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Article

A colorimetric investigation of copper(II) solutions

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SUMMARY

Complex ions containing transition metals, elements with incompletely filled d-orbitals, are usually colored, while similar ions from non-transition metals are not. Copper (Cu) is a transition metal with a flexible coordination sphere, meaning it can adopt many coordination geometries, and therefore have various colored complexes. Addition of Chloride (Cl^-) to a $CuCl_2$ solution causes color change away from blue toward a yellowish green. We hypothesized that adding acetone to an $CuCl_2$-water solution would cause a similar shift in solution color. We made aqueous $CuCl_2$ solutions with increasing acetone concentrations ranging from 0 to 100 percent and compared the resulting colors to aqueous $CuCl_2$ solutions with increasing added amounts of NaCl to find the closest visual fit in color from the acetone solutions for each added NaCl equivalent. Our experiment showed that increasing the percent acetone in aqueous $CuCl_2$ solutions gave rise to a color change parallel to that of adding Cl^-, shifting solution color away from blue and toward yellow. We propose an explanation of this relationship by considering Cu^{2+} reduction in high acetone concentrations and discussing ligand field strength and the possible effects of tetrahedral versus octahedral geometries on splitting: weaker splitting may similarly affect color through equilibria leaning towards green/yellow products. This investigation could support our understanding of copper coordination and copper complex color behavior with future implications for other copper complex experiments or, in a broader perspective, detection and evaluation of Cu^{2+} levels in environmental and biological systems.

INTRODUCTION

Light with wavelengths between 380 nm (violet) and 700 nm (red) falls in the portion of the electromagnetic spectrum that is visible to humans (1). When white light, a mixture of all wavelengths in the visible spectrum, passes through a solution, the solution absorbs some of the wavelengths in the light and transmits all other wavelengths. The resulting color observed is a mixture of all unabsorbed wavelengths, usually the color opposite of the absorbed color on the color wheel. Solutions containing transition metals that form ions with incompletely filled d-orbitals are colored; for example, Cu^{2+} in solution absorbs light in the red region of the spectrum to give a solution that appears pale blue/cyan in color (2).

The color that emerges from such solutions is related to ligands. Ligands are molecules or ions surrounding the central metal in a complex ion. Simple tetrahedral complexes have four ligands arranged around the central metal ion, while simple octahedral complexes have six (**Figure 1**). This coordination structure, along with a metal's oxidation state (whether it is 3+ or 2+, for example), and the nature of the ligands bound all affect the color displayed. Cu^{2+} specifically can be present in many coordination geometries, which is why many of its complex ions produce colors.

Because $CuCl_2$ is water soluble, it dissociates in pure water, and the water molecules are attracted to the Cu^{2+} ions through ion-dipole forces, forming octahedral $[Cu(H_2O)_6]^{2+}$ complex ions ($Cu^{2+}(aq) + 6H_2O(l) \rightarrow [Cu(H_2O)_6]^{2+}(aq)$) (2,3). $[Cu(H_2O)_6]^{2+}$ absorbs red light, giving the solution a cyan/pale blue color (4). Adding NaCl to $[Cu(H_2O)_6]^{2+}(aq)$ adds the common ion of Cl- after disassociation as well. The water molecules in the $[Cu(H_2O)_6]^{2+}(aq)$ are replaced one at a time by ionically bonded Cl^-, giving a stronger attraction than the ion-dipole-bound waters (5). Based on Le Chatelier's principle, adding more Cl^-, a reactant, shifts each equilibrium towards the right, which we observe as a change to a color that is closer to that of the yellow/green tetrahedral complex (**Figure 2**) (7).

We tested the effect of increasing acetone percent concentration compared to adding NaCl to an aqueous $CuCl_2$ solution and hypothesized that they would both similarly shift the equilibrium towards the products, which are yellow compared to the initial blue. Our data supported this hypothesis. We propose that both changes occur as a result of the replacement of H_2O with weaker molecules/ions, although it is also possible that the reduction of Cu^{2+} in acetone transforms the solution into a tetrahedral complex ion.

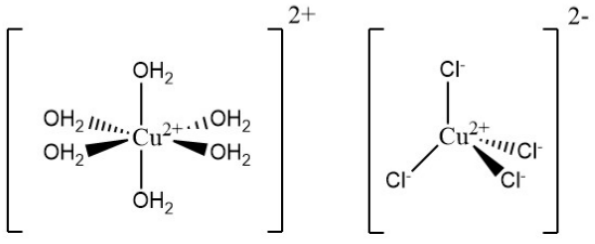

Figure 1: Examples of octahedral (left) versus tetrahedral (right) molecular shapes. The octahedral structure is of molecule $[Cu(H_2O)_6]^{2+}$ while the tetrahedral structure is of molecule $[CuCl_4]^{-2}$.

$$[Cu(H_2O)_6]^{2+}_{(aq)} + Cl^-_{(aq)} \rightleftharpoons [Cu(H_2O)_5Cl]^+_{(aq)} + H_2O_{(l)}$$

$$[Cu(H_2O)_5Cl]^+_{(aq)} + Cl^-_{(aq)} \rightleftharpoons CuCl_2(H_2O)_{2(aq)} + H_2O_{(l)}$$

$$CuCl_2(H_2O)_{2(aq)} + Cl^-_{(aq)} \rightleftharpoons [CuCl_3(H_2O)]^-_{(aq)} + H_2O_{(l)}$$

$$[CuCl_3(H_2O)]^-_{(aq)} + Cl^-_{(aq)} \rightleftharpoons [CuCl_4]^{-2}_{(aq)} + H_2O_{(l)}.$$

Figure 2: Equilibria showing stepwise replacements of H_2O by Cl^- around Cu^{2+} central ion, resulting in $[Cu(H_2O)_6]^{2+}$ from $CuCl_2$. Complex ions are color-coded based on expected color of molecule (6).

RESULTS

Water-$CuCl_2$ solutions are colorful, and by investigating the related impacts of varying percent acetone concentration versus adding Cl^- ions to such solutions, we hoped to better understand the mechanism behind the color changes. To look at this mechanism, we varied the molarity of Cl^-, by changing the added mass of NaCl (0 g, 0.150 g, 0.300 g, 0.450 g, 0.600 g) to a $CuCl_2$-water solution. Under controlled lighting and temperature conditions, we visually compared each $CuCl_2$-water solution we made to our spectrum of acetone-water-$CuCl_2$ solutions ranging in 10% increments from 0% to 100% acetone, and the percent acetone concentration of the closest color match was recorded.

As the molarity of Cl^- from added NaCl increased, so did the percent acetone concentration of its color match, with the final 6.000 g of NaCl matching the 80% acetone solution (**Figure 3**). Increasing the percent acetone concentration only made a large difference in color once there was at least 50% acetone (**Figure 4**). Both changing the percent acetone concentration and Cl^- molarity in the water-$CuCl_2$ solutions had similar effects in color, with the solutions going from blue to more green/dark yellow (**Figure 3**). Further testing of 60%-90% acetone-water-$CuCl_2$ solutions with neocuproine showed the 80% and 90% acetone solutions were red, the 70% acetone solution was yellow, and the 60% acetone solution was yellow with some slightly green areas.

DISCUSSION

We observed similar color changes of blue to yellowish-green when adding both NaCl as well as acetone. However, these similarities in color change cannot be from forming the same compound because we are adding different ligands.

In complex ions, ligands are attracted to the transition metal ion, and the repulsion between the ligand's electrons and metal ion's d-orbital electrons raises the energy of the d-orbitals (3). Due to the spatial arrangement of the d-orbitals, not all of the d-orbital energies are raised by the same amount, and the splitting of energy is dependent on the complex configuration. The d-orbitals are split into two groups– in an octahedral complex, two of them have a higher energy than the other three, while in a tetrahedral complex, three d-orbitals have higher energy than the other two (**Figure 5**) (2). When white light passes through such a solution, some of the light's energy promotes an electron from the lower set of orbitals into an empty space in the upper set. Each wavelength of light is associated with a particular energy, and the energy gap in the d-orbitals corresponds to the energy of a certain light. Shorter wavelengths of light can excite electrons across greater energy gaps (2). Because the amount of splitting in a tetrahedral field is smaller than in an octahedral field, the color could change with a change of coordination/number of ligands, as it does with the addition of Cl^- (3). The problem is that an ion would normally only change coordination if the ligand changed, and changing the ligand would change the color as well. It is difficult to isolate the impact of coordination. This difficulty is important when considering possible explanations of the coordination behavior of acetone $(CH_3)_2CO$ and Cu^{2+} (2).

In addition to coordination, the size of the energy gap between d-orbitals of the transition metal ion also varies with the nature of the ion, its oxidation state (whether it is 3+ or 2+, for example), and the nature of the ligands (2). In this experiment, we used the same transition metal ion throughout, so the main impacting factor is either oxidation

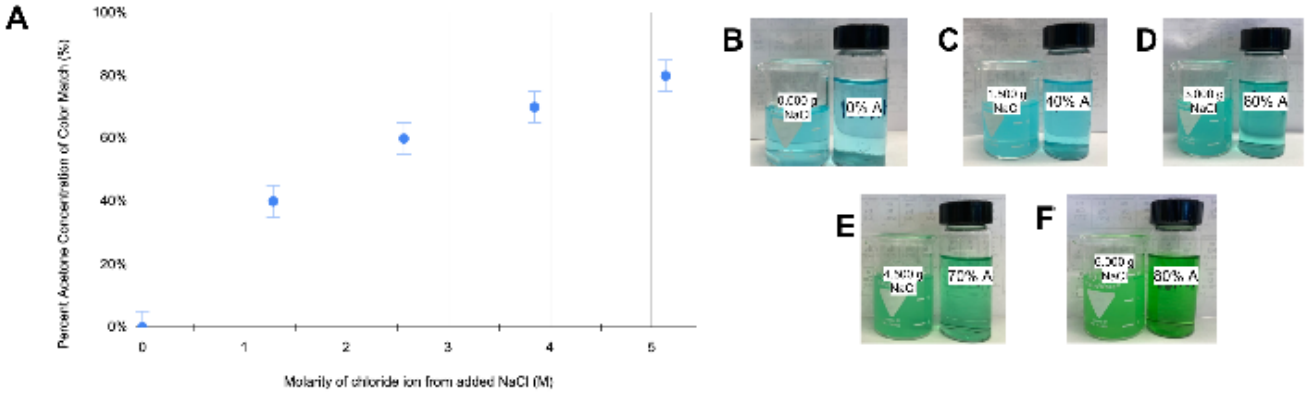

Figure 3. Acetone and chloride ion similarly shift the color of aqueous Cu^{2+} solutions from blue to green. A) The percentage of the acetone concentration chosen as the best color match for a given chloride solution. Data is shown as mean ± 10% (n=3); 10% increments was chosen as possible uncertainty from qualitatively categorizing color match through the acetone spectrum. Color match was performed through visual comparison with a spectrum of $CuCl_2$-water-acetone solutions increasing in 10% increments and ranging from 0% to 100% acetone concentration under controlled lighting. B-F) $CuCl_2$-water solution increasing in 1.500 g increments of NaCl is shown next to its color match from the acetone-water-$CuCl_2$ spectrum labeled with percent acetone.

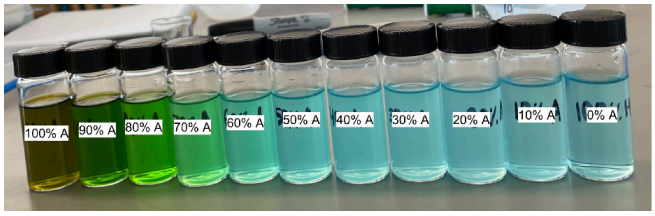

Figure 4: Increasing acetone concentration in aqueous Cu^{2+} solution shifts the color from blue to green to yellowish green. A spectrum of $CuCl_2$-water-acetone solutions was generated. The image shows the resulting spectra, decreasing in 10% increments of acetone concentration from left to right, ranging from 100% to 0% acetone (A) concentration.

state or the different ligands with different electrical field strengths. Stronger fields cause a larger energy gap than weaker fields, and greater splitting requires more energy to promote an electron to the higher group of orbitals. So, with a weaker ligand field and decreased splitting, the absorption band moves from the middle of the red region to the near red portion of the spectrum (9). In the case of Cu^{2+}, ligands that cause greater splitting would give a more intense blue solution while ligands that cause less splitting would produce a more yellow-green solution (2).

We believe the similar effects in color from both molarity of Cl^- and percent acetone changes could be partially because both increasing percent acetone concentration and adding Cl^- could result in the replacement of H_2O ligands around Cu^{2+} with weaker ligands. In the Cl^- replacement equilibria, Cl^- is a weaker ligand than H_2O and eventually forms tetrahedral complexes, leading to the shift from blue to green displayed (10). In the acetone solutions, we propose replacement of water by acetone. When acetone is added to $[Cu(H_2O)_6]^{2+}(aq)$, the acetone, which is more polar than water and thus attracted to the Cu^{2+} through stronger ion-dipole forces, could replace the water ligands (8, 10, 12, 13). Two equilibria have been proposed for this occurrence (11):

$$[Cu(H_2O)_6]^{2+}_{(aq)} + (CH_3)_2CO_{(aq)} \rightleftharpoons [Cu(H_2O)_5((CH_3)_2CO)]^{2+}_{(aq)} + H_2O_{(l)} \qquad K_f = 3.7$$

$$[Cu(H_2O)_5((CH_3)_2CO)]^{2+}_{(aq)} + (CH_3)_2CO_{(aq)} \rightleftharpoons [Cu(H_2O)_4((CH_3)_2CO)_2]^{2+}_{(aq)} + H_2O_{(l)}. \quad K_f = 4.0 \times 10^{-3}$$

From pure water to pure acetone as solvent, the completely hydrated ion could convert to the ion $[Cu(H_2O)_4((CH_3)_2CO)_2]^{2+}(aq)$ through the stepwise replacements of two H_2O molecules in $[Cu(H_2O)_6]^{2+}(aq)$ by two acetone molecules. The formation constant of the first equilibrium is much higher than that of the second, indicating that the equilibrium of the first step favors its products more than the second one (11,14). Therefore, we would expect that the majority of the Cu^{2+} complex ions would be converted to the monoacetone complex before any of them formed the diacetone complex. As acetone is also a weaker ligand than water, the proposed $[Cu(H_2O)_4(acetone)_2]^{2+}(aq)$ being more green than blue could be explained by the same splitting reasoning as the Cl^- replacement equilibria (11).

An alternative explanation to consider for Cu^{2+} behavior in acetone would involve the reduction of Cu^{2+} to Cu^+ in high concentrations of acetone (15). Once reduced, the Cu^+ may form a complex ion with up to four acetone molecules, which is the case when Cu^+ is added to 100% acetone that has been dried with potassium nitrate (16). In such a case, the color change could be explained by either the same concepts of splitting differences from ligand types and shape or by the change in copper oxidation state affecting splitting independently. In the highest concentrations of acetone, this Cu^+ behavior may be the sole cause of the color change, but we propose the possibility of color change resulting from both reduction to Cu^+ and the Cu^{2+} stepwise replacement equilibria occurring simultaneously at certain acetone concentrations, as supported by our separate further testing. In an effort to determine the composition of our acetone spectrums, we remade the solutions of acetone concentrations from 60%-90% and tested these solutions with neocuproine, which turns red with Cu^+ and green with Cu^{2+}. The results, showing red at 80% and 90% acetone, yellow for 70%, and yellow with some slightly green areas at 60%, point to the reduction of Cu^{2+} to Cu^+ at acetone concentrations of 70% and above. Between 50% and 70%, the solutions still may involve the formation of the new ligand structure we proposed, and below 50%, the Cu^{2+} reduction may not take place.

The acetone-water-$CuCl_2$ solutions showed only minimal color changes in solutions with less than 50% acetone concentration. This may not be solely due to the absence of Cu^+; instead, it could be because only one water ligand was being replaced in the complex. The replacement of only one water ligand with one acetone would not cause much splitting difference, so the first five solutions of the spectrum would be similar colors. By increasing NaCl by increments of 1.500 g, the color itself seems to increase quite linearly, but because the first five of the spectrum are similar, the increase between data points of Cl^- molarities 1.283 M and 2.567 M appear more drastic. At around 50% acetone concentration, the acetone

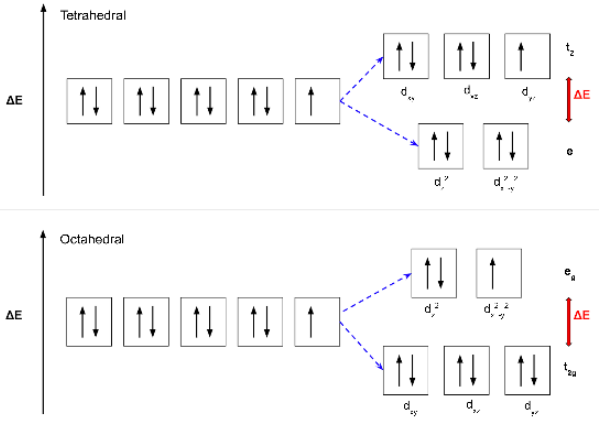

Figure 5: Example diagrams of splitting in tetrahedral versus octahedral complex ions. The arrangement of d-orbitals in a Cu^{2+} ion before and after bonding with four chloride ions (tetrahedral) or six water molecules (octahedral). In both cases, the orbitals are differently affected by repulsion because of their spatial arrangement. ΔE refers to the energy gap between the d-orbitals. Diagrams show Cu^{2+} $3d^9$ (quantum numbers: n = 3, l = 2 with 1 unpaired electron), and labels show orbital sets and individual orbital orientations after Jahn Teller distortion is considered (8).

may start the second replacements, which would result in larger splitting difference and a more visually noticeable color change. For solutions higher than 50% acetone concentration in the spectrum, the colors start changing more consistently, likely because of the additional effects of Cu^{2+} reduction, so the graph increases more linearly as well, as shown by data points of Cl^- molarities between 2.567 M and 5.133 M, signaling a correlation in color change. Eventually, the graph would flatten once the solution reaches salt saturation. We believe the correlating color patterns between acetone and Cl^- concentration are caused by the combination of shifting of equilibria towards the complex ions with weaker ligand field strengths and a tetrahedral complex as well as the reduction of Cu^{2+} to Cu^+.

There are a few areas of uncertainty that could be addressed in future studies. As mentioned in the procedure, we measured our results through visual comparison. Although we tried to control the conditions of our comparisons, our way of doing so was broad and to some degree subjective. Additionally, we color matched to the closest fit among the limited choices, which could also cause generalization and/or lack of accuracy. We could try using a spectrometer and cuvettes that do not dissolve in acetone to measure the absorbance of the different wavelengths generated by the different copper complex ions. Furthermore, anhydrous $CuCl_2$ efficiently absorbs moisture from the air to form the dihydrate. Although we sourced anhydrous $CuCl_2$, a pure anhydrous sample should be yellowish brown, but our $CuCl_2$ was a pale green, indicating some small extent of hydration. This indicates there was slightly more water than calculated in our solutions, which as established, can impact the color of a solution. A possible although perhaps excessive suggestion to control this variable would be to perform our experiment in a manufactured water free atmosphere. As additional future experiments, we could try smaller percent increments of acetone and molar amounts of NaCl, specifically with the higher amounts, to see gradations and the range of color change more clearly. Overall, this work regarding these colored complexes may connect new ideas about copper's mechanisms of coordination and color change, important characteristics of copper complexes.

MATERIALS AND METHODS

Making the acetone reference spectrum

Eleven $CuCl_2$-water-acetone solutions were created to be used for color comparisons. Acetone concentration was increased in 10% increments by volume, giving a range from 0% to 100%. To get a desired concentration in the acetone-water-$CuCl_2$ solutions, the volume of acetone needed for each solution was calculated by multiplying the total volume of solution, 20 mL, by the desired percent acetone concentration. The volume of water needed was then calculated by subtracting the volume of acetone needed from the total volume of solution. To make the solutions, the appropriate amount of tap water for each solution was added to 30 mL beakers. A combination of 2 mL and 10 mL volumetric pipettes were used to measure out our solvent components. Then, the proper amount of acetone was quickly added with new pipettes of the same sizes to the water, followed by 0.300 g of anhydrous $CuCl_2$ that had been measured on an electronic scale. The solution was mixed with a plastic scoopula until the $CuCl_2$ visibly dissolved and poured into a 20 mL glass vial before sealing it. This process was repeated for each percent acetone concentration and the vials were stored in our classroom for color comparisons.

Comparing the NaCl-water-$CuCl_2$ solutions to the spectrum

Twenty milliliter solutions of NaCl-water-$CuCl_2$ were made as follows and color was compared visually to the acetone spectrum - 20 mL of tap water was measured into a 30 mL beaker using a 10 mL volumetric pipette and 10 mL pipette filler. A scale was used to measure 0.300 g of anhydrous $CuCl_2$, which was added to the same beaker. The beaker, with a stir bar, was placed on a stir plate on speed 1 until the solid was visibly dissolved. The color of this solution was then recorded by finding the most similar color amongst the spectrum of acetone-water-$CuCl_2$ solutions. Visual comparisons were completed under the fume hood light with white papers underneath and behind the solutions. Color comparisons were done from the actual solutions instead of photos of the solutions, so the temperatures of the spectrum solutions were the same as the new ones during comparison. NaCl was added in 1.500 g increments to the above solutions, up to a maximum of 6.000 g, and the same comparison explained above was completed to find the matching acetone percentage for each increment. Three NaCl-water-$CuCl_2$ solutions were made in total.

Controls

All testing was conducted within a two-hour time frame to minimize the variation of temperature and humidity levels. These variables were measured with a Vernier probe at the start and midpoint of the experiment. To minimize changes due to exposure to the atmosphere, the hydration levels of the acetone and $CuCl_2$ were controlled by using a new bottle of anhydrous acetone that was capped whenever possible. The $CuCl_2$ was always measured right before it was added into the solution then capped immediately. After making them, the solutions were also stored in vials of minimum volume closed tightly. The same equipment (pipettes, beakers, stir bars, stir plate and stir plate speed) was used consistently, which kept precision the same and prevented possible variables introduced through the stirring process.

Further testing

In a later effort to determine the composition of our acetone spectrums, we remade the solutions of acetone concentrations from 60%-90% and tested these solutions with neocuproine, which turns red with Cu^+ and green with Cu^{2+}. The testing was performed by sprinkling neocuproine powder onto filter paper and using a plastic pipette to soak it with the acetone-water-$CuCl_2$-solution, then recording the color the neocuproine turned.

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REFERENCES

1. "Visible Light." NASA Science, National Aeronautics and Space Administration, 2010, science.nasa.gov/ems/09_visiblelight. Accessed 17 June 2022.
2. "The Colours of Complex Metal Ions." Chem Guide UK, www.chemguide.co.uk/inorganic/complexions/colour.html#:~:text=Copper(II)%20ions%20in%20solution,as%20pale%20blue%20(cyan). Accessed 7 June 2022.
3. National Center for Biotechnology Information. "PubChem Compound Summary for CID 24014, Cupric chloride." PubChem, pubchem.ncbi.nlm.nih.gov/compound/Cupric-chloride. Accessed 17 June 2022.
4. "An Introduction to Complex Metal Ions." Chem Guide UK, www.chemguide.co.uk/inorganic/complexions/whatis.html. Accessed 7 June 2022.
5. LumenLearning. "51. Intermolecular Forces." Introductory Chemistry, Pressbooks. UEN Digital Press, Pressbooks, uen.pressbooks.pub/introductorychemistry/chapter/intermolecular-forces/.
6. Kuntzleman, Tom. "A Multi-Colored Equilibrium Experiment." Chem Ed X, Division of Chemical Education, Inc. of the American Chemical Society, 5 Mar. 2020, www.chemedx.org/blog/multi-colored-equilibrium-experiment. Accessed 8 June 2022.
7. Clark, Jim. "Le Chatelier's Principle Fundamentals." Chemistry LibreTexts, Truro School in Cornwall, 14 Mar. 2021, chem.libretexts.org/@go/page/96656.
8. Bond, Marcus R. "Structural Diversity in Substituted Pyridinium Halocuprates(II)." 2022. Exploring Chemistry with Pyridine Derivatives, edited by Satyanarayan Pal, IntechOpen, 2023. IntechOpen, doi.org/10.5772/intechopen.107124.
9. Cotton, F. Albert, Geoffrey Wilkinson, Carlos A. Murillo, Manfred Bochman Advanced Inorganic Chemistry -6th ed. "A Wiley-Interscience Publication", 1999.
10. "5.4: Spectrochemical Series." LibreTexts Chemistry, Penn State University, 3 June 2021, chem.libretexts.org/@go/page/183320.
11. Friedman, Newton J., and Robert A. Plane. "Solvation of Copper(II) Ion in Acetone-Water and Ethanol-Water Solutions." PUBS, vol. 2, no. 1, Feb. 1963, doi.org/10.1021/ic50005a003.
12. Florida State University. "Polarity of Molecules." Chemistry LibreTexts, 6 June 2019, chem.libretexts.org/@go/page/30254. Accessed 17 June 2022.
13. Dept. of Chemistry. "Ion-Dipole Forces." Chem Purdue, Purdue University, www.chem.purdue.edu/gchelp/liquids/iondip.html#:~:text=An%20ion%2Ddipole%20force%20is,ionic%20compounds%20in%20polar%20liquids. Accessed 17 June 2022.
14. UCD. "Complex-Ion Equilibria." Chemistry LibreTexts, 21 May 2021, chem.libretexts.org/@go/page/516. Accessed 17 June 2022.
15. Kochi, Jay K. "The Reduction of Cupric Chloride by Carbonyl Compounds." Journal of the American Chemical Society, vol. 77, no. 20, Oct. 1955, pp. 5274-78, doi.org/10.1021/ja01625a016.
16. Chu, Y., et al. "Solvation of Copper Ions by Acetone. Structures and Sequential Binding Energies of Cu+(acetone)x, x = 1-4 from Collision-Induced Dissociation and Theoretical Studies." Journal of American Society for Mass Spectrometry, vol. 13, 2002, pp. 453-68, doi.org/10.1016/S1044-0305(02)00355-0.

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