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## On the existence of '*L*-alanine cadmium bromide'

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### Graphical Abstract

***L*-alanine + CdBr<sub>2</sub> ⇒ *L*-alanine**

**(C<sub>3</sub>H<sub>7</sub>NO<sub>2</sub>)**

**and NOT**

***L*-alanine cadmium bromide**

**[Cd(C<sub>3</sub>H<sub>7</sub>NO<sub>2</sub>)Br<sub>2</sub>]**

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### **Highlights**

- *L*-alanine cadmium bromide is actually *L*-alanine.
- *L*-alanine crystallizes in the orthorhombic crystal system.
- Thermal decomposition of *L*-alanine results in no residue.

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### Abstract

It is argued that the recently reported nonlinear optical crystal *L*-alanine cadmium bromide, grown by slow solvent evaporation method at room temperature [P. Ilayabarathi, J. Chandrasekaran, Spectrochim. Acta 96A (2012) 684-689] is the well-known *L*-alanine crystal. The isolation of *L*-alanine crystal is explained due to fractional crystallization.

**Keywords:** *L*-alanine; *L*-alanine cadmium bromide; nonlinear optical crystal; growth from solution; fractional crystallization.

### 1. Introduction

Compounds crystallizing in non-centrosymmetric space groups are of considerable research interest because they can exhibit several desirable physical properties including nonlinear optical (NLO) activity. In this frontier area of research on NLO materials, several papers reporting on new non-centrosymmetric solids are being published. For many of these investigations, naturally occurring *L*-amino acids are employed as reagents for the synthesis of new NLO materials. In addition to several valuable works, compounds which have not been properly characterized are being published under the name new nonlinear optical (NLO) crystals. Several such erroneous papers were brought to the attention of the scientific community by Fleck and Petrosyan in a case study of salts of amino acids [1]. A survey of the literature reveals that many compounds of *L*-alanine initially claimed as novel NLO crystals were later convincingly proved to be not novel *L*-alanine compounds but actually crystals of *L*-alanine (Table 1). For many of these „so called“ novel NLO materials, the unit cell parameters were found to be coincident with the reported data for pure *L*-alanine [2], thus

enabling their correct identification [1, 3-9]. In this comment, a „so called“ new semiorganic NLO crystal *L*-alanine cadmium bromide [10] is added to the list of incorrectly characterized compounds of *L*-alanine in Table 1.

**Table 1**

List of incorrectly characterized compounds of *L*-alanine

No	<b>Wrongly</b> characterized NLO crystal	Actual compound	Ref
1	<i>L</i> -alanine tetrafluoroborate	<i>L</i> -alanine	3
2	<i>L</i> -alanine acetate	<i>L</i> -alanine	3
3	<i>L</i> -alanine formate	<i>L</i> -alanine	4
4	thiourea <i>L</i> -alanine acetate	<i>L</i> -alanine	5
5	<i>L</i> -alanine alaninium nitrate	<i>L</i> -alanine	6
6	<i>L</i> -alanine sodium nitrate	<i>L</i> -alanine	6
7	<i>L</i> -alanine <i>DL</i> -malic acid	<i>L</i> -alanine	1
8	Urea <i>L</i> -alanine acetate	<i>L</i> -alanine	1
9	<i>L</i> -alaninium fumarate	<i>L</i> -alanine	1
10	<i>L</i> -alaninium succinate	<i>L</i> -alanine	1
11	bis <i>L</i> -alanine triethanolamine	<i>L</i> -alanine	8
12	bis <i>L</i> -alanine picrate	<i>L</i> -alanine	7
13	<i>L</i> -alanine lithium chloride	<i>L</i> -alanine	9
14	bis <i>L</i> -alanine lithium chloride	<i>L</i> -alanine	9
15	<i>L</i> -alanine cadmium bromide	<i>L</i> -alanine	This work

## 2. Comment

### 2.1 Synthetic aspects of metal-amino acid compounds

The product of a reaction of an amino acid with a metal salt (or any other reagent) depends on several factors which include the stoichiometry of the reagents employed in the reaction, temperature of reaction, pH of the reaction medium, the zwitter ionic nature of amino acid employed used in the reaction, the affinity of a given metal ion for O or N donor sites, oxidation state and stereochemical preference of the metal, counter anion in the metal salt, presence of other ligands, etc. In view of this, it is essential to accurately identify the formation of a new product crystal based on its initial characterization by elemental analysis, comparison of spectral and thermal properties to rule out the presence of any starting material, and finally by single crystal X-ray structure wherever crystals are available.

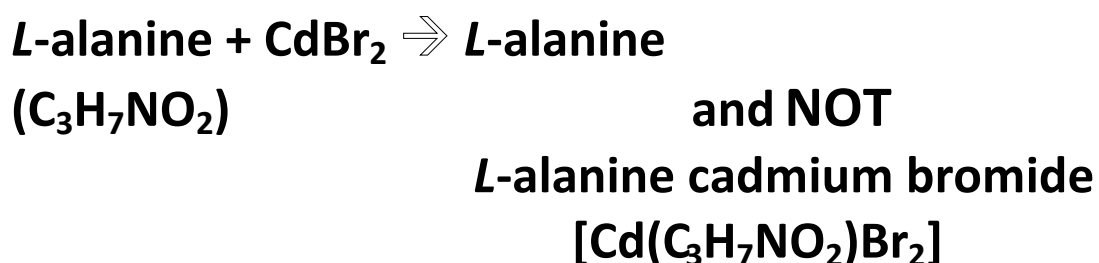
The role of pH can be understood by the synthesis of two different Cd(II) compounds viz.  $[\text{CdCl}_2(L\text{-alanine})]$  [11]  $[\text{Cd}(L\text{-alaninate})_2 \cdot 3\text{H}_2\text{O}]$  (Table 2) [12]. The *L*-alaninate compound wherein the Cd(II) is charge balanced by two *L*-alaninate anions, is formed under alkaline conditions while  $[\text{CdCl}_2(L\text{-alanine})]$  is obtained by reaction of equimolar quantities of  $\text{CdCl}_2$  with *L*-alanine in water at room temperature. Reaction of the isomeric  $\beta$ -alanine or the racemic *DL*-alanine instead of *L*-alanine with  $\text{CdCl}_2$  results in the formation of  $[\text{CdCl}_2(\beta\text{-alanine})]$  [13] or  $[\text{CdCl}_2(DL\text{-alanine})] \cdot \text{H}_2\text{O}$  [14]. Note that the Cd(II) crystal of *DL*-alanine has an additional water molecule in its formula, despite the same reaction conditions employed. To the best of my knowledge, the analogous bromo or iodo complexes of Cd(II) containing *L*-alanine have not yet been structurally characterized. The formation of a metal chloride-amino acid compound from a chloride salt, does not guarantee the formation of the corresponding bromo compound under identical conditions. In many instances, the possibility of no chemical reaction taking place cannot be ruled out and in these reactions only the starting materials are recovered either as a mixture of products or exclusively only one of the starting materials (often the amino acid) due to fractional crystallization of the less soluble reagent. Several such instances of formation of the starting amino acids have been documented by Fleck and Petrosyan in their case study of salts of amino acids [1].

**Table 2.** Unit cell data of L-alanine and Cd(II) compounds containing L-alanine

No	Compound	Space group	<i>a</i>	<i>b</i>	<i>c</i>	Unit cell volume $\text{\AA}^3$	Ref
1	$[\text{CdCl}_2(L\text{-alanine})]^*$	<i>C2</i>	16.240(2)	7.272(1)	7.987(2)	844.7(2)	11
2	$[\text{Cd}(L\text{-alaninate})_2 \cdot 3\text{H}_2\text{O}]$	<i>P3<sub>1</sub>21</i>	6.376(3)	6.376(3)	25.59(2)	901(1)	12
3	$[\text{CdCl}_2(\beta\text{-alanine})]$	<i>Pna2<sub>1</sub></i>	6.9391(10)	12.945(2)	7.9714(10)	716.05(18)	13
4	$[\text{CdCl}_2(DL\text{-alanine})] \cdot \text{H}_2\text{O}^\#$	<i>P2<sub>1</sub>/c</i>	7.1190(15)	14.408(3)	8.6396(13)	842.9(3)	14
5	<i>L</i> -alanine	<i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>	6.032(1)	12.343(1)	5.784(1)	430.6	2
6	<i>L</i> -alanine cadmium bromide monoclinic angle $\beta = 116.44(1)^{o*}; 107.98(2)^{o\#}$	---	5.771(2)	6.014(4)	12.298(2)	426.8(3)	10

## 2.2 On the non-existent *L*-alanine cadmium bromide

The authors of [10] claim to have grown crystals of *L*-alanine cadmium bromide [Cd(*L*-alanine)Br<sub>2</sub>] by slow evaporation solution growth technique, from an aqueous solution containing equimolar ratios of *L*-alanine and cadmium bromide. It is not clear why they call it *L*-alanine cadmium bromide and abbreviate it as LACB, since the corresponding chloride crystal [Cd(*L*-alanine)Cl<sub>2</sub>] is known as *catena*-poly[cadmium-di- $\mu$ -chloro- $\mu$ -*L*-alanine-O:O']. The abbreviation LACB is quite unusual. Disregarding the chemistry of a reaction which dictates product formation, the authors have formulated the crystal based on an incorrect assumption that a crystal grown from a mixture of precursor materials namely CdBr<sub>2</sub> and *L*-alanine represents their desired compound [Cd(C<sub>3</sub>H<sub>7</sub>NO<sub>2</sub>)Br<sub>2</sub>]. A scrutiny of the reported results in [10] confirms that the grown crystal is not *L*-alanine cadmium bromide as will be proved below (Scheme 1).



### Scheme 1

## 2.3 Importance of unit cell data for compound characterization

Although the authors claim to have characterized their „so called“ *L*-alanine cadmium bromide by a single crystal X-ray diffraction experiment, no refinement details of the single crystal work in the usual form of a cif file are available. The non-assignment of any space group only indicates that the structure was not determined. Since only unit cell data are provided the experiment should be actually called as unit cell determination and not single

crystal X-ray diffraction. Comparison of the reported unit cell data of *L*-alanine cadmium bromide crystal reveals that its cell parameters are in very good agreement (Table 2) with the respective parameters of pure *L*-alanine reported in 1966 [2] but for a change in the cell axes. A comparison of the unit cell data of *L*-alanine with those of the structurally characterized Cd(II) compounds of *L*-alanine and *DL*-alanine listed in Table 2 not only reveals that these compounds crystallize in a different space group but also exhibit a large increase in their unit cell volume as compared to that of *L*-alanine. The cell volume of [CdCl<sub>2</sub>(*L*-alanine)] at 844.7(2) Å<sup>3</sup> is almost double that of *L*-alanine. Unlike other structurally Cd(II) compounds in Table 2, the „so called“ *L*-alanine cadmium bromide crystal does not show any increase in its cell volume. In fact the volume is slightly less and shows very little variation compared to that of *L*-alanine ruling out the presence of any Cd in this crystal. Based on the comparison of unit cell data, especially the cell volume, it can be readily concluded that the semiorganic NLO crystal „*L*-alanine cadmium bromide“ is nothing but pure *L*-alanine. In their work Simpson and Marsh collected X-ray intensity data using Cu-K<sub>α</sub> radiation, by the multiple film Weissenberg photographs technique [2], unlike a four circle X-ray diffractometer and Mo-K<sub>α</sub> radiation used in [10]. The above observed result is only a testimony to the well-known fact that for a crystalline solid, the unit cell data are very characteristic.

#### 2.4 Infrared and thermal evidence for fractional crystallization of *L*-alanine

Based on the above result of the comparison of unit cell data of the product with that of the starting amino acid as mentioned above, the chemistry of the crystal growth of the „so called“ *L*-alanine cadmium bromide can now be explained. Unlike CdCl<sub>2</sub> which forms a one dimensional polymeric chain compound consisting of interlinked {CdCl<sub>4</sub>O<sub>2</sub>} octahedra on reaction with aniline, CdBr<sub>2</sub> does not exhibit any chemical reactivity towards *L*-alanine in water at room temperature. In view of this, an equimolar mixture of CdBr<sub>2</sub> and *L*-alanine in water results in the fractional crystallization of the less soluble *L*-alanine, with the freely

soluble  $\text{CdBr}_2$  remaining in solution (Scheme 1). The crystallization of *L*-alanine also reveals that presence of  $\text{CdBr}_2$  does not inhibit the growth of *L*-alanine crystals. That the crystal grown by the authors is *L*-alanine can be further confirmed by a comparison of the infrared spectrum reported in [10] which is identical to that of the spectrum of pure *L*-alanine. The same feature namely identical infrared spectrum with *L*-alanine has been used many times earlier to correctly formulate the wrongly characterized compounds listed in Table 1 [3-9]. A conclusive proof that the crystal under study in [10] is a pure organic compound namely *L*-alanine and not a „so called“ semiorganic NLO crystal can be evidenced from the reported TG thermogram (the authors incorrectly refer to this as TG spectrum) which shows no residue. In addition to unit cell data, infrared spectrum and thermal studies discussed so far, the authors of the commented paper have performed studies like fluorescence, photoconductivity, SHG test, etc. and explained these observations for the „so called“ *L*-alanine cadmium bromide which is actually *L*-alanine. In the absence of detailed studies, it is inappropriate to designate any compound as a novel NLO crystal based on a qualitative powder SHG test performed without even knowing the particle size of the solid. In view of the improper characterization of the grown crystal, all other studies for example dielectric study, microhardness study, etc. are meaningless and hence are not commented any further.

### 3. Conclusions

The conclusions of the present work are as follows: i) A product crystal of an aqueous reaction of an amino acid with a metal salt depends on several factors, and it is inappropriate to formulate a compound based on an assumption that a crystal grown from a mixture of precursor materials ( $\text{CdBr}_2$  and *L*-alanine) taken in a preferred ratio, will represent an expected product crystal. ii) Any compound should be represented by an appropriate chemical formula and should not be referred to by an arbitrary name or non-standard abbreviation. iii) Unlike  $\text{CdCl}_2$  which reacts with *L*-alanine in water at room temperature to



form [CdCl<sub>2</sub>(L-alanine)], CdBr<sub>2</sub> does not exhibit any chemical reactivity towards *L*-alanine under identical conditions. iv) The formation of pure *L*-alanine from an aqueous solution of CdBr<sub>2</sub> and *L*-alanine by slow solvent evaporation method at room temperature can be explained due to the fractional crystallization of *L*-alanine. v) A comparison of the unit cell and IR spectral data is one useful method to distinguish the products of a reaction from the starting materials. The usefulness of this procedure has been well demonstrated in several earlier papers [1, 3-9] and once again confirmed in the present work to correctly identify reported compounds and rectify errors in scientific literature.

In addition to providing a complete list of wrongly characterized *L*-alanine compounds, it is conclusively shown that the earlier reported crystal of „*L*-alanine cadmium bromide“ is not a semiorganic NLO material, but actually the well-known *L*-alanine crystal.

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