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On the existence of '*L*-asparagine cadmium chloride monohydrate' crystal

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Abstract

It is argued that the nonlinear optical single crystal '*L*-asparagine cadmium chloride monohydrate' grown by the slow evaporation solution growth technique by Masilamani et al (Optik, 123 (2012) 1304-1306) is actually the well-known *L*-asparagine monohydrate crystal.

Keywords: *L*-Asparagine cadmium chloride monohydrate; *L*-asparagine monohydrate; nonlinear optical crystal; growth from solution; improper characterization.

1. Introduction

Amino acids are known to react with metal salts to give new metal based amino acid compounds. The product thus formed depends on several factors which include the pH of the reaction medium, the zwitterionic nature of amino acid, extra functional groups in a given amino acid for example *L*-asparagine, the nature of the metal ion and its stereochemical preference, presence of other ligands, etc. The most suitable technique for an accurate characterization of any new crystalline material is a single crystal structure determination wherever crystals can be grown. The importance of X-ray crystallography work has been elegantly demonstrated by Fleck and Petrosyan in a case study of salts of amino acids [1]. However, formulating new compounds in the absence of single crystal X-ray structure result, with the aid of analytical data, infrared spectrum and powder pattern, leads to erroneous conclusions as can be evidenced in the paper entitled, '*Synthesis, growth and characterization of a novel semiorganic nonlinear optical single crystal: L-Asparagine cadmium chloride monohydrate*' by Masilamani et al [2]. Although, the authors believe that they have grown a so called novel semiorganic nonlinear optical crystal *L*-asparagine

cadmium chloride monohydrate (LACC), it will be proved that the crystal grown is not at all novel and does not contain any Cd.

2. On the non-existent *L*-asparagaine cadmium chloride monohydrate crystal

Crystals of *L*-asparagine cadmium chloride monohydrate $Cd(C_4H_8N_2O_3]_2Cl_2 \cdot H_2O$ are claimed to have been grown by slow evaporation solution growth technique by the authors of [2], from an aqueous solution containing *L*-asparagine and cadmium chloride monohydrate in 2:1 mole ratio (Scheme 1). The authors have formulated the crystal based on an incorrect assumption that a crystal grown from a mixture of precursor materials represents their desired compound $Cd(C_4H_8N_2O_3]_2Cl_2 \cdot H_2O$, disregarding the chemistry of the reaction which dictates product formation, when a metal salt reacts with amino acid.

$$2\,(C_4H_8N_2O_3) + CdCl_2 \cdot H_2O \xrightarrow{H_2O} \text{L-asparagine monohydrate}$$

L-asparagine

and NOT

L-asparagine cadmium chloride monohydrate

$Cd(C_4H_8N_2O_3)Cl_2 \cdot H_2O$

Scheme 1

The wrong assumption can be evidenced from their proposed (albeit incorrect) formula for the product as $Cd(C_4H_8N_2O_3]_2Cl_2 \cdot H_2O$, probably due to the fact that two moles of amino acid were used and the starting Cd(II) salt was a monohydrate ($CdCl_2 \cdot H_2O$). Although it is not clear as to why a compound with a proposed formula $Cd(C_4H_8N_2O_3]_2Cl_2 \cdot H_2O$ containing two *L*-asparagine molecules is called as *L*-asparagine cadmium chloride monohydrate, a scrutiny of the reported results clearly shows that the grown crystal does not contain any cadmium.

In order to characterize their so called novel NLO crystal, the authors have employed X-ray powder pattern, elemental analysis, UV-Vis and IR spectroscopy. Based on the X-ray powder diffractogram (without any data analysis) the authors concluded '*The prominent well defined*

sharp Bragg's peaks at specific 2θ angle reveals that the good crystalline nature of LACC crystal'. Since any of the two starting materials used for crystal growth can also give sharp peaks in their respective diffractogram, the sharp lines in the powder pattern cannot be taken as any valid proof for the formation of $Cd(C_4H_8N_2O_3]_2Cl_2 \cdot H_2O$. The same can be said for the UV-Vis spectral data because both $CdCl_2$ and *L*-asparagine are known to be transparent in the entire UV-Vis region.

The elemental analytical data (Table 1) provides the first clue that the crystal under study in [2] is a pure organic compound and does not contain any Cd whatsoever. Based on their experimental data for C (28.47%), H (6.57), and N (17.05), the authors declared in their paper '*This shows that the experimental values of C, H and N have good agreement with theoretical values of each other and confirming the formation of expected compound*'. Unfortunately, all theoretical values reported by the authors of [2] for the so called *L*-asparagine cadmium chloride monohydrate are incorrect and can at best be termed as conveniently chosen values.

Table 1. Theoretical elemental analytical data for *L*-asparagine cadmium chloride monohydrate, *L*-asparagine and *L*-asparagine monohydrate based on molecular formula

Compound	Formula weight	%C	%H	%N	%O	%Cd	%Cl
L-Asparagine cadmium chloride monohydrate (LACC) $Cd(C_4H_8N_2O_3)_2Cl_2 \cdot H_2O$	465.57	20.64 (**28.88**)*	3.90 (**6.08**)*	12.03 (**16.84**)*	24.06	24.14	15.23
L-Asparagine ($C_4H_8N_2O_3$)	132.12	36.36	6.10	21.20	36.33	---	---
L-Asparagine monohydrate $(C_4H_8N_2O_3) \cdot H_2O$	150.13	32.00	6.71	18.66	42.63	---	---
dichloro(*L*-asparagine)-cadmium(II) monohydrate $Cd(C_4H_8N_2O_3)Cl_2 \cdot H_2O$	333.45	14.41	3.02	8.40	19.19	33.71	21.26

*__Values in bracket__ are the **wrong** theoretical values reported by authors of [2].

The correct values are listed in Table 1 and the accuracy of the present theoretical calculation can be evidenced by the fact that for each entry, the sum of all atom percentages adds up to 100%. Although it is not clear if the wrong theoretical values are due to an unintentional error, or if some convenient numbers closer to the experimental values were chosen to support an arbitrary formula, it is very certain that the claim of the authors that the experimental and theoretical % are in agreement is untenable. A comparison of the experimental C, H and N % with the correct theoretical values in Table 1, reveals that these do not correspond to the proposed formula $Cd(C_4H_8N_2O_3)_2Cl_2 \cdot H_2O$ but instead are more reasonable for the well-known crystal namely *L*-asparagine monohydrate. More importantly, the data rule out the presence of any Cd in the grown crystal, including the 1:1 compound namely dichloro(*L*-asparagine)cadmium(II) monohydrate. Note that for any *L*-asparagine compound of cadmium, the theoretical % of C should be of the order of 20% or less due to the presence of Cd in the formula unlike a high carbon content for *L*-asparagine (36.36%) or its monohydrate. The absence of Cd in the grown crystal can be unambiguously confirmed from the IR spectrum reported in [2], which is identical to that of an earlier reported compound namely *L*-asparagine thiourea monohydrate (LATM), which does not contain any Cd in its formula. Based on a comparison of the spectral and unit cell data of LATM with that of *L*-asparagine monohydrate Petrosyan [3] reported that LATM and *L*-asparagine monohydrate are one and the same. The coincidence of the IR spectra permits the same conclusion to be drawn namely '*L*-asparagine cadmium chloride monohydrate' crystal is nothing but pure *L*-asparagine monohydrate.

Based on their interpretation (wrong assignment for NH_3 asymmetric vibration at 1643 cm^{-1}) of the infrared spectrum the authors stated '*These vibrations proved the presence of functional groups in the synthesized compound*'. The incorrect interpretation of the IR data can be evidenced by the fact that the authors did not assign stretching and bending vibrations

for the –OH moiety of water, for a compound which contains water in the proposed formula, and also any vibrations involving the Cd atom in accordance with their proposed formula. The authors were either unaware or did not take into consideration that a hydrated form of *L*-asparagine can as well give an identical spectrum as the one obtained by them. A comparison of the IR spectrum reported in [2] with that of *L*-asparagine monohydrate reveals their coincidence.

Based on the above mentioned analysis of the results reported by the authors of [2] the formation of *L*-asparagine monohydrate and not *L*-asparagine cadmium chloride monohydrate as the product (Scheme 1) can be explained due to the fractional crystallization of the less soluble *L*-asparagine with the more soluble $CdCl_2$ remaining in solution. The present finding that no new L-asparagine crystal of Cd(II) is formed under the reaction conditions and only the starting material namely *L*-asparagine is isolated is not at all surprising because several such instances of so called novel compounds turning out to be the starting amino acid are well documented in the literature [1, 3-7]. In this context it is worth mentioning that a so called NLO crystal *L*-alanine cadmium bromide claimed to have been grown from an aqueous solution containing equimolar ratios of *L*-alanine and $CdBr_2$ has been recently proved to be the starting amino acid namely *L*-alanine and not any Cd based compound [7]. Further, the present observation of no chemical reaction is very much in accordance with the chemistry of Cd(II) towards *L*-asparagine because no report of a structurally characterized Cd(II) compound containing *L*-asparagine in neutral form is known till date. Some studies pertaining to formation constants of cadmium *L*-asparaginate (anionic form) compound have been reported [8]. In view of the above mentioned facts, the growth of a crystal of formula $Cd(C_4H_8N_2O_3]_2Cl_2 \cdot H_2O$ can be conveniently ruled out. Hence, a report claiming the growth of such a non-existent compound without any proof in the form of a single crystal X-ray structure is completely erroneous.

3. Conclusions

In summary it is conclusively shown that the earlier reported '*L*-asparagine cadmium chloride monohydrate' is not a novel nonlinear optical single crystal, but instead the well-known *L*-asparagine monohydrate crystal. In addition to stressing the usefulness of analytical data for finding out the product composition, the present report once again highlights the fact that formulating new compounds based on assumption that a crystal grown from a mixture of precursor materials taken in a preferred ratio necessarily represents an expected compound in a desired mole ratio is an unscientific way of product characterization.

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