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Reinvestigation of crystal growth of thiosemicarbazide potassium chloride and thiosemicarbazide lithium chloride

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Abstract

Reinvestigation of the growth of thiosemicarbazide potassium chloride crystal (**1**) (J. Chandrasekaran, P. Ilayabarathi, P. Maadeswaran, S. Balaprabhakaran, K. Sathishkumar, B. Babu, Synthesis, crystal growth and characterization of a semiorganic material: Thiosemicarbazide potassium chloride, Optik 124 (2013) 31–34) and thiosemicarbazide lithium chloride crystal (**2**) (P. Maadeswaran, J. Chandrasekaran, S. Thirumalairajan, Synthesis, growth, spectral, thermal and photoluminescence properties of a new semiorganic NLO crystal — Thiosemicarbazide lithium chloride [TSLC] Optik 122 (2011) 259-262), unambiguously confirms that compounds **1** and **2** are pure thiosemicarbazide and do not contain any alkali metal or chloride ions. In this paper we demonstrate the use of classical halide test, flame test, as well as infrared (IR) spectra for correct product characterization.

Keywords: thiosemicarbazide; potassium chloride; lithium chloride; thiosemicarbazide potassium chloride; thiosemicarbazide lithium chloride; improper characterization.

1. Introduction

In the frontier area of non-linear optical (NLO) materials new non-centrosymmetric solids are being studied by several researchers for their material characteristics especially the optical properties. In such a study, the primary requirement is to unambiguously characterize the solid being studied in terms of its molecular formula and structure. However, this aspect is not taken into consideration by some research groups resulting in the publication of papers

reporting improperly characterized compounds under the name new nonlinear optical (NLO) crystals [1,2]. Based on a case study of salts of amino acids Fleck and Petrosyan [3] had shown that several amino acid based compounds reported as novel NLO materials are not actually novel but in most cases the amino acid itself. A survey of the literature reveals that improper characterization of the so called 'NLO' materials compounds is not limited to amino acid based compounds but to many other groups of compounds both inorganic and organic crystals [4-11]. Recently our group had shown that from the urea / thiosemicarbazide / water system no new compound can be isolated excepting the less soluble thiosemicarbazide as the only product due to its fractional crystallization [11].

In a recent paper, Chandrasekaran *et al* [1] have reported the growth of a so called thiosemicarbazide potassium chloride crystal **1** by the slow evaporation solution growth technique from water at ambient temperature. Compound **1** represented by the formula $K(NH_2\text{-}NH\text{-}CS\text{-}NH_2)Cl$ was abbreviated as TSCPC. We noted that the IR spectrum of **1** was identical to that of an earlier crystal namely thiosemicarbazide lithium chloride **2** represented by the formula $Li(NH_2\text{-}NH\text{-}CS\text{-}NH_2)_2Cl$ abbreviated as TSLC reported by the same group [2]. Both **1** and **2** were characterized by only IR spectra and X-ray powder pattern. It is not clear as to why a Li compound containing two thiosemicarbazide molecules is called as thiosemicarbazide lithium chloride, which is very same as the name thiosemicarbazide potassium chloride containing a single thiosemicarbazide in its formula. Such names as well as the strange abbreviations are very unusual and not in accordance with accepted chemical nomenclature. In view of this, compounds are represented by numbers **1** and **2** throughout this paper to avoid use of non-standard abbreviations like TSCPC and TSLC. It is well documented that the *s*-block metal ions are oxophilic in nature and a larger metal like K prefers a higher coordination number namely six unlike the lighter element lithium which prefers a coordination number of four. Hence the claim of growth of crystals of Li and K

containing a neutral S-donor ligand like thiosemicarbazide namely **1** and **2** appeared unacceptable. The assignment of C-Cl vibrations for compounds **1** and **2** which do not contain any C-Cl unit with the Cl shown as an anion in the formula, further indicated the dubious nature of the claims. Hence, we have reinvestigated the reported crystal growth reactions and we demonstrate the use of the classical halide test for correct product identification. The details are described in this paper.

2. Experimental

2.1. 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}.

*2.2 Reinvestigation of crystal growth of **1** and **2***

Potassium chloride (0.745 g, 10 mmol) and thiosemicarbazide (0.910 g, 10 mmol) were taken and dissolved in distilled water (~40 ml). The reaction mixture was stirred well to get a clear solution. The solution was filtered and the clear filtrate was left undisturbed at room temperature. Slow evaporation of the solvent resulted in the formation of transparent crystals after two to three days which were isolated by filtration, washed with little ice cold water and dried in air to get 0.690 g of crystalline product. These crystals were labeled as **1**. The use of LiCl (0.4239 g, 20 mmol) and thiosemicarbazide (1.82 g, 20 mmol) in the above crystal growth reaction resulted in the formation of transparent crystals (1.630 g) which were isolated by following the same procedure as for **1**. These crystals were labeled as **2**.

3. Results and Discussion

In this study, reported crystal growth reactions of thiosemicarbazide with KCl [1] or LiCl [2] have been reinvestigated to unambiguously characterize the crystalline product (Scheme 1). The grown crystals are referred to as compounds **1** and **2** respectively and were subjected to qualitative analytical tests to check for the presence of chloride by the Lassaigne's test [12] and alkali metal by flame test [13]. As the compound under study contains thiosemicarbazide an organic compound, the protocol given in Vogel's textbook of practical organic chemistry [12] was employed for performing the Lassaigne's test to check for the presence of chloride. In order to validate the test, two reference samples (~10 mg) namely pure thiosemicarbazide and an artificial 1:1 mixture of thiosemicarbazide and sodium chloride were first checked for the presence of chloride. For the reference compounds, a negative test and a positive test respectively were observed. The test clearly indicated the absence of any chloride in **1** and **2**. The flame test for the presence of K (or Li) was also found to be negative by the absence of characteristic lilac violet (or carmine red) flame colour. Instead the observation of a sooty flame indicated that **1** (or **2**) is a pure organic compound.

In order to determine the exact nature of **1** and **2**, IR spectroscopy was employed as a characterization tool. Both compounds exhibited identical IR spectra which in turn were coincident with that of pure thiosemicarbazide (Fig. 1) clearly showing that compounds **1** and **2** are nothing but pure thiosemicarbazide, which can also account for the negative tests for chloride and the alkali metals. This observation can be easily explained due to the fractional crystallization of thiosemicarbazide in both the crystal growth reactions depicted in Scheme 1. Both reactants used for crystal growth of **1** (or **2**) are water soluble but the less soluble (85 g / L) thiosemicarbazide crystallizes first, with the very highly soluble KCl (or LiCl) remaining in solution. Since the assignment of bands in the IR spectrum of thiosemicarbazide

is reported in the literature [14] and IR spectroscopy has been used as a characterization tool, no further discussion of the IR spectrum is presented.

$$KCl + (NH_2–CS–NH–NH_2) \xrightarrow{H_2O} NH_2–CS–NH–NH_2 \quad \text{... (1)}$$

(thiosemicarbazide)

and NOT

$K(NH_2–CS–NH–NH_2)Cl$

(thiosemicarbazide potassium chloride)

$$LiCl + 2\,(NH_2–CS–NH–NH_2) \xrightarrow{H_2O} NH_2–CS–NH–NH_2 \quad \text{... (2)}$$

and NOT

$Li(NH_2–NH–CS–NH_2)_2Cl$

(thiosemicarbazide lithium chloride)

Scheme 1

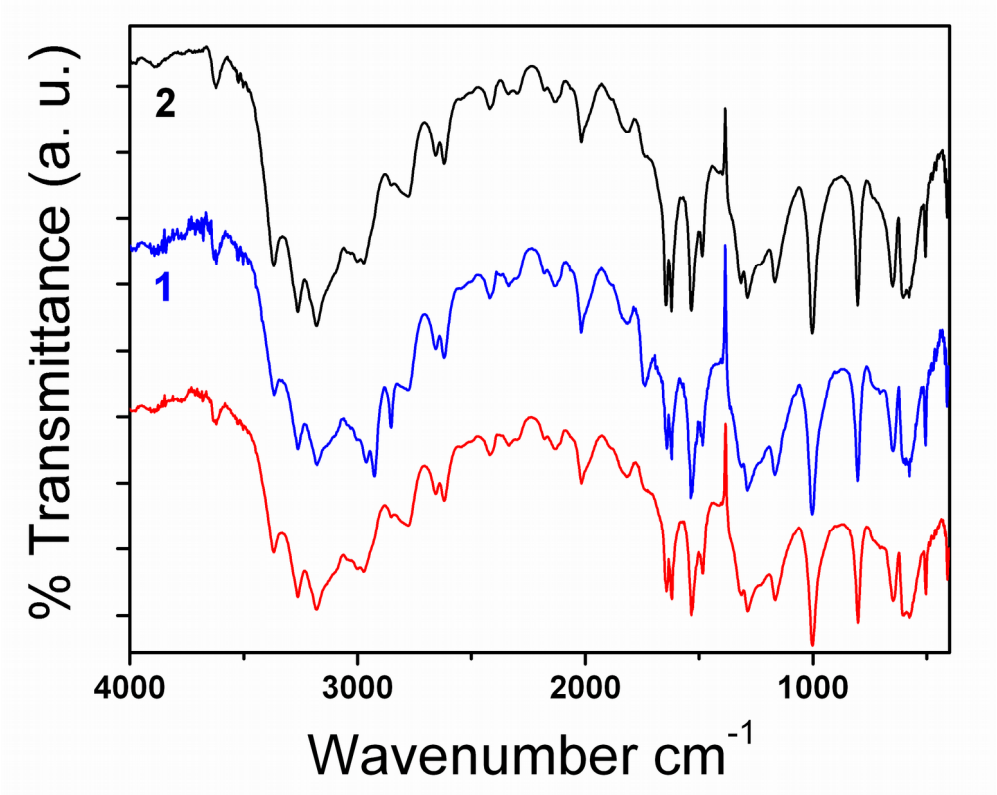

Fig.1. The IR spectra of pure thiosemicarbazide (bottom) compound **(1)** middle and compound (**2**) (top).

In order to confirm unambiguously, more batches of crystals of **1** and **2** were checked and in all cases the IR spectra were identical to that of thiosemicarbazide indicating that the product formed in the crystal growth reactions (Scheme 1) is always thiosemicarbazide, which was further corroborated by the negative tests for halide and alkali metal. The use of a large excess of thiosemicarbazide also did not result in any new product containing any chloride and in all these cases only thiosemicarbazide fractionally crystallizes and the presence of KCl or LiCl does not inhibit the crystallization of thiosemicarbazide. This result is not surprising at all but in accordance with the well-known chemistry of *s*-block metal ions like Li and K, which do not prefer to bind to a neutral S-donor ligand like thiosemicarbazide.

Formation of pure thiosemicarbazide as the only product was further confirmed by the melting point of **1** or **2** (180-181 ^{o}C) which is same as that of thiosemicarbazide. As it is well documented that thiosemicarbazide crystallizes in the centrosymmetric triclinic $P\bar{1}$ space group [11], it should not show any SHG signal. However, for so called thiosemicarbazide lithium chloride which is actually thiosemicarbazide the authors of [2] have reported a SHG response and we do not agree with this claim. In order to verify this, crystals of **1** and **2** were checked for their phase purity by X-ray powder pattern. The powder pattern of **1** and **2** were identical as expected and matched perfectly with that of pure thiosemicarbazide clearly indicating that its crystallization in the presence of KCl or LiCl did not result in the formation of any polymorphic modifications.

Crystals of another alkali metal compound namely *L*-asparagine potassium chloride (**3**) $K(C_4H_8N_2O_3{\cdot}H_2O)_2Cl$ are claimed to have been grown by slow evaporation solution growth technique by the same group of authors [15], from an aqueous solution containing *L*-asparagine and potassium chloride in 2:1 mole ratio. Although it is not clear as to why a compound with a proposed formula containing two *L*-asparagine molecules and two molecules of water is called as *L*-asparagine potassium chloride, a scrutiny of the reported

results especially the elemental analytical data clearly indicates that the grown crystal **3** cannot contain any K. Based on the coincidence of the reported IR spectrum of **3** with *L*-asparagine monohydrate, this crystal can be correctly formulated as pure *L*-asparagine monohydrate. The arguments recently described for the improper characterization of *L*-asparagine cadmium chloride [16] are equally applicable in this case.

In all the three above mentioned cases, it is noted that the product crystal obtained is not a novel material as claimed by the authors of these reports [1, 2, 15] but one of the starting materials namely thiosemicarbazide in the case of **1** and **2** and *L*-asparagine monohydrate for **3**. Several such instances of reporting of known compounds (or starting materials) as a novel NLO material have been critically commented [3-7, 11] in the literature. The frequent reporting of improperly characterized compounds as novel NLO materials, calls for a more careful scrutiny of papers reporting growth of NLO crystals without any single crystal X-ray structure evidence.

Conclusions:

In this report we have correctly formulated the products of crystal growth reactions of alkali metal compounds reported by the group of Chandrasekaran [1, 2, 14]. In all the examples discussed in this paper, the authors have not taken into account the chemistry of the reagents used in the crystal growth study. We have demonstrated the use of classical halide test, flame test, as well as infrared (IR) spectra for correct product characterization. This report once again highlights the fact that 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 is an unscientific method of product characterization.

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Footnotes:

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