



# Structural and spectroscopic characterization studies on metal - organic material: poly bis (thiourea) silver (I) nitrate (TUSN) single crystal

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**Abstract:** A metal-organic non-linear optical polymeric crystal, bis (thiourea) silver (I) nitrate (TUSN) has been synthesized from aqueous solution at room temperature. Powder and single crystal X-ray diffraction studies revealed that the crystal belongs to orthorhombic system with non centrosymmetric space group  $P2_12_12_1$ . Various functional groups present in the crystal are analyzed qualitatively by infrared and Confocal Raman spectral analysis. Effects due to coordination of thiourea with metal ions are also discussed. The chemical structure of the synthesized polymeric complex is further confirmed with NMR studies. The emission of green signal from second harmonic generation test confirms the optical nonlinearity of the material.

**Keywords:** crystal structure; organometallic compound; powder X-ray diffraction; spectral studies; SHG test.

## I. INTRODUCTION

In the recent past, materials scientists focused their attention to the growth of metal organic single crystals as these have wide applications in the field of laser technology, optical data storage, optical communication technology and frequency conversion processes<sup>1-3</sup>. In general, inorganic materials have high thermal stability, large mechanical strength and good optical transmittance. But these materials possess moderate optical nonlinearity due to the lack of extended  $\pi$ -electron dislocation in its molecular structure<sup>4</sup>. Thiourea is an organic compound which has a large dipole moment and having an ability to form an extensive hydrogen bond network with their co-compounds<sup>5</sup>. The centrosymmetric thiourea molecule coordinates with metal ions to form a non-centrosymmetric stable coordinated complex<sup>6</sup> which is the basic requirement for the material to have non-linear optical property (NLO). Recently we have reported the crystal structure<sup>7</sup> and thermal behaviour<sup>8</sup> of poly bis(thiourea) silver (I) nitrate synthesized at 60 °C.

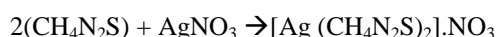
However, when it is synthesized at room temperature, it crystallizes in a different noncentrosymmetric crystal system with different morphology<sup>9</sup>.

The present chapter deals with the synthesis and characteristic studies such as structural, spectral, nonlinear optical properties of poly bis (thiourea) silver (I) nitrate (TUSN) single crystal and the results of which are discussed in detail.

## II. MATERIAL SYNTHESIS

The new poly bis (thiourea) silver (I) nitrate has been synthesized at room temperature. The TUSN complex is prepared by gently adding 0.01 mmol (1.6987 g) of  $AgNO_3$  to 0.02 mmol (1.5224 g) of thiourea, dissolved in 50 ml of millipore water.

The compound (TUSN) is synthesized according to the following chemical reaction:



The same chemical process is adopted for getting large quantities of TUSN salt. The final crystal product has been recrystallized many times to remove the impurity species present in the solution. The recrystallized salt of TUSN is taken in a beaker and saturated solution of TUSN is prepared at room temperature using a magnetic stirrer.

## III. RESULTS AND DISCUSSION

### Results and discussion

A quality single crystal of TUSN with dimension (0.24×0.22×0.20 mm<sup>3</sup>) was subjected to single crystal XRD study. Crystallography data were collected using Bruker Kappa APEX II CCD diffractometer at 298 K on a three circle X-ray diffractometer fitted with Mo-K $\alpha$

wavelength  $\lambda=0.71073 \text{ \AA}$ . The single crystal XRD data of bis (thiourea) silver (I) nitrate crystal indicate that the crystal belongs to orthorhombic system with the space group of  $P2_12_12_1$  and the calculated lattice parameters are  $a=13.022 \text{ \AA}$ ,  $b=14.394 \text{ \AA}$ ,  $c=18.362 \text{ \AA}$ ,  $\alpha=\beta=\gamma=90^\circ$  and  $V=3442 \text{ \AA}^3$

The TUSN crystal was characterized by powder X-ray diffraction technique using Rich Seifert X-ray powder diffractometer with  $\text{Cu-K}\alpha$  radiation of  $\lambda=1.5406 \text{ \AA}$ . Fig. 1 represents the indexed powder X-ray diffraction spectrum of TUSN crystal which was recorded in the  $2\theta$  range between  $5^\circ$  and  $40^\circ$  at the rate of  $1^\circ \text{ min}^{-1}$ . It shows the good crystalline nature of the sample and the prominent peaks present at different angles depict that the grown crystal belongs to the orthorhombic crystal system.

The crystal lattice parameters are measured using "XRDA" software using X-ray powder diffraction data. The obtained values are in good agreement with the single crystal X-ray diffraction results and are presented in Table 1.

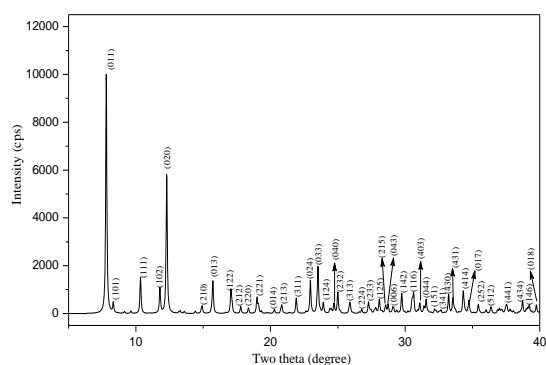


Fig. 1. Powder XRD pattern of the TUSN single crystal  
Table 1-Single crystal and powder XRD report of TUSN single crystal

Lattice parameters	Single crystal XRD	powder XRD
a (Å)	13.022	13.102
b (Å)	14.394	13.4587
c (Å)	18.362	18.6159
$\alpha$ (°)	90	90
$\beta$ (°)	90	90
$\gamma$ (°)	90	90
V (Å <sup>3</sup> )	3442	3282

### FT-IR and Confocal Raman spectral analysis

FT-IR spectral studies are used to demonstrate the composition and the information about the structure of the grown crystal. The product was characterized by the IR spectra (Fig. 2) using Perkin Elmer Spectrum one FT-IR spectrometer in the range  $4000 - 400 \text{ cm}^{-1}$  by employing a KBr pellet technique with a resolution of  $2 \text{ cm}^{-1}$ . A

number of reports are available on the IR studies of pure thiourea and metal complexes of thiourea<sup>10, 11</sup>.

Raman spectroscopy is also an efficient tool to identify the metal complex and functional groups present in the sample. Raman spectra of the samples can be analysed through either FT-Raman or Confocal Raman spectral studies. The differences between both techniques are the laser that is used and the way the Raman scattering is detected and analyzed. Compared to FT-Raman, Confocal Raman microscopy gives detailed chemical information at different positions of the sample. Since the laser source of  $532 \text{ nm}$  wavelength is used in Confocal Raman study, excitation energy of the source will be more and hence, several peaks which are not present in FT-Raman can be identified in Confocal Raman.

From the literature, it is found that there is a shift in peak position which confirms the metal coordination with thiourea. From the spectra of TUSN it is clear that the shifts of frequency bands are observed in the low frequency region and are agreed with the reported literature<sup>12, 13</sup>. In the complex, there are two possibilities by which the coordination of silver with thiourea can occur. The coordination with silver may occur either through nitrogen or through sulphur of thiourea<sup>14</sup>.

Among the several thiourea bands observed in the spectra, the two assigned bands for  $\nu_{\text{as}}(\text{CS})$  and  $\nu_{\text{as}}(\text{CN})$  confirm the complex formation of silver with thiourea ligand. This is consistent with the crystal structure, which shows a large number of different thiourea/Ag interactions. A larger effect of this kind is seen in the comparison of the  $\nu_{\text{as}}(\text{CN})$  wavenumbers for the complexes,  $\text{AgNO}_3/\text{thiourea}$  (1:3) and  $\text{Ag}_2\text{SO}_4/\text{thiourea}/\text{H}_2\text{O}$  (1:6:4)<sup>15</sup>. However, in the primary structural  $[\text{Ag}/\text{thiourea}]^+$  unit in which all three thiourea ligands are terminally bound to the silver which is consistent with the presence of a single asymmetric stretching C-N band at  $1479 \text{ cm}^{-1}$  in the IR spectrum.

Confocal Raman Spectra of TUSN (Fig. 3) has been recorded in the range  $0-3800 \text{ cm}^{-1}$  using WITEC alpha 300 Confocal Raman system with Nd:YAG laser of wavelength  $532 \text{ nm}$  and are shown in Fig. 3. The metal complex of thiourea under investigation may be considered to build up several chemical groups. Table 2 shows the Raman vibrational band assignments of both thiourea and metal coordinated thiourea.

In pure thiourea, C-S bonded with  $\text{NH}_2$  group where as in TUSN crystal C-S is bonded to  $\text{Ag}^+$ . The interaction between the C=S coordination of metal ions and  $\text{NH}_2$  lone pair electrons of thiourea is expected to shift its wavenumber of the N-C-N vibration at  $495 \text{ cm}^{-1}$  to  $484 \text{ cm}^{-1}$  in TUSN crystal. Stretching vibration band of  $\text{AgS}$  at  $204 \text{ cm}^{-1}$  further confirms the complex formation<sup>15</sup>. Thus, the observed spectral features associated with N-C-S,

N-C-S and S-M vibrations are due to the delocalization of lone pairs of electron<sup>16</sup>.

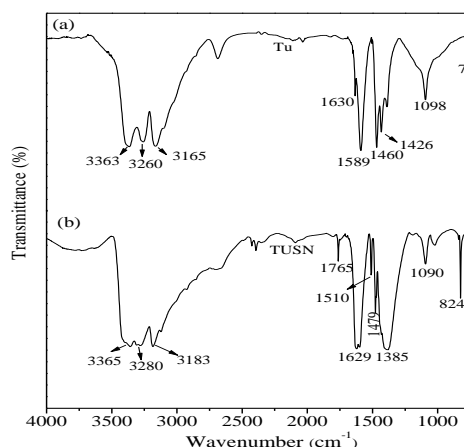


Fig. 2. FT-IR spectrum (a) pure thiourea (Tu) and (b) TUSN single crystal

Table 2- Molecular vibrational assignments of TUSN single crystal

Wavenumber (cm <sup>-1</sup> )		Assignments		
FTIR		Confocal Raman		
Thiourea	TUSN	Thiourea	TUSN	
3363	3365	3380	3326	$\nu_{as}(\text{NH}_2)$
3260	3280	3289	3213	$\nu_s(\text{NH}_2)$
3165	3183			$\nu(\text{NH}_2)$
1630,1589	1629,1765			$\delta(\text{NH}_2)$
	1510			$\nu_{as}(\text{NO}_2)$
1460	1479	1478	1507	$\nu_{as}(\text{C-N})$
1426	1385	1393	1402	$\nu_{as}(\text{C-S})$
1098	1090	1100	1110	$\nu_s(\text{C-N})$
	824			$\nu(\text{NO}_3^-)$
730	702	744	725	$\nu_s(\text{C-S})$
621	644			$\delta_{as}(\text{N-C-S})$
506	496	495	484	$\delta_{as}(\text{N-C-N})$
			204	$\nu(\text{AgS})$

$\delta$ : bending;  $\nu$ : stretching;  $s$ : symmetric;  $as$ : asymmetric

### NMR spectral analysis

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectral analysis are the important analytical techniques used to study the structure of organic compounds. The NMR spectra of TUSN crystal were recorded using D<sub>2</sub>O as solvent on a Bruker Advance III 500 MHz spectrometer at 22 °C to confirm the molecular structure and their spectra are presented in Figs. 4 and 5 respectively. The structural formula assigned for the resulting polymer shows the relation between the different structural components and the observed chemical shift values of the polymer. A strong peak of singlet at 4.703 ppm was attributed to the amide group of thiourea. Oxygen atom is more electronegative than sulphur atom. Hence the value (4.703 ppm) is slightly downfield which suggests the presence of some other hetero atom like sulphur which may be present in the

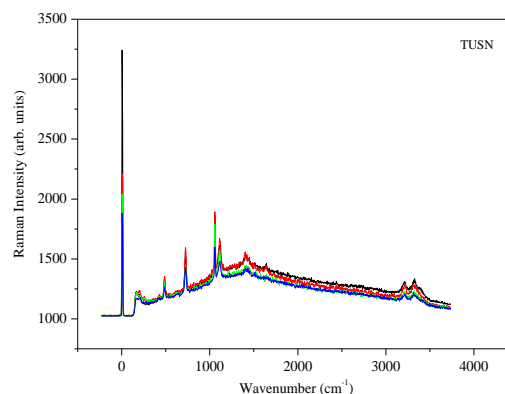


Fig. 3. Confocal Raman spectrum of TUSN single crystal

amide group. The equivalence of protons on the nitrogen atom in the TUSN crystal is shown as a singlet.

The carbon atoms present at different environments can be differentiated in the given proposed structure using C-13 NMR spectrum. Derivative with C=O groups will have their signals in the range from 150 to 185 ppm. The synthesized compound TUSN shows the signal at 176.425 in the upfield region which is due to sulphur in thiourea. Absence of any other peaks in the C-13 NMR spectrum represents the single carbon environment which is only due to thiourea in TUSN and not the other chemicals.

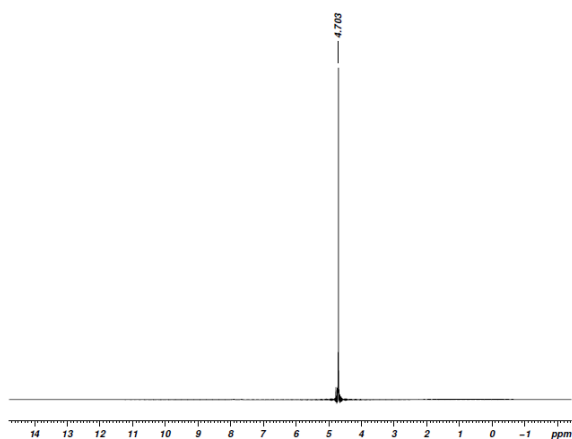


Fig. 4.  $^1\text{H}$  NMR spectrum of TUSN single crystal

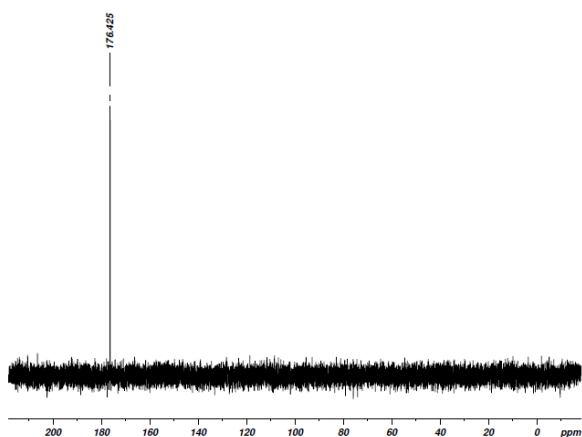


Fig. 5.  $^{13}\text{C}$  NMR spectrum of TUSN single crystal

### Second harmonic generation test

SHG property of the grown TUSN crystal was tested by the Kurtz and Perry technique<sup>17</sup> using Nd:YAG Q-switched laser beam with the input pulse of 5 mJ. The powdered crystal sample was densely packed in a micro-capillary tube of thickness 1 mm. The Nd:YAG laser produces IR radiation of fundamental wavelength 1064 nm, with 8 ns pulse width and 10 Hz pulse rate was made to fall normally on the sample tube. The fundamental beam was absorbed by IR filter and a photomultiplier tube detects the green signal which confirms the second harmonic generation property of the sample. The second harmonic signal of 8.4 mV was obtained for TUSN while the KDP gave an SHG signal of 14.8 mV for the same input beam energy of 5mJ.

## IV. CONCLUSION

A complex bis (thiourea) silver (I) nitrate (TUSN) was synthesized at room temperature. Single crystal X-ray diffraction study confirms the noncentrosymmetry space group  $P2_12_12_1$  which satisfies the basic requirement for any material to have NLO property. The powder X-ray

diffraction study supports the results of the single crystal XRD that the grown crystal belongs to the orthorhombic crystal system. Functional groups, the presence of metal nitrates and other chemical environments in the TUSN compound were completely discussed with the use of spectroscopic tools like FT-IR, Confocal Raman and NMR studies.

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