

Published in: Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy: 117; 2014; 805-809.

Reinvestigation of growth of thiourea urea zinc sulfate crystal

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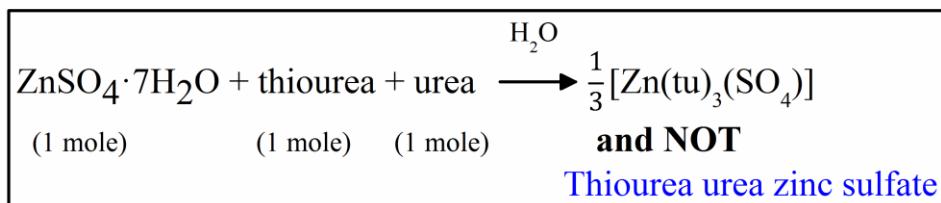
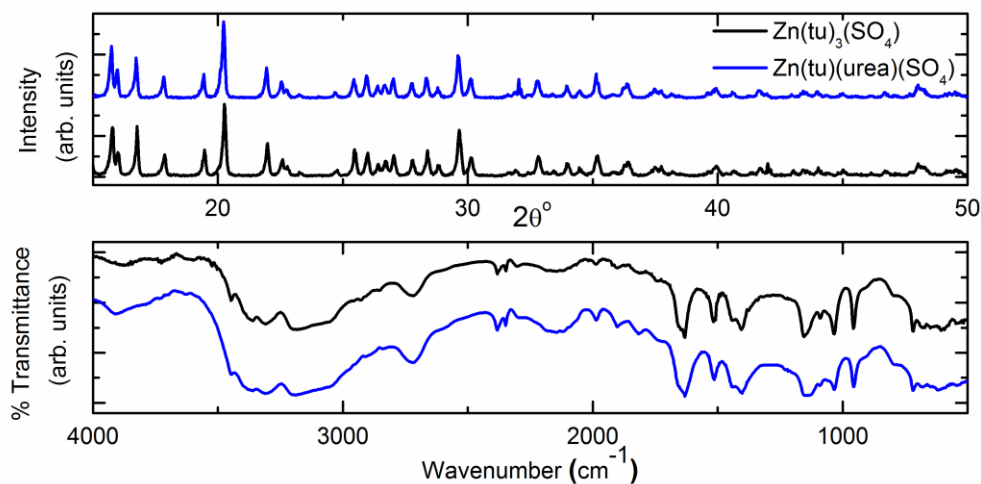
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Graphical Abstract

Reinvestigation of the reported work (Spectrochim. Acta A97 (2012) 456-463) on thiourea urea zinc sulfate crystal reveals that the crystal is actually the well-known $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ (tu = thiourea) crystal and not $[\text{Zn}(\text{tu})(\text{urea})(\text{SO}_4)]$.



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Highlights

- $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ (**1**) (tu = thiourea) crystallizes in the $Pca2_1$ space group.
- Reported NLO crystal thiourea urea zinc sulfate (**2**) is actually $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$.
- Compound (**1**) is distinguished from (**2**) by elemental analytical data.
- $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ exhibits a single ^{13}C resonance in its NMR spectrum.
- AAS is a sensitive technique for quantitative determination of metals.

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Abstract

Reinvestigation of the growth of thiourea urea zinc sulfate crystal is reported. Aqueous reaction of thiourea, urea and zinc sulfate in 1:1:1 mole ratio results in the formation of the well known $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ (**1**) (tu = thiourea) crystal and not the „so called“ novel semiorganic nonlinear optical thiourea urea zinc sulfate (**2**) crystal, as claimed by Redrothu Hanumantha Rao, S. Kalainathan, Spectroscopic investigation, nucleation, growth, optical, thermal and second harmonic studies of novel semi-organic nonlinear optical crystal – Thiourea urea zinc sulfate, Spectrochim. Acta A97 (2012) 456-463. In this work, we demonstrate the usefulness of elemental analytical data, infrared and NMR spectra and X-ray powder pattern, for accurate product characterization.

Keywords: thiourea; urea; thiourea urea zinc sulphate; nonlinear optical; powder pattern; infrared.

1. Introduction

Study of non-centrosymmetric solids is currently a topical area of research. Many research groups are investigating the synthesis, crystal growth and characterization of new examples of organic and inorganic compounds crystallizing in non-centrosymmetric space groups. For metal-organic compounds, metals with a closed shell electronic configuration like alkali or alkaline-earth metal ions, Zn(II), Cd(II), Cu(I) etc. and organic ligands like urea and thiourea, which are transparent in the visible region, are often investigated. An extensive chemistry of the complexes of the S-donor ligand thiourea (tu) has been developed and several structurally

characterized thiourea compounds are well documented in the literature since the pioneering structural work of Herbstein [1, 2]. Representative examples of thiourea compounds of the d^{10} metal ion Zn(II) are $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ [3], $[\text{Zn}(\text{tu})_2(\text{acetate})_2]$ [4], $[\text{Zn}(\text{tu})_2\text{Cl}_2]$ [5], $[\text{Zn}(\text{tu})_2(\text{NO}_3)_2]$ [6], and $[(\text{Zn}(\text{tu})_4)(\text{NO}_3)_2]$ [7]. It is interesting to note that in all these compounds the central metal adopts a tetrahedral geometry and thiourea functions as a monodentate ligand binding via the soft S site. In $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ (compound **1** hereinafter), the Zn(II) is coordinated to three S from three thiourea molecules and one O from the sulfate resulting in a $\{\text{ZnS}_3\text{O}\}$ tetrahedron (Fig. S1). The compound $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ which crystallizes in the non-centrosymmetric $Pca2_1$ space group has been the subject of several research investigations [8-16] and its crystal structure was reported as early as 1968 with the name tris(thiourea)zinc(II) sulfate [3]. Sulfatotris(thiourea)zinc [8, 15] and zinc tris(thiourea) sulfate (ZTS) [9, 10] are other names used in the literature for $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ (**1**).

A recent paper (title paper) describes the growth of a „so called“ novel semiorganic nonlinear optical thiourea urea zinc sulfate $[\text{Zn}(\text{tu})(\text{urea})(\text{SO}_4)]$ single crystal [17]. The compounds $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ and $[\text{Zn}(\text{tu})(\text{urea})(\text{SO}_4)]$ are referred to by numbers **1** and **2** respectively throughout this paper, to avoid use of non-standard abbreviations like TUZS. Based on the proposed formula $[\text{Zn}(\text{tu})(\text{urea})(\text{SO}_4)]$ it is noted that in **2**, two monodentate thiourea ligands of **1** are substituted by a single urea (O donor) ligand. However, no structural features of the single crystal of $[\text{Zn}(\text{tu})(\text{urea})(\text{SO}_4)]$ (for example the coordination sphere of Zn(II)) were reported in [17] despite the claim of a single crystal study having been performed. The unit cell data of **2** reported by the authors of [17] which were in agreement for the known compound $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ (**1**) and the several unusual features like use of AAS and SEM-EDS to check the presence of zinc, NMR solvent signal assigned as compound signal, incorrect molecular mass etc. indicated that compound **2** was not correctly characterized. As no structurally characterized zinc compound containing both urea and thiourea has been

reported in the literature so far, other than the above mentioned compound **2**, a reinvestigation of its reported crystal growth has been undertaken in this study, in order to establish its correct identity.

2. Materials and Methods

All chemicals and reagents were purchased from commercial sources and were used as received without any further purification in this study. Double distilled water was used as solvent. Infrared spectra of the samples diluted in KBr were recorded in the region 4000 – 400 cm^{-1} using a Shimadzu (IR Prestige-21) FT-IR Spectrometer, at a resolution of 4 cm^{-1} . ^1H (in $\text{DMSO-}d_6$) and ^{13}C (D_2O) NMR spectra were recorded using a Bruker 400 MHz (Avance) FT-NMR spectrometer. Thermal decompositions were performed using a temperature controlled furnace. C, H, N and S analyses were performed using a Vario Micro (Elementar) equipment. Zinc content was determined by EDTA titrations [18] after thermal decomposition of compounds followed by dissolving of the residue in dilute HCl. X-ray powder patterns were recorded using Rigaku X-ray diffractometer fitted with a diffracted beam monochromator, employing $\text{Cu K } \alpha$ ($\lambda = 1.5418\text{\AA}$) radiation in the 2θ range of 15° to 80° with a step size of 0.02° .

2.1 Synthesis of $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ (**1**)

The known compound sulfatotris(thiourea)zinc (**1**) was prepared by the method of Udupa [8]. The crystalline product thus obtained analysed satisfactorily (Table 1).

2.2 Reinvestigation of crystal growth of thiourea urea zinc sulfate

An aqueous solution of zinc sulfate heptahydrate (2.876 g, 10 mmol) was added to an aqueous solution containing a mixture of thiourea (0.761 g, 10 mmol), urea (0.600 g, 10 mmol) and the reaction mixture was stirred well for ~10 min. After this, the 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 of compound **2** which were isolated by filtration, washed with a little acetone, followed by ether and dried in air to yield 0.98 g of crystalline product.

Table 1

Comparative data for tris(thiourea)zinc(II) sulfate and thiourea urea zinc sulfate

	[Zn(tu) ₃ (SO ₄)] (1)	[Zn(thiourea)(urea)(SO ₄)] (2)
Molecular formula	C ₃ H ₁₂ N ₆ O ₄ S ₄ Zn	C ₂ H ₈ N ₄ O ₅ S ₂ Zn
Molecular weight	389.82	297.63
% Chemical composition		
% C	9.24 (9.39)*	8.07 (9.37)*
% H	3.10 (2.91)*	2.71 (2.87)*
% N	21.56 (21.76)*	18.82 (21.77)*
% O	16.42	26.88
% S	32.90 (32.71)*	21.55 (32.59)*
% Zn	16.77 (16.00)*	21.97 (15.99)*
% ZnO residue expected on pyrolysis	20.88 (20.17)*	27.35 (20.08)*
% (SO ₄)	24.64	32.27
M ⁺ ion peak expected in mass spectrum	389.82	297.67
Number of Signals expected in ¹ H NMR	One (for the equivalent protons of thiourea)	Two (one each for the -NH ₂ protons of urea and thiourea)
Number of Signals expected in ¹³ C NMR	One (for the C atom of thiourea)	Two (one each for the C of thiourea and urea)
Unit cell parameters	Reported in [15]	Reported in [17]
<i>a</i> (Å)	11.1738(2)	7.78
<i>b</i> (Å)	7.80110(10)	11.15
<i>c</i> (Å)	15.5424(2)	15.47
$\alpha = \beta = \gamma$	90°	90°
<i>V</i>	1354.80 Å ³	---

* Values in bracket are the experimental analytical values obtained in this work.

3. Results and discussion

3.1 Synthetic aspects and infrared spectral characterization

The recently reported growth of thiourea urea zinc sulfate crystal [17] is reinvestigated in order to unambiguously characterize the crystalline product. The crystalline material obtained

from the reaction is referred to as compound **2**. The elemental analytical data of **2** (Table 1) gives the first clue that the proposed formula is incorrect. As can be seen, the analytical data especially for S is 11% more than the theoretically calculated value for the formula proposed by authors of [17]. More interestingly the experimental analytical data and the ZnO residue obtained by pyrolysis perfectly match for compound **1** clearly indicating that compound **2** does not contain any urea whatsoever. The identical nature of the infrared spectra of compounds **1** and **2** (Fig. 1) adds further credence to the analytical data revealing that compounds **1** and **2** are one the same. In order to confirm this unambiguously, more batches of crystals of **2** were checked and in all cases the IR spectrum of **2** was always the same as that of **1** indicating that no thiourea urea zinc sulfate crystal (Fig. 1) is formed. Since the $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ (**1**) compound is a well-known compound and has been extensively studied in the literature [8-14] and IR spectroscopy has been used as a characterization tool to infer if a new product is formed, no discussion of the IR spectrum and the assignment of bands is presented here.

3.2 Phase pure nature of compound 2 based on X-ray powder pattern and ^{13}C NMR

A comparison of the powder pattern of compound **2** with that of the known compound **1**, serves to demonstrate its phase pure nature. The matching pattern (Fig. 1) thus prove that compounds **1** and **2** are identical and **2** contains no trace of inorganic (for example Zn(II)-urea compound) or organic impurities. The absence of any organic (urea) impurities in **2** is also revealed by its ^{13}C NMR spectrum recorded in D_2O . A compound whose proposed formula is thiourea urea zinc sulfate crystal is expected to give two distinct ^{13}C signals, one for the thiocarbonyl C atom of thiourea, and one for the carbonyl C of urea. However, compound **2** shows a single ^{13}C resonance at 181.66 ppm (Fig. S2). A comparison of this

signal with that of pure thiourea (181.95 ppm) thus serves to confirm that compound **2** has a single unique thiocarbonyl type C atom and rules out the presence of any urea.

3.3 Additional proof for the non-formation of thiourea urea zinc sulfate

As the exact identity of the product formed in the aqueous reaction of zinc sulfate with thiourea and urea was established as $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ based on analytical data, IR and NMR spectra and X-ray powder pattern, we considered the determination of single crystal structure a superfluous exercise and did not perform the same. In this context, we wish to mention that it is not surprising to note that the unit cell data reported by the authors of [17] are in agreement (Table 1) with those of $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ [15] excepting for an interchange of a and b values. Since, no structural features in terms of the ligands around zinc were reported, it is not clear if these authors determined the structure and prepared a cif file as is normally done in single crystal work. However the space group for this compound was reported as $Pca2_1$ (without any Flack parameter [19]) and one wonders how the space group can be reported without structure determination. The authors do not give any reason in terms of systematic absences for their choice of the $Pca2_1$ space group from out of a total of 59 space groups in the orthorhombic crystal system. The unit cell data reported by the authors of [17] and the absence of a cif file for an alternate structure model thus provide one more proof, that crystals of **2** are not the „so called“ thiourea urea zinc sulfate but simply $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$.

The residual protons and water present in the deuterated solvents used for recording NMR spectra exhibit characteristic chemical shifts which are listed in standard spectroscopy text books [20]. For DMSO- d_6 these signals appear at $\delta = 2.49$ ppm (residual proton signal) and $\delta = 3.35$ ppm (DMSO water). The authors of [17] have not taken this aspect into consideration and have assigned the solvent signal for compound and vice versa. In the NMR spectrum, the authors' assignment of a signal at ~ 2.4 ppm, for the thiourea protons is incorrect, because

this signal is actually due to the residual protons of DMSO- d_6 which was used as NMR solvent [20]. The broad signal at ~ 7.2 ppm in [17] is actually due to the protons of thiourea as can be evidenced by the fact that a similar signal is also observed for pure thiourea (Fig. 2). A compound whose proposed formula is thiourea urea zinc sulfate crystal is expected to give two distinct NMR signals, one each, for the equivalent protons attached to the N in thiourea and the protons attached to N in urea at ~ 5.47 ppm. In contrast, the ^1H NMR spectrum of $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ is expected to exhibit a single signal for the equivalent protons of thiourea. It is interesting to note that the ^1H NMR spectrum of pure thiourea recorded in DMSO- d_6 (Fig. 2) is nearly identical to that of the spectrum in [17], indicating yet again the non-formation of any new zinc compound containing urea.

Thus a combination of elemental analyses, IR and NMR spectra and X-ray powder pattern serve to unambiguously confirm that compounds **2** and **1** are one and the same. The reported mass spectrum does not show the expected ($m/z = 297.67$) molecular ion peak for the formula proposed by the authors once again showing the wrong characterization. A well-known compound $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ was incorrectly formulated by the authors as a novel thiourea urea zinc sulfate crystal, due to i) incorrect interpretation of experimental results ii) inappropriate use of AAS and SEM-EDS for example to check presence of zinc instead of well-known spot tests [21] iii) assigning an arbitrary signal for the molecular ion peak in mass spectrum, iv) comparing SHG properties of a zinc-organic compound with amino acid compounds instead of relevant compounds [22-26]. Details of these several inconsistencies in the earlier reported paper [17] are given in Supplementary material.

3.4 Chemistry of the aqueous reaction of zinc sulfate with thiourea and urea

The authors of the title paper attempted to grow crystals of a „so called“ thiourea urea zinc sulfate by use of equimolar ratios of urea, thiourea and zinc sulfate in water. It appears that the grown crystals were formulated based on an incorrect assumption that use of thiourea:

urea:ZnSO₄ in a 1:1:1 mole ratio will result in a „so called“ thiourea urea zinc sulfate crystal, disregarding the chemistry of the reaction which dictates product formation. Contrary to the authors“ assumption, the reaction resulted in the formation of a totally different product namely the known compound [Zn(tu)₃(SO₄)] **1** which contains zinc and thiourea in a 1:3 mole ratio. From the yield of product, one can easily make out that the compound formed is different from the assumed crystals of thiourea urea zinc sulfate, but the authors missed this. Note that neither the amounts of starting materials nor the yield of the crystalline product are given in [17]. Instead of this detail, the resistivity of water used in the experiment is given. Based on the phase rule studies of the system zinc sulfate-thiourea-water at 30 °C it has been shown that only one complex of composition [Zn(tu)₃(SO₄)] is formed between zinc sulfate and thiourea [8]. It has been reported that the low solubility of [Zn(tu)₃(SO₄)] as compared to those of ZnSO₄·7H₂O and thiourea and its occupancy of the largest area in the saturation region of the phase diagram are factors, which makes its isolation easy in pure state [8]. In view of this chemistry of Zn(II) towards thiourea namely facile formation of the tris(thiourea) compound, the attempt of the authors to grow crystals of thiourea urea zinc sulfate from an aqueous solution containing urea, thiourea and zinc sulfate, only resulted in the formation of the known compound [Zn(tu)₃(SO₄)] with the more soluble urea and unreacted zinc sulfate remaining in solution resulting in low yield.

In this study we have observed that the use of the reagents ZnSO₄·7H₂O, thiourea and urea in 1:1:1 mole ratio results in a low yield (~25%) of [Zn(tu)₃(SO₄)]. This can be explained by the consumption of only a third of ZnSO₄·7H₂O (1/3 mole) for product formation with thiourea (1 mole) to maintain a 1:3 mole ratio of zinc:thiourea. The more soluble urea and the unreacted ZnSO₄·7H₂O (2/3 mole) do not participate in any chemical reaction and remain in solution and the less soluble [Zn(tu)₃(SO₄)] crystallizes out as the product. Thus our observation is perfectly in accordance with the reported results of the phase rule studies of the

system zinc sulfate-thiourea-water at 30 °C [8]. Our observation that the product yield can be enhanced by addition of thiourea adds more credence. It has been observed that use of two moles of urea also does not result in any urea containing zinc compound clearly indicating that two monodentate thiourea ligands in $[\text{Zn}(\text{tu})_2(\text{SO}_4)]$ cannot be substituted by a single urea ligand which has to function as a bidentate ligand in order to satisfy the preferred four coordination of Zn(II). The compounds $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ and thiourea urea zinc sulfate differ widely in their chemical formula (Table 1) and can be easily distinguished based on analytical data and spectral characteristics as has already been shown in this work.

3. Conclusions

The main findings of the present work are as follows: i) The formation of a product crystal in a crystal growth study, is dictated by the chemistry of the reactants. Hence it is incorrect to formulate compounds based on an assumption that a certain crystal grown from a mixture of precursor materials (for example ZnSO_4 , urea, thiourea) taken in a preferred ratio, will represent a desired crystal namely thiourea urea zinc sulfate; ii) It is inappropriate to use AAS and or EDAX for verifying the presence of a certain metal ion (zinc in the present case). Mere observation of the presence of a certain element in an EDAX study is no valid proof for the confirmation of a new product [27]; iii) It is incorrect to formulate a new compound based only on unit cell data and also to report space group without structure determination; iv) The present work demonstrates the importance of elemental analytical data for accurate characterization of a product crystal; In the case of the thiourea urea zinc sulfate crystal, elemental analytical data are more than sufficient to rule out its formation and hence it can be termed as a hypothetical compound. A combined use of analytical data, IR and NMR spectra and X-ray powder data provides not only complimentary but also confirmatory data to unambiguously and correctly formulate the „so called“ novel semi-organic nonlinear optical thiourea urea zinc sulfate crystal as $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$.

Acknowledgments

The BRUKER 400 MHz FT-NMR instrument used in this study was procured by the Department of Chemistry, Goa University, out of DST-FIST grants sanctioned by the Department of Science & Technology (DST), New Delhi.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at *****

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Captions for figures:

Fig. 1. Matching X-ray powder pattern (top panel) and IR spectra (middle panel) showing $[\text{Zn}(\text{tu})_3(\text{SO}_4)]$ (**1**) and $[\text{Zn}(\text{tu})(\text{urea})(\text{SO}_4)]$ (**2**) are one and the same. No urea is incorporated into (**1**) to form thiourea urea zinc sulfate as shown in the reaction scheme (lower panel).

Fig. 2 ^1H NMR spectrum of pure thiourea in $\text{DMSO}-d_6$

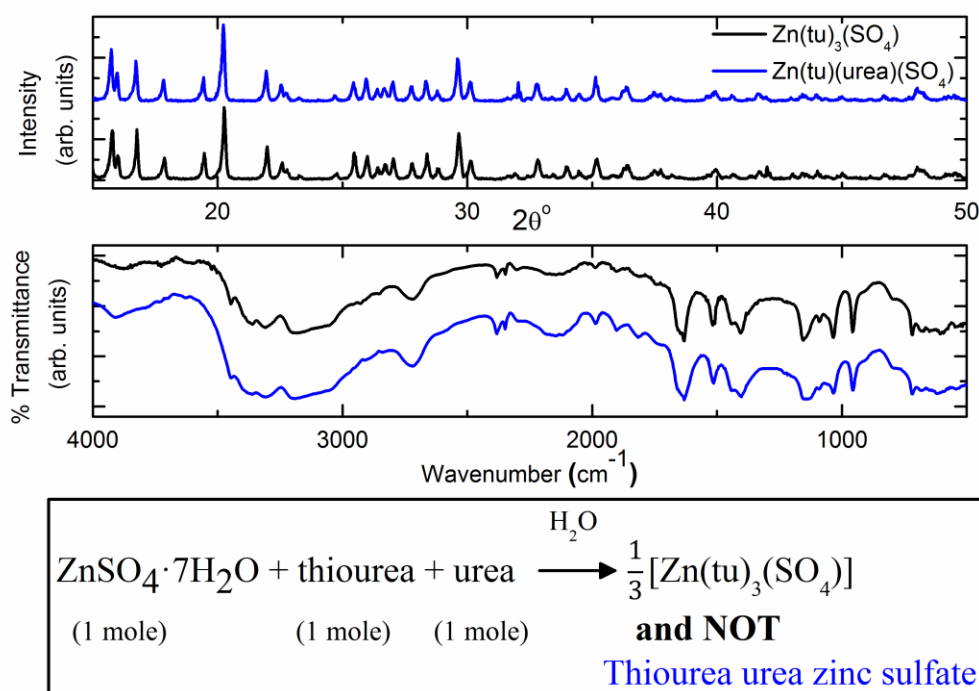


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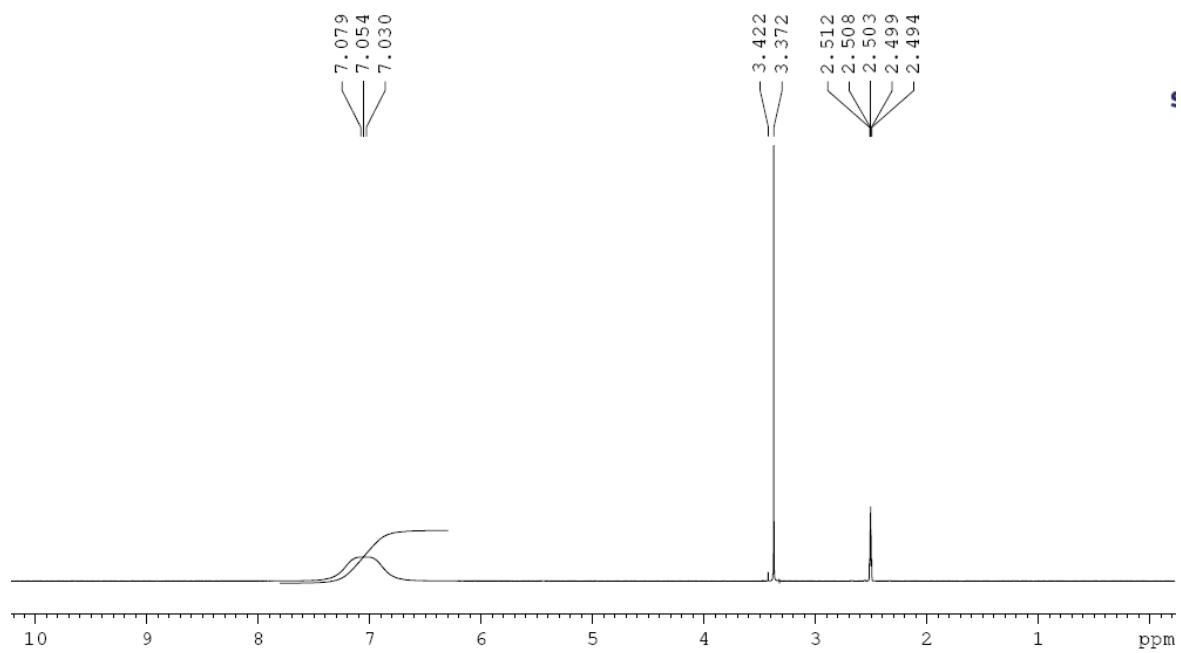


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