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**EFFECTS OF LIGAND CONCENTRATION ON THE
STRUCTURAL CHARACTERISTICS OF A COORDINATION
COMPOUND**

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Abstract

In this project, effects of ligand (NH_3) concentration on the characteristics of tetraammine copper (II) sulfate monohydrate were investigated by using different analysis technique such as DTA/TGA, IR spectroscopy and Magnetic Susceptibility measurement.

Firstly, amine complexes of copper were prepared by using different concentrations of ammonia at a fixed copper concentration. Then, these complexes were analysed to determine the differences at coordination and related properties such as thermal behaviour and chemical binding in the complexes.

Results demonstrated that there are significant differences between the prepared complexes. Using different ammonia concentrations in the synthesis resulted in different compounds with different thermal stabilities. Also it was seen from IR spectra that chemical bindings change with respect to the ammonia concentration.

(119 Words)



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Aim Of This Project

In this project, effects of ligand (NH_3) concentration on the characteristics of tetraammine copper (II) sulfate monohydrate were investigated by using different concentrations of ammonia during the synthesis of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$. Synthesized complexes were analysed by some techniques such as DTA/TGA, IR spectroscopy and Magnetic Susceptibility measurement to determine their structures and some of their chemical and physical properties (such as thermal stability and their magnetism).

Research Question

Can we change the properties of a coordination compound by changing the ligand concentration during the synthesis at a fixed central atom concentration ?



1) INTRODUCTION

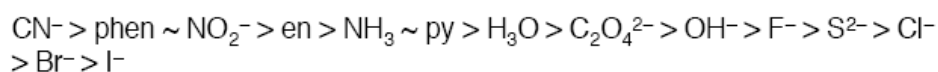
A) Coordination Chemistry

Metal complex or coordination compound can be defined as an adduct of a Lewis acid and a Bronstedbase. A coordination compound is formed by the chemical bonds between electron donating ions or molecules and central metal atom via electron transfer. Electron donating groups are named as ligands and those groups accepting electrons are named as central atom (usually transition metal atoms) [1].

The coordination number in a complex is the number of ligands bonding to the metal directly. Ligands coordinate to the metal ion in a special manner and this manner determines the coordination geometry of the complex (octahedral, tetrahedral, square planar) [2].

B) Spectrochemical Series

The order given below refers to the ordering of ligands with respect to their ligand strength and called as “spectrochemical series”. The strongest ligand is the cyanide and the weakest one is the iodide. The electron donating ability determines the place of a ligand in this order. Most electron donor one is the strongest ligand and vice versa.



[1] <http://science.jrank.org/pages/1771/Coordination-Compound.html>

[2] R. G. V. Ewens and H. Bassett, *Chem. Ind.*, 1949, 27, 131.

C) Tetrahedral Complexes

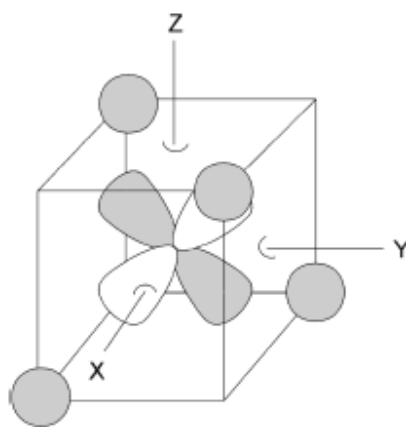


Fig.1 Schematic illustration of tetrahedral arrangement

Fig.1 shows the tetrahedral arrangement of four ligands on each axis.

The e orbitals are therefore lower in energy. The interaction of the four ligands with the t_2 orbitals (d_{xy} , d_{xz} and d_{yz}) is considerably greater than with the e type orbitals (d_{z^2} and $d_{x^2-y^2}$) (Fig.2). [3].

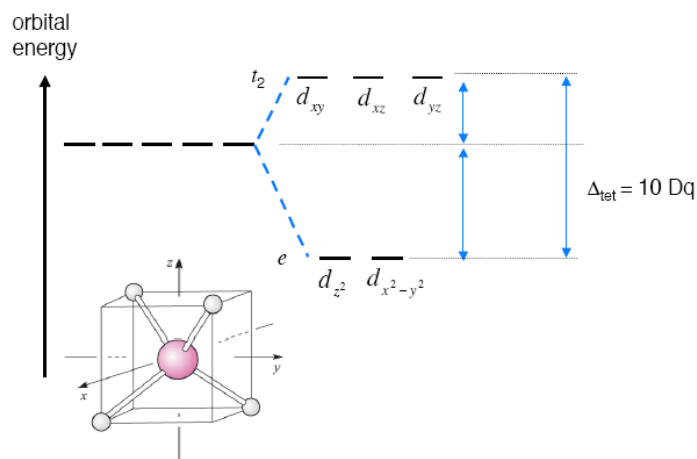
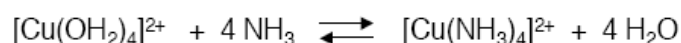


Fig.2 Orientation of d-orbitals of a metal ion in the tetrahedral coordination.

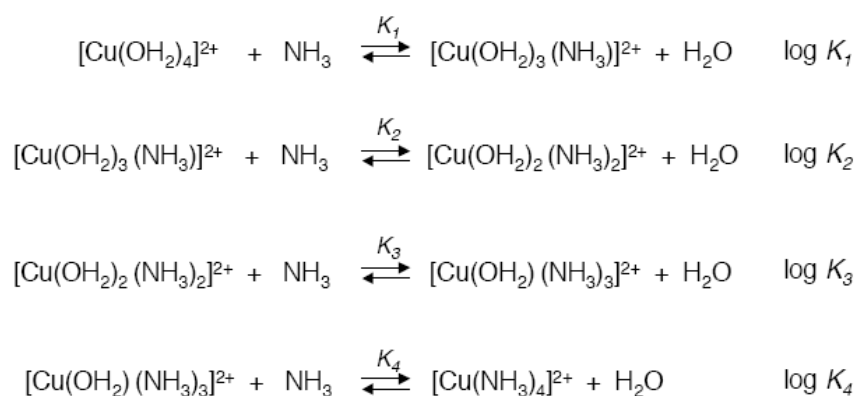
[3] *Advanced Inorganic Chemistry, Third Edition Summary*, By F.Albert Cotton, Sir Geoffrey Wilkinson, John Wiley & Sons Inc.

D) Thermodynamic Stability

Equilibrium constant is an indication of the thermodynamic stability of a coordination compound formed with the reaction of the metal ion with the corresponding ligand:



The overall equilibrium constant for this reaction can be expressed as K_n (here $n = 4$).



$$\log \beta_4 = \log K_1 + \log K_2 + \log K_3 + \log K_4 = 12.82$$

E) Thermal analysis

Thermal analysis is an analysis method where the properties of materials are studied as a function of temperature. There are several types of thermal analysis such as;

- Differential scanning calorimetry (DSC)
- Thermogravimetric analysis (TGA)

During the analysis temperature can be controlled by a continuous increase or decrease in temperature at a constant rate (during heating and cooling) or by carrying out a series of determinations at different temperatures.

In addition to the temperature control, it is also possible to control the environment (e.g. atmosphere). Measurements may be carried out in air or under an inert gas (e.g. nitrogen or helium). Reactive atmospheres can also be used. Some measurements are even carried out with the sample surrounded by water or other liquids [4].

i) Thermogravimetric Analysis:

Thermogravimetric Analysis (TGA) is a method in which the changes in weight is recorded against to the change in temperature with high degree of precision. Sometimes, derivative of the weight loss curves can be used to make the analysis easier. Because, many weight loss curves look similar in usual. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. TGA is commonly used to determine characteristics of materials (such as polymers, inorganic and organic materials). This technique can also be used to carry out some high temperature reactions. For example, some hydrogenation reactions or some reduction reactions using H₂ gase can be carried in this instrument.

ii) Analyzer

During the analysis samples are loaded with a platinum or alumina pan. The pan is placed in a small electrically heated oven in which the temperature is measured sensitively by a thermocouple. The atmosphere can be made inert by purging the medium with inert gases such as nitrogen, argon in request. A computer is connected to the system to control the instrument and to process the collected data.

Analysis is carried out by recording the raising temperature against to the weight of sample. After the data is obtained, additional operations can be done (such as curve smoothing) to find the exact points of inflection [5].

[4] http://en.wikipedia.org/wiki/Thermal_analysis.

[5] http://en.wikipedia.org/wiki/Thermogravimetric_analysis.

Differential thermal analysis:

Differential thermal analysis (DTA) is a thermoanalytic technique in which the material under study and an inert reference are made to undergo identical thermal cycles. During this cycles temperature differences between sample and reference are recorded. This differences is then plotted against time, or against temperature (DTA curve). Exothermic and endothermic changes in the sample is detected relative to the (Al_2O_3) inert reference. Thus, a DTA curve gives information about the transformations such as glass transitions, crystallization, melting and sublimation. The area under a DTA peak refers to the enthalpy change which is not affected by the heat capacity of the sample [6].

F) Infrared Spectrometers

Infrared (IR) spectrometers measure the wavelength and intensity of the absorption of infrared light by the sample. IR light lies between the visible and microwave portions of the electromagnetic spectrum. Near infrared light is closest in wavelength to visible light. Conversely, far infrared light is closest to the microwave region. Mid-infrared light has enough energy to excite molecular vibrations to higher energy levels. Changes in the molecule's dipole moment causes these vibrations which occur only at those frequencies where the molecule absorbs infrared light. As is well known, the wavelengths of infrared absorption bands are characteristic for a specific chemical bonds. Hence, IR measurements can be used to identify the structure of the molecules [7].

G) Magnetic Susceptibility

Magnetic Susceptibility can be defined as "the ratio of the intensity of magnetism induced in a substance to the magnetising force of field to which it is subject." Basic principles of magnetic behaviour is based on their magnetic properties. All substances can be classified into the three groups. Those attracted by a strong magnetic field are paramagnetic and those repelled designated diamagnetic. Finally, the most recognised class, ferromagnetic, unique in their ability to retain their own magnetic field. [8].

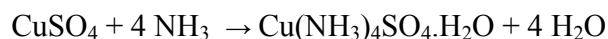
[6] Bhadeshia H.K.D.H. "Thermal analyses techniques. Differential thermal analysis". University of Cambridge, Material Science and Metallurgy.

[7] http://laboratoryequipment.globalspec.com/LearnMore/Labware_Scientific_Instruments/Spectrometers_Analytical_Photometers/Infrared_Spectrometers.

[8] <http://www.sherwood-scientific.com/msb/msbindex.html#def>

2) EXPERIMENTAL

i) *Synthesis of tetraammine copper (II) sulfate monohydrate, $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$*



2 grams of copper sulfate 5-hydrate are dissolved in a mixture of 3 mL of concentrated ammonia and 2 mL of water. The resulting deep blue solution is cooled in ice and stirred continuously while 3 mL of alcohol is added drop-wise from a buret or tap-funnel. The mixture is allowed to stand in the cold for at least 4 hours, preferably overnight ; the supernatant liquid should be almost colorless. The crystalline product is filtered off , washed first with 12.5 mL of a cold equivolume mixture of alcohol and concentrated aqueous ammonia and then with 12.5 mL of 95% alcohol and ether. The salt is dried in air. Conversion almost quantitative.



ii) Variation of structural properties with decreasing ammonia concentration

In this part, the synthesis procedure given above was followed. Only, ammonia concentration was changed. By diluting with water, 6.9, 7.9 and 8.9 M ammonia solutions were prepared and then used in the synthesis of tetraammine copper (II) sulfate monohydrate.



iii) Characterization of the synthesized coordination compounds

In this part, all the coordination compound synthesized were characterized by using several experimental techniques such as FT-IR, UV-Vis, DTA/TGA and Magnetic Susceptibility Balance. Our aim was to determine the structural differences resulted after the variation of the ammonia concentration. As it is known, in this study NH_3 is used as a ligand and a decrease in its concentration will affect the coordination behavior of the central atom copper.

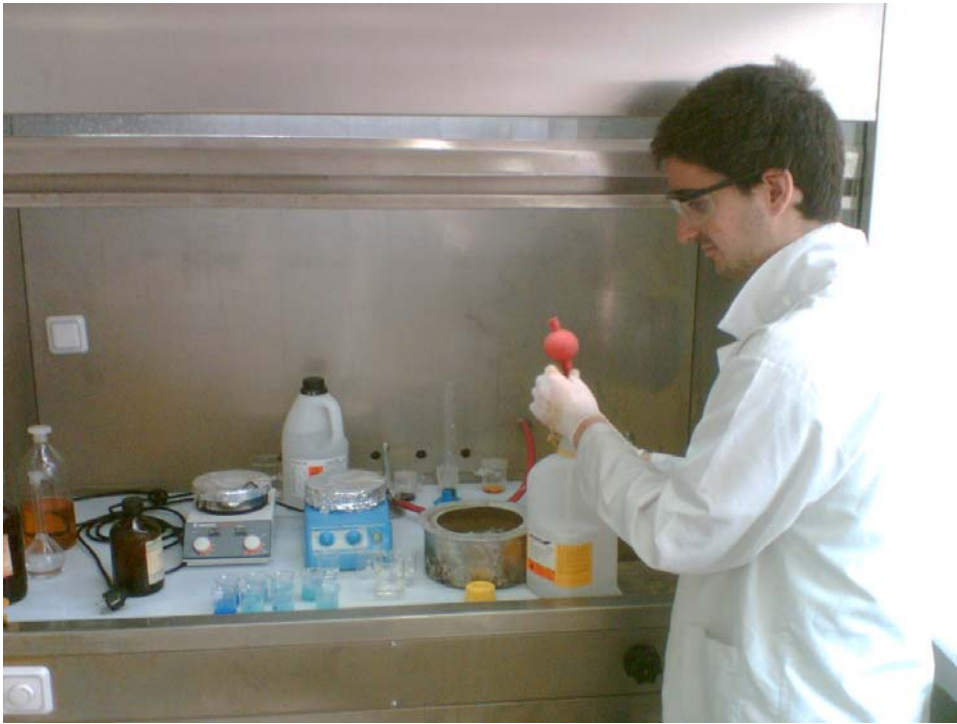
So, we will obtain different compounds at the end and it is probable to observe some structural differences when these compounds are analysed by the techniques mentioned above.

a) FT-IR: The infrared (IR) spectra of the zeolite samples were measured from 400 to 4000 cm^{-1} by a FTIR-Spectrometer (Nicolet 380) with a pellet of powdered potassium bromide (80mg) and sample (3mg).

b) UV-Vis: 10mg sample was dissolved in 5mL water and then analyzed by using (Varian, UV-VIS Spectrometer, Cary 100) between 250-900nm against a water blank and spectrum was recorded.

c) DTA/TGA: Thermal analysis was carried out with Shimadzu DTG-60 instrument. Nearly, 5 mg sample was heated with a reference containing the same amount of α -alumina by heating between 30 and 900 $^{\circ}\text{C}$. During this measurement, weight loss and endo/exothermic behavior of the sample were recorded on a thermogram.

d) Magnetic Susceptibility Balance: By using this balance (Sherwood Scientific Magnetic Balance), presence of copper was evidenced with the calculation of number of unpaired electrons. This value is "1" for the copper 2+ ion. That is, Cu^{2+} has only one unpaired electron in its valence orbitals. During the magnetic susceptibility measurement, firstly, empty capillary tube was placed into the balance and R_0 value was recorded. Then, certain amount of the sample was placed in a 3 mm diameter capillary tube and R value was measured. Also, the height of the sample in the capillary was weighed on a balance.



3) RESULTS AND DISCUSSION

DTA/TGA study:

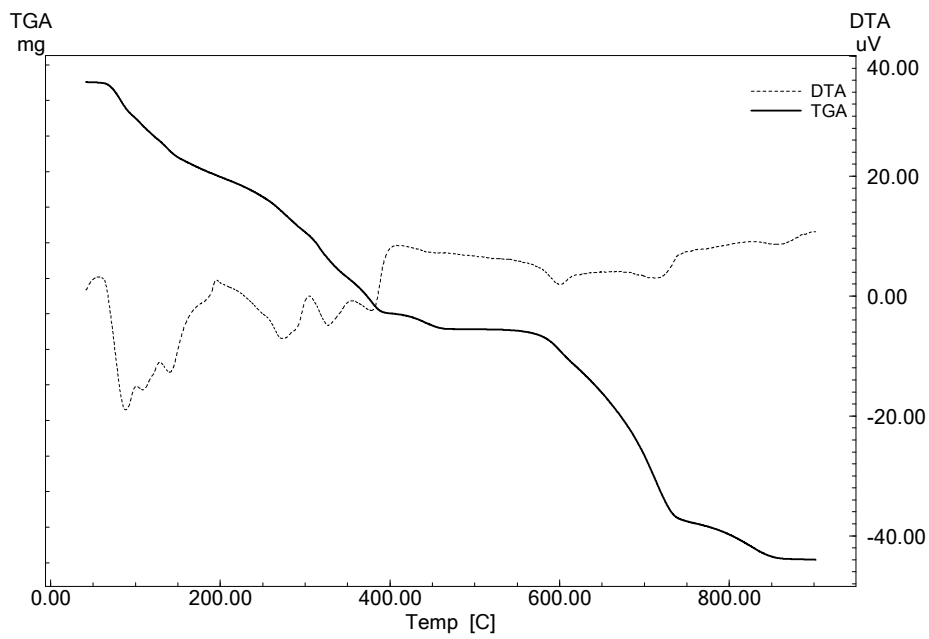


Fig. 3. DTA/TGA curves of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ prepared (concentrated ammonia used) Weight loss between 30-900°C= 68.8%

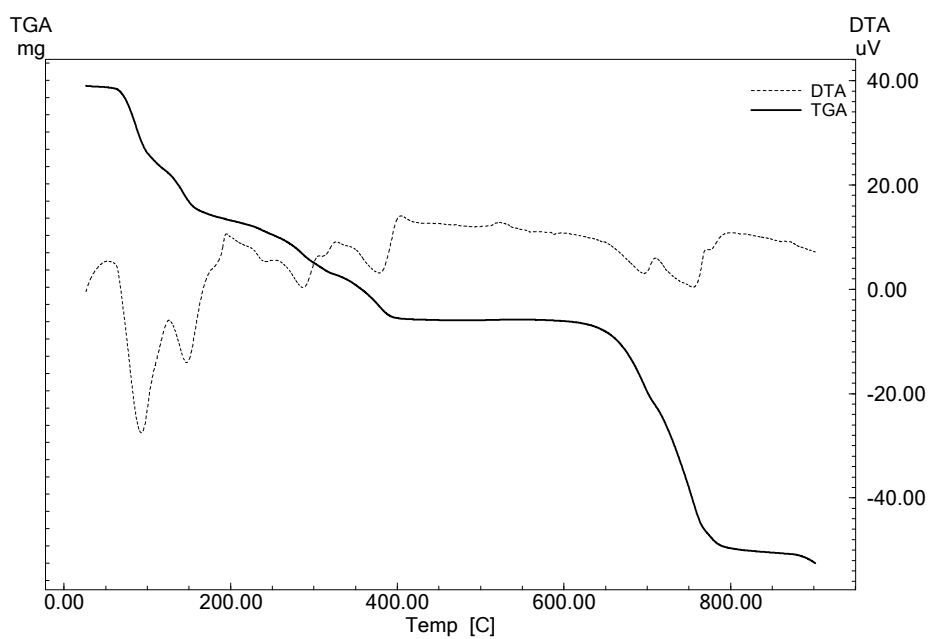


Fig. 4. DTA/TGA curves of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ prepared (8.9M ammonia used) Weight loss between 30-900°C= 71.0%

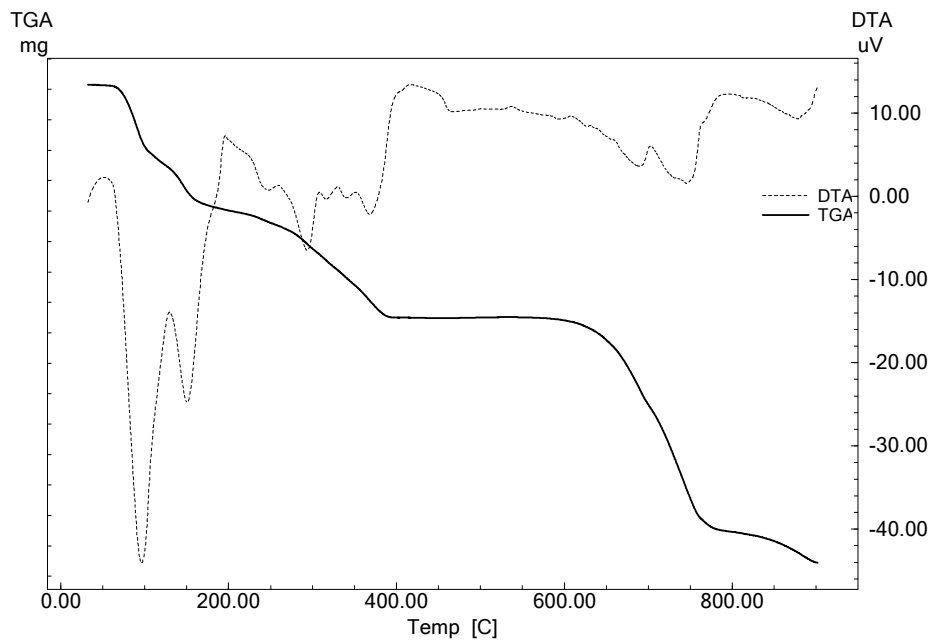


Fig. 5. DTA/TGA curves of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ prepared (7.9M ammonia used) Weight loss between 30-900°C= 70.8%

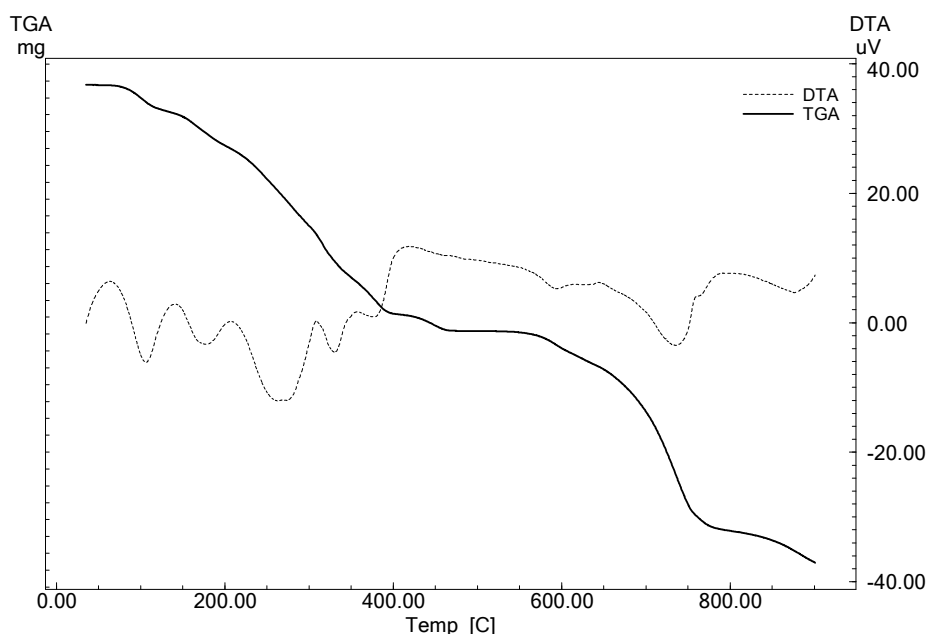


Fig.6 DTA/TGA curves of [Cu(NH₃)₄]SO₄.H₂O prepared (8.9M ammonia used) Weight loss between 30-900°C= 66.2%

Evaluation of The DTA/TGA study:

As it is seen from the TGA curves, there are two region belong to the weight losses due to the H₂O and NH₃ present in the coordination compound [Cu(NH₃)₄]SO₄.H₂O. Weakly bound NH₃ ligands and H₂O molecules present in the voids of crystal are removed between 30-200°C. Beyond 200°C, observed weight loss is due to the removal of NH₃ molecules strongly bound to the central atom copper (II). When we compare the thermal behavior of the coordination compound produced with the standart procedure to the other coordination compounds prepared by varying the NH₃ concentration, we can say that especially DTA curves are completely different. Except the sample prepared by using 6.9M NH₃, there is an increase of the intensity in the endothermic peak, for the 8.9 and 7.9M NH₃ used samples.

This is probably due to the incorporation of higher amounts of H₂O molecule as a ligand and crystal water with decreasing NH₃ concentration. Increasing endothermic nature with 7.9M NH₃

used sample shows us that in this region there is another ligand bonded to the central atom. Because, endothermic peak observed in this sample has higher intensity than standart sample prepared by using concentrated ammonia. The probability of the attachment of H₂O molecule to Cu(II) increases with increasing H₂O content (or decreasing NH₃ concentration). Weight loss and endothermic peak observed beyond 600 °C is probably due to the decomposition of sulfate group of the coordination compound. The shape of TGA curves recorded between 30 – 400 °C is completely changed due to the usage of dilute (6.9M) ammonia solution. This is also another indication of the structural change of the coordination compound with varying ammonia concentration. Weight loss values are nearly same for all the samples studied. This is probably due to that NH₃ and H₂O are monodentate (means they can bind to the central atom via only one chemical bond) ligands and their exchange does not change the number of ligands in the coordination compound. And also, their molecular weights are very close to each other (NH₃: 17g/mol ; H₂O: 18g/mol). So, it is proper to expect minimal changes in the percentage of weight loss values.

IR Study:

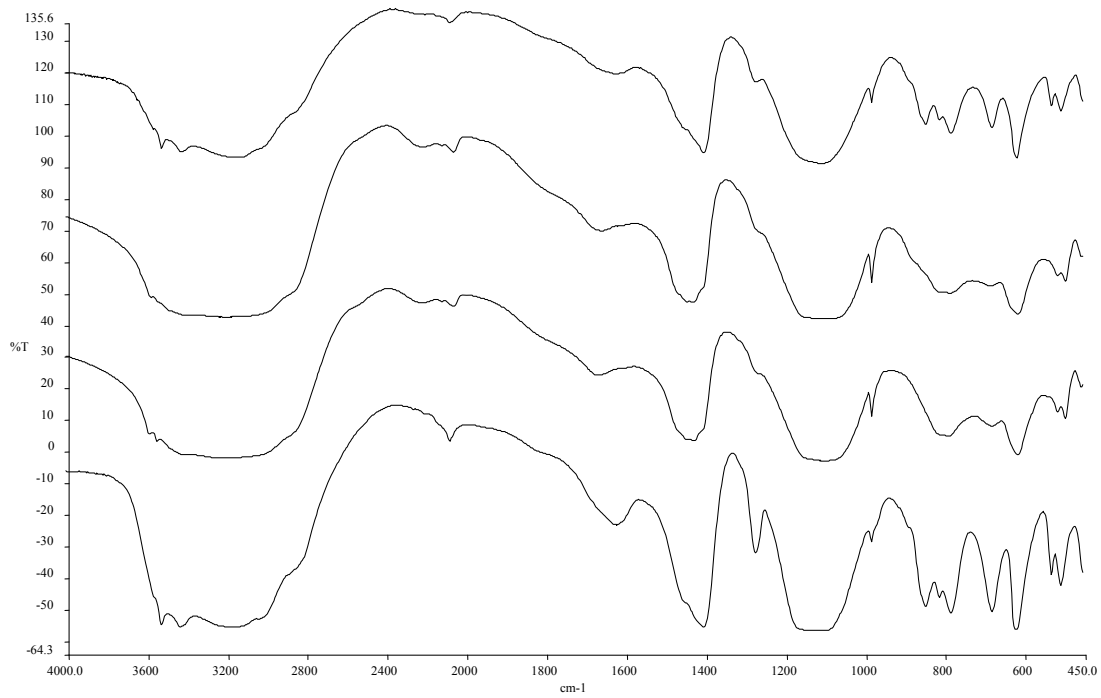


Fig.7 IR spectra of the copper complexes; standart (upper), 8.9, 7.9 and 6.9 M NH₃ used sample (down).

Evaluation of The IR Study:

As it is seen from the spectra, there area lot of evidence for the higher content of water for the diluted ammonia used samples. This means, with diluted ammonia solutions the probability for the incorporation of the additional water molecules to the coordination sphere of the Cu increases. First evidence is the increasing peak intensity in the 2800-3600 cm⁻¹ region. When the ammonia solution diluted, more H₂O coordinated to the Cu (II) ion and the O-H bonds increases the intensity of the peak in this region. The effect of these O-H bonds also seen at ~1600 cm⁻¹. With decreasing NH₃ concentration or increasing water content of the ammonia solution the intensity of this peak increases.

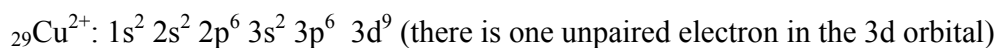
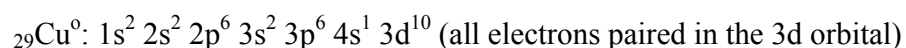
As it was given in Fig.7, peaks belong to the N-H bond are placed 3200-3400cm⁻¹ region. This region overlapped by the O-H bands. So, it is not possible to show the changes in N-H region after the incorporation of additional H₂O molecules. But, except the 6.9M NH₃ used sample, 8.9 and 7.9 M NH₃ used samples shows the expected changes. By diluting the ammonia solution, metal-NH₃ peaks are weakened. This is an evidence for the removal of some of the NH₃ ligand and the incorporation of H₂O molecule.



Magnetic susceptibility studies:

i) Determination of the presence of Cu(II) in the complex

To determine the presence of copper (II) ions in the coordination compound, magnetic susceptibility measurements were carried out. As it is well known diamagnetic compounds, with all electrons paired, are slightly repelled by a magnetic field. A compound with unpaired electrons is paramagnetic and is attracted into a magnetic field. The measure of this magnetism is called the magnetic susceptibility. When the electron configuration of copper (II) ion was written (scheme 1.), it will appear that copper (II) ion has one unpaired electron which means that n (number of unpaired electrons) =1 for Cu(II) ion.



ii) Formulation for the magnetic susceptibility

$$X_g = C_b \cdot L \cdot (R - R_0) / (10^9 \cdot m)$$

$$X_m = X_g \cdot MW$$

$$\mu = 2.8 \cdot (X_m \cdot T)^{1/2}$$

$$\mu = (n \cdot (n+2))^{1/2}$$

m: weight of sample used

C_b : constant (0.963)

L: height of the sample in the capillary tube (cm)

R_0 : measurement with empty capillary tube

R: measurement with sample containing capillary tube

X_g : gram susceptibility

X_m : molar susceptibility

T: temperature in Kelvin scale (298 K)

M: magnetic moment

n: number of unpaired electron (s) in the coordination compound studied

MW: molecular weight of the coordination compound $[\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}] = 245.5 \text{ g/mol}$

iii) Experimental data

Table 1. Data recorded from the magnetic susceptibility measurements

Sample	m	Ro	R	L
<i>Standart</i>	0.140	-3.0	189	3.0
<i>8.9</i>	0.151	-3.0	180	3.0
<i>7.9</i>	0.130	-3.0	181	3.1
<i>6.9</i>	0.167	-3.0	194	3.1

iv) Calculations

a) Calculation of gram susceptibility

For Standart Sample :

$$X_g = C_b \cdot L \cdot (R - R_o) / (10^9 \cdot m)$$

$$X_g = 0.963 \times 3.0 \times (189 - (-3.0)) / (10^9 \times 0.140)$$

$$X_g = 3.962 \times 10^{-6}$$

For 8.9 M Sample :

$$X_g = C_b \cdot L \cdot (R - R_o) / (10^9 \cdot m)$$

$$X_g = 0.963 \times 3.0 \times (180 - (-3.0)) / (10^9 \times 0.151)$$

$$X_g = 3.501 \times 10^{-6}$$

For 7.9 M Sample :

$$X_g = C_b \cdot L \cdot (R - R_0) / (10^9 \cdot m)$$

$$X_g = 0.963 \times 3.1 \times (181 - (-3.0)) / (10^9 \times 0.130)$$

$$X_g = 4.225 \times 10^{-6}$$

For 6.9 M Sample :

$$X_g = C_b \cdot L \cdot (R - R_0) / (10^9 \cdot m)$$

$$X_g = 0.963 \times 3.1 \times (194 - (-3.0)) / (10^9 \times 0.167)$$

$$X_g = 3.521 \times 10^{-6}$$

b) Calculation of molar susceptibility

$$X_m = X_g \cdot MW$$

For Standart Sample :

$$X_m = 3.962 \times 10^{-6} \times 245.5 \text{ g/mol} = 9.726 \times 10^{-4}$$

For 8.9 M Sample :

$$X_m = 3.501 \times 10^{-6} \times 245.5 \text{ g/mol} = 8.594 \times 10^{-4}$$

For 7.9 M Sample :

$$X_m = 4.225 \times 10^{-6} \times 245.5 \text{ g/mol} = 10.372 \times 10^{-4}$$

For 6.9 M Sample :

$$X_m = 3.521 \times 10^{-6} \times 245.5 \text{ g/mol} = 8.644 \times 10^{-4}$$

c) Calculation of dipole moment (μ)

$$\mu = 2.8 \cdot (X_m \cdot T)^{1/2}$$

For Standart Sample :

$$\mu = 2.8 \times (9.726 \times 10^{-4} \times 298)^{1/2} \Rightarrow 1.507$$

For 8.9 M Sample :

$$\mu = 2.8 \times (8.594 \times 10^{-4} \times 298)^{1/2} \Rightarrow 1.417$$

For 7.9 M Sample :

$$\mu = 2.8 \times (10.372 \times 10^{-4} \times 298)^{1/2} \Rightarrow 1.556$$

For 6.9 M Sample :

$$\mu = 2.8 \times (8.644 \times 10^{-4} \times 298)^{1/2} \Rightarrow 1.421$$

d) Calculation of the number of unpaired electron (n) in the coordination compound;

$$\mu = (n.(n+2))^{1/2} \Rightarrow \mu^2 = (n.(n+2))$$

For Standart Sample :

$$(1.507)^2 = (n.(n+2))$$

$$0 = n^2 + 2n - 2.271 \Rightarrow n = 0.806$$

For 8.9 M Sample :

$$(1.417)^2 = (n.(n+2))$$

$$0 = n^2 + 2n - 2.008 \Rightarrow n = 0.734$$

For 7.9 M Sample :

$$(1.556)^2 = (n.(n+2))$$

$$0 = n^2 + 2n - 2.421 \Rightarrow n = 0.850$$

For 6.9 M Sample :

$$(1.421)^2 = (n.(n+2))$$

$$0 = n^2 + 2n - 2.020 \Rightarrow n = 0.738$$

When the calculated n values are compared to the theoretical value of $n = 1$, all calculated values are very close to the expected value of 1. So, we can conclude that all coordination compound samples contain Cu(II) ion and also all of them are paramagnetic due to the presence of one unpaired electron. Paramagnetism arises because each unpaired electron behaves as tiny magnet. With a paramagnetic sample, the tube (in which sample placed) and magnet attract each other and the magnet appears slightly lighter. Conversely, with a diamagnetic sample, the tube (in which sample placed) and magnet repel each other and the magnet appears slightly heavier.



4) CONCLUSION

In this study, effects of ligand concentration on the structural characteristics of the coordination compound were investigated. Results demonstrated that ligand concentration has a significant effect on the structure of the complex. Both thermal properties and chemical bindings are different for each coordination compound prepared by using different concentrations of ammonia. But, weight loss values are nearly same for all the samples studied. This is probably due to that NH_3 and H_2O are monodentate ligands and their exchange does not change the number of ligands in the coordination compound. And also, their molecular weights are very close to each other. So, it is proper to expect minimal changes in the percentage of weight loss values.

IR spectra showed that, with decreasing ammonia concentration, hydroxyl group region $3400\text{-}3600\text{ cm}^{-1}$ becomes distorted and some shoulders appeared. Additionally, the peak located at $\sim 1600\text{ cm}^{-1}$ becomes much more intense with decreasing ammonia concentration. This is an evidence for the incorporation of water to the coordination sphere of copper at low ammonia concentration.

Also, the presence of copper ion (as Cu^{2+}) is evidenced by using magnetic susceptibility balance. It was seen that ammonia concentration does not effect the oxidation state of copper. Calculated values are very near to the theoretical value $n=1$. This means that there is only one unpaired electron in the structure of the coordination compound. Hence, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4\cdot\text{H}_2\text{O}$ can be said to be a paramagnetic compound.

5) REFERENCES

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