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On the existence of "potassium *para*-nitrophenolate dihydrate"

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Abstract

The author of a paper titled, "Growth, optical, mechanical and electrical studies of nonlinear optical single crystal: potassium *para*-nitrophenolate dihydrate" in *Science Postprint* (2014) (http://www.spp-j.com/spp/1-1/spp.2014.07A0001/) reports to have grown a nonlinear optical (NLO) single crystal namely potassium *para*-nitrophenolate dihydrate 1 by the slow evaporation technique. Many points of criticism, concerning the crystal growth and characterization of this so called NLO crystal, are highlighted in this comment to show that the paper reporting this crystal is completely erroneous.

Keywords: crystal growth, slow evaporation, nonlinear optical, *para*-nitrophenol, potassium, dubious crystal.

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Introduction

Para-Nitrophenol also known as 4-nitrophenol (4NP) having chemical formula ($C_6H_5NO_3$) exhibits polymorphism [1]. The acidic character of the phenolic proton of 4NP has been investigated by studying its reaction with a variety of reagents. This research has resulted in the structural characterization of several new compounds containing the 4-nitrophenolate $(C_6H_4NO_3)^-$ anion. Examples of 4NP based solids crystallizing in non-centrosymmetric as well as centrosymmetric space groups are well documented in the literature [2–13]. Of the many 4-nitrophenolate ($4NP^-$) salts, the sodium (Na) and potassium (K) salts viz. $Na^+(4NP^-)\cdot 2H_2O$ [2], and $K^+(4NP^-)\cdot H_2O$ [11] obtained by the reaction of 4NP with NaOH (or KOH) deserve special mention. It is interesting to note that the $Na^+(4NP^-)\cdot 2H_2O$ crystallizes in the non-centrosymmetric *Ima*2 space group while potassium 4-nitrophenolate monohydrate $K^+(4NP^-)\cdot H_2O$ (molecular formula = $[K(C_6H_4NO_3)H_2O]$) crystallizes in the centrosymmetric $P2_1/c$ space group. No structurally characterized potassium compound of 4NP other than $[K(C_6H_4NO_3)H_2O]$ is available in the Cambridge Crystallographic Data Centre (CCDC) database till date. Hence the paper entitled, "Growth, optical, mechanical and electrical studies of nonlinear optical single crystal: potassium *para*-nitrophenolate dihydrate" [14] (title paper hereinafter) claiming growth of a nonlinear optical (NLO) crystal namely potassium *para*-nitrophenolate dihydrate **1** by the slow evaporation technique attracted my attention and has been taken up for discussion in the following comment. In this paper, the title crystal is referred to as compound **1**.

Comment

The author of the title paper [14] claims to have grown a so called potassium *para*-nitrophenolate dihydrate **1** crystal by the slow evaporation of an aqueous solution containing KOH and 4-nitrophenol (4NP) in equimolar ratios. No quantities of reagents and solvent employed for crystal growth and the yield of product crystal **1** is given. It is also not clear why this method of crystal growth involving the reaction of equimolar amounts of KOH and 4NP should result in the formation of a dihydrate and not the potassium 4-nitrophenolate monohydrate $[K(C_6H_4NO_3)H_2O]$ obtained by Andersen et al [11] who also used the same method. Unfortunately the author of the title paper is not aware of the existence of the monohydrate $[K(C_6H_4NO_3)H_2O]$ as the work of Andersen et al. [11] is not cited. No elemental analytical data (for C, H and N), or spectra (IR or NMR) has been reported for **1**. Although the author claims to have employed methods like single crystal and powder X-ray diffraction for product characterization, no CIF file is available to substantiate the single crystal study. It is also noted that no molecular formula of **1** is given in the entire paper in spite of a single crystal study. However under the discussion for single crystal XRD the author states "*The asymmetric unit of the crystal shows two water molecules, one nitrophenolate moiety and another potassium atom and nitrophenol moiety. The water, nitrophenolate and nitrophenol are co-ordinated to the potassium atom through oxygen. It is nitro oxygen that is bonded to potassium rather than the phenoxide oxygen of the nitrophenolate. The water molecules are co-ordinated to potassium ions of the asymmetric unit and its b-translation*" along with a diagram of the so called potassium *para*-nitrophenolate dihydrate single crystal (Figure 2 of the commented paper) and has cited the work of Boaz et al. [15] (Ref. 4 of title paper). It is also not clear why the compound **1** containing one nitrophenolate moiety, a nitrophenol moiety and two water molecules in its asymmetric unit is called potassium *para*-nitrophenolate dihydrate and not potassium *para*-nitrophenolate *para*-nitrophenol dihydrate. It is noted that the above mentioned structure description including the ORTEP diagram has been perfectly reproduced (copied) from the work of Boaz et al. [15]. The same structure figure is also available in another paper by the group of Jerome Das [16]. In addition, the author claims that the unit cell data of **1** (Table 1) agrees well with the available reported literature values of Mahadevan and Ramachandran [17] (Ref. 3 of title paper). A scrutiny of this paper reveals that these authors [17] have also not reported any CIF file for their single crystal work on a so called potassium *para*-nitrophenolate dihydrate. From the ambiguous statement of authors of [17] "*From single crystal X-ray diffraction analysis it is found and reported that the crystal has monoclinic system with the lattice parameters,*" it is not very clear if these authors report the earlier literature data of [15] or their own measured cell data.

From the title of the paper of Boaz et al. [15] it can be inferred that a so called potassium para-nitrophenolate dihydrate was

Table 1: Single crystal unit cell data for a so called potassium *para*-nitrophenolate dihydrate

a (Å)	*b* (Å)	*c* (Å)	β (°)	Reference
22.076	3.682	21.283	111.52°	Title paper [14]
22.098(2)	3.7911(3)	21.391(3)	121.513°	[17]
22.098(2)	3.7911(3)	21.391(3)	121.513°(9)	Boaz et al. [15]
22.098(2)	3.7911(3)	21.391(3)	121.513°(9)	Boaz et al. [16]

a new material when it was published in 2005. However these authors also did not submit a CIF file for their new compound (A normal practise while publishing a new structure is to submit the CIF file to CCDC) as no CIF file is available in the CCDC database for a potassium *para*-nitrophenolate dihydrate. No CIF file is also available for the same compound when it was once again published as a novel compound by the same (Jerome Das) research group [16].

In a case study of NLO crystals Fleck and Petrosyan have highlighted the importance of a structure determination [18] for the correct identification of any new compounds and have shown with examples that use of only unit cell data results in improper characterization of a crystalline material. In addition Petrosyan et al. have reported that it is inappropriate to characterize a new solid based only on unit cell and has termed as dubious any claim of single crystal structure determination in the absence of refinement results and a CIF file [19]. In recent papers it has been shown that formulating compounds based only on unit cell data will result in erroneous identification of a solid [20–22]. This aspect has been well explained in the case of *L*-valine zinc sulphate (actually *L*-valine) and bis *L*-glutamine sodium nitrate (actually *L*-glutamine) both of which were claimed to have been grown by the author of the title paper.

It is to be noted that the structure description in the title paper is neither in accordance with the Ortep diagram (as there is no *para*-nitrophenol moiety) and the claim of observation of binding of nitro oxygen to K and not the phenolate O is not only in accordance with the known chemistry of an oxophilic metal like K, but quite different from the reported structure of $[K(C_6H_4NO_3)H_2O]$ [11]. The structural description based on single crystal data can be termed as unfortunate considering the identical nature of the explanation (including figure) with that of Boaz et al. [15] and the absence of a CIF file and other supporting spectral data. Reporting data from an earlier paper as one's own data in a later paper is not a good scientific practice.

The author of the title paper claims that the results of powder X-ray diffraction studies are found to be in good agreement with the results of single crystal XRD and earlier reported values. A constant shift is observed for all the peaks in the powder pattern (Figure 3 of title paper) when compared with the pattern in [17]. It is not clear if this is due to an instrumental error or due to some other factor. Although the author states in the introduction of the title paper "*In the present work, a systematic investigation has been carried out on the growth of semi organic single crystals of potassium para-nitrophenolate dihydrate and the ….*" no such attempt has been made in this work. Note that the author is unaware of the literature on the potassium compound of 4NP namely the work of Andersen et al. [11]. It is customary for any author to describe in the introduction as to what has happened in the area of research reported in the paper. Going by this the author should have stated in the introduction as to what is known in the area of compounds of K containing 4NP namely the main findings of Ref. 3 to 5 cited in the title paper. Instead it is noted that the author reports that his unit cell and powder pattern is in agreement with previous work. In fact most studies starting from crystal growth and others (for example dielectric study) have already been reported for a so called potassium *para*-nitrophenolate dihydrate by earlier authors (Ref. 3 to 5 of the title paper) and the title paper does not show in what way the results differ from the earlier work, for example if the earlier reported dielectric measurements are incorrect. Most of the studies are just a repetition and the reproduction of data from an earlier paper is unacceptable.

From the above mentioned discussion it is clear that the crystal reported in the title paper is not properly characterized despite the fact that this paper is the fifth in a series of papers [14–17, 23] on a so called potassium *para*-nitrophenolate dihydrate **1**. Three of these papers are by Jerome Das group [16, 17, 23]. All reports till date on compound **1** are unsupported by CIF file for the structure work. None of the authors of [14–17, 23] are aware of the reported structure of potassium 4-nitrophenolate monohydrate $[K(C_6H_4NO_3)H_2O]$ as the work of Andersen et al. [11] is not cited. In order to understand the exact nature of compound **1**, an analysis of the synthetic details in all these papers is presented. None of these reports provide quantities of reagents employed for crystal growth and yield of product crystal. In one of the reports [16] it is mentioned that the pH of the solution is maintained between 3.2 and 3.4 for growing the crystals while in all other reports no mention of reaction pH is made. Interestingly the method of synthesis of the so called potassium *para*-nitrophenolate dihydrate crystal of the authors of [14, 17] is the same as the one used by Andersen et al namely reaction of equimolar ratios of KOH and 4-nitrophenol. Hence it is strange that these authors [14, 17] could not get the monohydrate reported by Andersen [11]. Based on the synthetic protocol, it can be argued that the crystal grown by the authors of [14, 17] can at best be considered as the monohydrate salt namely $[K(C_6H_4NO_3)H_2O]$ and not any potassium *para*-nitrophenolate dihydrate **1**.

The reports of the Jerome Das group are examined in order to understand the exact nature of a crystal which is called as potassium *para*-nitrophenolate dihydrate **1**. In this context, it is to be noted that Davydov et al. [24] suggested in 1977 that the sodium nitrophenolate hydrate can be a promising NLO crystal. Minemoto et al. determined the structure and further investigated its NLO properties [2]. Later this crystal was studied by others [5, 6]. The Jerome Das group tried to obtain a potassium analog of sodium 4-nitrophenolate dihydrate [15], without being aware of previously published important papers [11] and [8]. In [11] the potassium analog was obtained already, which proved to be potassium nitrophenolate monohydrate with centrosymmetric structure, while the authors of [8] unexpectedly isolated at pH 7, the crystal of sodium *para*-nitrophenolate *para*-nitrophenol dihydrate $Na^+(4NP^-)(4\text{-}NP)\cdot 2H_2O$ (space group *C*2). *Para*-nitrophenolate and *para*-nitrophenol form dimeric nitrophenolate-nitrophenol anion with short O-H···O hydrogen bond. The authors of [15] determined the crystal structure of their crystal prepared from a reaction of equimolar quantities of KOH and 4NP. However, they were so sure that they obtained potassium *para*-nitraphenolate dihydrate that they completely ignored their own structural data: "*The asymmetric unit of the crystal shows two water molecules, one nitrophenolate moiety and another a potassium atom and nitrophenol moiety.*" In spite of this, the authors assume that the formula unit is $C_6H_8KNO_5$ and Z = 2. For this formula unit and Z = 2 they calculated a fantastic density equal to 21.532 g cm^{-3} and measured not less fantastic 21.586 g cm^{-3} density. Actually, calculated value of density for $C_6H_8KNO_5$ and Z = 2 makes 0.463 g cm^{-3}. So, this paper of Jerome Das group [15] which is erroneous, created the first confusion. Later the same research group reported more detailed structural data [16] and also some additional data on synthesis: "*Good quality seed obtained from spontaneous nucleation in the pH range 3.2–3.4 is suspended in the saturated solution.*" It is noted that this pH information was not provided in [15] but the reported unit cell for the crystal in both papers is identical. On the structure the authors of [16] wrote: "*The asymmetric unit of the crystal shows two water molecules, one nitrophenolate moiety, a disordered potassium atom and nitrophenol moiety.*" Actually there are two crystallographically independent K^+ ions and they are not disordered but are in special positions and the actual

formula unit is $C_{12}H_{13}KN_2O_8$. The authors of [16] could have rectified their earlier error and correct the paper [15] and realize that they actually obtained a potassium analog of sodium *para*-nitrophenolate *para*-nitrophenol dihydrate [8]. Instead of this, the authors in spite of obtained structural data continue to assume that the crystal is "potassium *para*-nitrophenolate dihydrate." In a still later paper [23] the same research group continues to believe that the crystal is "potassium *para*-nitrophenolate dihydrate" and interpreted the vibrational spectroscopic results based on this assumption. The above mentioned discussions reveal that there is no valid scientific proof for the crystal structure of potassium *para*-nitrophenolate dihydrate in the literature and thus all the three papers (which are erroneous) are responsible for the confusion in the literature in this area. Recently two more papers [14] and [17] have been published believing that the crystal obtained in [15, 16, 23] is "potassium *para*-nitrophenolate dihydrate" which add to this confusion. The authors of [14, 17] are responsible for noncritical approaching to the reported work in [15, 16, 23] and are certainly at fault for not analysing the chemical composition or determining the structure. The compounds "potassium *para*-nitrophenolate dihydrate" and "potassium *para*-nitrophenolate *para*-nitrophenol dihydrate" can be easily distinguished based on a simple chemical analysis.

Conclusions

In summary, it is proved that all papers in the literature till date (including the title paper) reporting crystal growth of potassium *para*-nitrophenolate dihydrate are completely erroneous.

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