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Microwave Assisted Nano Structured Tetrakis (4- Aminopyridine) Copper (II) Tetrachloro Cobaltate (II)

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Abstract: The cementish blue $[Cu\ (C_5H_6N_2)_4]^{2+}.[CoCl_4]^{2-}$ adduct crystals have been prepared with the help of microwave oven at the room temperature. The grown crystals have been characterized by UV-visible and FTIR spectra. The size of adduct crystals were observed using high-resolution transmission electron microscopy-HRTEM. The results show that, the-grown adduct crystals have the size within the range of 0-2 nm, and have the structure of Tetrakis (4-aminopyridine) copper (II) tetra chloro cobaltate (II). Very strong peaks were observed at 254 nm and 205 nm. The electronic transition in copper ion and cobalt ion were not observed due to the strong UV absorption. The elemental analysis conforms that it has 35.94 % of carbon, 3.22 % of hydrogen and 16.54 % of nitrogen.
Key words :Nano structured adduct crystal, FTIR spectrum, UV-visible spectrum, elemental analysis, HRTEM.

1. INTRODUCTION

The microwave assisted wet chemical synthesis of compounds have advantages in terms of accelerated reaction, yield improvement, enhanced physicochemical properties and evolvement of new phases. In this technique, the rate enhancement of up to two orders of magnitude and higher yield were reported for many organometallic compounds[1].

The first metal-base caged compound capable of releasing organic biomolecules was [Ru(bpy)2(4AP)2]2+, where 4AP is 4 aminopyridine, a K^+ (potassium) channel blocker[2]. Only a few caged neurochemicals have been prepared so far using the metal coordination strategy, the technique has a promising future. A caged compound must contain an interior cavity in which one or more molecules in ions can be trapped. Metal – assembled cages consists of multi-denate ligands held together by metal cations [3] which are unique because their bonds are more easily broken allowing the movement of guest molecules through the cavity [4]. These cages have potential applications in the area of molecular recognition, light harvesting, bio molecular transport and delivery systems, waste clean-up and time-released medicine [5].

Fampyridine, a new sustained release oral tablet of 4-AP is currently under phase III clinic trial

for its therapeutic efficacy in patients with multiple sclerosis (MS) and chronic spinal cord injury. Low concentration of 4-AP are considered to block transient, voltage activated, outward K^+ currents [6].

Potassium ions (K^+) and sodium ions (Na^+) flow between the neurons and the extracellular fluid to set up the state of electrical charge potential when the neuron is at rest (the resting potential) and to release that potential when the neuron is sending a nerve impulse (the action potential). Sodium ions flow through other special gates called "sodium channels". . Voltage – gated channels open or close in response to the surrounding electro – potential while chemically gated ones open and close in response to chemical stimuli. Dendrites, the branched filaments that receive nerve transmissions from other neurons, tend to have more chemically – gated potassium channels and fewer voltage – gated potassium channels by comparison with axons, the long extensions that send these transmissions onto other neurons.

Clinically for Lambert – Eaton myasthenic syndrome 4aminopyridine is used because it is blocking potassium channels. It prolongs action potentials thereby increasing transmitter release at the neuromuscular junctions [7,8,9,10]. The structure of 4- aminopyridine $C_5H_6N_2$ has been redetermined at 150 K [11]. Also for the same compound, the structure has been reported at room temperature [12]. Though this compound was not analysed and reported for its physical properties from our literature survey, the synthesis and characterization of crystals as well as other nano structured behaviour have been reported in this paper based on their potential applications in biomedical and industrial need.

This paper was aimed at developing green approach based synthesis of nanomaterial viz. microwave assisted nano structured 4-aminopyridine adduct crystal with the suitable green solvent , Also analysis was made with reference to its spectroscopic characteristics (FTIR , UV and HRTEM) and composition of elements present in the material.

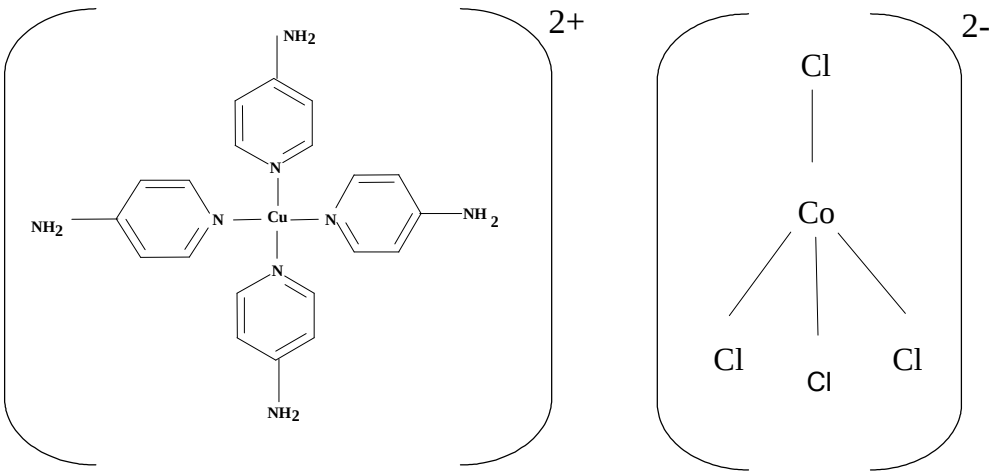
2. EXPERIMENTAL PROCEDURE

All the reagents used for the preparation of sample are analytical grade and the solutions are prepared using pure de-ionized distilled water. A solution of 4-aminopyridine (0.3768 g) in 99.9% pure distilled water (20 ml) was added to a solution of $CuCl_2 . 2H_2O$ (1.7048 g) in 99.9% pure distilled water and a solution of $CoCl_4^{2-}$ (0.475 g) in 99.9% pure distilled water and mixture was prepared at 30°C. The crystal was prepared under microwave assisted condition. To have fast and complete dissolving, the mixture was kept inside the microwave device for one minute. This time is enough for dissolving the solute in the solvent. After one minute the container having the mixture was removed from the microwave device and a cementish blue solution was obtained and cooled and it was filtered and the filtrate was dried at the room temperature. The chemical reaction taking place in the growth process is:

$CuCl_2.2H_2O+4C_5H_6N_2 \rightarrow [CuCl_2(C_5H_6N_2)_4] .H_2O+H_2O$

$[CuCl_2(C_5H_6N_2)_4] .H_2O+CoCl_2 \rightarrow [Cu(C_5H_6N_2)_4](CoCl_4)$

The cementish blue $[Cu(C_5H_6N_2)_4]^{2+} . [CoCl_4]^{2-}$ nano structured adduct crystals of the titled compound were obtained after 2 weeks whose molecular structure is shown below.



The structure of Tetrakis (4-aminopyridine – $_kN^1$) – dichlorocopper (II) monohydrate has been reported [13] in which the pyridine nitrogen is co-ordinated to copper $(II)^+$ ion along with the 2 chloride ions. This compound is treated with $CoCl_2$ resulted the cementish blue nanostructured crystals of adduct of Tetrakis [4-aminopyridine] copper (II) tetrachloro Cobaltate (II) with grain size of about 0-2 nm.

3. RESULTS AND DISCUSSION

3.1 UV-Vis Spectrum

UV spectrum was measured using Perkin – Elmer Lambda 35 UV spectrophotometer over the range of 190 nm – 1100 nm at room temperature. Figure 1 and Figure 2 show the UV – visible absorbance and UV-visible transition characteristics of as grown $[Cu(C_5H_6N_2)_4]^{2+}$. $[CoCl_4]^{2-}$ nano structured adduct crystals respectively. In Figure 1, the peaks at 254 nm and 205 nm in the spectrum are very strong. Normally for the four coordinated copper complexes there will be a transition in the electronic spectrum in the visible region. However due to strong absorption in the UV region, the transition in the visible region is absent. So the electronic transition in copper ion and cobalt ion were not observed due to the strong UV absorption.

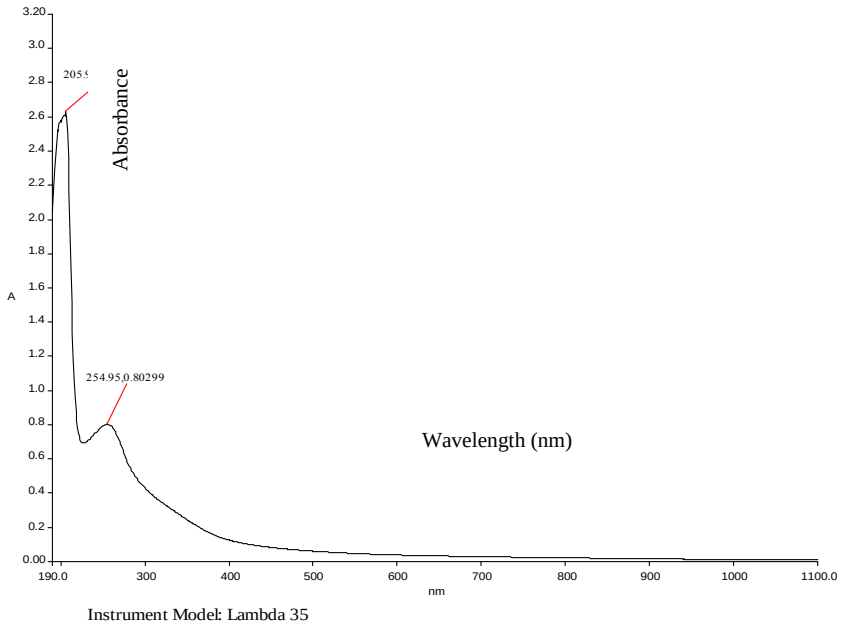


Figure 1: UV Absorption Spectrum

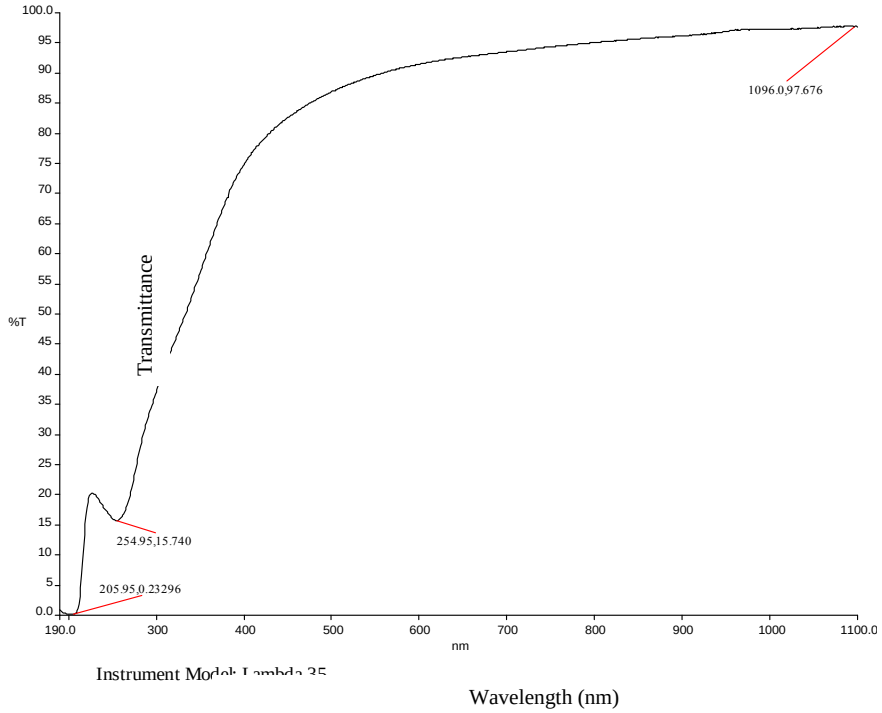


Figure 2: UV Transition Spectrum

3.2 FTIR Spectrum

FTIR spectrum was measured using Perkin – Elmer FTIR spectrophotometer over the range of ± 400 cm^{-1} – 4000 cm^{-1} at room temperature. Figure 3 shows the IR spectrum of as grown $[Cu(C_5H_6N_2)_4]^{2+}$ $[CoCl_4]^{2-}$ nano structured adduct crystals. The Cu – Cl stretch found at 530 cm^{-1} in Tetrakis (4-aminopyridine - $_kN^1$) – Dichloro Copper (II) monohydrate was missing in the FTIR spectrum of the titled nano particle. In the IR spectrum of adduct, the co-ordination of copper is similar to that of the parent compound except the co-ordination of chloro with copper ion. Because there is a positive shift in the NH stretch of the amino group, the amino nitrogen co-ordination with copper ion is ruled out. The negative shift of the C = N stretch of the pyridine nitrogen found at 1638.01 cm^{-1} conforms the co-ordination of pyridine nitrogen with copper ion. There is a decrease in C = N stretch in the adduct. This value is less than the C = N decrease found in $[CuCl_4(C_5H_6N_2)_4]H_2O$. The cation and anion of the adduct are divalent and are represented by 2^+ and 2^- . Thus the structure of the adduct is $[Cu(C_6H_5N_2)_4]^{2+}$. $(CoCl_4)^{2-}$. The cementish blue color is due to the tetrahedral $CoCl_4^{2+}$ ion.

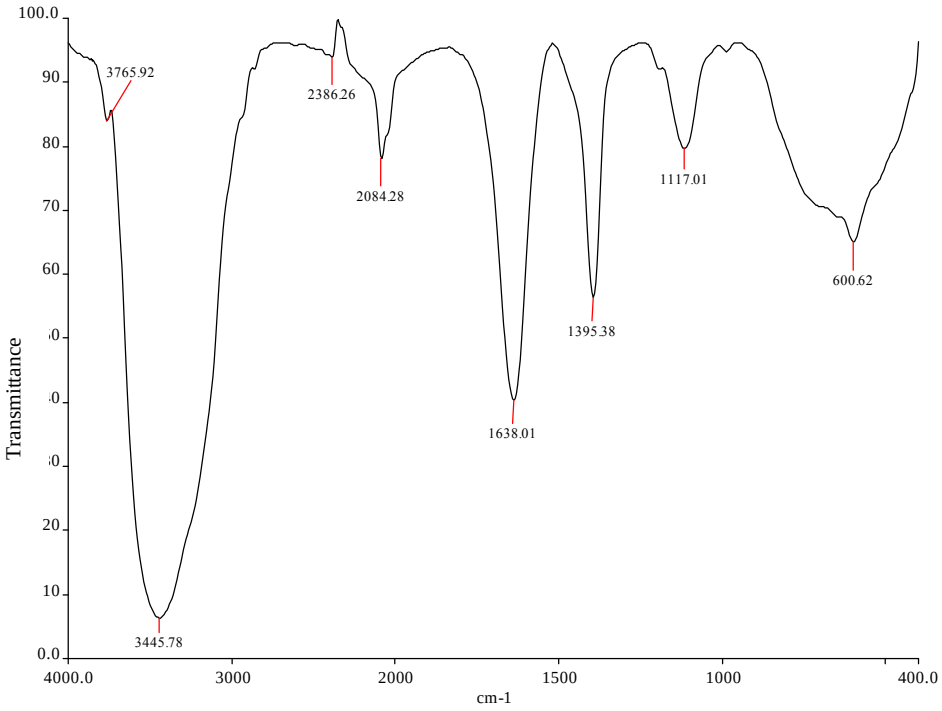


Figure 3: FTIR S Wavelength (cm^{-1})

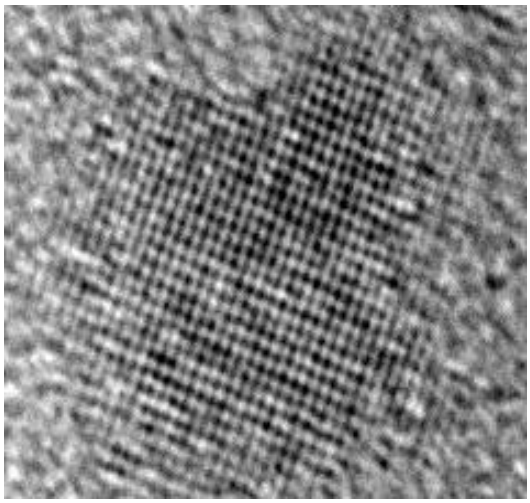
3.3 HRTEM Images

High-resolution transmission electron microscopy HRTEM values are recorded using JEOL 3010 with accelerating voltage 200 KV. Figure 4 and Figure 5 show the HRTEM results, in imaging mode and diffraction mode respectively. Lattice image is represented by the black dots in Figure 4(a, b, c), arranged in a pattern to that of tetrahedral sites. Figure 4(a, c) shows the stacking of atoms in 5 nm scale for different resolution of the image. Figure 4(b) shows the stacking of atoms in 2 nm scale. The imaging mode shows that the as grown crystals having one dimensional nanostructure of the size about 0 – 2 nm. Stacking arrangement of atoms has different orientation. Grain distribution is uniform in each orientation, conforming the grain periodicity. The diffraction mode conforms that this new compound has crystalline nature.

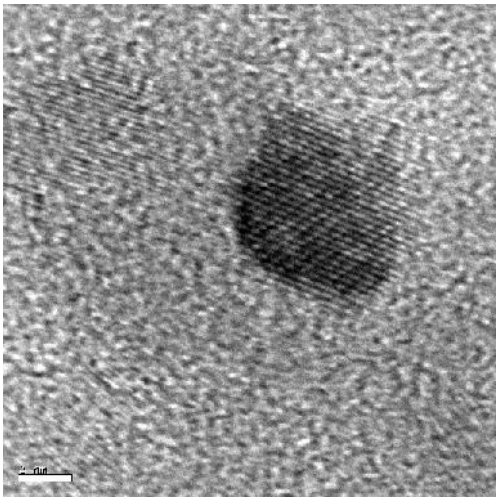
C.H.N. analysis was carried out using Perkin Elmer : series II CHNS/O elemental Analyser. Table 1 shows the composition of CHN in percentage and this table has the % of metal ion found out by titrimetric method and the % was consistent with theoretical values.

The adoption of this method offers a low cost procedure with green approach for synthesis of insertion of materials at higher efficiency and to generate new material structures that could not be obtained from the conventional methods. The grown one dimensional nanostructured adduct crystals have the size within the range of 0-2 nm, and have the structure of Tetrakis (4-aminopyridine) copper (II) tetra chloro cobaltate (II). Very strong peaks were observed at 254 nm and 205 nm. The electronic transition in copper ion and cobalt ion were not observed due to the strong UV absorption. The elemental analysis conforms that it has 35.94 % of carbon, 3.22 % of hydrogen and 16.54 % of nitrogen.

The structural investigation of the chosen pharmaceutically interested compound and understanding the mechanism involved in these compound, needs interdisciplinary research. Since the synthesized crystals are potentially helpful to stimulate the central nervous systems of human beings, the same is subjected to vitro-vivo study to conform its relevance as drug with necessary precautionary measures. Its response in the weak electric field will be a very good procedure through implantable medical device as targeted drug delivery for treating injuries in the spinal chord. A detailed study on the behaviour of the compound would enhance its importance to the society.



4 (a)



4 (b)

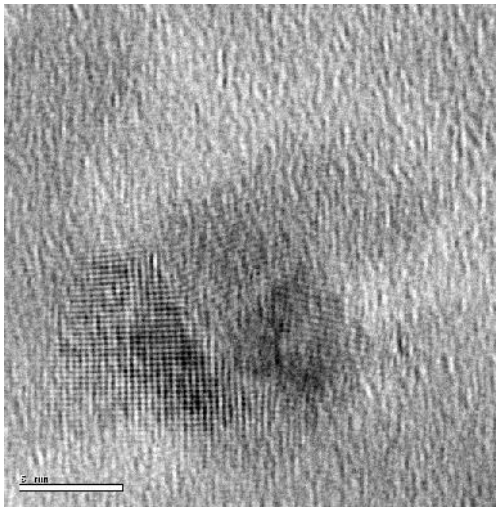


Figure 4(c)

Figure 4: HRTEM Image in Imaging Mode

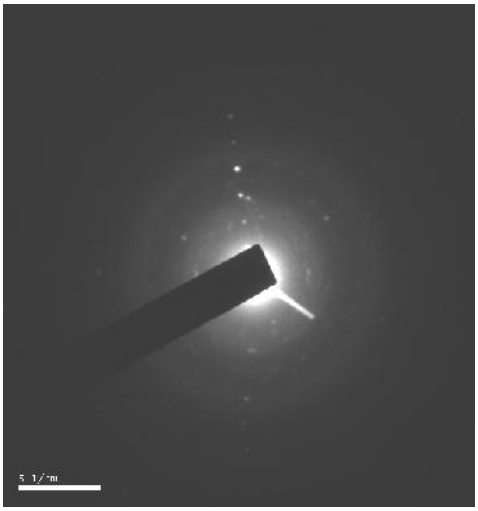


Figure 5

Figure 5: HRTEM Image in Diffraction Modes

Table 1: Elemental analysis

Symbol	Atomic weight + Number of atoms	Mass present %	
		Theoretical value	Experimental value
Co	58.9331955	9.1975	8.94
Cl	141.8128	22.1322	21.36
Cu	63.5463	9.175	9.14
C	240.2156	37.4896	35.94
H	24.190728	3.7754	3.22
N	112.05376	17.4878	16.54

The molecular weight: 640.7524 g/mol.

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