Published in *Journal of Thermal Analysis and Calorimetry*: 119(2); 2015; 985-988

Letter to the Editor

On the existence of 'thiourea urea magnesium chloride' and 'urea thiourea sodium chloride'

Bikshandarkoil R. Srinivasan
Department of Chemistry, Goa University, Goa 403206, India
Email: srini@unigoa.ac.in Telephone: 0091-(0)832-6519316; Fax: 0091-(0)832-2451184

Abstract

Gopinath et al report to have grown single crystals of thiourea urea magnesium chloride (**1**) (J Therm Anal Calorim 2012, 109:841–5) and urea thiourea sodium chloride (**2**) (J Therm Anal Calorim 2012, 110:789–92) from an aqueous solution containing thiourea, urea and magnesium chloride (sodium chloride for **2**) by the slow evaporation method. In this letter it is proved that (**1**) and (**2**) are not new metal-thiourea compounds but pure thiourea. In view of no chemical reaction among the reagents employed for crystal growth, thiourea is formed due to fractional crystallization.

Keywords: Crystal growth; Urea; Thiourea urea magnesium chloride; Urea thiourea sodium chloride; Thiourea; Fractional crystalization.

Published in *Journal of Thermal Analysis and Calorimetry*: 119(2); 2015; 985-988

Introduction

The synthesis and characterization of new materials and investigation of their spectroscopic, optical and thermal properties is an area of ongoing research in materials science. In order to characterize any new crystalline material, it is essential to unambiguously identify the solid being studied in terms of its correct molecular formula and crystal structure wherever suitable crystals are available. It is inappropriate to refer to a new solid in terms of only a name (without any formula) for example thiourea urea magnesium chloride (TUMC) [1] or urea thiourea sodium chloride (UTNC) [2]. Abbreviations or codes should not be used as alternates for molecular formula of new compounds. In addition to X-ray structure determination, a crystalline material should be characterized for its composition based on analytical data for C, H, N and S for organic crystals and % of metal in addition to C, H, N and S data for metal-organic crystals. In the absence of X-ray structure, the composition is very important for characterization of any material. New crystalline materials cannot be characterized based on an assumption that mixing of a few reagents in aqueous solution (for example thiourea, urea and magnesium chloride) will result in the crystallization of a new product crystal (for example thiourea urea magnesium chloride). We and others have shown in several recent reports that disregarding the chemistry of the reagents used for crystal growth leads to improper characterization of product crystals [3-10]. It is well-known that many Mg(II) compounds isolated from aqueous solution contain the $[Mg(H_2O)_6]^{2+}$ unit in view of the high affinity of Mg(II) for aqua ligands [11] the name thiourea urea magnesium chloride indicating absence of water for a so called TUMC crystal isolated from an aqueous medium appeared unusual and the claim questionable. In an extensive study of metal-thiourea compounds Boeyens and Herbstein [12] had reported that no lithium or sodium salts give complexes with thiourea. Hence the claim of growth of urea thiourea sodium chloride UTNC crystal also appeared dubious. For both these crystals no chemical formula was reported by the authors [1, 2] but very interestingly the infrared spectra, the powder pattern and thermal behavior were identical. In the following comment it will be proved that both TUMC and UTNC are not metal-thiourea compounds but pure thiourea.

A so called thiourea urea magnesium chloride

Gopinath et al [1] report to have grown a new nonlinear optical crystal based on an incorrect assumption that slow evaporation of an aqueous solution containing thiourea, urea and $MgCl_2 \cdot 6H_2O$ will result in the formation of a so called thiourea urea magnesium chloride TUMC (**1**)[1]. For the name of **1** the authors have not taken into consideration that a Mg(II) compound isolated from an aqueous solution normally contains coordinated water molecules especially $[Mg(H_2O)_6]^{2+}$ unit [11]. A scrutiny of the reported results reveals that the authors have not assigned any chemical formula for compound **1** excepting an unusual code TUMC. The amounts of reagents taken for crystal growth and the % yield of the product crystal are not given excepting the statement, '*TUMC was prepared by dissolving the required quantities of thiourea, urea and magnesium chloride in Millipore water*'. Although the exact ratio of Mg:thiourea:urea ratio in **1**is not clear, the name indicates that **1** contains a mole of each thiourea and urea per Mg metal.

The authors neither performed single crystal study nor determined any elemental composition of **1**. Instead they employed IR and UV-Vis spectra, X-ray powder pattern and TG-DTA thermogram for its characterization. Although the spectra and thermal study do not provide any information on the exact formula of **1**, an examination of the IR spectrum rules out the presence of any urea due to the absence of the carbonyl (C=O) vibration which is expected to be seen as an intense signal. The authors have also not assigned this vibration and did not think it important to look for this strong signal in a urea containing compound. Although the sharp Bragg lines indicate the crystalline nature of compound **1**, this cannot be taken as any clue for new product formation because each one of the starting materials which are crystalline can also give sharp lines. The high thermal stability indicates the absence of water in **1**and the observed thermal event is close to the melting point of thiourea. Other than these immediate hints, no clues on the exact composition or structure of **1**can be obtained. Although, the authors have stated in the abstract, '*Detailed structural analysis of the compound is under progress*' no such study has been reported for**1**. Instead the authors have reported on the growth of another so-called urea thiourea sodium chloride UTNC (**2**)[1] crystal [2].

A so called urea thiourea sodium chloride

It is not clear why a sodium compound which is supposed to contain thiourea and urea is called as urea thiourea sodium chloride and not thiourea urea sodium chloride. Such contradictory names for **1** and **2** clearly indicate that the nomenclature employed by the authors is arbitrary. The authors formulated compound **2** also based on an incorrect assumption that slow evaporation of an aqueous solution containing thiourea, urea and NaCl will result in the formation of a so-called urea thiourea sodium chloride **2**. This is in disagreement with the fact that Na does not form any thiourea compounds [12]. The characterization of **2** is exactly on very similar lines like for compound **1**. No chemical analysis or single crystal structure was performed for this so-called UTNC. In the entire paper [2] no molecular formula (or composition) is given for compound **2**. However it is interesting to note that the IR and UV-Vis spectra, powder pattern, thermogram, solubility curve and crystal morphology of **2** are very similar to those of **1** indicating that both products are one and the same. The absence of urea inferred from the IR spectrum combined with the thermal event at ~182^{o} provides the clue that both **1** and **2** are nothing but thiourea since this is the only common reagent other than urea in both crystal growth reactions.

Fractional crystallization of thiourea

The metals Mg(II) and Na(I) are oxophilic and prefer to bind to O-donor ligands and not the soft S site of thiourea ligand. The few known Mg(II) compounds bonded to S donors are prepared by non-aqueous method in view of the high affinity of Mg(II) for water [13]. Recently we had shown that slow evaporation solution growth actually results in the fractional crystallization of the less soluble S-donor ligand namely thiosemicarbazide and not any *s*-block metal-thiosemicarbazides [14]. The formation of thiourea can be similarly explained due to fractional crystallization as shown in Fig. 1. When a crystal growth reaction is performed at room temperature in aqueous medium employing thiourea, urea and magnesium chloride, no chemical reaction takes place between Mg(II) and thiourea (or urea) resulting in the fractional crystallization of the least soluble reagent namely thiourea (1 g in 11 ml) with the more soluble urea (1 g in 1 ml) and magnesium chloride (1g in 0.6 ml) remaining in solution. This result is in accordance with the fact that no Mg(II)–thiourea complexes are known in the literature. A similar explanation can be extended for the crystal growth reaction performed by the authors employing thiourea, urea and sodium chloride. In view of no chemical reaction between NaCl and thiourea (or urea) the least soluble of the three reagents namely thiourea fractionally crystallizes. Thus, the isolation of thiourea crystals by the authors of [1, 2] as their product not only explains the absence of the carbonyl (C=O moiethy) vibration in the IR spectra of both **1** and **2** but also their thermal stability. Had the authors calculated the yield of the product crystals they would have noted that the product yield is equal to or less than the amount of thiourea taken for crystal growth. However no such exercise was done. This is the importance of reporting the amount of reagents employed and yield of product obtained.

thiourea + urea + $[Mg(H_2O)_6]Cl_2$ → thiourea
and NOT
thiourea urea magnesium chloride (~~TUMC~~)

thiourea + urea + NaCl → thiourea
and NOT
urea thiourea sodium chloride (~~UTNC~~)

Fig. 1 – Crystal growth reactions resulting in fractional crystallization of thiourea

Reinvestigation of reported crystal growth reactions

In order to prove that fractional crystallization of thiourea does indeed take place, the crystal growth reactions were reinvestigated by dissolving thiourea, urea and the metal (Mg or Na) chloride in 1:1:1 ratio in water (For details see supplementary material). The product crystals thus isolated were subjected to qualitative analysis to check for the presence of chloride by the Lassaigne's test [15] and *s*-block metal by spot tests [16]. These tests showed absence of chloride, Mg and Na. The yield of the product crystal was always less than the amount of thiourea employed for the crystal growth. Infrared (IR) spectroscopy was employed for product confirmation as has been done for several NLO crystals recently [17-19]. The IR spectrum of both products coincided with that of pure thiourea unambiguously confirming the fractional crystallization of thiourea.

Conclusions:

The main conclusions are as follows: i)Any new compound should be represented by a proper chemical formula and not by arbitrary names like thiourea urea magnesium chloride and urea thiourea sodium chloride. ii) Codes like TUMC or UTNC cannot be substitutes for the chemical formula of any compound. iii) Formulating new compounds based on an assumption that a crystal grown from a mixture of precursor materials taken in a preferred ratio necessarily represents an expected compound (for example thiourea urea magnesium chloride or urea thiourea sodium chloride) is an unscientific method of product characterization as proved for the title compounds. iv)The fractional crystallization of thiourea reveals that the chlorides of magnesium and sodium do not exhibit any chemical reaction towards thiourea and urea in aqueous solution.

Acknowledgements:

BRS thanks Rita N Jyai for helpful discussions.

References

[1] Gopinath S, Barathan S, Rajasekaran R. Growth and studies of thiourea urea magnesium chloride (TUMC) single crystals, J Therm Anal Calorim 2012, 109:841–5.

[2] Gopinath S, Barathan S, Rajasekaran R. Growth and characterization of semiorganic crystal, J Therm Anal Calorim 2012, 110:789–92.

[3] Fleck M, Petrosyan AM. Difficulties in the growth and characterization of non-linear optical materials: A case study of salts of amino acids, J Cryst Growth. (2010) 312:2284-90.

[4] Srinivasan BR, Moovendaran K, Natarajan S. Comments on ‘‘Crystal growth, spectral, optical, and thermal characterization of glycyl-L-alanine hydrochloride (GLAH) single crystal’’ J Therm Anal Calorim http://dx.doi.org/10.1007/s10973-014-4164-x

[5] Baran J, Petrosyan AM. Comments on the Paper by R. Ezhil Vizhi et al. “Synthesis, Crystal Growth, Structural, Dielectric and Ferroelectric Properties of N-Acetyl Glycine Phosphite (AGPI) Single Crystals, Ferroelectrics. (2012) 432:117-8.

[6] Srinivasan BR. On the existence of *L*-alanine cadmium bromide. Spectrochim Acta. (2013) 116A:639-41.

[7] Petrosyan AM, Ghazaryan VV, Fleck M. On the existence of “bis-glycine maleate” J Cryst Growth (2012) 359:129-31.

[8] Srinivasan BR. Does an ‘*L*-arginine doped orthophosphoric acid’ crystal exist? J Lumin. (2014) 148: 370-72.

[9] Srinivasan BR. On the existence of ‘glycine barium nitrate potassium nitrate’ crystal, Optik. (2014) 125:3606-7.

[10] Petrosyan AM, Ghazaryan VV, Fleck M. On the existence of “*L*-threonine formate”, “*L*-alanine lithium chloride” and “bis *L*-alanine lithium chloride” crystals, Spectrochim Acta (2013) 105A:623-5.

[11] Bock CW, Kaufman A, Glusker JP. Coordination of water to magnesium cations, Inorg Chem 1994, 33:419-27.

[12] Boeyens JCA, Herbstein FH. Ionic Complexes of Thiourea. II. Chemical and Crystallographic Survey and Determination of the Crystal Structures of Some Representative Complexes, Inorg Chem (1967) 6:1408-25

[13] Pedrares AS, Teng W, Ruhlandt-Senge K. Syntheses and Structures of Magnesium Pyridine Thiolates–Model Compounds for Magnesium Binding in Photosystem I, Chem Eur J 2003, 9:2019-24.

[14] Srinivasan BR, Keerthika N. Reinvestigation of crystal growth of thiosemicarbazide potassium chloride and thiosemicarbazide lithium chloride, Optik 2014, 125:4807-9.

[15] Furniss B S, Hannaford A J, Rogers V, Smith PWG, Tatchell AR. Vogel’s Textbook of Practical organic Chemistry, 4th ed, London: ELBS / Longman, 1978. p 933-7.

[16] Svehla G, Vogel’s Qualitative Inorganic Analysis, 7th ed. New Delhi: Pearson, 2011. p164-7.

[17] Srinivasan BR, Jyai RN. Reinvestigation of growth of ‘*L*-valine zinc sulfate crystal’ Spectrochimica Acta, 2014, 120A:621-4.

[18] Srinivasan BR, Naik TA, Tylczyński Z, Priolkar KR. Reinvestigation of growth of thiourea urea zinc sulfate crystal, Spectrochimica Acta 2014, 117A:805-9.

[19] Natarajan S, Srinivasan BR, Moovendaran K. Reinvestigation of crystal growth of ‘*L*-proline succinate’ & ‘*L*-threonine zinc acetate’ showing use of IR spectra for product identification, J Crystallization Process & Technology 2014, 4:121-5.

Footnotes:

[1] Compounds are referred to by numbers to avoid use of non-standard abbreviations.