



Comments on: “Crystal growth and comparison of vibrational and thermal properties of semi-organic nonlinear optical materials”

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Abstract. In *Pramana – J. Phys.* **75**, 683 (2010), Gunasekaran *et al* reported that they have grown the nonlinear optical crystals, urea thiourea mercuric chloride (UTHC) and urea thiourea mercuric sulphate (UTHS). We argue that UTHC and UTHS are dubious crystals and are not what the authors propose.

Keywords. Crystal growth; urea thiourea mercuric chloride; urea thiourea mercuric sulphate.

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During the course of a literature survey of metal compounds containing both thiourea and urea ligands, the title paper by Gunasekaran *et al* [1] reporting on the growth of the so-called urea thiourea mercuric chloride (UTHC) and urea thiourea mercuric sulphate (UTHS) crystals attracted our attention. For formulating these crystals, the authors did not take into consideration the known chemistry of Hg(II) towards thiourea [2]; instead they assumed that the mixing of urea, thiourea and mercuric chloride (or sulphate) in water will result in the formation of UTHC (or UTHS) crystals by slow evaporation method. Our assumption is based on the fact that (i) both compounds are not represented by proper chemical formula but by unusual names which are not in accordance with chemical nomenclature and abbreviated by strange codes UTHC and UTHS and (ii) no results of single-crystal X-ray structure determination and chemical analysis are given in the entire paper to support the exact composition of the UTHC and UTHS crystals. Interestingly, the authors claimed to have used atomic absorption spectroscopy (AAS) to determine the mole percentage of dopants incorporated in their grown doped crystals, which only adds confusion because in the synthetic details of crystal growth there

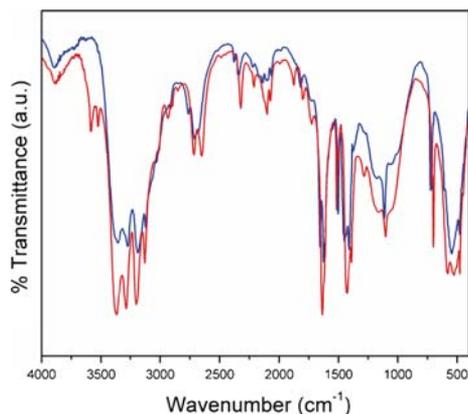
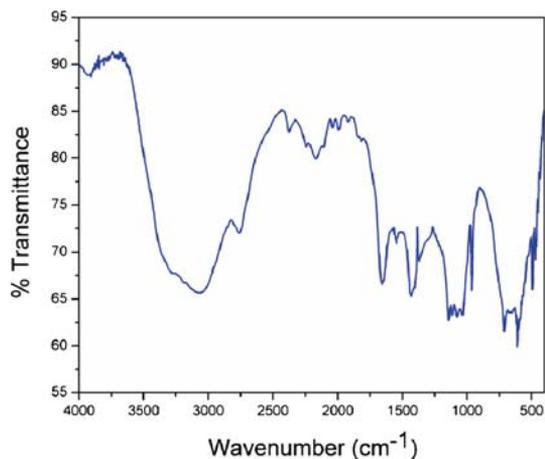


Figure 1. The IR spectrum of the known compound $[\text{Hg}(\text{tu})_2]\text{Cl}_2$ (blue) coincides with the spectrum of urea thiourea mercury chloride (UTHC) (red) isolated by growing a crystal using urea (u), thiourea (tu) and HgCl_2 , in 1 : 1 : 1 mole ratio showing that both are one and the same.

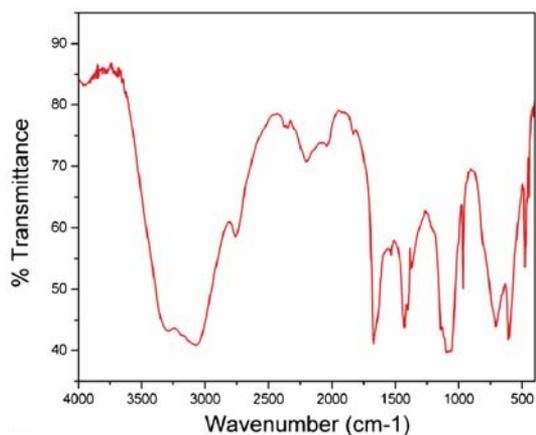
is no mention of growth of any doped crystals other than the UTHC and UTHS. Further, it is unfortunate that the exact nature of the dopant cannot be inferred from the following claim of the authors: *The low percentage of incorporation of dopants into the crystal may be because of the large difference between the ionic radii.* The UV–visible spectral data do not provide any clue on the exact nature of UTHC and UTHS because all the reagents used in the crystal growth, namely urea, thiourea, mercuric chloride (or sulphate) are colourless solids and are known to be transparent in the visible region.

The authors claimed to have used infrared (IR) spectroscopic studies to identify the functional groups present in the crystals and to determine the molecular structure. Urea represented by the formula $\text{CO}(\text{NH}_2)_2$ exhibits an intense band at 1675 cm^{-1} for the carbonyl (CO) vibration, which is absent in the reported IR spectra of UTHC and UTHS and also in the bands assigned by the authors. Thus, the IR spectra serve to infer the absence of urea in both UTHC and UTHS proving their dubious nature. This is not surprising and can be explained as the expected behaviour of a softer Hg(II) ion preferring to bind to the soft S donor of thiourea rather than to the hard O of urea. This explanation gains credence from the fact that no example of a well-characterized Hg(II) compound containing both urea and thiourea ligand in the same compound is reported in the literature unlike in a series of mercury–thiourea complexes described half a century ago [2]. An earlier claim of the growth of a thiourea urea zinc sulphate (TUZS) crystal has been shown to be erroneous and TUZS was correctly formulated as the well-known tris(thiourea)zinc sulphate $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ (tu = thiourea) [3]. To verify if any Hg(II) compound containing both urea and thiourea can be isolated from an aqueous medium by the reaction of urea, thiourea and a mercuric salt, we reinvestigated the crystal growth reactions under conditions identical to the conditions

Comment



(a)



(b)

Figure 2. The IR spectrum of (a) $[\text{Hg}(\text{tu})_2]\text{SO}_4$ is identical with that of the (b) urea thiourea mercury sulphate (UTHS) isolated by growing a crystal using urea (u), thiourea (tu) and HgSO_4 , in 1 : 1 : 1 mole ratio showing that both are one and the same.

given in the title paper and compared the IR spectra and powder pattern of the product (UTHC and UTHS) thus obtained with those of the reported $\text{Hg}(\text{II})$ -thiourea complexes. The perfect matching of the spectra and powder pattern of UTHC (or UTHS) with those of $[\text{Hg}(\text{tu})_2\text{Cl}_2]$ (or $[\text{Hg}(\text{tu})_2(\text{SO}_4)]$) reveal (i) the crystals reported in the title paper are dubious and (ii) confirm unambiguously that they do not contain any urea. The present comment thus points out the risk of formulating new compounds based on an incorrect assumption that mixing of a few reagents in aqueous solution will result in the crystallization of a desired product (figures 1–3 are given to support our argument).

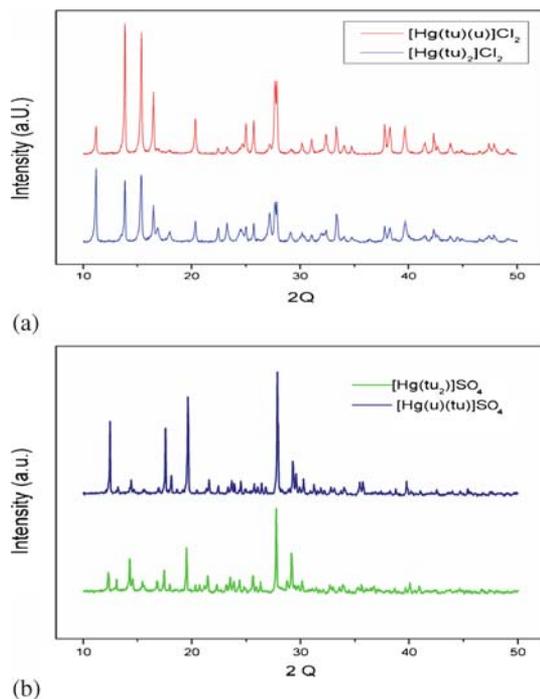


Figure 3. The identical powder pattern of (a) UTHC and (b) UTHS with those of the urea free compounds $[\text{Hg}(\text{tu})_2]\text{Cl}_2$ and $[\text{Hg}(\text{u})(\text{tu})]\text{SO}_4$ confirming the dubious nature of UTHC and UTHS.

References

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