

# Synthesis And Spectroscopic Studies Of Tetrakis(Acetato)Copper(II) Dihydrate Complex.

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## Abstract

Copper(II) tetrakis(acetato) dihydrate complex has been synthesized using standard laboratory methods involving precipitation, filtration, evaporation and recrystallization. The synthesis was carried out in order to re-establish the chemical nature of metal complexes in their dimeric state. Infrared spectra of ligand and complex were recorded. Atomic Absorption, Ultraviolet-Visible Spectroscopic Studies and melting points of the complex were also recorded. The colour change in the complexation of metal to the ligand was also recorded. Infrared spectral peak for the oxygen-metal (M-O) was  $490\text{ cm}^{-1}$  for copper acetate. The Infrared Spectroscopic Studies showed that copper complexed with acetate ligand by the replacement of hydrogen in the OH bond of the acetate in one hand and another via a dative bond brought about by the oxygen atom in the C=O lone pair of electrons.

Key words: Synthesis, Spectroscopy, Tetrakis(Acetato)Copper(II), Complex.

## Introduction

Historically, the existence of co-ordination complexes, such as Prussian blue and copper vitriol was known since the beginning of Chemistry, but their nature was not well understood initially. A better understanding of coordination complexes however, began with the theories proposed by Alfred Warner (Anusiem, 2004; Shrivvers & Atkins, 2010). Other than metal vapours, plasmas and alloys, all other metal compounds are complex compounds. Metals and metalloids bond to ligands almost in all circumstances, although gaseous “naked” metal ions can be engendered in high vacuum. The metal ions are usually formed from transition metals, although some non-transition elements such as Mg are known and employed in the formation of complexes such as chlorophyll that is responsible for photosynthesis and the conversion of solar energy to life energy.

Transition metal complexes are important because of their chemical, optical and magnetic properties (Davies, 2007; Grande, 2008; Li, 2009 and Torrisi, 2010). They are also important in catalysis, material synthesis, photochemistry and biological systems (Mueller; 2006). For example, haemoglobin, a complex of iron, is vital to the transport of oxygen by the red blood cells (RBC). Hemocyanin, a complex of copper is vital to the transport of oxygen in the hemolymph of most molluscs and some arthropods e.g horseshoe crab and snails. Ferrocene and metallocene are also complexes of iron used industrially as ligand scaffolds, anti-knock formulations, precursors to oxide materials and as an internal standard for calibrating redox potentials in non-aqueous electrolytes. Chromium also forms complexes of importance; for example, chromium(IV) oxide is used to manufacture magnetic tapes and because of its higher coercivity than iron, chromium oxide tapes give better performance than iron oxide tapes. In well drilling mud, chromium(IV) oxide is also used as an anti-corrosive. In medicine, chromium(III) chloride, chromium(III) picolinate and chromium(III) polynicolinate or amino acid chelate such as chromium(III) D-phenylaniline are used as dietary supplement or slimming aids. Chromium hexacarbonyl is also used as a gasoline additive. Biologically, chromium(III) is required in trace amounts in sugar metabolism in humans and its deficiency may cause a disease called chromium deficiency (Spitsyn *et al*, 1982 and Zaitseva *et al*, 1982). However, there is dearth of literature about complexes of copper(II) in comparison to those of chromium and iron of which all of them belong in the outer transition elements.

Ligand selection therefore, is a critical consideration in many practical areas, such as medicine and homogeneous catalysis (Wikipedia, 2009). The identity of the coordinating atoms and the number of electrons donated to the metal classify a given ligand. In this work acetate is the ligand selected to complex with copper metal.

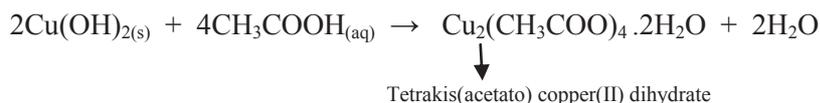
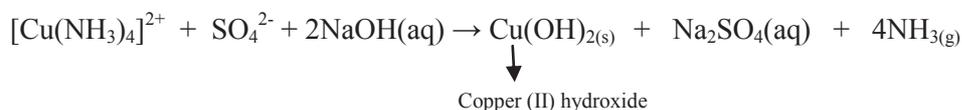
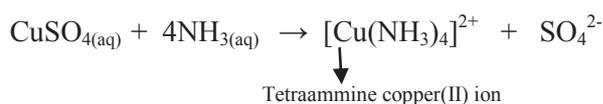
## Methodology

Into a clean beaker equipped with a magnetic stirrer, 6.25 g of analytical grade copper sulphate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) was dissolved in 125 ml of deionized water. The mixture was stirred and warmed to  $50^\circ\text{C}$  to aid dissolution. 15 ml of 50% v/v ammonia solution was added, warmed and stirred until the pale blue coloured solution became intense deep blue. 2.0 g of NaOH pellets were added to the deep blue solution and then stirred for 30 minutes at  $55\text{-}65^\circ\text{C}$ . The mixture was allowed to cool and a light blue solid precipitated out which was collected by suction filtration using a Buchner funnel. The precipitate was triply washed with 50 ml portions of warm water. Thereafter the solid was transferred to a 250 ml beaker and dissolved in 20 ml of 10% acetic acid.

The solution was warmed and stirred until a clear dark blue solution was formed. The solution was then crystallized by warming nearly to dryness. The product was dried on a filter paper and then subjected to:

1. Ultraviolet-Visible spectroscopic study using the THERMO ELECTRO – VISIONpro SOFTWARE V4.20
2. Atomic absorption spectroscopic study using RAYLEIGH WFX-320 AA Spectrophotometer
3. Infrared spectroscopic study of the ligand and complexes using the SHIMADZU IR spectrophotometer.
4. Melting point determination of the complex.

### Chemistry of the reactions involved:



### Results and discussion

In the infrared spectrum of the acetic acid ligand (Fig.1) Four distinct peaks were identified, between (a) 2800 - 3600  $\text{cm}^{-1}$ , (b) 2400 - 2800  $\text{cm}^{-1}$ , (c) 1730 - 1700  $\text{cm}^{-1}$ , 1400 and 3900  $\text{cm}^{-1}$ . The strengths of these peaks and their corresponding vibrations are presented in table 1.

**Table 1: Infra red spectrum of acetic acid ligand**

Peak value ( $\text{cm}^{-1}$ )	Strength	Remarks
3600-2800	Broad	O-H stretching vibration (intermolecular hydrogen bonding)
2800-2400	Strong	C-H stretching vibration
1730-1700	Very Strong	C=O stretching vibration
1400-3900	Strong	C-H bending vibration $\text{sp}^3(\text{CH}_3)$

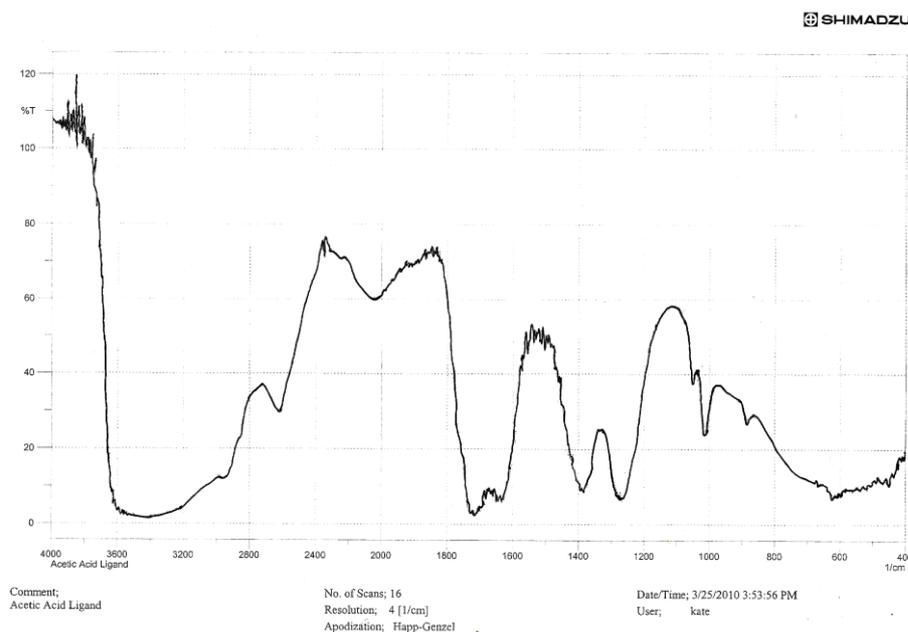


Fig. 1: IR spectrum of the Acetic Acid ligand

Fig.2 represents the IR Spectrum of the Tetrakis(acetato) copper(II) dihydrate Complex. Two distinct peaks were identified, between 2800 – 3600  $\text{cm}^{-1}$  and 1400 - 1600  $\text{cm}^{-1}$ . Their respective strengths are presented in Table 2.

**Table 2: Infra red spectrum tetrakis(acetato) copper(II) dehydrate complex**

3900-3200	Very weak and broad	Metal- O bond formation
2970-2800	Strong	C-H stretching vibration
1600-1500	Strong	C=O $\rightarrow$ metal bond
1400-3900	Strong	C-H bending vibrations
490	Strong	M-O

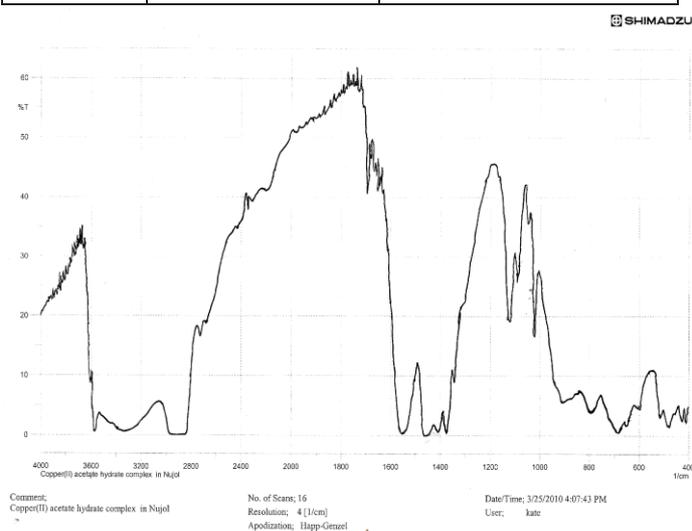
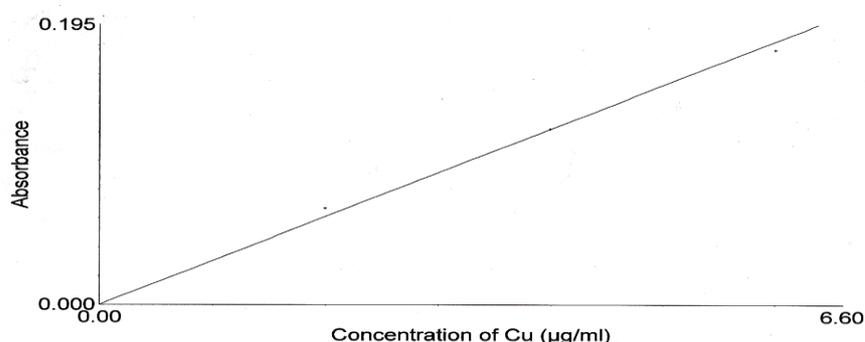


Fig.2: IR Spectrum of tetrakis(acetato)copper(II) dihydrate complex.

A comparison of the IR spectra of the free ligand and that of the metal complex revealed broad band absorption of  $3600-3200\text{ cm}^{-1}$  due to OH vibrational frequency, and  $1300-1200\text{ cm}^{-1}$  due to OH bending vibration for the ligand. In the complex however, these two peaks were absent indicating the displacement of hydrogen in the OH bond by the metal. Again in the ligand, a very strong stretching vibration, seen between  $1730-1700\text{ cm}^{-1}$  due to C=O, was shifted to about  $1600-1500\text{ cm}^{-1}$  in the metal complex indicating that  $\pi$ -bonding bond system of the free ligand was not involved in the bonding but rather the lone pair of electrons in the oxygen atom was donated to the metal for bonding via a dative bonding (co-ordinate covalency).

The IR spectra for M-O bonding for (Th) (Pb) and (La) have been reported to absorb at  $412\text{ cm}^{-1}$   $402\text{ cm}^{-1}$  and  $340\text{ cm}^{-1}$  respectively (Uzoukwu *et al* 1995). In this study, the M-O complex absorption peak of about  $490\text{ cm}^{-1}$  was recorded, this peak was absent in the free ligand. In the Periodic Table, IR spectra below  $600\text{ cm}^{-1}$  for M-O { iron(II) through zinc(II) } have been studied(Inskeep,1962).

Qualitative and quantitative analysis of the complex through AAS Fig. 3 confirmed the presence of Cu with a concentration of  $426,381\mu\text{g/l}$



Sample Label	Weight(g)	Volume(Ml)	Sample Label	Weight(g)	Volume(Ml)
Cu 50 DIGE	0.13324	1000.00	DISTILLED	0.13324	1000.00
Cu 50 DIGE	0.13324	1000.00	Cu 50 DIGE	0.13324	1000.00
Cu 50 DIGE	0.13324	1000.00			

Sample Label	Conc. (µg/ml)	%RSD	Mean Abs.	Replicates	Dilution factor	Final conc. µg/l.
Cu 50 DIGESTED	High	----	1.0206	1.0206		
DISTILLED WATER	ND	----	-0.1434	-0.1434		
Cu 50 DIGESTED	410.138	----	0.1361	0.1361		
Cu 50 DIGESTED	442.623	----	0.1469	0.1469		
Cu 50 DIGESTED	High	----	1.5366	1.5366	1000	410,138
Cu 50 DIGESTED	73.171	----	0.0243	0.0243	1000	442,681
						<u>426,381</u>

Analysis  
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**AAS of copper(II) acetate complex**

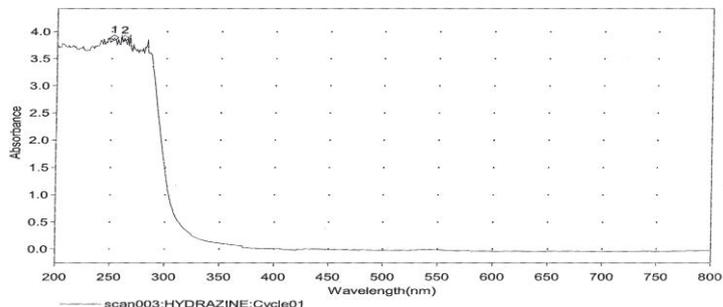
Fig. 3: AAS of the tetrakis(acetato)copper(II) dihydrate complex.

Figs.4 and 5 represent results for the UV/visible spectroscopic studies of the free ligand and the copper acetate complex respectively.

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 Department (None Entered) Time of Report 10:28:05PM  
 Organization (None Entered)  
 Information (None Entered)

**Scan Graph**



Results Table - scan003, HYDRAZINE, Cycle01

nm	A	Peak Pick Method
252.00	3.886	Find 8 Peaks Above -3.0000 A
262.00	3.879	Start Wavelength 200.00 nm
		Stop Wavelength 800.00 nm
		Sort By Wavelength

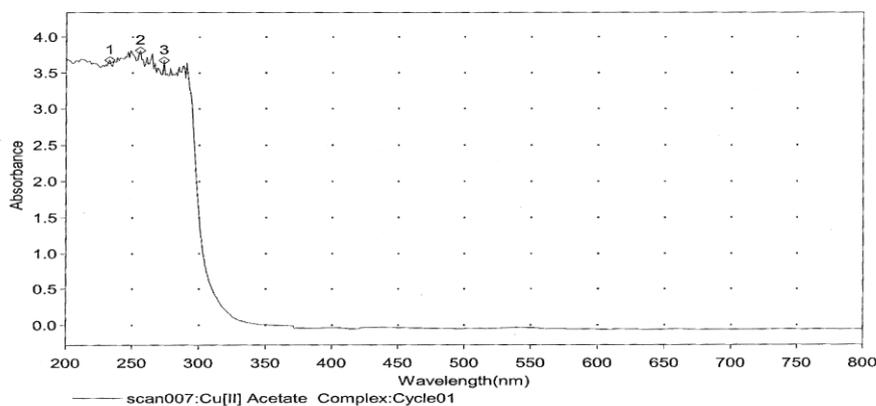
Sensitivity Auto

Fig.4: UV/Visible Spectrum Acetic Acid ligand

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Operator Name (None Entered) Date of Report 8/6/2010  
 Department (None Entered) Time of Report 11:00:55PM  
 Organization (None Entered)  
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**Scan Graph**



Results Table - scan007, Cu[II] Acetate Complex, Cycle01

nm	A	Peak Pick Method
233.00	3.680	Find 8 Peaks Above -3.0000 A
256.00	3.812	Start Wavelength 200.00 nm
274.00	3.676	Stop Wavelength 800.00 nm
		Sort By Wavelength

Sensitivity Auto

Fig. 5: UV/Visible Spectrum of the Copper(II) Acetate Complex

**Elemental Analysis**

Elemental analysis for tetrakis(acetato) copper(II) dihydrate complex was carried out at London Metropolitan University. The result for % carbon and hydrogen are shown on Table 3.

**Table 3. Elemental analysis for tetrakis(acetato)copper(II) dihydrate complex**

Compound	%C	%H
tetrakis(acetato) copper(II) dihydrate complex	29.7	4.1

Also a comparison of the UV/Visible spectra of both Figs 4 and 5, i.e. ligand and complex show that both absorbed in the visible region of the electromagnetic spectrum, although the complex synthesized was dark greenish gray in colour. This indicates an intraligand  $\pi \rightarrow \pi^*$  transition of a 6-bonding system. Consequently, the reaction between copper ion and the ligand resulted in the 6-bond formation as a result of the deprotonation of the OH group of the ligand.

The AAS result for the metal Fig.3 showed that out of 0.13324g/L of the sample used for the AAS analysis 426,381 $\mu$ g/L of copper was found to be present. Thus the % of copper in 0.13324g/L of sample was **32.00%**. The metal complex melted between **225-235 °C** with decomposition.

Thus with IR spectra, UV study, AAS, elemental analysis, melting point and even colour changes it is clear that the copper metal bonded with the acetate ligand via the displacement of the H in the OH bond, thereby forming a 6-bond and another bond via the C=O due to non-bonding electrons of the oxygen. Transition metal complexes in their dimeric form, have quadruple bonds ( Cotton and Wilkinson, 1988 and Lee, 1996), the structure of the tetrakis(acetato)copper(II) dihydrate complex may be seen to be as presented in Fig. 6

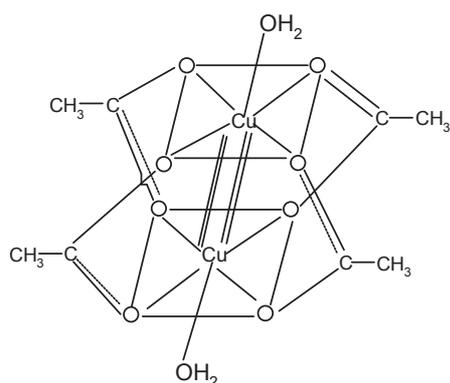


Fig.6: Proposed structure of Tetrakis(acetato) copper(II) dihydrate

### Conclusion

The procedures described in this study are successful pathways for the synthesis of the tetrakis(acetato)copper(II) dihydrate complex. Melting point measurements and spectroscopic studies (IR, AAS, UV and elemental analysis) confirm this. However, subject to the availability of necessary equipment, it is recommended that further studies on this complex should include X-ray diffraction crystallography (single and powder) for the determination of metal-metal bond lengths as well as thermogravimetric analysis of the complex.

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