Synthesis and Characterization of Dichloro bis-thioacetamide Nickel(II) and bis-thioacetamide Copper(II) Chloride Complexes and Formation of Metal Sulphides

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ABSTRACT

Metal complexes of the type [M(L)\textsubscript{2}X\textsubscript{2}] (where M= Ni\textsuperscript{2+}, Cu\textsuperscript{2+} and L = thioacetamide, X = chloride ion) have been synthesised by reacting thioacetamide with the metal chlorides in 2:1 molar ratio in ethanol. The observed complexes were characterised by elemental analysis, UV-visible, FT-IR spectroscopy and magnetic susceptibility measurements. For nickel complex, two thioacetamide molecules are acting as bidentate chelating (N-S) ligands, occupy trans positions and two chloride ions satisfy the six-coordinated geometry. On the other hand, for copper complex, two thioacetamide molecules are acting as bidentate chelating (N-S) ligands and occupy trans positions to fulfil square planar geometry. These complexes were then used as precursors for synthesis of the corresponding nickel sulphides and copper sulphides through thermolysis method at 120°C in ethylene glycol without using any surfactant or additives under gentle reaction conditions.

Keywords: Metal complex, UV-Vis, FT-IR, magnetic susceptibility, Thermolysis, Metal sulphide.

1. INTRODUCTION

The development and prosperity of human society are being challenged by energy crisis and climate change related to the burning of fossil fuels, placing these issues at the forefront of the global concern\textsuperscript{1}. Much effort has been invested into identifying and converting renewable energies to help relieve the global energy demand and reduce the greenhouse gas emissions\textsuperscript{2}. Solar energy is the most promising option for renewable energy in terms of scale\textsuperscript{3}. 
The photovoltaic solar cell has been identified as one of the most promising conversion devices for solar energy because it is clean and scalable. At present transition metal chalcogenides are very interesting materials because of the unusual physical and chemical properties including electrical conductivity, chemical sensing capability and ideal characteristics for solar energy conversion. These transition metal sulfides have different shapes and sizes such as nanoplates, spheres, nanorods, tubes and can be prepared by number of methods like hydrothermal/solvothermal route, microwave assisted chemical bath deposition and sonochemical method.

This study reports the synthesis of transition metal [Cu(II), Ni(II)] thioacetamide complexes, reacting the chloride salts of these metals with thioacetamide in ethanolic medium under stirring conditions at room temperature. Then the corresponding metal sulfides have been prepared by thermolysis method from thioacetamide complexes of these metal. The benefits of using thioacetamide complexes of these transition metals [Cu(II), Ni(II)] as precursor is the mildness of the reactions to simplest way of preparing metal sulfides at 120°C and for 2 hr.

2. EXPERIMENTAL

2.1. Materials

Ethanol, thioacetamide, nickel chloride, copper chloride, acetone, dichloromethane and ethylene glycol were purchased from Mark India. All the reagents were of analytical grade and were used, without purification.

2.2. Physical Measurements

The elemental analysis of the precursor was performed using FISONs EA-1108 CHN analyzer. Infrared spectra were recorded on Perkin Elmer Spectrum2 FT-IR Spectrophotometer with sample prepared by KBr pellets. Optical measurements were recorded on a Shimadzu UV-Vis 1800 Spectrometer at room temperature. The samples were placed in glass cuvettes using water and acetone as reference solvents for all measurement.

2.3. Synthesis of transition metal complexes

2.3.1. Dichloro bis-thioacetamide nickel(II)

Nickel chloride (1.0 gm; 4.0 mmol) taken in a 100 ml beaker and dissolved in 20 ml ethanol. After that ethanolic solution (10 ml) of thioacetamide (0.63 gm; 8.0 mmol) was added drop by drop during 10 minutes with vigorous starring. Starring was continued for another 30 minutes. During the starring, a green precipitation was observed. The precipitation was filtered off and the residue was washed with ethanol-water mixture (1:1) for several times. Purification was done by recrystallization. Yield: 80 %. Anal. Calc. for NiCl₂H₄N₂S₂Cl₂: C, 17.41; H, 3.98 and N, 9.61%. Found: C, 17.17; H, 4.05 and N, 10.01%.
2.3.2. *bis*-thioacetamide copper(II) chloride

Same procedure was followed for the synthesis of copper complex. Copper chloride was taken 1.0 gm (6.0 mmol) in 20 ml ethanol, instead of nickel chloride and thioacetamide was taken 0.63gm (8.0 mmol) in 10 ml ethanol. The reaction mixture was stirring for 45 minutes. During the stirring, a white precipitation was observed. The precipitation was filtered off and the residue was washed with dichloromethane for several times. Purification was done by recrystallization. Yield: 65 %. Anal. Calc. for CuC₂H₁₀N₂S₂Cl₂: C, 16.95; H, 4.02 and N, 9.52 %. Found: C, 16.87; H, 4.14 and N, 9.34 %.

![Reaction Scheme](https://via.placeholder.com/150)

2.4. Synthesis of Metal Sulphide

Both the prepared compounds were taken separately and dried to remove if any solvents are present there. After that the dried complexes were used for growth of metal sulphides, details are given below. Both the experiments were performed separately.

Nickel complex (335 mg), and copper complex (500 mg) were taken separately and disperse in 10 ml of ethylene glycol in separate beaker. Then the solutions were injected separately into three-neck round bottom flask (250 ml) containing preheated (at 120°C) 60 ml ethylene glycol, with vigorous stirring. Stirring with heating were continued 2 hours. During stirring, black precipitates were observed for both the experiments. After that the solution was cooled to room temperature and the precipitates were separated through centrifuge. The products were washed with water and ethanol for a number of times for purification. Finally, the products were dried and used for spectral analysis.
3. RESULT AND DISCUSSION

3.1 Elemental analysis of metal complexes

Both the complexes were prepared by the reaction between metal salts to ligand, L molar ratio of 1:2. The observed analysis is agreed with the proposition having a 1:2 metal to ligand molar ratio. I have tried different reaction with 1:1 and 1:3, metal salts to ligand molar ratio but the products were same as above and elemental analysis having 1:2 molar ratio. These experiments indicated that the stable complexes are formed in 1:2 stoichiometric ratios.

3.2. Magnetic study for metal complexes

The observed values of magnetic moment for nickel(II) and copper(II) complexes are generally diagnostic of the coordination geometry about the metal ion. The magnetic moment observed for the nickel(II) complex lies in the range of 2.91–2.97 BM which is consistent with the octahedral stereochemistry of the complex with two unpaired electrons. Room temperature magnetic moment of the copper(II) complex lies in the range 1.92–1.96 BM corresponding to the square planar geometry with one unpaired electron.

3.3. UV-visible spectral study of metal complexes

Absorption spectra of free ligand and corresponding complexes have been performed in water [for Ni(II) complex] and acetone [Cu(II) complex] solvent. The slight absorption for the complexes occurred at lower energy region may be attributed to electronic transitions in the sulphur group and be slightly metal ligand charge transfer transition occur in the complex.

![Fig 1(a) UV-visible spectra of ligand, L](image)
4.1. FT-IR Spectra of metal complexes

The assignments of the significant complexes are presented in the Table-1.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\nu_{as}$(NH$_2$) cm$^{-1}$</th>
<th>$\nu$(NH$_2$) cm$^{-1}$</th>
<th>$\delta$(NH$_2$) cm$^{-1}$</th>
<th>$\nu$(C=S) cm$^{-1}$</th>
<th>$\nu$(M-N) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>3298</td>
<td>3081</td>
<td>1648</td>
<td>1028</td>
<td>708</td>
</tr>
<tr>
<td>[CuL$_2$]Cl$_2$</td>
<td>3449</td>
<td>3339</td>
<td>1624</td>
<td>984</td>
<td>591</td>
</tr>
<tr>
<td>[NiL$_2$Cl$_2$]</td>
<td>3422</td>
<td>3336</td>
<td>1558</td>
<td>935</td>
<td>619</td>
</tr>
</tbody>
</table>

The highest frequency bands of thioacetamide at 3298 cm$^{-1}$ and 3081 cm$^{-1}$ can be assigned to asymmetric and symmetric stretching frequency of -NH$_2$ group respectively. For the complexes, the corresponding frequencies increase due to complexation$^{10}$. The
deformation mode $\delta(\text{NH}_2)$ in thioacetamide occur at 1648 cm$^{-1}$, which is observed in copper complex at 1624 cm$^{-1}$ and nickel complex at 1558 cm$^{-1}$. These bands shifted to lower frequencies in the complexes due to coordination of -NH$_2$ group in metal complexes$^{11}$. The stretching band at 514 cm$^{-1}$ (for copper complex) and at 501 cm$^{-1}$ (for nickel complex), which is absent in free ligand, are due to the formation of new M-N bond in these complexes. For ligand, bands having contribution for $\nu(\text{C=S})$ observed at 1028 cm$^{-1}$ and 708 cm$^{-1}$, which are observed comparatively lower frequencies in metal complexes due to complexation.

Thus, in each complex, two thioacetamide ligands were coordinated to the central metal ion through two N atoms and two S atoms. So, it is concluded that the ligand acts as a bidentate N, S-chelating fashion. Two thioacetamide ligands and two chloride ions satisfied the octahedral geometry (for nickel complex) and containing two thioacetamide ligands, copper (II) satisfied square planar geometry.

**Fig.2(a):** FT-IR spectra of [CuL$_2$]Cl$_2$

**Fig.2(b):** FT-IR spectra of [NiL$_2$Cl$_2$]
5. Infrared study of metal sulfide

IR spectra of obtained products (metal sulphieds) are shown in Fig. 3. It is clearly shows that the nature of the stretching frequencies are different from the corresponding source complexes. Literature survey reveals that the stretching frequencies of metal sulphides are generally shows around 400 cm\(^{-1}\) [12]. Nickel sulphided shows a stretching band at \(\sim 418\) cm\(^{-1}\) and that of copper sulphided it is \(\sim 420\) cm\(^{-1}\), which confirm that the formation of NiS and CuS respectively, through complex decomposition.

![Fig. 3(a): FT-IR spectra of CuS](image)

![Fig. 3(b): FT-IR spectra of NiS](image)

CONCLUSION

In summary, metal complexes, dichloro bis-thioacetamide nickel(II) and bis-thioacetamide copper(II) chloride have been successfully synthesized and were characterised by elemental analysis, UV-visible, FT-IR spectroscopy and magnetic susceptibility measurements. Nickel complex is formulated as octahedral geometry having two
thioacetamide molecules are acting as bidentate chelating (N-S) ligands and two chloride ions satisfy the geometry. On the other hand, for copper complex, two thioacetamide molecules are acting as bidentate chelating (N-S) ligands and occupy trans positions to fulfil stable square planar geometry. These complexes were then used as precursors for synthesis of the corresponding nickel sulphides and copper sulphides through thermolysis method at 120°C in ethylene glycol without using any surfactant or additives under gentle reaction conditions.

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