

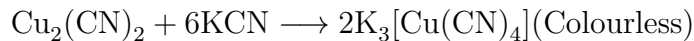
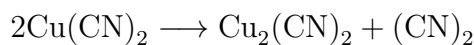
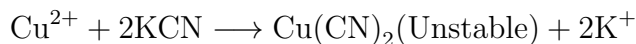
2.11 en

Ethylene diamine forms a purple coloured complex [10] with $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.

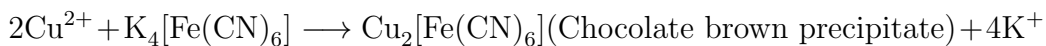


2.12 CN^-

Copper-cyanide complexes can be attempted to be made in the following manner:



Thus we obtain a colourless Cu(I) complex when try to make a copper(II)-cyanide complex. Incidentally, one of the famous confirmatory tests for detection of aqueous Cu(II), which involves the formation of a chocolate brown precipitate, has Cu^{2+} outside the coordination sphere, and thus is rejected.



Thus like in the case of iodide, where it is not possible to make a Cu(II)-iodine complex in aqueous media, similarly we remove the case of aqueous Cu(II)-cyanide from our case of study.

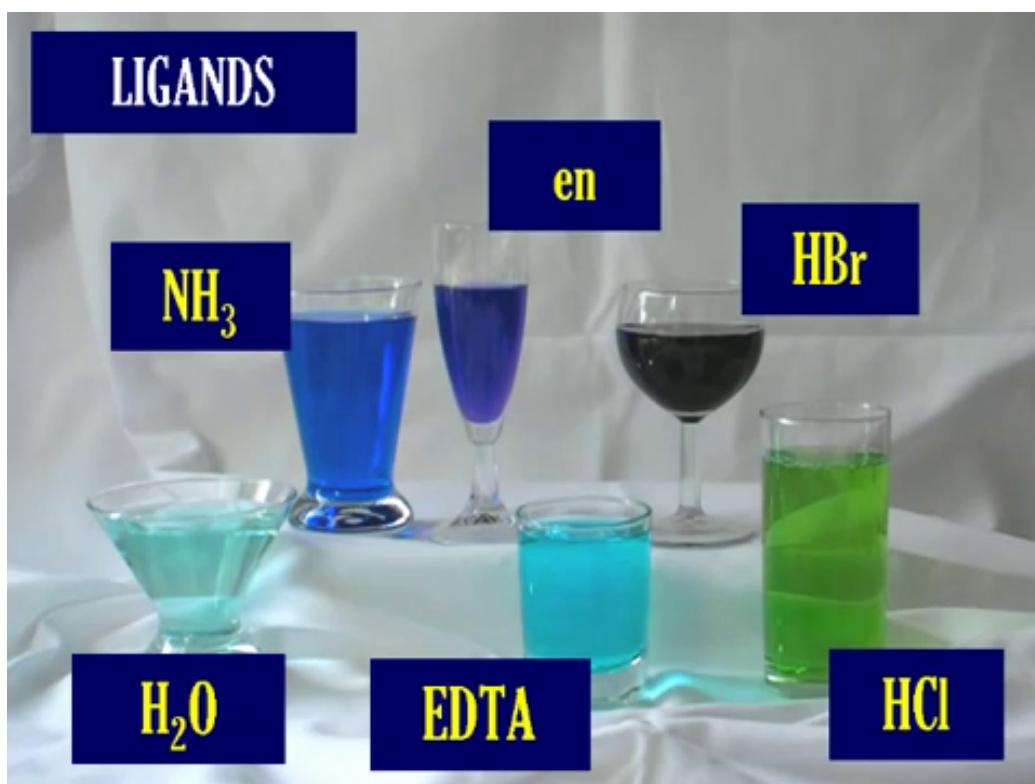


Figure 1: Colours of various copper complexes [10]



Figure 2: Result of lab demonstration



Figure 3: Crystals of $K_2Cu[C_2O_4]_2$ [12]

3 A few Salient Points

Since we were describing the formation of complexes with some detail, we thought it was pertinent to include the cases of iodide and cyanide and describe how it is not possible to make their complexes with divalent copper in aqueous media.

Now we come to describe the point of SCN^- and NCS^- where things are a bit complicated. Copper, according to Pearson's HSAB-concept is at a position where its equally likely to form both thiocyanate and isothiocyanate complexes having colours ranging from green to black. Moreover, $Cu(SCN)_2$ like CuI_2 undergoes internal redox reaction(s) forming white $CuSCN$ and a polymeric Thiocyanate [14]. Thus, the mechanism described above is solely the personal view of the person posting in that thread from which it has been cited [3].

Now, coming to the issue of the copper-fluorine complexes; Though it was not possible to determine the colours of the copper-fluorine anionic complexes, we could have perhaps extrapolated as follows:

In cases of complexes where the complex is formed by the attack of excess of the anions on a salt of copper and that anion (say for example the preparation of $[CuCl_4]^{2-}$ from $CuCl_2$), the colour of the complex usually resembles



Figure 4: $\text{Cu}(\text{OH})_2$ [13]



Figure 5: CuF_2 crystals [8]

the colour of the simple salt from which it was made. Thus we can perhaps predict that the colour of the copper-fluorine complexes would be similar to the turquoise colour of CuF_2 , and if our prediction comes out to be true, then the colour of the fluorine complexes would fit in very well with the trend (described in the conclusion below) as the wavelength of turquoise-coloured light would be intermediate between the green of $[\text{CuCl}_4]^{2-}$ and the blue of $[\text{Cu}(\text{OH})_4]^{2-}$.

4 Conclusions

Overall our prediction that the frequencies of light reflected by the copper complexes will be in their order of splitting energy in the spectrochemical series fits in quite well, except for a few compounds like $[\text{CuBr}_4]^{2-}$ which seem to defy the trend.

Otherwise, note that we begin off with $[\text{Cu}(\text{H}_2\text{O})_4(\text{SCN})_2]$ and $[\text{Cu}(\text{H}_2\text{O})_2(\text{SCN})_4]^{2-}$ being apple green and pale yellow respectively, then moving on to the bright green colour of $[\text{CuCl}_4]^{2-}$ having a higher frequency.

Then $[\text{Cu}(\text{OH})_4]^{2-}$, $[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CuEDTA}]^{2-}$ all have roughly the same colour (blue), with $[\text{Cu}(\text{OH})_4]^{2-}$ having a slightly lower shade of blue than $[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$, and $[\text{CuEDTA}]^{2-}$ having a higher shade of blue than $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.

Then $[\text{Cu}(\text{NH}_3)_4]^{2+}$ has a noticeably higher frequency of colour than $[\text{CuEDTA}]^{2-}$, being dark blue-violet in colour, and $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ having an even lower wavelength than the wavelength of colour of tetraammine copper by being completely violet.

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