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‘Urea oxalic acid’ is not parabanic acid

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Abstract

We prove that the recently published “urea oxalic acid” is not parabanic acid but is in fact the well-known bis-urea oxalic acid. Hence the paper by Jeeva *et al.* (Chin. J. Phys. 56 (2018) 1449-1466) is completely erroneous.

Keywords: *urea oxalic acid; parabanic acid; improper characterization; misinterpretation; dubious crystal*

Highlights

- Urea oxalic acid (UOA) is not a non-centrosymmetric crystal.
- Urea oxalic acid is not parabanic acid.
- Parabanic acid can never be prepared from aqueous solution of urea and oxalic acid.

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Graphical abstract

Slow evaporation of an aqueous solution containing equimolar amounts of urea and oxalic acid does not result in dehydration to provide parabanic acid or oxalylurea.

Urea + oxalic acid → bis-urea oxalic acid
NOT
~~parabanic acid~~

Introduction

The purpose of writing the present comment is to prove unambiguously that a recently published report on “urea oxalic acid” [1] is completely erroneous. In a very early paper Dalman [2] studied the urea-oxalic acid-water solubility diagram and demonstrated that in addition to the previously known compound bis-urea oxalic acid (2:1) which is readily formed, a mono-urea oxalic acid (1:1) adduct having incongruent solubility can also exist in this system. The urea adducts of oxalic acid are generally referred to as urea oxalic acid (2:1) (I) and urea-oxalic acid (1/1) (II) and their crystal structures were determined by Harkema et al. [3, 4]. Both (I) and (II) crystallize in centrosymmetric structures. The space group and unit cell parameters are as follows: $P2_1/c$; $a=5.110(3)$ Å, $b=12.400(3)$ Å, $c=7.035(2)$ Å, $\beta=98.13(7)^\circ$, $Z=4$ for (I). $C2/c$; $a=13.0625(7)$ Å, $b=6.6437(2)$ Å, $c=6.8478(3)$ Å, $\beta=92.474(6)^\circ$, $Z=4$ for (II). The authors of

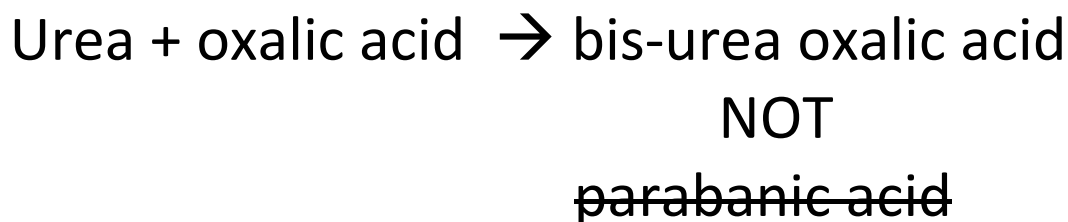
[5-7] claimed ferroelectric properties for “urea oxalic acid” crystals. In their papers on “urea oxalic acid” the authors actually were referring to bis-urea oxalic acid namely the 2:1 compound. In a mini review [8] we have proved that the papers [5-7] are erroneous. If the erroneous claims in [1] are not brought to the attention of the scientific community, then the paper by Jeeva et al [1] can become the basis of subsequent erroneous publications, like the recently commented papers [5-7]. In view of this, we prove that paper [1] is completely erroneous in the following discussion.

Comments

From the title of the paper [1] it appears that the authors are reporting on the (1/1) compound namely mono-urea oxalic acid adduct. However, the first line of the abstract “A *non-centro symmetric single crystal of Urea Oxalic acid (UOA) has been grown from aqueous solution*” indicates that the authors are dealing with an altogether new polymorphic modification. In the abstract the authors further reported, “*Single crystal X-ray diffraction (SXRD) evinces UOA corresponding to the triclinic system with the space group P*”. This does not appear to be a typographic error, since this is found in the text twice more (Section 3.1 and Table 1). In the introduction of their work, the authors reported: “*The title compound has been reported earlier by Chithambaram et al and Ezhil Vizhi et al in the ratio (2:1) of UOA [13,14]*”, where the citations “[13, 14]” are presently [5,6]. Thus, the authors consider that the obtained crystal is identical to those obtained in [5,6], and is the 2:1 adduct namely the bis-urea oxalic acid. In the section on Materials synthesis, the authors claimed without any substantiation and literature citations that from an aqueous solution of urea + oxalic acid in 1:1 ratio, parabanic acid (also known as oxalylurea) can be obtained as a result of a dehydration reaction, with the removal of two water molecules. The authors reported cell parameters ($a=5.204 \text{ \AA}$, $b=7.20 \text{ \AA}$, $c=12.30 \text{ \AA}$, $\alpha=89.23^\circ$, $\beta=88.86^\circ$, $\gamma=79.19^\circ$), but did not compare these parameters with those of parabanic acid [9] (space group $P2_1/n$; $a=10.685(1) \text{ \AA}$, $b=8.194(1) \text{ \AA}$, $c=5.054(1) \text{ \AA}$, $\beta=92.73(3)^\circ$, $Z=4$). Instead the authors declared: “*The unit cell parameters accord with the reported work [14]*”, where “[14]” is [6], and the provided unit cell parameters coincide with those of [5].

In the above circumstances, the authors should have determined the structure of the obtained crystal [10]. Instead, they provided the infrared and Raman spectra. However, the interpretation is contradictory. Although the authors reported: “*The clarification on the IR absorption reports of synthesized Urea with Oxalic acid is well understood in the previous literature [14]*”, the spectra were interpreted assuming the obtained crystal to be parabanic acid. In doing so, some absorption bands and Raman-lines were ignored. The authors provided thermogravimetric and DSC curves, which were wrongly interpreted. They consider that the effects on DSC curve are exothermic. Moreover, the authors consider that melting can be an exothermic process. Perhaps the impact of [5] has affected, where it is also reported that “... *a sharp exothermic peak at 180 °C shows the melting point of the crystal*”. For the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves reported in [5], the caption reads “*TG/DTA spectrum of the grown crystals*”.

Considering the issue as to what material was actually obtained in [1], first of all we can say that it cannot be parabanic acid, as it can never be obtained from aqueous solution by simple mixing of urea and oxalic acid. So, all results of calculations on parabanic acid do not relate in any way to the crystal obtained in [1]. Also, it is not the mono-urea oxalic acid (II) because (II) has incongruent solubility and cannot be obtained at room temperature by evaporation from an aqueous solution containing urea and oxalic acid in 1:1 molar ratio. The conditions of preparation of (II) at 40 °C are given in [2]. The only possible compound in the system urea-oxalic acid-water under slow evaporation is bis-urea oxalic acid (I) (Scheme 1). So, we consider that the so called “urea oxalic acid” obtained in [1] is bis-urea oxalic acid, which can be confirmed by the reported infrared spectrum and thermal curves. Obviously the choice of the triclinic system instead of the monoclinic was erroneous. Attention is to be paid to the closeness of the values of unit cell parameters a , b , c of “urea oxalic acid” (a to a , b to c and c to b) with the values of (I) [3] (*vide supra*) which supports formation of (I) for the crystal growth reaction in Scheme 1.



Scheme 1: Product of slow evaporation of aqueous solution of 1:1 urea and oxalic acid

Conclusion

The above critical analysis allows us to conclude that the crystal "urea oxalic acid" obtained in [1] is neither mono-urea oxalic acid (**II**) nor parabanic acid, but is bis-urea oxalic acid (**I**).

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