Chapter 3

EXPERIMENTAL STUDIES ON TRIS THIOUREA COPPER CHLORIDE (TTCC)

Copper has two common oxidation states +1 and +2 [69] which are both relatively stable. In addition to stability considerations, the physical and chemical properties vary considerably between the two oxidation states. Copper(II) has an electron configuration of [Ar]3d\(^9\) [69], which means that it has a vacancy in its d-subshell. Because of ligand field splitting, the d orbitals in copper complexes are nondegenerate. The energy required to promote an electron into the higher energy orbital is corresponding to a wavelength in the visible light region. As a result, copper(II) compounds tend to be highly colored, generally blue or green. Copper(I) has the electron configuration [Ar]3d\(^{10}\) [69]. That is, it has no vacancies in its d orbitals. Electronic promotion cannot occur within the d subshell, so the energy required for excitation is greater than that of visible light. This results in copper (I) compounds typically being white. The most prevailing coordination environment of copper(I) is 4-coordinate. The most common geometry for a 4-coordinate copper(I) is tetrahedral, illustrated in Figure 3.1. The coordination chemistry of copper(II) has been well documented, but studies focusing primarily on copper(I) are less common. By expanding the knowledge of copper(I) compounds, one can more accurately predict and pursue potential applications of such molecules. Ureas and thioureas are
Figure 3.1 Tetrahedral coordination of Copper (I)
widely recognized for their ability to hydrogen-bond. In addition, they can act as ligands in coordination complexes. This combination has led to their increasing use in an array of self-assembled network materials. Moreover, Thiourea, a centrosymmetric molecule has formed the non-centrosymmetric complexes by co-ordinating with different metal ions leading to nonlinear optical properties [70]. Thiourea molecule has been co-ordinated with several transition metal ions to form stable coordination complexes. They can be crystallized either by solution growth technique [71, 72] or by gel growth technique [73-75]. In these coordination complexes, thiourea has been linked to the central metal through sulfur atom rather than nitrogen [76]. Thiourea possess a large dipole moment and it forms number of semiorganic materials. The pure organic materials are having the disadvantages of low optical transparencies, poor mechanical properties and low laser damage thresholds and an inability to produce large crystals [77-81]. These crystals are soft in nature and difficult to polish and intense absorption in the UV region. Pure inorganic crystals have modest optical properties. Therefore, new class of semi organic crystals which share the properties of both organic and inorganic crystals receives greater attention. They have the advantages of large non-linearity, high resistance to laser induced damage, low angular sensitivity and good mechanical properties. Recently, the copper(I) thiourea complex finds potential applications in industrial catalysis for the development of heterogeneous carbonylation catalysts, in medicinal chemistry as carriers of small molecules such as nitric oxide to tumor cells, in storage and delivery for hemocyanin (respiratory proteins) and as luminescent material due to $d^{10}$-$d^9p^1$ orbital interaction. Motivated by these considerations, the Tris thiourea Copper (I) Chloride has been selected for the present study. The crystals have been grown and characterized by single
crystal and powder XRD, FTIR, UV-Vis, low temperature PL, TGA, DTA, DSC, EPR and low temperature magnetic susceptibility studies. The results have been discussed in detail and reported in this chapter.

3.1 Synthesis and Crystal growth

Tris thiourea Copper (I) Chloride (TTCC) compound was synthesized by mixing GR (99% purity Merck) grade thiourea and Copper(II) Chloride dihydrate (CuCl₂.2H₂O) in the stoichiometric ratio (1:4). The calculated quantities of thiourea and Copper (II) Chloride salts were dissolved in the mixed solvent of water-methanol taken in the ratio of 1:1. The synthesized salt was purified by repeated recrystallization process for three times. Then, the good quality crystals were obtained by slow evaporation technique at ambient temperature.

3.2 Experimental details

The compositions of Carbon, Hydrogen, Nitrogen and Sulfur in the grown crystals were determined by using Vario EL-III elemental analyzer and the copper content by AAS analysis using Perkin Elmer Instrument Analyst 100. The grown crystals were subjected to single crystal XRD (Four circle diffractometer with MoKα source), Powder XRD (Richseifert diffractometer), FTIR analysis (Perkin Elmer spectrum BX model at a resolution 2 cm⁻¹), UV-Visible spectral analysis (Perkin Elmer Lamda 35) and Low temperature PL studies (VARIAN Cary Eclipse Fluorescence Spectrophotometer employing 150 Watts Xe arc discharge lamp as the excitation source). The TGA and DTA scans were performed using Perkin Elmer, Diamond TG / DTA thermal analyzer in the temperature
range 42°C to 1200°C. High temperature DSC was carried out in Mettler Toledo DSC 822e instrument in the temperature range of 40°C to 460°C. The rate of heating in all thermal scans was 10°C per min. The EPR powder spectrum of Cu (II) ion in the TTCC crystal was recorded with Bruker EMX plus model spectrometer at room temperature. The Low temperature magnetic susceptibility study was recorded with Quantum Design PPMS.

3.3 Results and Discussions

3.3.1 CHNS analysis

The elemental composition of grown crystals from experiment are in agreement with that of calculated one and the crystallization of 1:4 anhydrous complexes of CuCl₂ and thiourea have been reported here. The addition of thiourea to a Cu(II) salt results in reduction of Cu(II) to Cu(I) leading to Cu(I) complexes in aqueous solution. It can be well followed by the change of the colour of the CuCl₂ solution from blue to greenish to colourless. Figure 3.2 presents well developed bright, transparent and colourless crystals with well defined external faces.

Experimental:  C: 11.32%, H: 3.709%, N: 26.30% and S: 25.58%.
Calculated :  C: 10.99%, H: 3.680%, N: 25.66% and S: 29.41%.

3.3.2 Atomic Absorption spectra

The AAS analysis determined the copper content of TTCC crystals as 15.37% which is in agreement with the calculated value 14.48%.
Figure 3.2 Photograph of grown TTCC crystal
3.3.3 Single crystal XRD

The single crystal XRD study has shown that the chlorine atom remains free in the lattice and the compound contains inter molecular hydrogen bonds. The structure of TTCC crystal has been solved as tetragonal structure with P4\textsubscript{3}2\textsubscript{1}2\textsubscript{1} space group using SHELXL-97 and the lattice parameters are deduced as a=b=13.3911 Å, c=13.7859 Å and α=β=γ=90°. The cell volume V is 2472.11Å\textsuperscript{3} and the number of molecules per unit cell (z) is 8. The molecular formula determined is Cu[CS(NH\textsubscript{2})\textsubscript{2}]\textsubscript{3}Cl.

3.3.4 Powder XRD

The Powder XRD of the grown crystal is shown in Figure 3.3. The experimentally observed XRD peaks in the range 10° ≤ θ ≤ 80° indexed using CELN programme by cell refinement using least square fit method is presented in Table 3.1. The value of the inter atomic distance d, between the hkl planes for the tetragonal system has been found out by using the equation

\[
\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}
\]

The crystal is found to be crystallized in tetragonal structure with a=b=13.409±0.02Å, c=13.774±0.02 Å, V=2476.58Å\textsuperscript{3} and α=β=γ=90°. The particle size of the crystal is deduced as 36.6nm by using Scherrer formula

\[
t = \left(\frac{0.9 \, \lambda}{\beta \, \cos \theta}\right)
\]

where t is averaged dimension of the crystallites, 0.9 is the Scherrer constant, \(\lambda\) is the wavelength of the x-ray, θ is the peak position and \(\beta\) is the integral breadth of the reflections (in radian 2θ) located at 2θ [68].
Figure 3.3 X-ray powder diffraction pattern of TTCC crystal
Table 3.1 The observed interplanar d-spacing of TTCC crystal with hkl index

<table>
<thead>
<tr>
<th>d in Å</th>
<th>hkl</th>
<th>d in Å</th>
<th>hkl</th>
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<td>6.6758</td>
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</table>
3.3.5 FTIR

The FTIR spectrum of the TTCC crystal is shown in Figure 3.4. The Table 3.2 presents the observed absorption frequencies and their assignments of characteristic vibrational modes. The broad absorption band observed in the high frequency range between 4000 and 2000 cm\(^{-1}\) is attributed to symmetric and asymmetric (NH\(_2\)) hydrogen bond vibrations. In the frequency range of 2000 to 1600 cm\(^{-1}\), the absorption bands at 1747 and 1612 cm\(^{-1}\) are assigned for Cu (II) complexes and also attributed to NH\(_2\) deformation [84-87]. The occurrence of asymmetric N-C-N stretching, symmetric N-C-N stretching and N-C-N bending vibrational modes in the molecule, are evident from the peaks at 1476, 1426 and 592 cm\(^{-1}\) respectively. The bands at 1426 and 1395 cm\(^{-1}\) for TTCC against absorption of pure thiourea at 1412 cm\(^{-1}\) confirms the formation of coordination. It has been reported that the increase of C-N and decrease of C-S stretching frequencies are corresponding to the complex formation [60, 82, 83]. The band at 1162 cm\(^{-1}\) is assigned for Cu (II) complex [84]. In the low frequency region called finger print region, two peaks at 1101 and 714 cm\(^{-1}\) for metal complex has been compared to 1081 and 730 cm\(^{-1}\) peaks of thiourea [60]. The peaks at 1101 cm\(^{-1}\) attributed to NH\(_2\) rocking mode is not affected by the co-ordination. Lower shift of C=S stretching frequency (730 to 714 cm\(^{-1}\) ) confirms the formation of metal sulfur coordination bond [82]. The metal sulfur bonds present in the compound are evident from the peak at 475cm\(^{-1}\) due to antisymmetric S-Cu-S stretching as well as C-N deformation. The results are in close agreement with those of thiourea complexes [60, 82, 83].
Figure 3.4 FTIR spectrum of TTCC crystal
Table 3.2 Assignment of IR absorption bands for the TTCC crystal from the FTIR spectrum

<table>
<thead>
<tr>
<th>Frequency in cm(^{-1})</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Cu (II) complex and NH(_2)</td>
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<tr>
<td>1612</td>
<td>Cu (II) complex and NH(_2)</td>
</tr>
<tr>
<td>1476</td>
<td>Antisymmetric N-C-N stretching</td>
</tr>
<tr>
<td>1426</td>
<td>C-N stretching</td>
</tr>
<tr>
<td>1395</td>
<td>C=(\text{S}) stretching</td>
</tr>
<tr>
<td>1162</td>
<td>Cu (II) complex</td>
</tr>
<tr>
<td>1101</td>
<td>NH(_2) rocking</td>
</tr>
<tr>
<td>714</td>
<td>C=(\text{S}) stretching</td>
</tr>
<tr>
<td>592</td>
<td>N-C-N bending</td>
</tr>
<tr>
<td>475</td>
<td>Antisymmetric S-Cu-S Stretching and C-N deformation</td>
</tr>
</tbody>
</table>
3.3.6 UV Spectrum

The UV-Vis spectrum of TTCC crystal (Figure 3.5) reveals the transparent wavelength region in the visible region. The cutoff wavelength is observed as ~ 400nm and the energy gap is deduced as 3.00eV. Generally the energy gap of the insulator lies above 3eV [3]. This confirms that the TTCC crystal is an insulator nearer to semiconductor region. It has also been reported that the nature of the crystal also gives the hint whether the crystals are insulator or semiconductors. Semiconductor crystals are mostly coloured crystals and insulator crystals are transparent. To be very clear, a crystal can have no strong electronic and vibronic transitions in the visible spectral region of 740nm to 360nm or 1.7eV to 3.5eV [3]. It is notable that the present grown crystals are found to be colourless, transparent and clear. It exhibits no strong electronic or vibronic transitions in the visible spectral region between 740 and 360nm. This confirms the nature of the TTCC crystal as an electrical insulator.

The absorption spectrum of the diffused Cu\(^{2+}\) ion in the crystal is shown in Figure 3.5. The broad absorption at about 850 nm is identified as the d-d transition band due to Cu\(^{2+}\) ions. The broad absorption band on the right side has not yet been assigned. The crystal may include various kinds of defects other than Cu\(^{2+}\) sites such as colour centers [85-86]. The spectrum contains intense and broad absorption band in the UV range at 336 nm, which may be, probably charge transfer transition bands since it arises from the higher lying energy levels. The four bands at \(\lambda_1=689\)nm, \(\lambda_2=583\)nm, \(\lambda_3=559\)nm and \(\lambda_4=463\)nm in the visible range are weak in intensity. They may be regarded as d-d transfer bands which show the uniqueness of the
Figure 3.5  UV-Vis optical absorption spectrum of TTCC crystal
presence of Cu\textsuperscript{2+} ion [87,88] due to the preparation of the crystal from copper (II) chloride.

3.3.7 Low temperature PL spectra

The low temperature PL emission spectrum of TTCC crystal at a fixed excitation wavelength of 385 nm for temperature ranging from 300K to 77K during cooling process is shown in Figure 3.6 and the same PL emission spectra during heating process is shown in Figure 3.7. Copper is a transition metal impurity which can strongly affect the optical properties. It is fast diffuser even at low temperatures and gives rise to both radiative and nonradiative centers [89]. The room temperature PL spectrum at 300K comprises two prominent blue emission peaks at 410.92 nm, 422.87 nm and one very weak shoulder peak at 484.92 nm. Besides these one green emission peak is identified at 526.86 nm.

It is generally believed that in the tetrahedral crystal field of four S\textsuperscript{2-} ligands, the Cu\textsuperscript{2+} 3d\textsuperscript{9} ground state has two levels [90]. When an electron is excited to the conduction band and subsequently trapped by shallow (delocalized) donor level, a green luminescence can occur by the recombination at Cu impurity. This so called G-Cu emission has been extensively studied by Shinoya and Co-workers. In TTCC crystal, Cu\textsuperscript{+} ions are tetrahedrally co-ordinated by the sulfur atoms of four thiourea ligands [80, 91]. The recombination of thiourea with Cu (II) chloride reduces Cu\textsuperscript{2+} to Cu\textsuperscript{+} leading to Copper (I) complex [80,81]. Before recombination, copper excites as Cu\textsuperscript{2+} and after recombination Cu\textsuperscript{+} 3d\textsuperscript{10} is formed which has nondegenerate ground states. Therefore green luminescence arises from transitions from a high energy state Cu\textsuperscript{2+} to lower energy state Cu\textsuperscript{+} and it is

81
Figure 3.6 Temperature dependent PL spectra of TTCC crystal during cooling process.
Figure 3.7 Temperature dependent PL spectra of TTCC crystal during heating process.
thought to be due to recombination between sulfur vacancy and Cu related acceptor centre [92].

Becker and Bard have attributed the blue emission band at 428 nm to $S^{2-}$ vacancies [93]. Bhattacharjee et al [94, 95] have ascribed 418 nm peaks to $S^{2-}$ vacancy. Therefore, the Blue emission at 422.87 nm may be attributed to $S^{2-}$ vacancy [94]. The weak blue peak at 484.92 nm may arise due to native point defects [92]. The similar trend has been observed during heating process.

The band gap luminescence at 410.92nm has shown red shift with decrease of temperature from 410.92nm at 300K to 411.84 nm at 77K whereas the position of all the other peaks remains almost constant with respect to temperature. The band gap has been deduced during heating and cooling process by using the formula

$$E = \frac{hc}{\lambda}$$

where $\lambda$ is the wavelength of the band gap luminescence. The Figure 3.8 has shown the variation of energy gap with temperature which exhibits interesting hysteresis loop.

3.3.8 Stokes shift

The difference between the position of the band maxima of the absorption and emission spectra of the same electronic transition is known as Stokes shift [96-98] which is shown in Figure 3.9. When a system absorbs a photon it gains energy and enters an excited state. One way for the system to
Figure 3.8 Plot of energy gap versus temperature for TTCC crystal
Figure 3.9 Stokes Shift
release is to emit photon, thus losing its energy. When the emitted photon has less energy than the absorbed photon, this energy difference is the Stokes shift. If the emitted photon has more energy, the energy difference is called as anti-stokes shift. The PL and UV-Vis spectra have shown maximum emission at 410.92 nm and maximum absorption at 336 nm respectively. Therefore, the stokes shift is determined as 75 nm or 16.5 eV.

3.3.9 Thermal analysis

The TGA curve of TTCC is shown in Figure 3.10. When the TTCC crystal is heated from ambient temperature to 1200°C, a prolonged decomposition starts at 205°C and extends up to 593°C leading to a total weight loss of 327 molecular units is equivalent to 70% at this temperature range can be accounted for the liberation of CS₂, S, CH₄, N₂ and H₂. The decomposition reaction is formulated as given below

\[\text{Cu} [\text{CS(NH}_2\text{)}_2\text{]}_3 \text{Cl} \rightarrow \text{CuCl} + \text{CS}_2 + \text{S} + 2\text{CH}_4 + 3\text{N}_2 + 2\text{H}_2\]

Molecular mass units: 327 99 228 [76+32+32+84+4]

The CuCl residue is stable beyond 593°C. The above decomposition pattern fits well with the formula of the compound.

The DTA curve is shown in Figure 3.11. The DTA analysis confirms the melting point of the sample through sharp endothermic peak at 172°C. The endothermic peak at 258°C reveals the volatile nature of the sample. The peak at 589°C indicates the large energy requirement for the decomposition process that starts at 205°C.

When high temperature DSC scan was run from room temperature to 460°C, two sharp peaks were observed as shown in Figure 3.12. The endothermic peak at 178.8°C corresponds to melting of compound. The
Figure 3.10 TGA curve of TTCC crystal
Figure 3.11 DTA curve of TTCC crystal
Figure 3.12 High temperature DSC curve of TTCC crystal
exothermic peak at 294.9°C indicates a structural phase transition of the residue CuCl which is also observed in DTA thermogram.

3.3.10 EPR

Generally, the EPR spectrum does not exhibit signals due to the absence of unpaired electrons in the copper (I) compounds. But, since the present TTCC crystal has been prepared from copper (II) chloride, EPR active signals have been observed as shown in Figure 3.13. This may be due to Cu$^{2+}$ ions entering from copper (II) chloride to the host lattice substitutionally and therefore the exhibited resonance lines are observed to be weak. Cu (II) has S=1/2 and nuclear spin I=3/2 (for both $^{63}$Cu and $^{65}$Cu naturally abundant isotopes). A group of four resonance lines is expected per complex. In any general orientation, the number of such resonance lines will provide the number of distinguishable complexes in the host lattice [99]. The 3d$^9$ ion Cu (II) exhibits four lines from single complex. Generally, Cu$^{2+}$ ion can enter the lattice substitutional or interstitially. In this present structure, it is assumed that Cu$^{2+}$ ion enters substitutionally [87, 88]. The observed EPR powder spectrum (Figure 3.13) starts from 3300 Gauss to 3600 Gauss. It shows that the symmetry of the complex in the crystal is not axial. The powder EPR spectrum was partially resolved into three components. The measured values are $g_{xx}=2.051$, $g_{yy}=2.000$, $g_{zz}=2.098$; $A_{xx}=2.37$mT, $A_{yy}=2.33$mT, $A_{zz}=2.37$mT. Kivelson and Neimann [100] pointed out that compounds having $g_{a}<2.3$ are covalent in nature where as the compounds having $g_{a}>2.3$ are ionic. The g - values obtained from present EPR spectral study suggests that the compound is having covalent character. It is notable that the coupling constant $A_{xx}=A_{zz}$ which favours tetragonal crystal structure deduced from XRD study. Since the lines are quite weak and
Figure 3.13 EPR powder spectrum of TTCC crystal
the spectrum is complex in appearance, the $^{63}$Cu and $^{65}$Cu hyperfine lines are not clearly resolvable [101].

3.3.11 Low Temperature Magnetic Susceptibility study

Magnetic susceptibility measurements provide a powerful tool for determining electronic configuration [102, 68]. The field dependence magnetization for TTCC crystal at room temperature 300K has been recorded ranging from 0 to 10000 Oe and the results have been shown in Figure 3.14. It clearly shows the diamagnetic behavior of the crystal. The temperature dependence of magnetic susceptibility measurements has been performed on TTCC crystal at temperatures extending from room temperature to helium temperature (300K-4K) at field strength of 500 Oe and the behavior is well clearly shown in Figure 3.15. The magnetic susceptibility is found to be negative and seems to be constant throughout the temperature range which confirms the diamagnetic nature of the crystal.

3.4 Conclusions

Pure TTCC crystals of good crystalline quality have been grown by slow evaporation technique. They are bright, transparent and colorless with well defined external faces. The CHNS analysis deduces C, H, N and S content and the AAS analysis determines the Cu content in TTCC. The values are in good agreement with calculated values. The single crystal and powder XRD confirms the tetragonal structure of TTCC with space group P4$_{2}$2$_{1}$2. The granularity of the crystal is found to be 36.6nm. The FTIR study assigns vibrational frequencies and confirms the growing of TTCC from
Figure 3.14  Field dependence magnetization of TTCC crystal at
T=300K
Figure 3.15  Low temperature magnetic susceptibility of TTCC crystal at $H=500$ Oe
Cu (II) chloride. It has suggested that the thiourea is linked to the metal copper through chlorine atom. The FTIR study has also confirmed the presence of Cu$^{2+}$ ions in the TTCC crystal. Since it has been prepared from Copper(II)chloride. The UV-Vis study deduces the cut off wavelength as 400nm and energy gap as 3.00eV. The PL spectrum shows maximum emission at 410.92 nm which confirms the energy gap as 3.02eV. These confirm that the TTCC crystal is an insulator nearer to the semiconductor region. The PL spectra collected from room temperature to 77K by cooling have shown two blue prominent emissions at about 410.92 nm, 422.87 nm, one very weak shoulder peak at 484.92 nm and green emission peak at 526.86 nm. When thiourea combines with Copper (II) chloride, Cu$^{2+}$ is reduced to Cu$^+$. The green emission peak arises due to the reduction of Cu$^{2+}$ to Cu$^+$. The blue emission at 422.87 nm corresponds to S$^2$ vacancies. The blue emission at 484.92 nm is due to native point defects. The band gap luminescence have shown red shift from 410.92 nm to 411.84 nm with decrease of temperature. The band gap exhibits interesting hysteresis loop with respect to temperature. The stokes shift has been determined as 75nm or 16.5eV. The decomposition patterns in the thermogravimetry gives the molecular formula of the compound. The decomposition starts from 205°C and extends up to 593°C. The DTA peaks illustrate the large energy requirement of decomposition. The endothermic peak found in high temperature DSC scan indicates the melting temperature as 178.8°C. The exothermic peak found in DSC scan indicates the structural phase transition of the decomposition residue CuCl. The copper (I) complexes are EPR inactive which give evidence for the diamagnetic nature of the complex [103]. The present recorded EPR spectrum exhibits weak four lines which indicates the presence of copper (II) centers. Since the crystal has been
prepared from copper (II) chloride, copper (II) ions enter the host lattice substitutionally. The +2 oxidation state of the copper which is a d⁹ electronic system of unpaired electrons is confirmed by the peaks present in EPR spectrum. The g - values obtained from present EPR spectral study suggests that the compound is having covalent character and ionic in nature. The optical absorption spectrum confirms the uniqueness of Cu²⁺ ion combination by the presence of d-d transition bands. The study of low temperature magnetic susceptibility and the field dependence magnetization confirm the diamagnetic nature of the crystal. The magnetic susceptibility is found to be negative throughout the temperature range from 300K to 4K. Thus the characterization of the TTCC crystal have been made and reported in this chapter.