



Raman spectral investigation of thiourea complexes

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ABSTRACT

Spectroscopic properties of metal complexes of thiourea single crystals (tris thiourea zinc acetate, bis thiourea cadmium zinc acetate and bis thiourea ammonium chloride) which are non-linear optic materials were investigated by Raman scattering spectroscopy. The vibrational frequencies of the functional groups are identified and assigned. Effects due to the coordination of thiourea with metal ions are analyzed. Hydrogen bonding interactions involved in the metal complexes are observed in the Raman spectra.

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1. Introduction

Thiourea (TU) is one of the few simple organic compounds having high crystallographic symmetry. It crystallizes in the rhombic bipyramidal division of the rhombic system and behaves as a good ligand [1]. The crystal structure of thiourea has established the coplanarity of the C, N and S atoms in the molecule [2]. Thiourea molecules also possess a large dipole moment and have the ability to form an extensive network of hydrogen bonds. Due to these two properties thiourea molecules can be used as inorganic matrix modifier [3,4]. The thiourea molecule can also coordinate with metal ions to form stable coordinate complexes. Thiourea as such is a centrosymmetric one, but when it is coordinated with metal ions it becomes a non-centrosymmetric material, which is an essential property for a crystal to exhibit non-linear optical activity [5]. Metal complexes of thiourea are commonly called semiorganics, and benefit from both the advantageous properties of the organic and the inorganic part of complex [6]. In particular the coordination compounds formed by the organic ligand thiourea and metal ions with d¹⁰ electronic configuration (Zn²⁺, Cd²⁺, Hg²⁺) have recently received renewed attention. This interest arises due to its high non-linear optical properties and the convenient preparation of semiconducting materials based

on CdS through the thermal decomposition of these complexes [7,8].

Raman scattering is a versatile non-destructive tool for characterization of crystalline materials. It is effectively used to identify functional groups to help determining the molecular structure of synthesized complexes and it can also be used in conformational analysis of samples. To broaden insight into the NLO metal complexes of thiourea crystals, we have carried out Raman studies of three metal complexes of thiourea namely, tris thiourea zinc acetate, bis thiourea cadmium zinc acetate and bis thiourea ammonium chloride, determining vibrational modes and the study of molecule interactions.

2. Experimental details

Metal complexes of thiourea single crystals were grown as described in Ref. [6]. The grown crystals have been subjected to single crystal X-ray diffraction studies. The single crystal X-ray diffraction analysis of the thiourea complex crystals were carried out using Eshref CAD-4 diffractometer with Mo K α ($\lambda = 0.71069 \text{ \AA}$) and the lattice parameter and the cell volume were determined [9,10,11].

Micro-Raman measurements were performed from the crystals using a Dilor XY double spectrometer, under 514.5 nm excitation from an Ar⁺ ion laser, using a 50 \times objective lens to focus the laser and to collect the scattered light. Before the spectra were recorded, the Raman instrument was calibrated using the Raman line of

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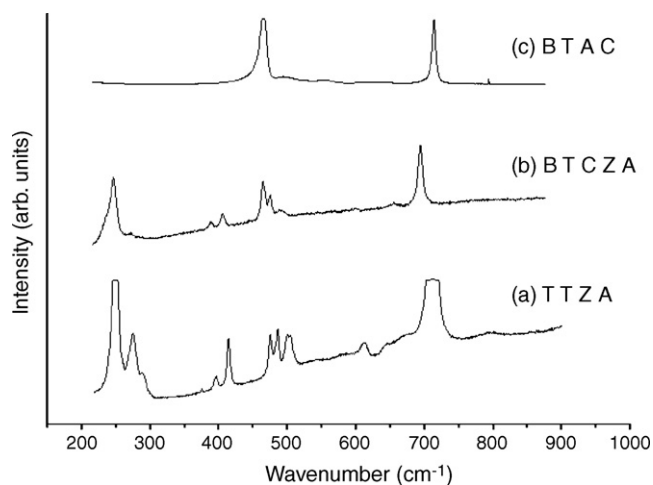


Fig. 1. Raman spectrum in the 200–900 cm^{-1} region: thiourea complex, (a) TTZA, (b) BTCZA, and (c) BTAC.

Si. The total power of laser excitation at the sample was about 1.05 mW.

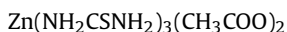
3. Results and discussion

3.1. Tris thiourea zinc acetate (TTZA)

The colorless single crystal of TTZA structure belongs to the monoclinic system with space group $P2_1$ [9,10]. The unit cell parameters are

$$a = 7.121 \text{ \AA}; \quad b = 17.665 \text{ \AA}; \quad c = 11.129 \text{ \AA}$$

TTZA is a semiorganic NLO material with molecular formula:



Spectra of thiourea complexes in four different regions in the 200–3400 cm^{-1} range (Stokes region) are shown in Figs. 1–4. The thiourea metal complexes under investigation may be considered to be built up of several chemical groups. Their Raman spectrum, both intensity and wavenumber, depends on the crystalline states and the nature of bonding. In order to understand the role the metal ions play in the crystallographic properties of divalent metal thiourea complexes, a comparison is made to a free ligand (TU) which is shown in Table 1.

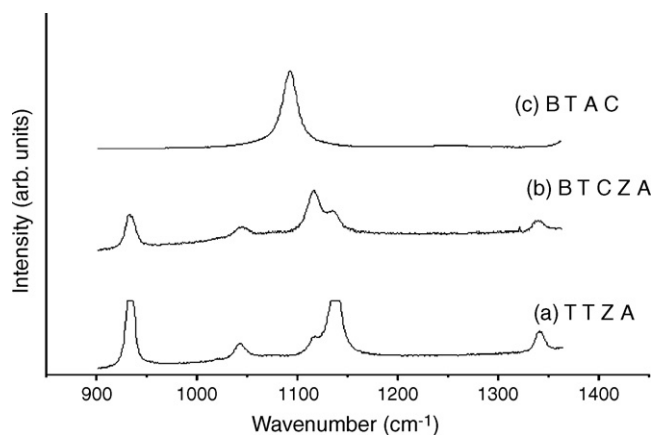


Fig. 2. Raman spectrum in the 900–1360 cm^{-1} region: thiourea complex, (a) TTZA, (b) BTCZA, and (c) BTAC.

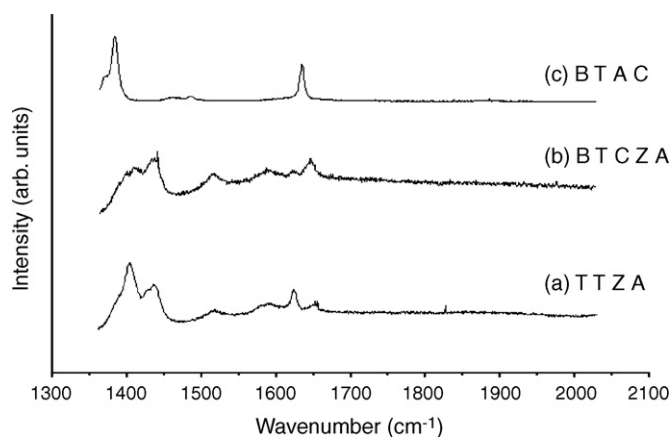


Fig. 3. Raman spectrum in the 1360–2100 cm^{-1} region: thiourea complex, (a) TTZA, (b) BTCZA, and (c) BTAC.

In thiourea metal complex crystals there are two possibilities by which the coordination can occur with the metal ions. The molecular structure of pure thiourea molecule is given in Fig. 5. It may be either through bonding to the nitrogen or through sulphur of the thiourea [4,9]. The formation of S–M bonds is also expected to increase the polarity of the thiourea molecules (Fig. 6) resulting in a greater double bond character for the nitrogen to carbon bond and a greater single bond character for the carbon to sulphur bond [2,12].

In thiourea, due to delocalization of lone pair electrons of the NH_2 group (Fig. 7), the electron density on the sulphur atom is

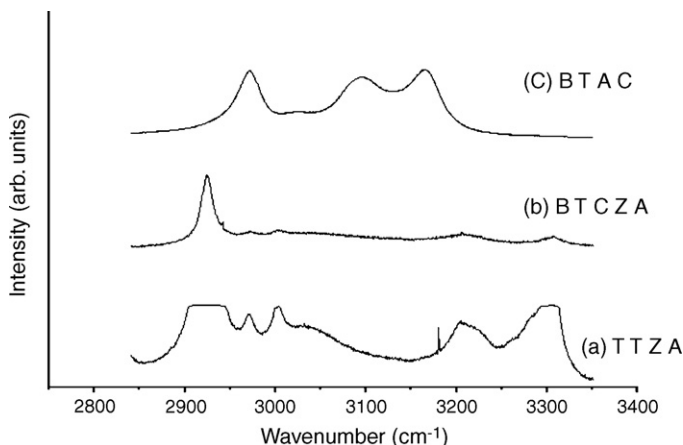


Fig. 4. Raman spectrum in the 2800–3400 cm^{-1} region: thiourea complex, (a) TTZA, (b) BTCZA, and (c) BTAC.

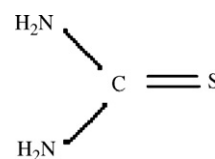


Fig. 5. Molecular structure of pure thiourea molecule.

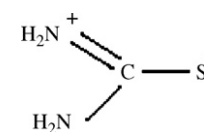


Fig. 6. Polar structure of pure thiourea molecule.

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