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Short Communication

Reinvestigation of growth of 'L-valine zinc sulphate' crystal

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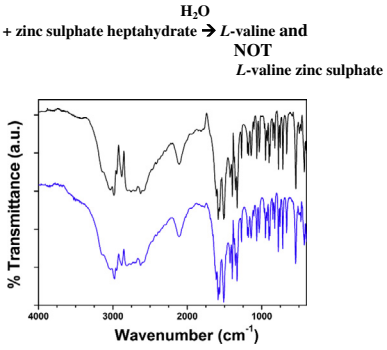
HIGHLIGHTS

- Growth of L-valine zinc sulphate crystal is reinvestigated.
- Earlier reported L-valine zinc sulphate crystal is actually L-valine.
- $ZnSO_4 \cdot 7H_2O$ does not show any chemical reaction towards L-valine.
- $ZnSO_4 \cdot 7H_2O$ does not inhibit crystal growth of L-Valine.

GRAPHICAL ABSTRACT



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ABSTRACT

A reinvestigation of the growth of L-valine zinc sulphate crystal is reported. The slow evaporation of an aqueous solution containing L-valine and zinc sulphate heptahydrate results in the fractional crystallization of L-valine and not the organic inorganic hybrid nonlinear optical L-valine zinc sulphate crystal, as reported by Puhal Raj and Ramachandra Raja (2012).

Introduction

An extensive biochemistry of zinc has been developed and it is now well recognized that zinc is a key element of life [1–3]. The coordination compounds of zinc, especially the zinc-amino acid chelates, find application in medicine and nutrition [4,5]. In addition to the biological relevance, zinc complexes of the naturally occurring chiral amino acids are of interest in view of their possible nonlinear optical (NLO) behavior. Many examples of structurally characterized amino-acid compounds of zinc [6–12] including a five coordinated Zn(II) compound namely $[Zn(val)_2(H_2O)]$ (val = L-valinate) obtained by the reaction of zinc sulfate with L-valine and NaOH in a 1:2:2 mol ratio are well documented. Although a thermochemical study of a zinc compound of composition $[Zn(valH)SO_4 \cdot H_2O]$ (valH = L-valine) has been reported [13], no structural details were given.

A recent paper describes the slow evaporation solution growth of a so called nonlinear optical (NLO) organic inorganic hybrid crystal L-valine zinc sulphate (**1**) having formula $C_5H_{11}NO_2ZnSO_4 \cdot 7H_2O$ and abbreviated by a strange code namely LVZS [14]. Although it is not clear why a compound with seven molecules of water in its formula was named as L-valine zinc sulphate, this compound is referred to as compound **1** in this paper, to avoid use of the non-standard abbreviation LVZS. Another paper also describes the growth of a crystal with the same name L-valine zinc sulphate but without any

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chemical formula or the code LVZS [15]. In both these papers, the details pertaining to crystal growth in terms of amounts of reagents taken and the yield of product crystal are not available. Although the authors of both papers [14,15] claim to have performed a single crystal structure determination no structural details of **1** (for example the coordination sphere of zinc) were reported. The authors have not substantiated the claim of their single crystal work with a CIF file. Based on a comparison of the unit cell data of the starting materials, L-valine [16], $ZnSO_4{\cdot}7H_2O$ [17] with the unit cell data of **1**, the authors of [14] made a remarkable conclusion, '*A notable increase in cell volume strongly recommends the presence of both molecules* (L-*valine and zinc sulphate*) *within the unit cell*'. Such a finding cannot be considered as an acceptable result of a single crystal structure determination. Instead of providing the structural features of the zinc site based on their single crystal exercise, the authors state '*SHG test confirmed the bonding between* L-*valine and zinc sulphate increases its NLO efficiency*'. In spectral discussion, the authors reported '*Slight variations are observed in frequencies of C–C bond* (L-*valine*) *is due to mixing of zinc sulphate heptahydrate*'. The above statements reveal that **1** is an improperly characterized compound. In view of this and also the possible importance of zinc(II) amino acid compounds in biological applications, a reinvestigation of the reported crystal growth of L-valine zinc sulphate [14] has been undertaken in this study, in order to establish the correct identity of the so called L-valine zinc sulphate.

Materials and methods

Chemicals used in this study were purchased from commercial sources and were used as received without any further purification. Double distilled water was used as solvent. Infrared (IR) 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 NMR spectra were recorded (in D_2O) using a Bruker 400 MHz (Avance) FT-NMR spectrometer. X-ray powder pattern were recorded on a Rigaku Miniflex II powder diffractometer using Cu Kα radiation with a Ni-filter. Optical rotation of the crystals dissolved in water, were measured in a Rudolph research analytical (Autopol IV) polarimeter.

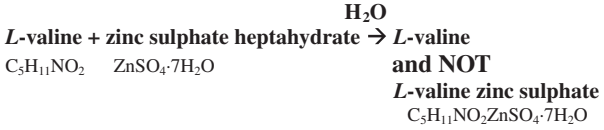
Reinvestigation of crystal growth of L-*valine zinc sulphate* **1**

A mixture of zinc sulphate heptahydrate (1.438 g, 5 mmol) and L-valine (0.586 g, 5 mmol) was taken in water ~25 ml and the reaction mixture was stirred well to obtain a clear colorless solution. The clear reaction mixture (pH ~4.5) was left undisturbed at room temperature. Slow evaporation of the solvent resulted in the separation of transparent crystals, which were isolated by filtration and dried in air to yield 0.45 g of crystalline product labeled as **1**. In addition, we investigated crystal growth reaction by taking L-valine (0.586 g, 5 mmol) and zinc sulphate heptahydrate (0.144 g, 0.5 mmol) in a 10:1 mol ratio and the crystalline product from this experiment was isolated as before. We performed one more crystal growth experiment by employing a large excess of zinc sulphate heptahydrate (10 mmol) and L-valine (1 mmol) and the crystalline product from this experiment was isolated and analysed.

Results and discussion

Synthetic aspects of crystal growth and spectral characterization

The recently reported growth of L-valine zinc sulphate crystal [14] is reinvestigated in order to unambiguously characterize the crystalline product. For the system L-valine/Zn(II)/water, the authors report that from an aqueous solution containing L-valine and zinc sulphate heptahydrate in a 10:1 mol ratio, 10 mm long crystals of **1** having formula $C_5H_{11}NO_2ZnSO_4{\cdot}7H_2O$ could be grown but did not mention the reason for use of a tenfold excess of L-valine for crystal growth of this so called nonlinear optical (NLO) organic inorganic hybrid **1**. In this work, we have investigated crystal growth reactions using (i) equimolar quantities of L-valine and $ZnSO_4{\cdot}7H_2O$ in view of the formula of **1** (Scheme 1) (ii) a crystal growth reaction using a tenfold excess of L-valine and (iii) a crystal growth reaction employing a tenfold excess of zinc sulphate heptahydrate. The products obtained in the first two crystal growth experiments involving equimolar quantities and large excess of L-valine were the same as evidenced by their identical IR spectra and the spectra were coincident with that of the spectrum of pure L-valine (Fig. 1) as evidenced by a comparative study of the infrared spectra of pure $ZnSO_4{\cdot}7H_2O$, pure L-valine and an artificial mixture of $ZnSO_4{\cdot}7H_2O$ and L-valine (Figs. S1–S4). The IR spectrum of the crystals of **1** is in good agreement with the spectrum reported for L-valine by the Natarajan group [16]. Since L-valine is a known compound and its spectrum is reported in the literature [16] and IR spectroscopy is used as a characterization tool to infer new product formation, no discussion of the IR spectrum and band assignment is presented here. In contrast, the IR spectrum of the crystals isolated from the crystal growth reaction using a large excess of $ZnSO_4{\cdot}7H_2O$ coincides with that of pure zinc sulphate hepthahydrate (Fig. S5) showing no incorporation of L-valine in the product. This was further confirmed by the presence of zinc and sulphate with the aid of standard qualitative spot tests [18]. It is noted that the IR spectrum and the TG thermogram reported in [14] can be better explained as belonging to a sample whose major composition is $ZnSO_4{\cdot}7H_2O$. It is not clear as to how the authors of [14] managed to get such an IR spectrum after performing a crystal growth reaction using L-valine: $ZnSO_4{\cdot}7H_2O$ in a 10:1 mol ratio. This only indicates that the details reported in the paper [14] and the actual experimental conditions were not the same.



Scheme 1.

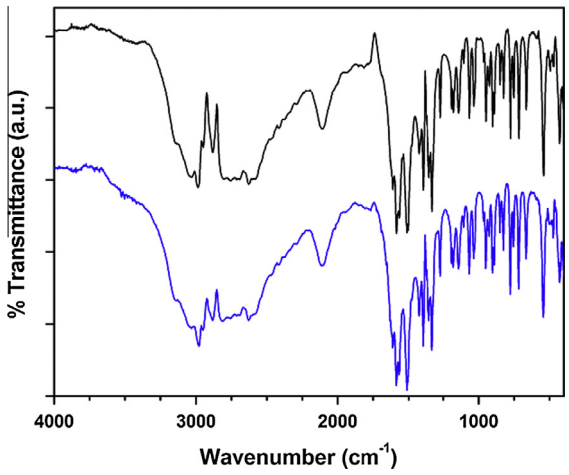


Fig. 1. IR spectral comparison reveals that L-valine (top) and the so called L-valine zinc sulfate (**1**) (bottom) are one and the same.