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What is alanine adipate, in fact?

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Highlights

A so-called alanine adipate is, in fact, adipic acid

Adipic acid is a centrosymmetric solid

Determination of crystal structure is mandatory

Abstract

We show that a recently published paper "Spectroscopic evaluation of Alanine Adipate nonlinear optical materials growth dynamics: Mechanical and thermal optimization" (Akilandeswari & Jothi, *J. Mol. Struct*. 1240 (2021) 130577) is completely erroneous. A so-called "alanine adipate" is, in fact, adipic acid, which is centrosymmetric and therefore cannot be a nonlinear optical crystal showing second harmonic activity.

Keywords: *adipic acid, improper characterization, IR spectra, crystal structure*

Introduction

We became aware of a recently published article [1] reporting on a new nonlinear optical "alanine adipate" (**I**) crystal. A quick glance, however, indicated its dubious nature. The authors claim to have observed SHG in **I**, without reporting its symmetry (space or point group) but giving only the unit cell parameters. The authors restricted to mentioning only the name, but did not report anywhere the composition (molecular formula) of **I**. Unfortunately, there are many similar publications in the literature which have been shown to be erroneous. This made us analyze the article in more detail to find out what the "alanine adipate" crystal really is.

Comments

Since, the term alanine can refer to L-alanine or D-alanine or DL-alanine or β-alanine, it is not clear what the authors mean by "alanine adipate". As "adipate" refers to the doubly charged anion of adipic acid, the correct name should be, e.g., (bis)L-alaninium adipate. Otherwise, it can be L-alaninium hydrogen adipate for the monoanion of adipic acid. Under the heading "Synthesis and crystal growth" authors reported "*Analytical grade alanine was dissolved in ethanol and stirred continuously for an hour to get the saturated solution. The saturated solution may contain impurities such as solid and dust particles and therefore it was filtered using filter paper.*" It is unclear how much alanine was dissolved in what amount of ethanol, given the low solubility of L-alanine in ethanol [2].

Determination of cell parameters for identification of the resulting crystal is a normal practice. However, characterization of new crystals based on cell parameters is the most common mistake leading to the publication of erroneous results [3]. The authors write: *It is observed from the X-ray diffraction data that the grown crystal belongs to monoclinic system and space group P. The lattice parameters*

values are a = 7. 41 Å, b = 5. 19 Å, c = 10. 14 Å, α= 90. 00 °, β= 110. 74 °, γ= 90.00 °, Volume = 365 Å^3. It is not clear what the authors mean by "space group P". In the IR and Raman spectral discussion, it is not clear how bands could be assigned for NH_2^+ and CH_2^+ group vibrations in the absence of a proposed molecular formula, when they are absent in alanine and adipate anion. The results of thermal analysis are contradictory. Despite reporting "*In the DSC curve the peak at 186. 4 °C indicates the melting point of the material"*, the authors claimed *"The DSC traces for both cooling and heating are shown in Fig. 14. The heating curve produces a sharp endothermic peak at 150 °C due to melting".* However, *Fig. 14* in [1] displays TG and DTG curves. Under the heading "Second harmonic generation (SHG) studies" it is mentioned "*…the SHG efficiency was found to be 1.06 higher than that of standard potassium dihydrogen orthophosphate (KDP)"*, indicating that **I** is noncentrosymmetric.

It is important to determine what the authors of [1] actually got. Very often, in the absence of reaction between the components, one reagent crystallizes [3]. Since the cell parameters do not correspond to those of L-alanine [4], D-alanine [5], DL-alanine [6] and β-alanine [7], we decided to compare with the parameters of adipic acid [8]. Unit cell parameters of adipic acid at 298°C are: *a*= 7.3712(2) Å, *b*= 5.1540(2) Å, *c*= 10.1449(4) Å, β= 112.360(2)°, V= 356.44(2) Å^3, space group $P2_1/c$ and T_m=153°C [8]. These parameters satisfactory correspond to those of [1], which allows us to conclude that "alanine adipate" is actually adipic acid. The coincidence of the IR spectrum of "alanine adipate" [1] with the IR spectrum of adipic acid [9] adds credence to our conclusion. We opine that only the authors can explain how they managed to observe SHG in the centrosymmetric crystal of adipic acid. It is unfortunate that articles like [1] appear on the pages of the Journal of Molecular Structure. We had hoped that our recent critical comments [10-12] would help to avoid the publication of articles on "new" crystals without determination of their structures.

Conclusion

The commented article [1] is a typical example of works on "new" crystals of unknown composition without determining their crystal and molecular structure. The alleged "new nonlinear optical crystal of Alanine Adipate" is proved to be a centrosymmetric crystal of adipic acid. Through this comment, we once again urge the editors of Journal of Molecular Structure not to accept for publication, articles reporting on new crystals in the absence of a valid proof (CIF file) of the crystal structure.

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