



## Short Communication

## Reinvestigation of growth of urea thiosemicarbazone monohydrate crystal

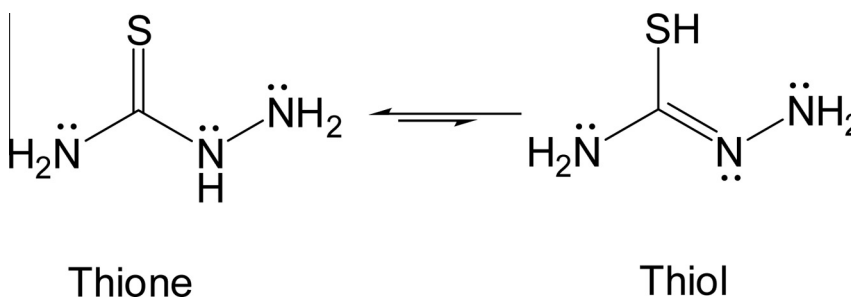
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## HIGHLIGHTS

- Reaction of urea with thiosemicarbazide is reinvestigated.
- Urea being an amide does not form any thiosemicarbazone product.
- Thiosemicarbazide crystallizes in the triclinic  $P\bar{1}$  space group.
- Thiosemicarbazide exhibits thione–thiol tautomerism in solution.
- Thiosemicarbazide exists as the thione tautomer in solid state.

## GRAPHICAL ABSTRACT

Reinvestigation of the reaction of urea with thiosemicarbazide **1** reported in Spectrochim. Acta A91 (2012) 345–351, reveals that the crystal obtained is the starting material namely thiosemicarbazide. Compound **1** exhibits thione–thiol tautomerism in solution.



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## ABSTRACT

The reaction of urea with thiosemicarbazide in 1:1 mole ratio in aqueous solution does not result in the formation of urea thiosemicarbazone monohydrate crystal, as reported by Hanumantharao, Kalainathan and Bhagavannarayana [Spectrochim. Acta A91 (2012) 345–351]. A reinvestigation of the reported reaction reveals that the crystal obtained is the starting material namely thiosemicarbazide, which has been unambiguously confirmed with the aid of infrared and <sup>1</sup>H NMR spectra and single crystal X-ray structure determination. Analysis of <sup>1</sup>H NMR spectrum reveals that thiosemicarbazide exhibits thione–thiol tautomerism in solution. In contrast, thiosemicarbazide exists as the thione tautomer in the solid state.

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## Introduction

Urea is the chief nitrogen-containing end product of protein metabolism and is thus an important biochemical. It is synthesized on a large scale for use as a fertilizer and as a raw material for the manufacture of urea–formaldehyde plastics and drugs. The chemistry of urea has been well studied since its first laboratory synthesis was reported by Wöhler in 1828 [1] and is described in

standard organic chemistry text books [2]. Urea crystallizes in the non-centrosymmetric space group  $P4_21m$  [3]. In nonlinear optical (NLO) materials research, the ready availability of high pure urea, has made it as an useful reference compound for reporting (as well as comparing) second harmonic generation (SHG) efficiency of non-centrosymmetric compounds [4,5].

Urea is a carbodiimide as its structure consists of a central carbonyl moiety (>C=O) flanked by two –NH<sub>2</sub> (amine) groups on either side. Unlike its hydrolysis to ammonia (or ammonium) and carbon dioxide under alkaline (or acidic) conditions or by the enzyme urease, where the >C=O group is converted to CO<sub>2</sub>,

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formation of urea–formaldehyde plastics, barbituric acid etc. are reactions in which the carbonyl group remains intact. While substitution reactions at the amino functionalities are known to result in products retaining the original  $>C=O$  moiety, transformations of urea involving the carbonyl group, which are typical of aldehyde or ketone are seldom known.

Thiosemicarbazone is a crystalline derivative of thiosemicarbazide and is usually prepared by reacting it with an aldehyde (or ketone) [6–8]. The formation of thiosemicarbazone is an addition reaction wherein the N atom of  $-NH_2$  group (nucleophile) of thiosemicarbazide adds onto the carbon center of the  $>C=O$  functionality of the aldehyde (or ketone) resulting in an imine ( $-C=N-$ ) compound with the elimination of a water molecule. In a recent report (title paper hereinafter), Hanumantharao et al. [9] have claimed growth of urea thiosemicarbazone monohydrate ( $C_2H_9N_5OS$ ) crystals by reacting urea with thiosemicarbazide and reported that the reaction mechanism is similar to that of benzaldehyde thiosemicarbazone monohydrate.

Urea being an amide is not expected to behave like an aldehyde (or ketone). If the  $>C=O$  group of urea can couple with the  $-NH_2$  functionality of thiosemicarbazide in a facile manner just by mixing aqueous solutions of urea and thiosemicarbazide, as claimed by the authors of [9], to give an imine namely urea thiosemicarbazone, then it should also be possible that the  $-NH_2$  group of one urea molecule couples with a neighboring molecule to form an urea dimer or a trimeric compound in view of the fact that the carbonyl group is flanked by  $-NH_2$  on either side. However, there is no literature report on the formation of any self condensation product of urea from an aqueous solution. In view of this, the reported crystal growth of urea thiosemicarbazone monohydrate appeared quite unusual. The inconsistencies in the reported spectral data [9] for the characterization of the grown crystal, for example assignment of the DMSO- $d_6$  signal (NMR solvent) for the compound, assignment of a signal at  $m/z = 133$  (Formula weight of  $C_2H_9N_5OS = 151.04$ ) as the molecular ion peak, reporting a higher carbon weight% (42.92) and a lower weight% of N (29.30) for the formula  $C_2H_9N_5OS$  (for elemental composition see Table S1), raised serious doubts about the correctness of the reported molecular formula. Since spectral data were inconsistent for  $C_2H_9N_5OS$ , the possibility that the crystal was incorrectly formulated could not be ruled out. The urea thiosemicarbazone crystal is a nitrogen rich compound containing five N atoms in  $C_2H_9N_5OS$ . In order to establish the correct identity of the crystal in view of the possible applications of a nitrogen rich compound, we have reinvestigated the reaction of urea with thiosemicarbazide reported by Hanumantharao et al. [9] and have characterized the crystals obtained with the aid of infrared and  $^1H$  NMR spectra and single crystal X-ray structure. The results of this reinvestigation are described in this report.

## Materials and methods

Reagent grade urea and thiosemicarbazide were purchased from commercial sources and were used as received without any further purification in this study. Infrared spectra of the samples diluted in KBr were recorded in the region  $4000-400\text{ cm}^{-1}$  using a Shimadzu (IR Prestige-21) FT-IR Spectrometer, at a resolution of  $4\text{ cm}^{-1}$ .  $^1H$  NMR spectra were recorded in DMSO- $d_6$  using a Bruker 400 MHz (Avance) FT-NMR spectrometer. X-ray intensity data were collected at room temperature using Oxford X Calibur, Gemini diffractometer equipped with EOS CCD detector. Monochromatic Mo  $K\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) was used for the measurements. Data were collected and reduced by using the "CrysAlispro" program [10]. An empirical absorption correction using spherical harmonics was implemented in "SCALE3 AB-SPACK" scaling algorithm. The structure was solved by direct

**Table 1**  
Crystal data and structure refinement for compound 1.

Empirical formula	$C_2H_9N_5OS$
Formula weight	91.14
Temperature	293(2) K
Wavelength	0.71073 $\text{\AA}$
Crystal system, space group	Triclinic $P\bar{1}$
Unit cell dimensions	$a = 4.9239(5)\text{ \AA}$ ; $\alpha = 77.201(9)^\circ$ $b = 6.0118(6)\text{ \AA}$ ; $\beta = 77.043(9)^\circ$ $c = 7.3175(7)\text{ \AA}$ ; $\gamma = 83.737(8)^\circ$
Volume	$205.45(4)\text{ \AA}^3$
Z, Calculated density	2, 1.473 $\text{mg/m}^3$
Absorption coefficient	$0.589\text{ mm}^{-1}$
$F(000)$	96
Crystal size	$0.38 \times 0.32 \times 0.28$
$\theta$ range for data collection	$2.92-26.36^\circ$
Limiting indices	$-6 \leq h \leq 4$ , $-6 \leq k \leq 7$ , $-7 \leq l \leq 9$
Reflections collected /unique	1302/835 [ $R(\text{int}) = 0.0130$ ]
Completeness $\theta = 25.00^\circ$	100.0%
Absorption correction	Multi scan
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	835/0/46
Goodness-of-fit on $F^2$	1.038
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0331$ , $wR2 = 0.0893$
R indices (all data)	$R1 = 0.0376$ , $wR2 = 0.0930$
Largest diff. peak and hole	0.313 and $-0.171\text{ e \AA}^{-3}$

methods using SHELXS97 [11] and refinement was carried out by full-matrix least-squares technique using SHELXL97 [11]. Anisotropic displacement parameters were calculated for all non-hydrogen atoms. H atoms attached to the N atoms were located in a difference fourier map and refined isotropically. Technical details of data acquisition and selected refinement results are listed in Table 1.

## Reaction of urea with thiosemicarbazide

A mixture of urea (0.300 g, 5 mmol) and thiosemicarbazide (0.455 g, 5 mmol) was taken in distilled water ( $\sim 40\text{ ml}$ ). The mixture was stirred well for  $\sim 15\text{ min}$  to get a clear solution. The reaction mixture was filtered and the clear filtrate was left undisturbed at room temperature. Slow evaporation of the solvent resulted in the separation of transparent crystals after three to four days. The crystals were isolated by filtration, washed with a little ice-cold water and dried in air to yield 0.231 g of crystalline product.

## Results and discussion

### Synthetic aspects and infrared characterization

The recently reported reaction of urea and thiosemicarbazide has been reinvestigated to unambiguously characterize the crystalline product. The crystalline material obtained from the reaction is referred to as compound 1 and investigated for its infrared and  $^1H$  NMR spectral characteristics. The IR spectrum of 1 was compared with that of the starting materials namely urea and thiosemicarbazide. The comparison revealed that the IR spectrum of 1 is identical to that of pure thiosemicarbazide (Fig. S1). In order to confirm this unambiguously, more batches of crystals of 1 were checked and in all cases the IR spectrum of 1 was always the same as that of thiosemicarbazide indicating that no urea thiosemicarbazone compound (Fig. 1) is formed. This observation can be easily explained due to the fractional crystallization of thiosemicarbazide. Both reactants are water soluble (Table S1) but the less soluble (85 g/L) thiosemicarbazide crystallizes first, with the more soluble urea (824 g/L) remaining in solution. The yield of isolated crystals amounted to  $\sim 50\%$  of reagent taken. In view of the isolation of only starting material, no efforts were taken to isolate more product. Since the assignment of bands in the IR spectrum of thiosemicarba-

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