



## Synthesis and Characterisation of Poly (Vinylpyrrolidone)–Copper (II) Complexes

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### Abstract

Transition metals show many remarkable applications in the field of biological sciences, chemical and pharmaceutical industries. Coordination compounds of the transition metals find their use in almost every field of human life. In the proposed work we have selected a copper salt for complexing with poly(vinylpyrrolidone) ligand. Copper compounds are used as bacteriostatic substances, fungicides and food preservatives. Poly(vinylpyrrolidone) is a water soluble polymer having many eco-friendly uses which are the results of its unique properties like low toxicity, biological compatibility, inert behavior towards many compounds, complexing ability, resistant to thermal degradation and film forming ability. Keeping these properties of copper and poly(vinylpyrrolidone) in view and with the objective of synthesizing more environment friendly compounds, complexes of poly(vinylpyrrolidone) and copper were prepared by using aqueous solution of PVP(30K) and alcoholic solution of hydrated copper chloride at room temperature with different molar composition. Crystalline polymer-metal complexes were obtained by evaporation of the solvent. They were characterized by solubility studies, CHN analysis, FTIR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. Procedure was repeated with aqueous solution of the salt also. The spectral analysis of the reactants and the complexes confirmed the formation of expected complexes. The conditions for better complexation were optimized.

**Keywords:** <sup>13</sup>C-NMR, FTIR, <sup>1</sup>H-NMR, Copper chloride dihydrate, Poly (vinyl pyrrolidone).

### Introduction

Coordination compounds of transition metals find their use in almost every field of human life. Now-a-days complexes of metals with polymer ligands are gaining importance as they exhibit many interesting characteristics such as improved thermal stability<sup>1</sup>, hardness and especially catalytic behavior. These properties differ from those of the corresponding ordinary metal complexes having low molecular weights<sup>1-3</sup>. The polymer – metal complexes possess characteristic structure in which the central metal ions are surrounded by a giant polymer chain. Consequently they serve as excellent models for metallo-enzymes<sup>4,5</sup>. This has led to the development of highly efficient catalysts<sup>5</sup>. These complexes are the basis for the synthesis of wide range of biomedical preparations and drugs also<sup>6-8</sup>. Organic polymers like poly (vinyl pyrrolidone), poly (vinyl alcohol), etc which have donor sites viz. oxygen atom, nitrogen atom, can act as ligands and form complexes with transition metal ions through coordinate bonds.

Poly (vinyl pyrrolidone), henceforth abbreviated as PVP, is a non-toxic, water soluble, physiologically compatible, pH stable, non-ionic polymer<sup>9-11</sup> and hence it is an environment-friendly polymer<sup>12</sup>. Its solution is resistant to degradation at high temperatures. It is almost inert towards action of many of the acids and salts. With PVP as ligand, it is easy to achieve the desired success as it exhibits a strong tendency towards formation of complexes<sup>13-14</sup>.

Copper is a transition metal of 3d series which exhibits variable oxidation states from 0 to +4 in its compounds. Copper compounds are used as bacteriostatic substances, fungicides and food preservatives. Copper is also one of the important trace elements in the human body<sup>15-16</sup>.

Keeping these properties of copper and poly (vinylpyrrolidone) in view and with the objective of synthesizing more eco-friendly compounds, complexes of poly(vinylpyrrolidone) and copper were prepared and characterized. The conditions for the synthesis were optimized.

### Material and Methods

**Materials:** Copper (II) chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O) of molecular mass = 170.48 and poly (vinyl pyrrolidone) sample of molecular mass 30K with molecular formula (C<sub>6</sub>H<sub>9</sub>NO)<sub>n</sub> were used for the synthesis of complexes. Water used was double distilled. The reactants and other solvents used were of AR grade from SD Fine Chemicals, India. The supplied chemicals were used without any purification.

**Synthesis of PVP - Copper Complexes:** Poly (vinylpyrrolidone) - copper complexes were prepared in aqueous medium. Aqueous solutions of PVP (w/v %) were mixed with alcoholic solutions (Molar) of copper (II) chloride dihydrate in different compositions as given in the table-1. The resulting mixtures were stirred on magnetic stirrer at room temperature till the volume was reduced to

about half of the initial volume. The thickened masses were evaporated to dryness in oven at 70-80°C for 9-10 hours.

One more complex namely CP5A with 25% aqueous solution of PVP (30K) and 0.5 molar aqueous solution (instead of alcoholic solution) of copper (II) chloride was also prepared, by taking the same volumes of reactants as in the case of CP5. This sample was prepared to study the effect of solvent on the formation of complex by the metal with the polymer. Crystals thus obtained were characterized by solubility studies, elemental analysis (CHN), VSM (Vibrating Sample Magnetometer) analysis, FTIR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR.

**Studies on Solubility:** The solubility of PVP-copper complexes was examined in water and other polar and non-polar organic solvents. 5 mL each of different solvents was taken in standard test tubes and about 8-10 mg of PVP-Cu complexes were added and kept aside for 24 hours. Solubility of prepared samples in these solvents was observed after 24 hours.

**Elemental Analysis:** CHN – Elemental analysis of the sample was done at SAIF, Cochin, Kerala.

**FTIR Spectral Analysis:** Fourier Transform Infra Red (FTIR) spectra of the prepared samples, pure samples of PVP and copper (II) chloride dihydrate were obtained on a Jasco model FTIR – 4100 spectrophotometer in 400 – 4000 cm<sup>-1</sup> range, in the form of KBr pellet, at Sapala Organics PVT Ltd, Hyderabad.

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were obtained on JNM-400model, Jeol 400-MHz spectro-photometer respectively, at Sapala Organics PVT Ltd, Hyderabad.

## Results and Discussion

**Synthesis:** 50 mL of aqueous solution of PVP was mixed with 10mL of alcoholic solution of copper (II) chloride dihydrate in different molar compositions as given in the table-1. The aqueous solution of PVP was colourless and alcoholic solution of copper salt was pale blue in colour. The complexes were synthesized as per the procedure explained in the section 'Materials and Methods'. Shining crystals having golden yellow colour, with

slightly different intensities were obtained. These crystals obtained showed deliquescent properties.

**Table-1**  
**Different molar compositions of aqueous solution of PVP and alcoholic solution of dihydrate copper chloride**

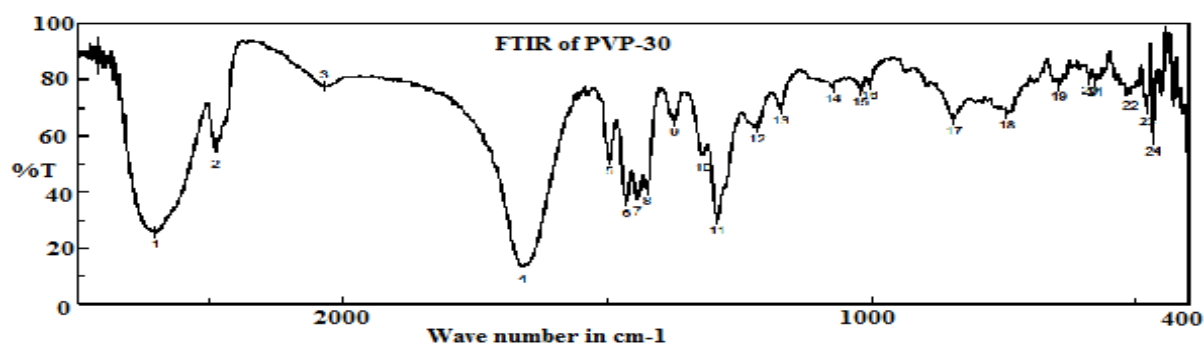
PVP↓ / Salt Solution→	0.1M	0.5M	1M
10%	CP1	CP4	CP7
25%	CP2	CP5	CP8
40%	CP3	CP6	CP9

**Solubility:** The solubility of the prepared complexes was checked in the solvents with both polar and non polar nature. Good solubility was shown in polar solvents like water, methanol, ethanol, 2-propanol, DMF and DMSO. But they were found insoluble in THF and chlorobenzene, which are also polar solvents. Slight turbidity was observed in chloroform. They were insoluble in non-polar solvents like acetone, diethyl ether, n-hexane, n-heptane, toluene, carbon tetrachloride and 1, 4 – dioxane. The behavior of the reactant, PVP was also exactly similar with the solvents listed above.

**Elemental Analysis:** The expected elements in the prepared samples are C, H, N, O and Cu. Elemental analysis of the sample for carbon, hydrogen and nitrogen indicates the respective percentages as C = 50.22%, H = 8.26%, N = 9.79%. Total of these three elements = 68.27%. Since number of oxygen atoms is equal to the number of nitrogen atoms in the polymer, the percentage of oxygen is approximately equal to 11-12%, which comes up to a total of 80%. The rest must be due to metal in the complex. This confirms the presence of metal in the complex prepared.

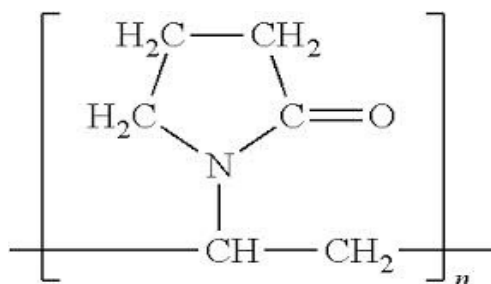
**FTIR Spectra:** The structure and structural transformation of materials can be well examined by FTIR spectroscopy and NMR spectroscopy. IR spectroscopy is the most useful and simple physical method for determining the functional groups on polymers and the formation of complexes with metal ions. IR spectroscopy helps in the location of coordination sites in the metal complexes with polymeric ligands.

The FTIR spectrum of pure PVP sample used for the synthesis of the complexes show the absorptions peaks which correspond to the characteristic chemical bonds present in PVP (figure- 1.)



**Figure-1**  
**FTIR spectrum of PVP-30**

In the FTIR spectrum, the prominent peak corresponding to C=O groups of pure PVP was observed at  $1659.4\text{ cm}^{-1}$  in FTIR spectrum which is characteristic of C=O bond in PVP (i.e., amide C=O bond). The peak at  $1443.5\text{ cm}^{-1}$  corresponds to C-N-C stretching. These characteristic peaks can be investigated to explore the interaction between PVP and metal ions.



**Partial Structure of the polymer, PVP is,**

Formation of polymer-metal complex is a result of the interaction between functional groups present on macromolecule and  $M^{n+}$  ions. Here  $M^{n+}$  ion acts as acceptor and groups such as  $-NH_2$ , heterocyclic N,  $-CO-$ , etc, of polymer chain act as donors.

Table 2 gives the stretching frequencies of C-N-C,  $-N-C$  and C=O groups in pure PVP sample and in the prepared PVP - copper complexes.

**Table-2**  
**Comparison of Stretching Frequencies of C-N-C, N-C and C=O bonds in Poly (vinyl pyrrolidone)-Copper Complexes**

Sample	CNC Stretching	N-C Stretching	C=O Stretching
PVP - 30K	1443.5	1292.1	1659.4
CP1	1439.6	1291.1	1661.4
CP2	1440.6	1291.1	1658.5
CP3	1442.5	1292.1	1652.7
CP4	1441.5	1292.1	1651.7
CP5	1438.6	1291.1	1662.3
CP5A	1439.6	1291.1	1661.7
CP6	1439.6	1290.1	1661.4
CP7	1440.6	1291.1	1659.4
CP8	1439.6	1290.1	1654.6
CP9	1439.6	1291.1	1662.3

Since both O-atom of C=O group and N-atom of heterocyclic ring possess lone pair of electrons, both can form coordinate bonds with  $M^{n+}$  ions. From the table it is evident that there is no observable change in N-C stretching frequencies in all the samples.

However, in some samples there is shift in stretching frequencies of the carbonyl ( $-C=O$ ) group to the lower wave number region. In pure PVP, peak for  $-C=O$  group appears at  $1659.4\text{ cm}^{-1}$  and in the PVP-copper complex (CP4), prepared with composition 10% PVP solution and 0.5 M copper chloride solution, peak is at  $1659\text{ cm}^{-1}$ . The shift in the peak towards lower wave number region indicates that C=O bond is getting weakened and there exists an interaction between copper ions and PVP through oxygen of C=O group of the polymer.

It is also observed that there is slight decrease in C-N-C stretching frequencies in all the samples. This suggests that there is also interaction between copper ions and N-atom of the heterocyclic ring of the polymer. Interestingly, the maximum decrease in C-N-C stretching frequency (CP5) is observed when there is slight increase in the stretching frequency of  $-C=O$  group. From this we may conclude that the two interactions viz. Cu - O and Cu - N, may not take place simultaneously.

Moreover, in both CP5 and CP5A, the magnitude of the shift in the stretching frequency of C=O towards the lower wave number direction is same. This indicates that the extent of interaction between PVP and copper ions is same with both aqueous solution and with alcoholic solution of copper salt. In other words the change in the solvent used, for dissolving the metal salt, from alcohol to water has little effect on the complex formation.

**$^1\text{H}$  NMR:**  $^1\text{H}$  NMR gives the information about the types of protons, number of each type of proton and their environments. Thereby it helps in arriving at important conclusions about the structure of the polymer-metal complex<sup>17-18</sup>.

$^1\text{H}$  NMR spectrum of the polymer-metal complex is shown in figure-4. The main chain methylene proton signals resonate at chemical shift ( $\delta$ ) of 3.2 ppm. Methine proton ( $-CH$ ) of PVP resonates at  $\delta = 3.74$  ppm. Ring methylene protons of PVP resonate at  $\delta = 1.87$  ( $^4\text{CH}_2$ ) ppm,  $\delta = 1.62$  ( $^2\text{CH}_2$ ) ppm and  $\delta = 1.31$  ( $^3\text{CH}_2$ ) ppm.

**$^{13}\text{C}$  NMR:** Carbon atoms form the skeleton of an organic molecule. Hence information about these carbon atoms of a molecule is very useful in the identification of the structure of a newly synthesized compound.  $^{13}\text{C}$ -NMR spectrum of the prepared complex is shown in the Figure- 5.

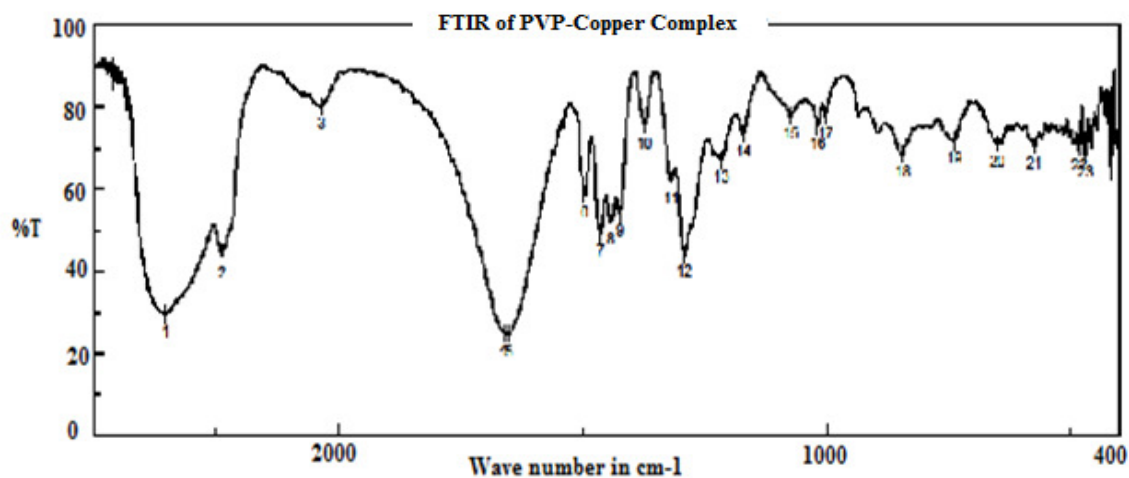


Figure-2  
FTIR spectrum of PVP-Copper complex

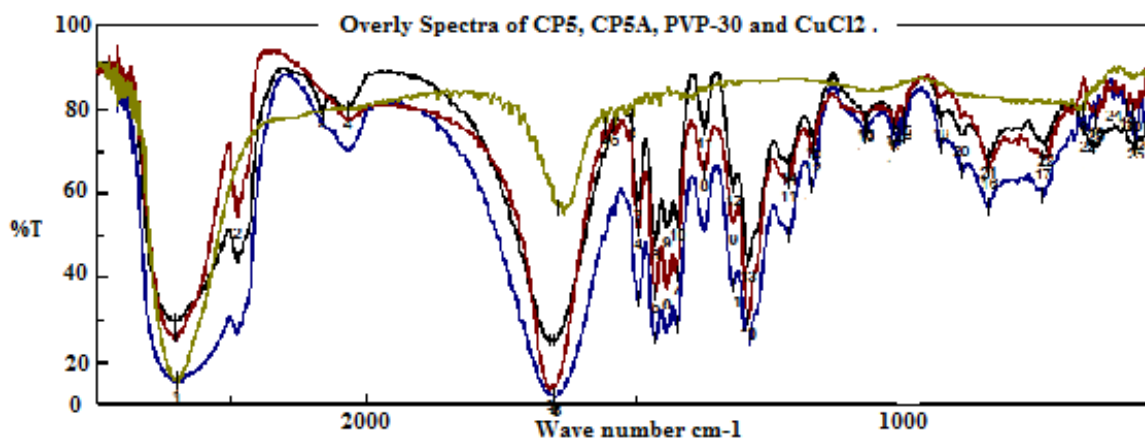


Figure-3  
Overly spectra of PVP – Copper complex, pure PVP and pure copper salt

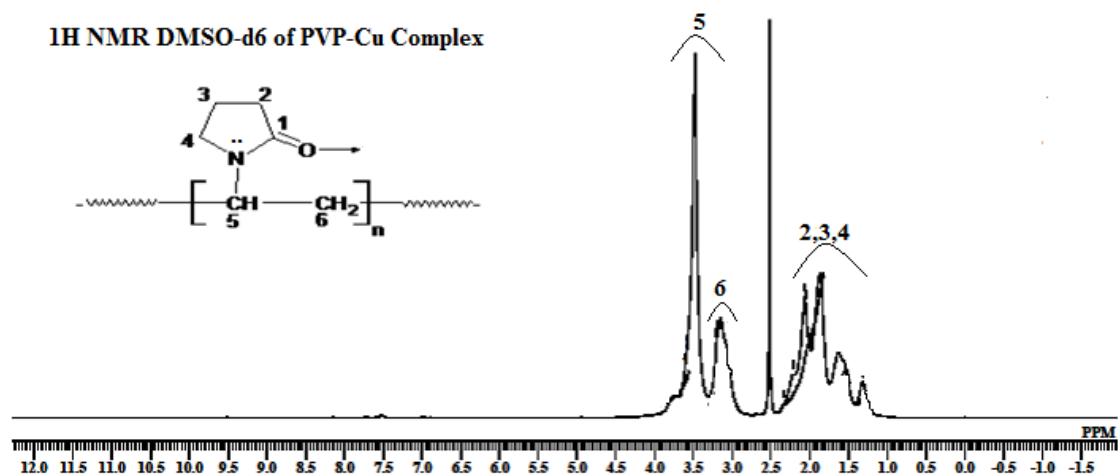
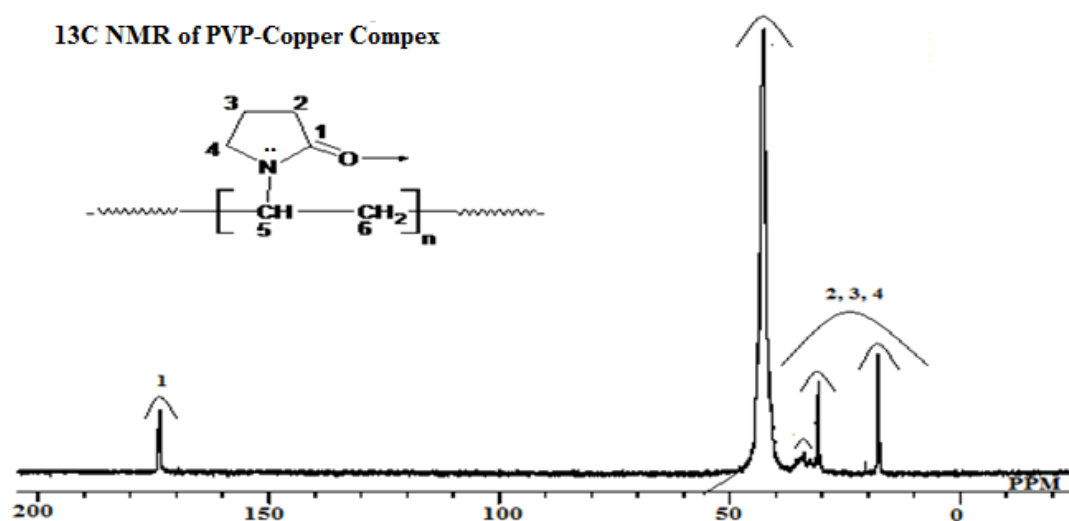


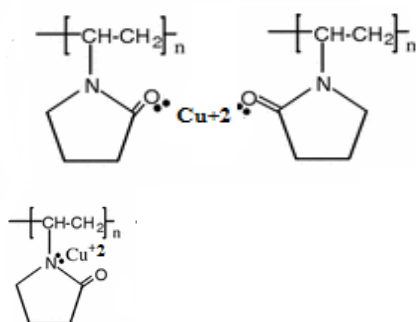
Figure-4  
<sup>1</sup>H-NMR spectrum of PVP-Copper complex



**Figure-5**  
**<sup>13</sup>C-NMR spectrum of PVP- Copper complex**

The peaks<sup>19</sup> in the range of 17.93 ppm to 34.48ppm are due to carbon atom in the side chain (<sup>2</sup>CH<sub>2</sub>, <sup>3</sup>CH<sub>2</sub>, <sup>4</sup>CH<sub>2</sub>). The carbonyl carbon (<sup>1</sup>C=O) resonates at  $\delta = 173.84$  ppm.

Based on the above spectral data<sup>20</sup>, the possible structures of the complex may be given as



**Structures of the Complex**

## Conclusion

The PVP-Copper metal complexes were prepared in different molar compositions. FTIR spectra of all the complexes were taken and studied for the optimization of the conditions for better complexation of PVP with copper. The <sup>1</sup>H- NMR and <sup>13</sup>C-NMR spectral studies confirm the formation of PVP – Copper complexes. The shift in stretching frequencies of C=O and C-N-C bonds in PVP-Cu complexes from that in pure PVP reveals that the formation of complex may be through oxygen of PVP in some compositions and through nitrogen of the heterocyclic ring in some other compositions. Spectral data also confirm that the heterocyclic ring of the polymer is intact.

Based on the shifts in the stretching frequencies of C=O group and C-N-C stretching frequencies in the samples, we can decide in which case the bond between copper and PVP is through oxygen of the carbonyl group and in which it is through nitrogen of the heterocyclic ring. Hence this comparative study may help to predict the possible structures and optimizing the conditions for the preparation of PVP-metal complexes. Further, the solvents water and absolute alcohol used for the dissolution of copper salt showed very little effect on the complex formation.

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