CHAPTER 2

SYNTHESIS, GROWTH AND CHARACTERIZATION OF METAL-ORGANIC CRYSTAL: TETRA THIOUREA COBALT CHLORIDE

2.1 INTRODUCTION

The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds (Bhat and Dharmaprakash 1998). Most of the thiourea complexes are from metal sulphur bonding in the metal structured center (Andreazza 1992). Metal complexes of thiourea, generally called semiorganic, include the advantages of both organic and inorganic part of the complex. The advantages of semiorganic crystals are that they can be grown from aqueous solution and form large three-dimensional crystals. Moreover, metal organic complexes offer higher environmental stability combined with greater diversity of tunable electronic properties by virtue of the co-ordinated metal center.

In general, crystals of the type $M\,[TU]_2\,X_2$, where $M = \text{Cd}, \text{Co}, \text{Hg}, \text{Pb}, \text{Ti}$ or $\text{Zn}$, $TU$ is thiourea and $X$ is a halogen, have been found to exhibit good NLO properties (Angeli Mary and Dhanuskodi 2001). Some examples of such complexes are bis thiourea cadmium chloride (Venkataramanan et al 1997), bis thiourea zinc chloride (Angeli Mary and Dhanuskodi 2001) and bis thiourea cadmium bromide (Ramachandraraja and Sundararajan 2008).
Motivated by these directions, we have synthesized thiourea cobalt chloride single crystals.

Forstat et al (1966) reported that the single crystals of CoCl$_2$·[(NH$_2$)$_2$ CS]$_4$ were grown at room temperature from an aqueous solution containing CoCl$_2$·6H$_2$O and (NH$_2$)$_2$ CS in the ratio of approximately 2:1 by weight respectively. Specific heat measurements were made on CoCl$_2$·[(NH$_2$)$_2$ CS]$_4$ single crystals in the temperature range 0.42–13.9 K. A λ type anomaly was observed at $T_N = 0.92$ K and is associated with a paramagnetic-antiferromagnetic transition. Weinstock (1968) reported the thermal conductivity measurements on Co [(NH$_2$)$_2$ CS]$_4$ Cl$_2$ crystals and it indicates an enhanced conductivity below the Neel temperature.

Chen-Chou Ni and Weinstock (1971) studied the thermal conductivity measurements on CoCl$_2$·[(NH$_2$)$_2$ CS]$_4$ in the temperature range 0.35-15 K as a function of magnetic field and direction of heat flow and results indicate that the probable existence of magnon conductivity below the Neel temperature. Ni et al (1972) studied the thermal conductivity measurements on CoCl$_2$·[(NH$_2$)$_2$ CS]$_4$ in the temperature range 0.35-20 K and in applied magnetic fields up to 20 kG. Below the Neel temperature of 0.92 K, an enhancement in conductivity for heat flowing in the <001> sublattice-magnetization is interpreted as due to the onset of spin-wave conductivity. Magneto-thermal-resistance resonances in the paramagnetic state have yielded information on the magnitude and anisotropy of the $g$ value for the unpaired electronic state of the cobalt ion.

In the present investigation, the efforts were made to synthesize the thiourea cobalt chloride compound. The growth parameters have been optimized. The grown crystals have been characterized by various characterization techniques.
2.2 SYNTHESIS AND CRYSTAL GROWTH

For thiourea cobalt chloride synthesis, thiourea and cobalt chloride hexahydrate solution (using Millipore water (resistivity 18.2 MΩcm) as solvent) were taken separately and mixed in the ratio of 1:1, 2:1, 3:1 and 4:1 respectively. The synthesized materials were allowed to evaporate at room temperature with controlled evaporation. It was observed that the resultant product was crystalline with good morphology from the ratio of 2:1 (pH value 5.4) and 3:1 (pH value 5.5). The resultant product did not have good morphology for the ratio of 1:1 (pH value 4.3) and 4:1 (pH value 6.3). But both the product crystals from the ratio 2:1 and 3:1 have same unit cell parameters as confirmed through single crystal X-ray Diffraction (XRD) analyses.

In the present study we have chosen the ratio of 2:1 for further crystal growth processes and characterization studies. The synthesized material was purified by repeated recrystallization for crystal growth. The saturated solution was prepared at 30°C and continuously stirred up to 35°C to avoid the nucleation during filtration of the solution. The solution was filtered twice to remove the suspended impurities. The solvent evaporation method was used to grow single crystals. After three weeks, the grown crystals were obtained including a crystal of size $25 \times 24 \times 7 \text{ mm}^3$ (Figure 2.1). The grown crystals were dark blue in colour and of nonhygroscopic nature.
Figure 2.1  As grown crystal of tetra thiourea cobalt chloride (TTCoC)

2.3. RESULTS AND DISCUSSION
2.3.1 Powder XRD Analysis

Powder XRD study of TTCoC crystal was carried out using Rich Seifert X-ray diffractometer employing CuKα (1.540 Å) radiation, scanning angle ranging from 10° to 60° at a scan rate 1°/min. The X-ray diffractogram (Figure 2.2) shows many diffraction peaks. The well defined Bragg’s peaks at specific 2θ angles show the high crystallinity of TTCoC crystal and all the prominent peaks were indexed.
2.3.2 Single Crystal XRD Studies

The single crystal XRD measurements for grown crystals were carried out using Enraf Nonius MACH3-CAT4 single crystal diffractometer with MoKα (λ = 0.717Å) radiation at room temperature. The calculated unit cell parameters of both ratios (2:1 and 3:1) are a = b = 13.542(5) Å, c = 9.099(2) Å with volume, V = 1668(1) Å³. After solving the crystal structure, it is found that the grown crystal is [CS (NH₂)₂]₄ CoCl₂. The crystal belongs to the tetragonal system and primitive lattice type with space group P4₂/n. The cell parameters are consistent with earlier report (Forstat et al 1966). Figure 2.3 (a) and (b) show the molecular structure and packing diagram of TTCoC single crystal respectively. The morphology of the grown crystal is shown in Figure 2.4. There are eight well developed faces.

Figure 2.2 Powder X-ray diffractogram of TTCoC
Figure 2.3 (a) Molecular structure of TTCoC

Figure 2.3 (b) Crystal packing diagram of TTCoC
2.3.3 Fourier Transform Infrared (FTIR) Analysis

FTIR spectrum of TTCoC crystal was carried out in the middle IR region between the wave number 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) at a resolution of \(\pm 5\) cm\(^{-1}\) by using Perkin Elmer Fourier transform infrared spectrometer equipped with a TGS detector, a KBr beam splitter, a He-Ne laser source, to confirm the functional groups. The FTIR spectrum of TTCoC is shown in Figure 2.5. In the complex, there are two possibilities by which the coordination of cobalt with thiourea can occur. The coordination with cobalt may occur either through nitrogen or through sulfur of thiourea (Ushashree et al 1998). Most of the metals form a complex through sulfur (Swaminathan and Irving 1964).

The broad envelope positioned in between 2700 and 3500 cm\(^{-1}\) corresponds to the symmetric and asymmetric stretching modes of \(\text{NH}_2\) grouping of thiourea. The bonds of thiourea were not shifted to lower
frequencies on the formation of the cobalt–thiourea complex. This indicates that the nitrogen to cobalt bonds is not present in the coordination compounds. The absorption observed at 1473 cm\(^{-1}\) in the spectrum of TTCoC corresponds to the N–C–N stretching vibration. The increase in the frequency can be attributed to the greater double bond character of the carbon to nitrogen bond on complex formation. Comparison of the vibration of thiourea and TTCoC is shown in Table 2.1. The metal–sulphur bond present in the TTCoC crystal is evident from the peak at 487 cm\(^{-1}\) which is due to antisymmetric S–Co–S stretching mode of deformation (Nakamoto 1978). The observations suggest that the complex formation was established through sulfur–cobalt bonds in TTCoC which confirms the presence of cobalt in the synthesized compound.

![Figure 2.5 FTIR spectrum of TTCoC](image-url)
Table 2.1 Assignments of IR band frequencies (cm\(^{-1}\)) of thiourea and TTCoC

<table>
<thead>
<tr>
<th>Thiourea</th>
<th>TTCoC</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1618</td>
<td>1615</td>
<td>NH(_2) bending</td>
</tr>
<tr>
<td>1470</td>
<td>1473</td>
<td>N-C-N stretching</td>
</tr>
<tr>
<td>1412</td>
<td>1414</td>
<td>CS symmetric band stretching</td>
</tr>
<tr>
<td>1087</td>
<td>1084</td>
<td>NH(_2) rocking</td>
</tr>
<tr>
<td>730</td>
<td>730</td>
<td>CS symmetric band stretching</td>
</tr>
</tbody>
</table>

2.3.4 Thermal Analysis

Thermo gravimetric and differential thermal analysis (TG/DTA) of TTCoC crystal was carried out using Perkin Elmer Diamond TG/DTA instrument. Simultaneous TG and DTA of TTCoC crystal was carried out between 35°C to 700°C at a heating rate 10°C/min in nitrogen atmosphere and the graph was plotted using PYRIS software.

The TG and DTA spectra of the TTCoC crystal are shown in Figure 2.4. From the TG curve it is obvious that TTCoC exhibits weight loss starting at 185°C. Below 185 °C there is no detectable weight loss. This illustrates the absence of physically adsorbed or lattice water in the crystal.

From DTA graph it is observed that the material is stable up to 110°C in which the material starts to melt. The endothermic peak at 118°C corresponds to the melting and the second endothermic peak at 226°C corresponds to the decomposition of the material.
2.3.5 High Resolution X-ray Diffraction (HRXRD) Analysis

A multicrystal X-ray diffractometer designed and developed at National Physical Laboratory (NPL), New Delhi (Lal and Bhagavannarayana 1989) has been used to study the crystalline perfection of the single crystals. Figure 2.7 shows the schematic diagram of multicrystal X-ray diffractometer. The divergence of the X-ray beam emerging from a fine focus X-ray tube (Philips X-ray Generator; 0.4 mm×8 mm; 2 kWMo) is first reduced by a long collimator fitted with a pair of fine slit assemblies. This collimated beam is diffracted twice by two Bonse-Hart (1965) type of monochromator crystals and thus diffracted beam contains well resolved MoKα₁ and MoKα₂ components. The MoKα₁ beam is isolated with the help of fine slit
arrangement and allowed to further diffract from a third (111) Si monochromator crystal set in dispersive geometry (+, -, -).

![Schematic diagram of multicrystal X-ray diffractometer](image)

**Figure 2.7 Schematic diagram of multicrystal X-ray diffractometer**

Due to dispersive configuration, though the lattice constant of the monochromator crystal and the specimen are different, the dispersion broadening in the diffraction curve of the specimen does not arise. Such an arrangement disperses the divergent part of the MoKα beam away from the Bragg diffraction peak and thereby gives a good collimated and monochromatic MoKα beam at the Bragg diffraction angle, which is used as incident or exploring beam for the specimen crystal. The dispersion phenomenon is well described by comparing the diffraction curves recorded in dispersive (+, -, -) and non-dispersive (+, -, +) configurations. This arrangement improves the spectral purity ($\Delta\lambda/\lambda << 10^5$) of the MoKα beam. The divergence of the exploring beam in the horizontal plane (plane of diffraction) was estimated to be $<< 3$ arc s.
The specimen occupies the fourth crystal stage in symmetrical Bragg geometry for diffraction in (+, -, -, +) configuration. The specimen can be rotated about a vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.2 arc s. The diffracted intensity is measured by using a scintillation counter. The rocking or diffraction curves for all the specimens were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position $\theta_B$ starting from a suitable arbitrary glancing angle (denoted as zero). The detector was kept at the same angular position $2\theta_B$ with wide opening for its slit, the so-called $\omega$ scan.

Before going to record the diffraction curve (DC), the sample surface was prepared by lapping and polishing and then chemically etched by a non-preferential chemical etchant mixed with water and acetone in the ratio of 1:2. These processes were carried out to get rid of non-crystallized solute atoms on the surface and also to remove surface layers, which may sometimes form for e.g. a complexating epilayer could be formed on the surface of the crystal due to organic additives (Bhagavannarayana et al 2006).

Figure 2.8 shows the high-resolution DC recorded for a typical TTCoC single crystal specimen using (300) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with MoK$\alpha_1$ radiation. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled rectangles. On deconvolution of the DC, it is clear that the curve contains a small additional peak, which is 126 arc s away from the main peak. This additional peak depicts a small internal structural low angle (tilt angle $\geq 1$ arc min but much less than a deg.) boundary (Bhagavannarayana et al 2005) whose tilt angle (misorientation angle between the two crystalline regions on both sides of the structural grain
boundary) is 126 arc s from its adjoining region. The dislocations from the boundaries may get elongated far into the bulk crystal and this causes broadening of the DC. However, 32 arc s of FWHM (full width at half maximum) of the main peak shows that the crystalline quality is fairly good.

![Rocking curve of TTCoC crystal](image)

**Figure 2.8 Rocking curve of TTCoC crystal**

### 2.3.6 Microhardness Study

Hardness does not produce a complete characterization of the strengths of materials, but it does sort them in a general way, so it is very useful for “quality control”; for the development of new materials; and for developing prototypes of devices and processes. Furthermore, mechanical hardness is closely related to chemical hardness, which is a measure of chemical bond stability (reactivity) (John J. Gilman 2009).
Vickers microhardness indentations were made on as grown surface of the TTCoC crystals at room temperature with the load ranging from 10 g to 50 g using Vickers microhardness tester. There were three trials made for each indentation. Time of indentation was kept at 5 seconds for all the trials. The Vickers hardness number was calculated using the expression:

\[ H_V = \left[ \frac{1.8544P}{d^2} \right] \text{kg} / \text{mm}^2 \]  \hspace{1cm} (2.1)

where, \( H_V \) is the Vickers hardness number in kg / mm\(^2\), \( P \) is the applied load in kg and \( d \) is the diagonal length of indentation impression in millimeter and 1.8544 is a constant of a geometrical factor for the diamond pyramid. A plot obtained between the hardness number and the load is depicted in Figure 2.9 (a). The Meyer’s law gives the relationship between \( P \) and \( d \): \( P = Ad^n \), where the exponent \( n \), the Meyer index (or number), which is known as work hardening coefficient, \( A \) is a constant. For normal Indentation Size Effect (ISE) behavior, the exponent \( n < 2 \), when \( n > 2 \) there is reverse ISE behaviour and when \( n = 2 \) the hardness is independent of applied load (Sangwal 2000). Figure 2.9 (b) reveals a plot of log \( P \) vs. log \( d \). The value of \( n \) was obtained using least squares fit method and it is 1.7, which is obeying the validity of Mayer’s relation.
Figure 2.9 (a) Vickers microhardness graph of TTCoC crystal

Figure 2.9 (b) Plot of log P vs. log d

\[ n = 1.7 \]
2.3.7 Dielectric Studies

If you apply an electric field, \( E \), across a material the charges in the material will respond in such a way as to reduce (shield) the field experienced within the material, \( D \) (electric displacement).

\[
D = \varepsilon E = \varepsilon_0 E + P = \varepsilon_0 E + \varepsilon_0 \chi_e E = \varepsilon_0 \left(1 + \chi_e\right) E
\]  

(2.2)

where, \( \varepsilon_0 \) is the dielectric permittivity of free space \( (8.85 \times 10^{-12} \text{ C}^2/\text{Nm}^2) \), \( P \) is the polarization of the material, and \( \chi_e \) is the electric susceptibility. The relative permittivity or dielectric constant of a material is defined as:

\[
\varepsilon_r = \varepsilon / \varepsilon_0 = 1 + \chi_e
\]  

(2.3)

The dielectric properties of material depend on the response of a material to an applied electric field. The total polarization of the material is sum of electronic polarizability, ionic polarizability, dipolar polarizability and space charge polarizability. When the relaxation time and the frequency of the applied field are similar, a phase lag occurs and energy is absorbed. This is called dielectric loss; it is normally quantified by the relationship:

\[
\tan \delta = \varepsilon_r'' / \varepsilon_r'
\]  

(2.4)

where, \( \varepsilon_r' \) is the real part of the dielectric constant and \( \varepsilon_r'' \) is the imaginary part of the dielectric constant.

The dielectric study for the grown crystal was carried out using Agilent 4284 A-LCR meter. The crystal is prepared and mounted between the copper platforms and electrodes. In order to ensure good electrical contact between the crystal and the electrodes, both sides of the crystal were coated
with silver paste. The capacitance and dissipation factor of the parallel plate capacitor formed by the copper plate and electrode having the sample as a dielectric medium have been measured. The dielectric constants have been calculated using the equation:

$$
\varepsilon_r = \frac{(C_{cryst} - C_{air} \cdot (1 - A_{cryst} / A_{air})) \cdot (A_{air} / A_{cryst})}{C_{air}}
$$  (2.5)

where $C_{cryst}$ is the capacitance of the crystal, $C_{air}$ is the capacitance of same dimension of air, $A_{cryst}$ is the area of the crystal and $A_{air}$ is the area of same dimension of air. The observations were made while cooling the sample in the frequency range 1 KHz to 1 MHz at the temperature 40°C to 100°C. Figure 2.10 (a) shows the plot of dielectric constant as a function of frequency. The dielectric constant has high values in the lower frequency region and then it decreases with the applied frequency. It is known that at low frequencies all kind of polarizations such as electronic, ionic, orientation and space charge are more active (Pillai 2001). At higher frequency, the orientation and ionic contributions of polarization are small at higher frequencies. This is due to the inertia of the molecules and ions (Charles Kittel 1993). So the total magnitude of polarization increases with the decrease of frequencies.

Figure 2.10 (b) shows the plot of dielectric loss as a function of frequency. At lower frequencies, the dielectric loss was found to be higher. This indicates that the frequency of the electric field is equal to that of natural frequency of bounded charge, which leads to the oscillation of the molecules with higher energy. Due to the presence of damping forces of solids, dipole energy is quickly dissipated, resulting in large radiation of electrical energy. At higher frequencies, the measure of dielectric loss is relatively low because the frequency of the electric wave is not equal to that of the natural frequency.
of the bounded charge and hence the radiation is very weak (Bhaskaran et al 2008).

Figure 2.10 (a) Dielectric constant of TTCoC crystal

Figure 2.10 (b) Dielectric loss of TTCoC crystal
2.3.8 Magnetic Study

Magnetic properties of the grown crystal have been analyzed using a vibrating sample magnetometer (lake shore 7410) at room temperature. Powder sample of the grown crystal was used for this measurement. Figure 2.11 shows the plot of magnetization versus the magnetic field strength for TTCoC crystal and it reveals the paramagnetic behavior. In general, antiferromagnetic order may exist at sufficiently low temperatures, vanishing at and above a certain temperature, called the Neel temperature. Above the Neel temperature, the material is typically paramagnetic. In general paramagnetic crystals are used in quantum-mechanical devices (Zverev et al 1962).

![Magnetic graph of TTCoC crystal](image)

**Figure 2.11** Magnetic graph of TTCoC crystal
2.4 CONCLUSIONS

The synthesized materials of both ratios (2:1 and 3:1) have same unit cell parameters confirmed by single crystal XRD. After solving the crystal structure, it is found that the grown crystal is tetra thiourea cobalt chloride \([\text{CS (NH}_2\text{)}_2\text{COCl}_2]\). Good quality TTCoC single crystals were successfully grown from aqueous solution by slow evaporation method. Powder XRD pattern shows that the well defined Bragg’s peaks at specific 2θ angles and all the prominent peaks were indexed. The presence of functional group was confirmed by FTIR spectrum. TG and DTA reveals that the crystal is thermally stable up to 110°C. The crystalline perfection of TTCoC crystal was analyzed by HRXRD technique. FWHM of the crystal contains a small additional peak which depicts a small internal structural low angle (tilt angle $\geq 1$ arc min but much less than a deg.) boundary. However, 32 arc s of FWHM of the main peak shows that the crystalline quality is fairly good. The mechanical behavior of TTCoC crystal was studied by Vickers microhardness measurements and it exhibits the normal ISE. The dielectric studies reveal that dielectric constant and dielectric loss are both inversely proportional to frequency. The characteristic of low dielectric loss with high frequency for TTCoC crystal suggests that it possesses good quality with lesser defects. The magnetic measurement of TTCoC crystal was carried out at room temperature and it shows the paramagnetic behavior.