

Comments on the paper “Growth and investigation of novel nonlinear optical single crystal of urea potassium dichromate by solution growth technique for photonic application”

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Abstract

The authors of the title paper (Journal of Optics **49**, 181–186 (2020)) claim to have grown a so-called urea potassium dichromate (UPDC) by slow evaporation of an aqueous solution containing equimolar amounts of urea and potassium dichromate and characterized it based on a unit cell study. A critical analysis reveals that the claims in the title paper are erroneous. Hence, we reinvestigated the crystal growth reaction and determined the structure of the product crystal. Based on these studies, we prove that due to no chemical reaction between the reagents fractional crystallization of potassium dichromate ($K_2Cr_2O_7$) occurs and not formation of any so-called UPDC crystal. Taking the title crystal as an example we show the importance of reporting single crystal structure for new compound characterization.

Keywords: *urea potassium dichromate; potassium dichromate; crystal structure; erroneous paper; fractional crystallization;*

Introduction

Recently we became aware of a paper by Chithambaram et al [1] published in the Journal of Optics reporting on the solution growth of a novel nonlinear optical urea potassium dichromate (UPDC) single crystal. This paper attracted our attention in view of our recent interest in urea-based materials [2,3]. Urea which crystallizes in the non-centrosymmetric tetragonal space group $P\bar{4} 2_1m$ [4], is well-known to form several

molecular adducts in 1:1 or 2:1 molar ratios with α,ω -alkanedicarboxylic acids many of which crystallize in centrosymmetric space groups [5-11]. In the literature, several urea-based crystals have been shown to be improperly characterized materials [12-17].

In an earlier paper the Chithambaram group had reported on a so-called glycine potassium dichromate crystal which we proved to be potassium dichromate [18]. The name urea potassium dichromate indicates that the title compound may be a molecular adduct of urea. However, a search of the Cambridge Structural Database (CSD) [19] reveals the absence of any entry with the name urea potassium dichromate or any structurally characterized compound containing both urea and $K_2Cr_2O_7$ in the same crystal. Hence, we perused the title paper reporting on a so-called UPDC (urea potassium dichromate) crystal and noted that the authors had characterized the crystal based on a unit cell measurement and an IR spectrum. We have shown in several critical comments [2, 3, 12-18] that characterization of new materials based on unit cell data results in incorrect compound identification. We note that the Chithambaram group employs similar procedure namely characterization based on unit cell in their papers. In this study we first show that the so called UPDC is in fact potassium dichromate based on a reinvestigation. In addition, we prove that four more papers of the Chithambaram research group [20-23] are erroneous. Together, these examples demonstrate the importance of single crystal structure determination for new compound characterization.

UPDC is in fact potassium dichromate

Authors of [1] reported in the introduction that they are making an attempt to grow novel single crystals of urea potassium dichromate by slow evaporation method to study the optical, mechanical and biological properties. Although it is mentioned that urea and potassium dichromate were taken in equal molar ratios, it is not clear what the authors mean by “*The calculated amount of urea potassium dichromate was dissolved in distilled water at room temperature.*” and left the solution for slow evaporation. As is usually observed in these papers, neither the quantities of reagents used for the crystal growth experiment nor the amount of UPDC obtained are reported. Under the heading, “single X-ray diffraction analysis” authors reported the

following: “It was observed that the crystal belongs to triclinic system with the following cell dimensions $a = 6.80 \text{ \AA}$, $b = 8.38 \text{ \AA}$, $c = 5.95 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 106^\circ$, $\gamma = 90^\circ$, with non-centrosymmetric space group P .” It is not clear why the authors refer to the unit cell of UPDC as triclinic cell despite reporting α and γ to be 90° . There is no space group identified by a single alphabet viz P and hence the reported unit cell is highly questionable. Under the heading powder X-ray diffraction analysis authors claimed, “The grown crystals were of high degree of crystallinity which can be revealed from the sharp and high-intensity peaks. The diffraction peaks were indexed using TREOR program for corresponding 2θ values and the estimated lattice parameter values. The sharp and well-defined Bragg peak at specific 2θ angles in the pattern attests the proper orientation of the grown crystal” that the peaks were indexed, no indices can be seen in the Bragg lines in the figure displaying the pattern. It is also not clear as to how a sharp Bragg peak in a powder pattern attests the proper orientation of a crystal.

Under the heading UV-Vis-NIR analysis authors claimed, “The resultant spectrum shows that the crystal has very low absorbance in the entire visible and IR region.” This discovery appears to be quite remarkable because the crystal is red coloured. In addition, it contradicts the infrared spectrum reported by the authors of [1] which shows quite a few strong infrared signals.

In view of the above contradictory claims we performed a crystal growth reaction on a ten millimolar scale by taking potassium dichromate (2.940 g, 10 mmol) and urea (0.600 g, 10 mmol) in ~60 ml of water. The reaction mixture was stirred well and then filtered. The clear red filtrate was left aside undisturbed for the slow evaporation of solvent water. After a few days bright red crystals were obtained. The crystals were filtered and washed with little cold water and allowed to air dry to obtain ~2.0 g of red crystals (**1**). No special efforts were taken to grow big crystals. A small crystal from the isolated product was used for the single crystal X-ray experiment which was performed in a Bruker D8 Ecoquest equipment. The details of data collection and refinement results in the triclinic space group ($P\bar{1}$) are given in Table 1. Our data are in very good agreement with the reported triclinic modification of potassium dichromate $K_2Cr_2O_7$ by Brandon and Brown [24]. The crystal structure of **1** consists of two unique dichromate anions and four

crystallographically independent K^+ ions (Fig. 1). Since this structure is well-documented in the literature [24], we do not wish to describe it any more. More importantly the formation of only potassium dichromate and not any urea potassium dichromate (UPDC) in very good yield reveals that there is no chemical reaction between the two reagents and the less soluble of the two namely $K_2Cr_2O_7$ fractionally crystallizes (Scheme 1). The more soluble urea remains in solution. A complete evaporation of the reaction mixture results in isolation of both unreacted products. Unlike urea which crystallizes in a non-centrosymmetric space group $K_2Cr_2O_7$ crystallizes in the centrosymmetric space group and hence is not expected to exhibit any second harmonic generation response (SHG). The observation of a very high SHG (2.5 times of KDP) for the so-called UPDC crystal indicates that the authors evaporated all the solvent and obtained a mixture of products. The unreacted urea in the product can explain the strong SHG signal. A similar explanation namely presence of unreacted starting material was provided by us for the observation of SHG signal in a so-called glycine potassium dichromate which was actually the centrosymmetric potassium dichromate [18].

Table 1 Crystal data and structure refinement for $K_2Cr_2O_7$ **1**

| | |
|---|--|
| Empirical formula | $K_2Cr_2O_7$ |
| Formula weight ($g\ mol^{-1}$) | 294.20 |
| Temperature (K) | 293(2) |
| Wavelength (\AA) | 0.71073 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions | |
| a (\AA) | 7.3888(2) |
| b (\AA) | 7.4733(2) |
| c (\AA) | 13.4044(4) |
| α ($^\circ$) | 96.3180(10) |
| β ($^\circ$) | 97.9770(10) |
| γ ($^\circ$) | 90.9270(10) |
| Volume (\AA^3) | 728.19(4) |
| Z | 4 |
| D_{calc} (mg/m^3) | 2.684 |
| Absorption coefficient (mm^{-1}) | 4.113 |
| $F(000)$ | 568 |
| Crystal size (mm^3) | 0.358 x 0.294 x 0.192 |
| θ range for data collection ($^\circ$) | 2.744 to 30.538 |
| Limiting indices | $-10 \leq h \leq 10, -10 \leq k \leq 10, -19 \leq l \leq 19$ |
| Reflections collected /unique | 19875 / 4451 [R(int) = 0.0226] |
| Completeness $\theta = 27.00^\circ$ | 99.6 % |
| Refinement method | Full- matrix least-squares on F^2 |

| | |
|--|---------------------------|
| Data / restraints / parameters | 4451 / 0 / 199 |
| Goodness of fit on F^2 | 1.115 |
| Final R indices [$I > 2\sigma(I)$] | R1 = 0.0224, wR2 = 0.0639 |
| R indices (all data) | R1 = 0.0249, wR2 = 0.0655 |
| Largest diff. peak and hole ($e \text{ \AA}^{-3}$) | 0.489 and -0.736 |
| CCDC deposit no. | 2032971 |

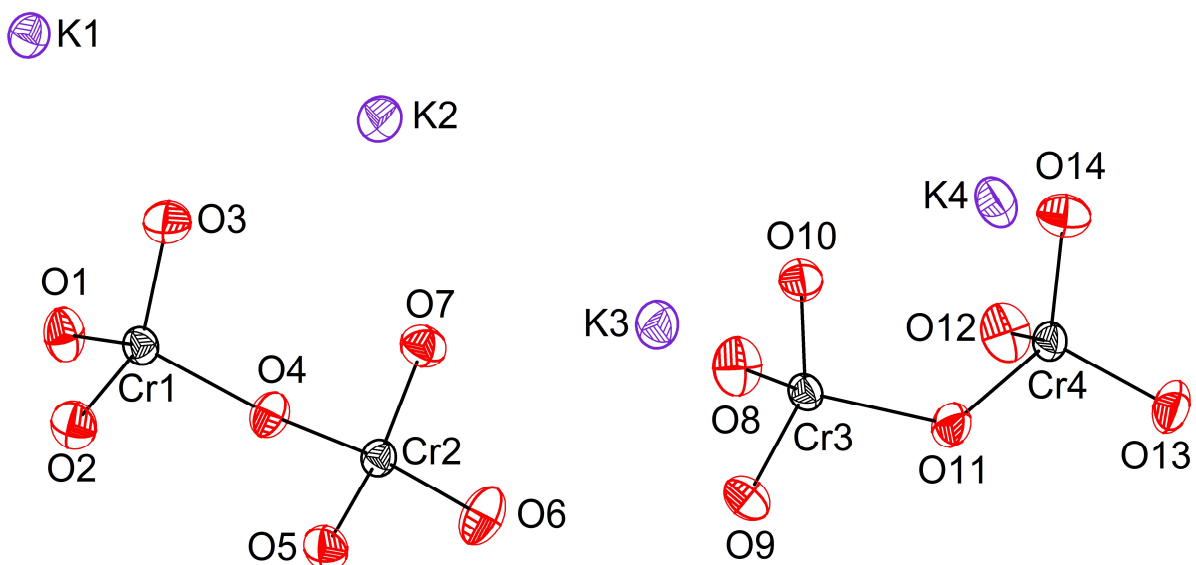


Fig.1 The asymmetric unit of $K_2Cr_2O_7$ showing the crystallographically unique dichromate anions and the four independent K^+ ions. Thermal ellipsoids are drawn at the 50% probability level.

Urea + potassium dichromate \rightarrow potassium dichromate
and NOT
~~urea potassium dichromate~~

Scheme 1: Fractional crystallization of potassium dichromate from an aqueous solution of 1:1 urea and potassium dichromate

We explain the formulation of UPDC crystal by the authors based on an incorrect assumption that stirring urea and potassium dichromate in equal ratios and allowing it to evaporate slowly will result in the formation of a so-called UPDC crystal. The above given discussions show the dangers associated with formulating compounds (especially so-called new materials) based on unit cell measurement. Had the

authors refined the structure they would have known that the so-called UPDC crystal obtained by them is not a novel material as claimed by them, but a known compound. As is the normal practice, we have deposited the CIF file of **1** with the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Improper characterization is also observed in four more articles of Chithambaram with other coauthors [20-23]. In [20] which is on a so-called “glycine manganous acetate” the authors reported: “*The calculated lattice parameter values are $a = 9.11 \text{ \AA}$, $b = 17.54 \text{ \AA}$ and $c = 10.41 \text{ \AA}$ Volume of the unit cell = 1552 \AA^3 . The XRD data prove that the crystal is monoclinic in structure with the space group of P* ”. The non-reporting of beta angle and reporting of a questionable space group for the monoclinic crystal and the absence of a CIF file makes this claim highly questionable. In [21] the authors report on “novel nonlinear optical L-threonine calcium chloride single crystal”. The crystal structure of this “novel” crystal was not determined. Instead, authors reported unit cell parameters, space group and infrared spectrum: “...*the LTCC crystal crystallizes in Orthorhombic system with non-Centro symmetric space group P_1 . The cell parameters are identified to be $a=5.18 \text{ \AA}$, $b=7.79 \text{ \AA}$, $c=13.71 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$ $\gamma = 90^\circ$ and $V = 553 \text{ \AA}^3$* ”. The space group P_1 is triclinic and provided unit cell parameters and infrared spectrum perfectly correspond to that of L-threonine (see [25] references therein). So, the crystal “L-threonine calcium chloride”, is in fact, L-threonine (see also [26]). In [22] the authors claim on obtaining a new L-tyrosine cadmium chloride crystal. Again, the structure was not determined. Moreover, the composition of the crystal is uncertain. The crystal is called L-tyrosine cadmium chloride, while the composition is assumed as $\text{Cd}(\text{C}_9\text{H}_{11}\text{NO}_3)_2\text{Cl}_2$. The authors report that the crystal is orthorhombic with the space group $Pmn2_1$. The lattice parameters were observed to be $a=13.0259 \text{ \AA}$, $b=5.8238 \text{ \AA}$, $c=6.4800 \text{ \AA}$ and cell volume is $V=491.582 \text{ \AA}^3$. However, the space group $Pmn2_1$ is incompatible with the existence of L-tyrosine in the crystal structure. For interpretation of the infrared spectrum the authors assume the presence of -COOH group, which is incorrect. In [23] the authors claim on obtaining a new “L-serine zinc acetate” crystal. Without structure determination, the authors reported lattice parameters $a=14.31 \text{ \AA}$, $b=5.28 \text{ \AA}$, $c=10.84 \text{ \AA}$, $\alpha=90^\circ$, $\beta=100^\circ$, $\gamma=90^\circ$, and volume 807 \AA^3

with non-Centro symmetric monoclinic space group C. Comparison of these parameters with those of zinc acetate dihydrate [27] ($a=14.50 \text{ \AA}$, $b=5.32 \text{ \AA}$, $c=11.02 \text{ \AA}$, $\alpha=90^\circ$, $\beta=100.0^\circ$, $\gamma=90$, $Z=4$, space group $C2/c$) show that the crystal “L-serine zinc acetate” is in fact zinc acetate dihydrate. It is not clear how the authors could observe SHG in this centrosymmetric crystal. Discussing the thermal properties of the crystal, the authors report: “...the exothermic peak of the materials is at 110°C is indicate to melting point of the crystal”. The authors consider that melting of a crystal can be exothermic, disregarding the fact that it is an endothermic effect caused by dehydration.

Conclusions

In this critique, we have proved that a so-called urea potassium dichromate crystal is in fact potassium dichromate. Four more publications by the Chithambaram research group report on questionable and improperly characterized crystals. Our present comment once again highlights the importance of single-crystal structure refinement for new compound characterization. We request all leading journals will make reporting of structure determination in the CSD or ICSD database an essential prerequisite for the publication of “new crystals”.

Supplementary Material

Deposition Number 2032971 (for **1**), contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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