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Comments on the growth of '*L*-threonine phthalate', '*L*-threonine phosphate', '*L*-threonine formate' and '*L*-threonine diformate' crystals

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Abstract

It is proved that the recently reported '*L*-threonine phthalate' (Theras et al. Optik 127 (2016) 3397-3401) '*L*-threonine phosphate' (Chinnappan et al. Optik 126 (2015) 5517-5521) '*L*-threonine formate' (Hanumantharao & Kalainathan, Optik 124 (2013) 2204-2209) and '*L*-threonine diformate' (Viju et al, Optik 125 (2014) 5926-5928) are dubious crystals. Taking the title crystals as examples the importance of nomenclature of nonlinear optical crystals is highlighted.

Keywords: *L*-threonine phthalate; *L*-threoninium cation; *L*-threonine phosphate; *L*-threonine formate; *L*-threonine diformate;

Introduction

A recently published paper [1] reporting growth of a so called '*L*-threonine phthalate' crystal attracted my attention in view of an unusual name for a solid crystalline material. It is well known that the zwitter ionic amino acid *L*-threonine is a neutral molecule, while phthalate is the dianion of phthalic acid. Hence the claim of having grown a crystal with the name *L*-threonine phthalate indicated that the crystal cannot be a charge imbalanced solid as suggested by its name but an improperly characterized crystal with an incorrect name instead of a scientifically acceptable name viz. bis(*L*-threoninium) phthalate or *L*-threoninium hydrogen phthalate. A perusal of the contents of the publication revealed that the paper is fundamentally wrong warranting the following comment on *L*-threonine phthalate and three more similar charge imbalanced crystals namely *L*-threonine phosphate [2], *L*-threonine formate [3] and *L*-threonine formate [4]. The purpose of the present communication is to ensure that the erroneous papers [1-4] on the four *L*-threonine based dubious crystals do not form the basis for further erroneous papers as shown recently by Petrosyan and Srinivasan [5] and in addition to highlight the importance of nomenclature of solids.

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Comment

The authors of the commented papers characterized the title crystals based on an incorrect assumption that reaction of *L*-threonine with phthalic acid (or phosphoric acid or formic acid) will result in the formation of so called *L*-threonine phthalate, *L*-threonine phosphate, *L*-threonine formate and '*L*-threonine formate crystal but not based on a scientific interpretation of the experimental data. For all the title crystals, no quantities of reagents employed for crystal growth and the yield of product obtained are reported in the commented papers. The names of all the title crystals indicate that they are charge imbalanced crystals containing free anions like phthalate or phosphate or formate without any positive charge on *L*-threonine and hence wrong. A positively charged *L*-threonine is to be called *L*-threoninium since the positive charge will be present on the N atom of the amine group. A scrutiny of the results reveals that none of the compounds contain either a *L*-threoninium species or phthalate, phosphate, formate as shown below.

L-threonine phthalate

The authors claim to have obtained a so called "*L*-threonine phthalate" LTP crystal by slow evaporation of a solution containing equimolar quantities of *L*-threonine and phthalic acid in mixed methanol-acetic acid solvent, and already have published another paper on "*L*-threonine phthalate" which has been commented [6]. The authors were unaware that a phthalate is formed by the reaction of phtahlic acid with a base. The crystal growth medium was acidic due to use of acetic acid thus ruling out formation of any phthalate containing product. According to authors single crystal X-ray diffraction study showed that the '*L*-threonine phthalate' crystal has centrosymmetric *C*2/c space group. The assignment of the C2/c space group for a solid supposed to contain a chiral amino acid confirms beyond doubt that '*L*-threonine phthalate' is a dubious crystal. Although it is not clear why the authors repeated their incorrect single crystal result in a second paper, it is obvious they did not compare the unit cell parameters with those of phthalic acid (Table 1). Had they done, they would have easily noted that their unit cell is in excellent agreement with that of phthalic acid [7].

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Table 1. Crystallographic data of L-threonine, L-threonine phthalate (LTP 1), L-threonine phosphate (LTP 2), L-threonine diformate (LTDF) and phthalic acid [**]

Compound	Crystal System	*Space group*	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	Ref
Phthalic acid	Monoclinic	*C2/c**	5.0698(4)	14.3178(4)	9.6305(5)	93.260(4)	7
LTP 1	Monoclinic[#]	*C2/c*[#]	5. 09	14.40	9.67	93.16	1
L-threonine	Orthorhombic	$P2_12_12_1$*	13.611	7.738(2)	5.142	90.0	8
LTP 2	Orthorhombic	*P*[#]	5.159	7.759	13.659	90.0	2
LTDF	monoclinic	--[#]	5.1447	13.6104	7.745	§	4

*Space group from structure determination; # No CIF file available; [§]No β reported but V = 542.3224 Å^3

L-threonine phosphate

The authors claim to have obtained a so called '*L*-threonine phosphate' (LTP) crystal by slow evaporation of a solution containing appropriate amounts of *L*-threonine and *ortho*-phosphoric acid acid [2]. Although the name indicates that the crystal is a phosphate salt of *L*-threonine, the reported structure given in the commented paper actually indicates it to be a phosphate ester viz. 2-amino-(3-phosphonooxy) butanoic acid obtained by the coupling the –OH group on the C2 of *L*-threonine with H_3PO_4. The dubious nature of this '*L*-threonine phosphate' can be evidenced from the strange orthorhombic space group *P* reported by the authors in the single crystal study. A closer examination of the unit cell data reveals the true identity of this LTP crystal as L-threonine in view of the good agreement of the cell [8] but for an interchanged cell axes.

L-threonine formate and L-threonine diformate

The authors of [3] claim to have grown a so called novel nonlinear optical *L*-threonine formate (LTF) crystal by using *L*-threonine and formic acid in equal ratios according to the following reaction.

$$C_4H_9NO_3 + H\text{-}COOH \rightarrow C_5H_9NO_4$$

The authors believe that the crystal growth involving loss of a water molecule (dehydration) could be performed in aqueous medium and already wrote two papers on this LTF crystal, both of which were commented by Petrosyan et al [9] who convincingly proved that the LTF is *L*-threonine. It is not clear why these authors claimed that LTF as a novel crystal in a third paper. It is unfortunate to mention that a substantial part of [3] is essentially from their earlier papers already commented. A similar undesirable practice by the same group has already been pointed out in the case of a so called 1-(4-fluorostyryl)-4-nitrostilbene [10].

According to authors of [4] '*The L-threonine diformate (LTDF) was synthesized from L-threonine and formic acid in the stoichiometric ratio of 1:2*'. Although the authors claim that LTDF is a monoclinic crystal no monoclinic angle β as well as a CIF file was reported. Interestingly the unit cell volume indicates that the angle β is 90^o indicating that the cell is orthorhombic. A scrutiny of the cell reveals that LTDF is *L*-threonine but for an intercahnged cell axes. The isolation of the starting reagent clearly reveals that there is no chemical reaction between *L*-threonine and formic acid due to which *L*-threonine is isolated and formic acid (being a liquid) stays in the aqueous medium.

The above mentioned discussions clearly prove that no crystal containing any anion like phthalate, phosphate or formate was grown by the authors of [1-4]. The crystals are not charge imbalanced as the name suggested. The product solid in each commented paper is one of the starting materials and all these papers are erroneous starting from the name of the crystals. Thus in addition to proving that the title compounds (all based on *L*-threonine) are dubious crystals, the present comment highlights the importance of proper nomenclature for crystalline solids.

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