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Ligand Exchange and Stability of Copper(II) Complexes

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GRAPHICAL ABSTRACT

Copper(II) sulphate pentahydrate as starting material

ABSTRACT

The purpose of this study is to synthesize a series of copper(II) complexes and investigate the stability of copper(II) complexes which are tetra-ammine copper(II) sulphate and bis-ethylenediamine copper(II) sulphate by using copper(II) sulphate pentahydrate as the starting material. The synthesized products were characterized and identified by melting point, Fourier transforms infrared (FTIR) spectrophotometer, and UV-Visible (UV-Vis) spectroscopy. The stability constant of these copper(II) complexes were determined by using the electrochemical cell layout. In general, the greater the positive charge density on the central ion, the greater is the stability of its complexes. To find the stability is based on the chelate effect of the compound. Chelation is a type of bonding of ions and molecules to metal ions. The chelate effect can be seen by comparing the reaction of a chelating agent and a metal ion with the corresponding reaction involving comparable monodentate ligands. It has been known for many years that a comparison of this type always shows that the complex resulting from coordination with the chelating ligand is much more thermodynamically stable. This can be seen by looking at the values of stability constant for adding two monodentate ligands compared with adding one bidentate ligand. A monodentate ligand has only one donor atom used to bond to the central metal atom or ion while bidentate ligands, are Lewis bases that donate two pairs of electrons to a metal atom and are often referred to as chelating ligands. From this study, it shows that ethylenediamine is a chelating ligand that is more stable compared to ammine. Therefore, the stability constant value for ethylenediamine is smaller than ammine.

Keywords: Copper complexes, ligand exchange, stability

1. INTRODUCTION

Transition metals have several key properties that differ from main group metals. One of the compelling aspects of transition metals is their potentiality to form coordination compounds. Coordination compounds are formed between a metal ion and molecule with one or more unshared electron which is known as a ligand [1],[2]. The number of ligands bound to the transition metal ion is called the coordination number. Ligands can be classified according to the number of donor atoms they contain. A monodentate ligand donates a single electron pair to metal or metal ion. Some examples of monodentate ligand are chloride ion, water, hydroxide ion, and ammonia. Bidentate ligands have two donor atoms which allow them to bind with a central metal atom or ion at two points. Common examples of bidentate ligands are the oxalate ion (ox) and ethylenediamine (en).

A metal ion in solution is present in combination with ligands such as solvent molecules, simple ion, or chelating groups that giving rise to complex ion or coordination compounds. These complexes contain a central atom or ion, often a transition metal, and a cluster of ions or neutral molecules are surrounding it. Copper often has coordination number 4 and consists of the ligand involved in coordination compound such as monodentate ligand which has only one atom that coordinates directly to the central atom of the complex. For example ammonia and chloride ion are monodentate ligand of copper in the complex $[Cu(NH_3)_6]^{2+}$and $[CuCl_6]^{2+}$. A copper (II) complex consists of a central metal atom or ion that is bonded to the ligands, which are ions or molecules that contain one or more pairs of electron that can be shared with a copper metal.

The electronic energy levels within the Cu(II) 3d electron configuration can be investigated through the UV-visible absorption spectra of the compounds in solution. The position and intensity of the absorption bands in the visible region show why the solutions have observably different colors, and a quantitative estimate of the ligand field stabilization energies can be derived from the positions of the absorption bands in the spectra.

It is frequently stated in the standard textbooks that in comparing two complexes with ligands which are otherwise similar but one of which is able to chelate, for example, the ligands NH_3 and en, then the letter complex will be far the more stable. This effect is known as the chelate effect, [3] and is ascribed to the favorable entropy change which results from the formation of the chelate. The primary objective of this experiment is to measure the relative stabilities of the two complexes shown in the equation and examine the magnitude of the chelate effect in this instance.

$$[Cu(H_20)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 6H_2O \qquad (\Delta G_{amm})$$

$$[Cu(H_20)_6]^{2+} + 2en \rightleftharpoons [Cu(en)_2]^{2+} + 6H_2O \qquad (\Delta G_{en})$$

2. EXPERIMENTAL

The experiment was focusing on prepare and isolate pure, dry samples of copper(II) sulphate pentahydrate,$CuSO_45H_2O$, tetra-ammine copper(II) sulphate, $[Cu(NH_3)_4]SO_4.H_2O$ and bis-ethylenediamine copper(II) sulphate, $[Cu(en)_2]SO_4.H_2O$. The IR spectra was recorded by Fourier Transform Infrared (FTIR) spectroscopy, Perkin Elmer series 1600. The absorption spectra was determined by Shimadzu UV-Visible spectroscopy. The stability constant for the tetra-ammine and bis- ethylenediamine copper(II) complexes in aqueous solution was determined by the electrochemical cell layout that give contributed to the chelate effect.

2.1. Synthesis of Copper(II) Sulphate Pentahydrate, $CuSO_45H_2O$

Firstly, 8 g (0.1mol) of copper oxide was placed in a 250 ml beaker and 100 ml dilute sulphuric acid was added. The mixture was heated to dissolve the black solid and the solution will be turned to blue. The hot solution was filtered by using a conical filter paper into a 250 ml conical flask. Use a glass rod to stir. After that, 50 mL of the copper sulphate was saved for the next two experiments. The remaining filtered solution was placed in the evaporating dish was heated until it evaporated. The filtered solution was allowed to cool and solidified. Then, the crystals can be isolated by suction filtration and washed with water.
Preparation of extracts

2.2. Synthesis of Tetra-ammine Copper(II) Sulphate, $[Cu(NH_3)_4]SO_4.H_2O$

Firstly 25 ml (0.021 mol.) of the residual copper sulphate solution from the reaction of CuO and sulphuric acid in the previous experiment were taken, and this was poured into a 150/250 ml conical flask. Dilute ammonia was added in small portions, and the flask was shaking after each addition. A light blue will form initially. When ammonia has added enough to dissolve all the pale blue solid, ethanol was added into the flask. The compound was isolated by suction filtration and washed with ethanol.

2.3. Synthesis of Bis-ethylenediamine Copper(II) Sulphate, $[Cu(en)_2]SO_4.H_2O$

The remaining 30 ml (0.021) of the copper sulphate solution from the first preparation was taken and the described preparation of tetra-amino copper (II) was repeated, but use ethylenediamine in place of ammonia. The dilute (10%) ethylenediamine solution provided was used, by adding to slight excess to obtain a dark blue/purple compound. The dark blue compound was isolated exactly as described for the ammonia complex.

2.4. Electronic Absorption Spectroscopy

100 ml of a solution (~0.08 – 0.10M) of copper sulphate pentahydrate was prepared in water. This solution will be needed for UV-visible spectrometry and later for the electrochemical measurements. The solution should be prepared in a 100 ml volumetric flask, using approximately 2.0 – 2.5 g $CuSO_45H_2O$, 10 ml dilute H_2SO_4, and water up to 100 ml. For the ammonia and ethylenediamine complexes, solutions of known concentration of approximately 0.02M should be prepared. In each case, a 100 ml volumetric flask was used and 10 ml of the appropriate ligand solution was added which is dilute ammonia or 10% ethylenediamine. In all cases, record the UV-visible region spectrum from 400-900 nm in polystyrene cells.

2.5. Electrochemical Cell

Firstly, 25 ml of the copper sulphate solution was put in each beaker, and make sure the electrodes and salt bridge are well dipped into the solution. 25 ml (2M) ammonia solution was added, take a reading, (mV). Three further 25 ml ammonia additions were made, and the reading was noted each time. By the third reading, the cell potential should have leveled off, somewhere around 400 – 500 mV. The experimental measurement was repeated but using ethylenediamine solution in place of ammonia (a 10% solution, ~1.5M, is provided for this experiment). The maximum stable reading in this case will be significantly larger than that obtained with ammonia.

3. RESULTS AND DISCUSSION

3.1. IR Spectroscopy

The IR spectrum copper(II) sulphate pentahydrate, $CuSO_4 5H_2O$, one peak is observed for the pentahydrate at 3398.57 cm^{-1} and it can assign to O-H stretching vibrations of water. A band of medium intensity was observed at 1376.89 cm^{-1} for S-O bond. This also assigns to the bending modes of water. Characteristic bands of C-H are observed at 1460.75 cm^{-1} with strong intensity. The C-O bond was observed at 1080.95 cm^{-1}. The spectral data is summarized in Table 1 and Figure 1 shows the IR spectrum of $CuSO_4.5H_2O$.

Table 1. IR spectral data for $CuSO_4 5H_2O$

Type of bond	Intensity	Frequency (cm^{-1})
O-H	Broad	3398.07
S-O	Strong	1376.89
C-H	Strong	1460.75
C-O	Broad	1080.95

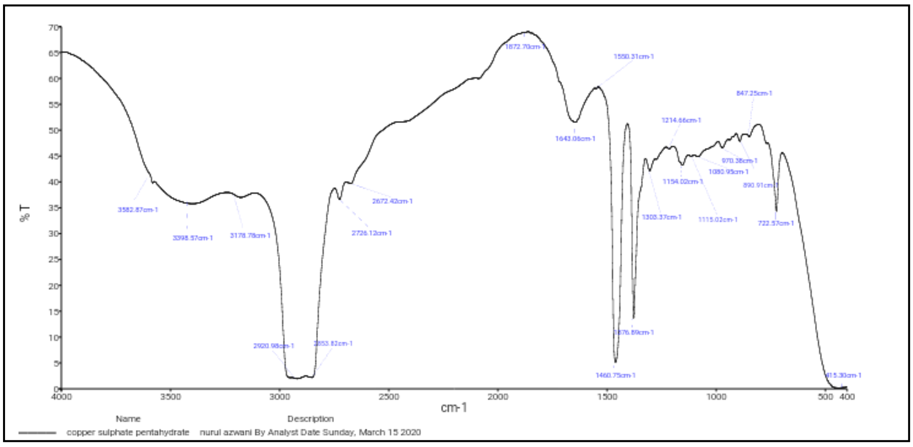

Figure 1. IR spectrum of $CuSO_4.5H_2O$

For spectrum of tetra-ammine copper(II) sulphate, $Cu(NH_3)_4]SO_4.H_2O$, first evidence is the increasing peak in the 3299.92 cm^{-1} regions. The effect of O-H bonds also seen at 1601.97 cm^{-1}. Peaks belong to the N-H bond located at 3231.14 $cm^{-1}$and 3299.92 cm^{-1}. This region overlapped by the O-H bands. It was summarized in Table 2. Figure 2 shows the IR spectrum of $Cu(NH_3)_4]SO_4.H_2O$.

Table 2. IR spectral data for $Cu(NH_3)_4]SO_4.H_2O$

Type of bond	Intensity	Frequency (cm^{-1})
O-H	Broad	3299.92
N-H (2° ammine)	Medium-strong	3231.14 & 3299.92
C-O	Strong	1268.67
S-O	Strong	1115.17
N-H (1°, 2° ammine)	Strong	776.75

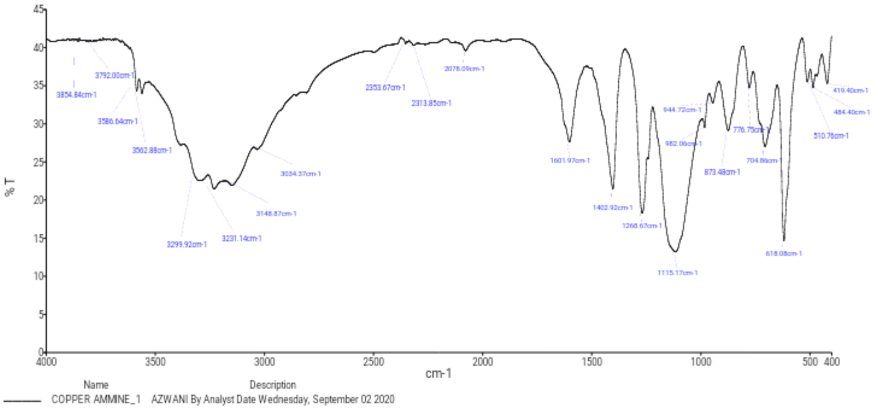

Figure 2. IR spectrum of $Cu(NH_3)_4]SO_4.H_2O$

For Bis-ethylenediamine Copper(II) Sulphate, $[Cu(en)_2]SO_4.H_2O$ these are some stretch as well as deformation modes of Cu-N and Cu-O bond. Two bands at 448.83 cm^{-1} and 475.52 cm^{-1} are due to Cu-N mode. The recognizable of strong band at 974.35 cm^{-1} correspond to the S-O bond. The CN band in the spectrum of the crystalline en was reported at 1120.42 cm^{-1}. The double band with maximums at 3129.35 cm^{-1} and 3297.79 cm^{-1} corresponds to symmetrical NH_2 and asymmetrical NH_2 respectively. In the IR spectrum of the solid state en, the title band are shifted and could be found at 3129.35 cm^{-1} and 3364.44 cm^{-1}. Symmetrical CH_2 and asymmetrical CH_2 at 2885.07 cm^{-1} and 2944.57 cm^{-1} in the solid en respectively were observed [6].

Table 3. IR spectra for $[Cu(en)_2]SO_4.H_2O$

Type of bond	Intensity	Frequency (cm^{-1})
Cu-N	Strong	448.63, 475.52
S-O	Strong	974.35
CN	Broad	1120.42
CH_2 (sym., asym.)	Strong	2885.07, 2944.57
NH_3 (sym., asym.)	Medium-strong	3129.35, 3297.79
en	Medium-strong	3219.71, 3364.33

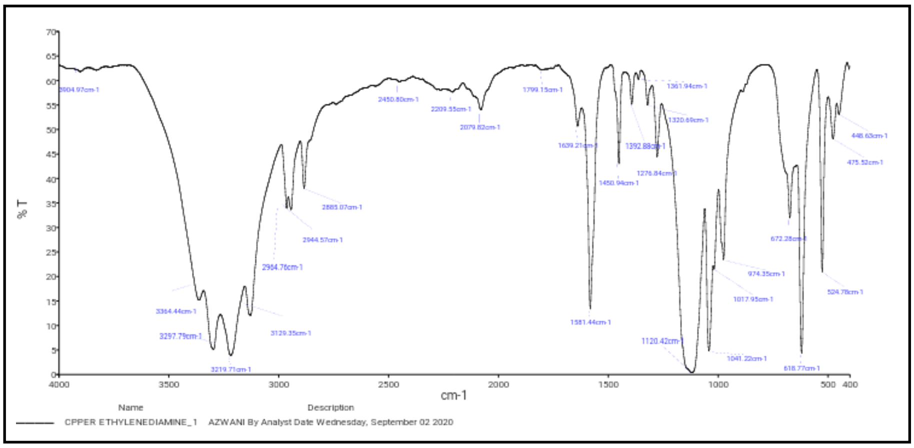

Figure 3. IR spectrum of $[Cu(en)_2]SO_4.H_2O$

3.2. UV-Visible spectroscopy

Anhydrous copper sulphate $(CuSO_4)$ is white, which means that it does not absorb light in the visible region of the spectrum. The hydrated copper sulphate $(CuSO_4.5H_2O)$ is blue. The structure of the compound can be represented more accurately as $Cu(H_2O)_4SO_4.H_2O$ where four water molecules are bound to the copper ion and the fifth is a water of crystallization. The water molecules are arranged at the corners of a square, with the copper at the center. Such an arrangement is called a square planar. Notice that the compound absorbs light of wavelengths from 400-900 nm. In order to absorb light in this region which is where the spectra are measured, the molecule must contain either pi bonds or atoms with non-bonding orbitals. A non-bonding orbital is an atom that has a lone pair such as nitrogen.

When ammonia is added to a solution of copper(II) cation, a deep blue color is formed immediately. The blue color is due to the complex. ion $[Cu(NH_3)_4]^{2+}$. The absorption spectrum of this complex ion in 0.02M ammonia is shown in Figure 4. Copper(II) ethylemediamine has the higher absorbance, 1.350 abs. It is shown that most of the lights are absorbed by the sample and only small light detects by the detector. This result was tabulated in Table 4.

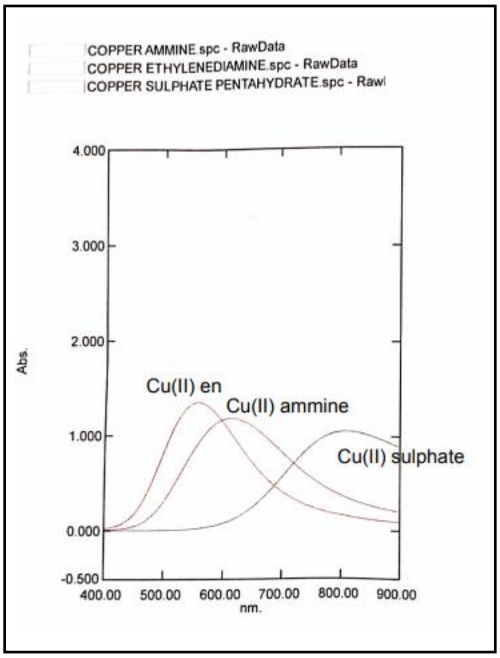

Figure 4. UV-Vis spectrum of copper(II) complexes

Table 4. UV-Vis spectral data of copper(II) complexes

Compounds	**Absorbance**	**wavelength, nm**
Cu(II) en	1.350	557.50
Cu(II) NH_3	1.185	612.00
Cu(II) sulphate	1.058	809.50
Cu(II) en	1.350	557.50

3.3. Stability of Copper(II) Complexes

From the graft of the copper(II) complex, it shows that free energy different, ΔG is inversely proportional to the volume of the compound, mL. The higher the volume of ammonia and ethylenediamine, the smaller the value of the free energy different. However, the value of copper(II) ethylenediamine is much smaller than copper(II) ammine. Therefore, the value of the equilibrium constant of copper(II) ethylenediamine is higher than copper(II) ammine. This is due to the stability of copper(II) ethylenediamine is stronger than copper(II) ammine. Ligands like ammonia is a monodentate ligand that attached to the metal via only a single atom. While ethylenediamine is a bidentate ligand that is attached to the metal at two sites that act as a chelating agent. Therefore, the bidentate ligand ethylenediamine forms a chelate complex with the copper ion.

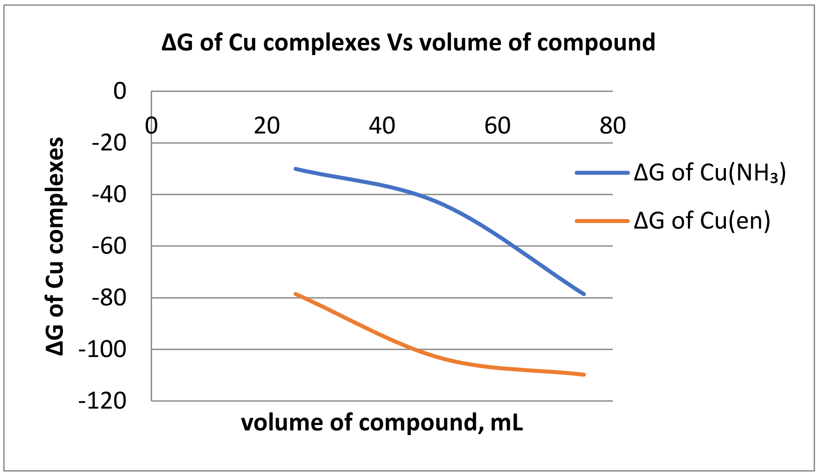

Figure 5. Free energy of Cu(complexes) as a function of the volume

4. CONCLUSION

This report has been successfully synthesize and characterize series of copper(II) complexes starting with copper(II) sulphate pentahydrate, $CuSO_4.5H_2O$ followed by tetra-ammino copper(II) sulphate, $Cu(NH_3)_4]SO_4.H_2O$ and bis-ethylenediamine copper(II) sulphate, $[Cu(en)_2]SO_4.H_2O$. Copper(II) sulphate pentahydrate give blue color of crystal, while tetra-ammino copper(II) sulphate formed dark blue color of solid powder and bis-ethylenediamine copper(II) sulphate formed dark purplish color of solid powder. From the result obtained, it can be concluded that copper(II) ethylenediamine is more stable compared to copper(II) ammine and the copper(II) sulphate solution as the starting material. This is due to the value of the equilibrium constant of copper(II) ethylenediamine is larger than copper(II) ammine that shows it is a bidentate ligand that can chelate with the center atom which is copper(II).

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