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Can zinc(II) ions be doped into the crystal structure of L-proline cadmium chloride monohydrate?

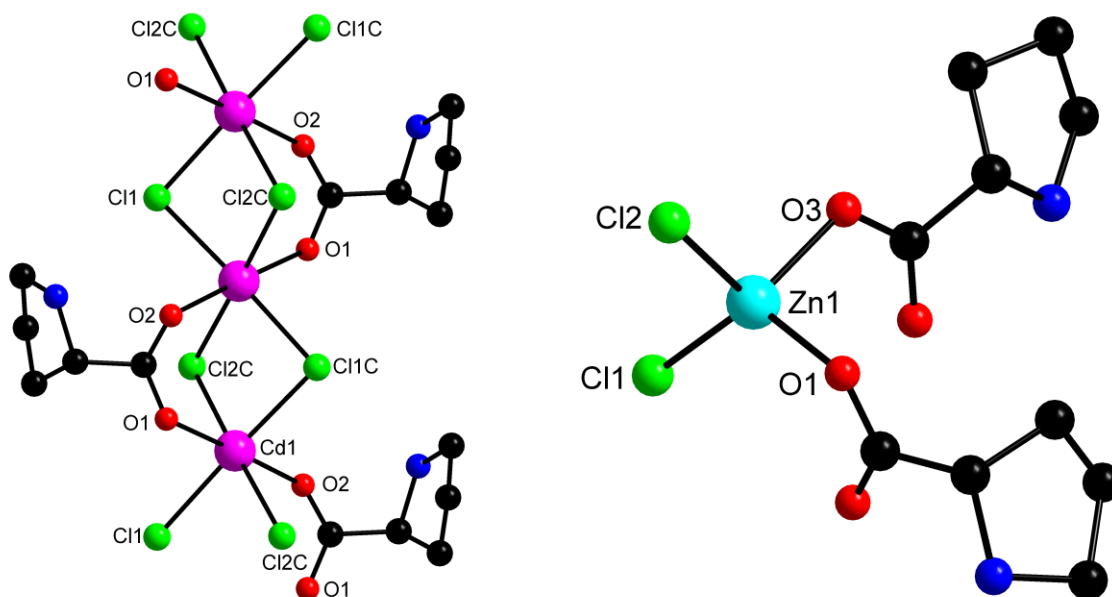
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Graphical Abstract

The differing stereochemistry of the bivalent metals Cd and Zn for the set of L-proline and chloride ligands precludes the substitution (doping) of Cd(II) ions by Zn(II) ions in the crystal structure of L-proline cadmium chloride monohydrate.



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Highlights

- Dichloro(L-proline)cadmium(II) hydrate **1** is a one-dimensional polymer.
- Dichlorobis(L-proline)zinc(II) **2** is a monomer.
- Tetrahedral Zn(II) ions cannot be doped into octahedral Cd(II) ions of **1**.
- $Zn_{(0.4mol)}$:LPCCM **3** is actually dichlorobis(L-proline)zinc(II) **2** crystal.
- $Zn_{(0.2mol)}$:LPCCM **4** is actually dichloro(L-proline)cadmium(II) hydrate **1** crystal.

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Abstract

The bivalent metals Cd(II) and Zn(II) exhibit different stereochemical requirements for the set of chloride and L-proline ligands, which precludes the doping of Zn(II) ions into the crystal structure of dichloro(L-proline)cadmium(II) hydrate also referred to as L-proline cadmium chloride monohydrate (L-PCCM). Hence, the reported claim of growth of zinc doped L-PCCM crystals namely $Zn_{(0.4\text{mol})}$:LPCCM and $Zn_{(0.2\text{mol})}$:LPCCM by S. Vetrivel *et al* (Spectrochim. Acta 110A (2013) 317-323), is untenable.

Keywords: Cadmium; zinc; dichloro(L-proline)cadmium(II) hydrate; L-proline; L-proline cadmium chloride monohydrate; doping;

1. Introduction

Several groups are working on the growth and characterization of new compounds, which can be used for applications in non-linear optics (NLO). The naturally occurring α -amino acids which are commercially available, are known to form several compounds with many inorganic and organic reagents, due to the reactivity characteristics of the amino ($-\text{NH}_2$) or the carboxylic acid ($-\text{COOH}$) functional groups. The compounds thus obtained crystallize in non-centrosymmetric space groups in view of the chiral nature of the α -amino acids (excepting glycine) and possess non-linear properties. This has prompted several new research groups to venture into the above type of work by employing chiral amino acids as starting materials for product syntheses. It is unfortunate to note that, the chemistry of the reactants used for crystal growth and analysis of the experimental observations are not taken into consideration while reporting the results of such research work, in the form of a

publication, resulting in erroneous reports. Several such erroneous reports were brought to the attention of the scientific community by Fleck and Petrosyan in a case study of salts of amino acids [1]. A commonly encountered error in many of these reports is the claim of the discovery of a „so called“ novel NLO crystal when the crystal grown is a known compound or even one of the starting materials [1-4]. Crystals of the well-known compound dichloro(L-proline)cadmium(II) hydrate (**1**) [5] are investigated under a different name viz. L-proline cadmium chloride monohydrate L-PCCM (for compound nomenclature see Supplementary Material) by Vetrivel *et al* [6] who claim to have grown the „so called“ zinc doped L-proline cadmium chloride monohydrate crystals namely $Zn_{(0.4mol)}:LPCCM$ (**3**) and $Zn_{(0.2mol)}:LPCCM$ (**4**). In this report, it will be shown that the structural features of compound **1** do not permit the doping of any zinc(II) ions into its crystal structure.

2. Structural chemistry of L-proline compounds of Cd(II) and Zn(II)

Yukawa *et al* have reported on the synthesis and single crystal X-ray structure (Table 1) of dichloro(L-proline)cadmium(II) hydrate **1** [5] and dichlorobis(L-proline)zinc(II) (**2**) [7]. The structure of compound **1** which consists of a central Cd(II), two unique μ_2 -bridging chloride ligands and a symmetrical μ_2 -bridging bidentate L-proline ligand is a one-dimensional polymer. Each Cd(II) in the infinite chain is six coordinated and bonded to four Cl atoms and two oxygen atoms of L-proline. In contrast, the structure of **2** consists of a central Zn(II), two terminal chloride ligands and two unique monodentate L-proline ligands and is a monomer. Unlike the Cd(II) compound **1** which exhibits a polymeric structure based on interlinked $\{CdCl_4O_2\}$ octahedra, the structure of the zinc compound **2** is based on discrete $\{ZnCl_2O_2\}$ tetrahedra (Fig. 1). The metric parameters of M-O, M-Cl bonds and O-M-O, Cl-M-Cl angles (M = Cd or Zn) (Fig. S1) also illustrate the differing structure of compounds **1** and **2**. Thus, it is interesting to note that compounds **1** and **2** which crystallize in the same orthorhombic Sohncke space group $P2_12_12_1$ (Table 1) are structurally different in terms of the

stereochemical requirements of the central metal and dimensionality (for more details see Supplementary Material). This difference in structure of **1** and **2** was attributed by Yukawa [7] to the halogeno L-proline Cd(II) or Zn(II) compounds retaining the traces of cadmium or zinc halide. It is well documented that the structure of CdCl_2 and ZnCl_2 consist of CdCl_6 octahedra and ZnCl_4 tetrahedra [8]. The preference of Cd(II) and Zn(II) for hexa and tetra coordination respectively for the set of L-proline and chloride ligands can be confirmed by the fact that the analogous Zn(II) and Cd(II) compounds of **1** and **2** namely dichloro(L-proline)zinc(II) hydrate and dichlorobis(L-proline)cadmium(II) are not known.

Table 1. Comparison of unit cell data of dichloro(L-proline)cadmium(II) hydrate **1**, dichlorobis(L-proline)zinc(II) **2** with zinc chloride doped LPCCM

Compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	Space Group	Ref
dichloro(L-proline)cadmium(II) hydrate 1	10.021(3)	13.562(4)	7.298(3)	991.833	$P2_12_12_1$ [#]	[5]
dichlorobis(L-proline)zinc(II) 2	13.527(3)	16.263(3)	6.598(1)	1451.49	$P2_12_12_1$ [#]	[7]
$\text{Zn}_{(0.4\text{mol})}$:LPCCM 3	16.2658*	13.5624*	6.6153*	1459.35	$P2_12_12_1$ [§]	[6]
$\text{Zn}_{(0.2\text{mol})}$:LPCCM 4	10.0123*	13.5496*	7.299*	990.18	$P2_12_12_1$ [§]	[6]

*No esd's given; [#]Space group from structure determination; [§]No cif files reported

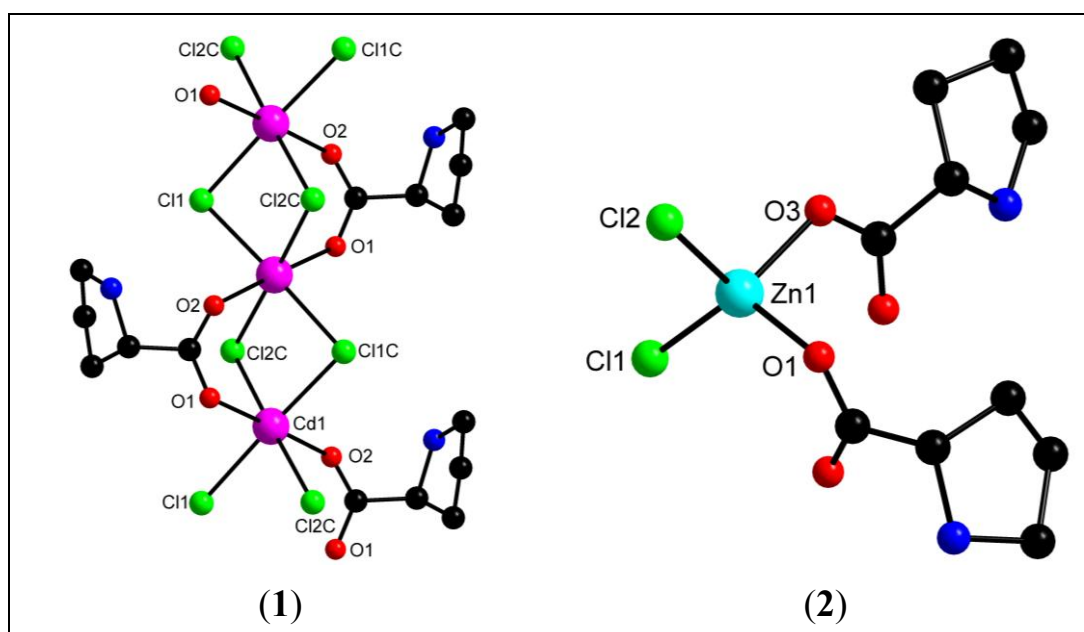


Fig. 1. Interlinked $\{\text{CdCl}_4\text{O}_2\}$ octahedra in the polymeric compound **1** (left) *versus* discrete $\{\text{ZnCl}_2\text{O}_2\}$ tetrahedra in **2** (right). For clarity, H atoms of L-proline (see Fig. S1-S3) are not shown here. (Note- Structures are drawn using the reported cif data in [5] and [7]).

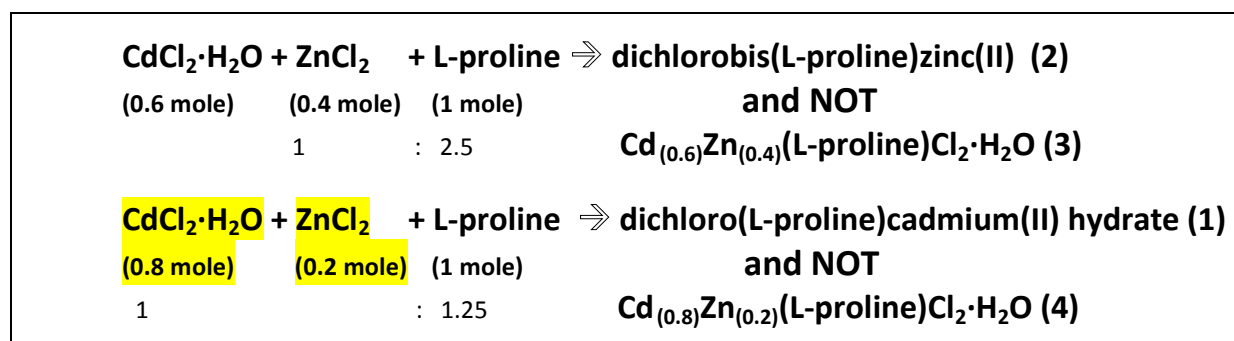
3. Can zinc(II) ions be doped into the crystal structure of compound 1?

The authors of [6] claim to have grown by the slow evaporation solution growth technique, the „so called“ zinc doped L-proline cadmium chloride monohydrate crystals namely $\text{Zn}_{(0.4\text{mol})}:\text{LPCCM}$ (**3**) or $\text{Zn}_{(0.2\text{mol})}:\text{LPCCM}$ (**4**) from an aqueous solution containing zinc chloride (0.4 mol or 0.2 mol), cadmium chloride (0.6 mol or 0.8 mol) and L-proline (1 mol) (Scheme 1). Disregarding the chemistry of a reaction which dictates product formation, these authors have formulated the grown crystals based on an incorrect assumption that the use of $\text{CdCl}_2:\text{ZnCl}_2:\text{L-proline}$ in a 0.6:0.4:1 or (0.8:0.2:1) mole ratio will result in their „so called“ Zn-doped compounds **3** or **4**. Although, these authors claim to have characterized both the Zn doped compounds **3** and **4** with the aid of single crystal and powder X-ray diffraction studies, only lattice parameters (without any esd's) and space group $P2_12_12_1$ (without Flack parameter [9]) are given and no other results of the single crystal studies (cif files) are reported. Based on unit cell volume, the authors claimed that zinc is doped in the structure of **1** and declared in the paper: „*The increase in unit cell volume of $\text{Zn}_{(0.4\text{mol})}:\text{LPCCM}$ and $\text{Zn}_{(0.2\text{mol})}:\text{LPCCM}$ crystals has confirmed that the doping of various percentage of zinc chloride in pure L-PCCM crystal*‘. Unfortunately the above conclusion of the authors of [6] is incorrect as will be proved below.

For compound **3** with a proposed chemical composition $\text{Zn}_{(0.4\text{mol})}:\text{LPCCM}$ where 0.4 mol (40%) of Cd(II) ions in the L-PCCM crystal **1** are supposed to have been doped (substituted) by Zn(II) ions, the unit cell volume is actually expected to decrease in view of the smaller size of zinc, but never increase, if any doping takes place. Hence, the observed very large (~46%) increase in unit cell volume for compound **3** (from 991.83 for **1** to 1459.35 \AA^3) compared to that of the Cd(II) compound **1** (Table 1) clearly indicates that no Zn(II)

incorporation (doping) has taken place. Instead, the reported cell volume unambiguously confirms that the „so called“ Zn doped crystal namely $Zn_{(0.4mol)}:LPCCM$ **3** is actually dichlorobis(L-proline)zinc(II) **2**, as can be evidenced by the very good agreement of the unit cell parameters of **3** with the respective parameters of the dichlorobis(L-proline)zinc(II) **2** crystal, reported by Yukawa *et al* [7] but for an interchange in the *a* and *b* axes (Table 1).

Thus the non incorporation of the tetrahedral zinc(II) ions at the octahedral Cd(II) sites in the one-dimensional polymeric chain compound **1** is perfectly in accordance with the differing structural chemistry of compounds **1** and **2**. The Zn(II) ions which exhibit four coordination and shorter Zn-Cl, Zn-O bond lengths and Cl-Zn-Cl, O-Zn-O angles cannot be incorporated into the structure of the polymeric compound **1** at the octahedral Cd(II) site which exhibits longer Cd-Cl and Cd-O bonds and a nearly linear O-Cd-O bond angle (Fig. S1). The growth of crystals of **2** as major product can be explained due to the presence of zinc (0.4 mole) and L-proline (1 mole) closer to the preferred ratio for its formation instead of **1**. Despite the presence of an excess of Cd(II) (0.6 mole) in the reaction medium, no Cd(II) was incorporated in the crystal structure of **2** (for the above same reason) resulting in the formation of pure **2** as evidenced by unit cell data. The above arguments can be extended to rule out the formation of the other „so called“ zinc doped crystal namely $Zn_{(0.2mol)}:LPCCM$ crystal (Scheme 1) which is nothing but dichloro(L-proline)cadmium(II) hydrate **1** crystal, as can be evidenced by a comparison of the unit cells of **4** and **1** (Table 1).



Scheme 1

4. Inappropriate use of EDAX for compound characterization

Although the authors wrote „An elemental analysis has been carried out for zinc doped LPCCM crystal specimen by the energy dispersive X-ray analysis (EDAX) in order to confirm the composition of zinc and chlorine radicals in the crystal“ they did not check to see if the EDAX values agreed with theoretical values for the proposed formula. In the crystal, zinc and chlorine do not exist as radicals but as Zn^{+2} and Cl^{-} ions. Contrary to the claim of the authors, the experimental EDAX values for compound **3** (Table 2) do not in any way correspond to the theoretical values. In addition to an unusually high value for C, the sum of the percentages of only four atoms namely Cd, Zn, Cl and C (excluding N and H) is 100 % showing that the EDAX result for compound **3** is not only unacceptable but also no valid proof. A listing of % content of a lighter element like C as a proof for product formation from an EDAX experiment is meaningless [3]. It is very strange to note that compounds were formulated based on incorrect EDAX data instead of refinement of single crystal data when single crystal X-ray diffraction studies are claimed to have been performed.

Table 2. Theoretical elemental analytical data for compounds **1**, **2**, **3** and **4** based on molecular formula

Compound code	Formula weight	%Cd	%Zn	%Cl	%C	%H	%N	%O
L-PCCM 1	316.46	35.52	---	22.41	18.98	3.50	4.43	15.17
Compound 2	366.56	---	17.84	19.34	32.77	4.95	7.64	17.46
Zn _(0.4mol) :LPCCM 3	297.65	22.66	8.79	23.82	20.18	3.72	4.71	16.13
		(12.99)*	(3.33)	(25.66)	(58.02)			
Zn _(0.2mol) :LPCCM 4	307.06	29.29 [#]	4.26	23.09	19.56	3.61	4.56	15.63

*Values in **bracket** were reported in [6] for compound **3** based on EDAX analysis.
[#]No experimental values were reported for **4**.

5. Conclusions

The conclusions of the present work are as follows: i) A new compound should not be formulated based on an assumption that a certain crystal grown from a mixture of precursor materials (CdCl_2 , ZnCl_2 , L-proline in the present case) taken in a preferred ratio, will represent an expected product crystal. ii) For doped crystals, an increase in unit cell volume is no valid proof for the doping to have occurred. iii) Mere observation of the presence of a few elements in an EDAX study is no valid proof for confirmation of a new product. iv) Structural chemistry principles are very useful to determine beforehand, which atom or ion or molecule can be incorporated into the known crystal structure of a compound. In the case of the L-proline compounds of Cd(II) and Zn(II) namely dichloro(L-proline)cadmium(II) hydrate **1** and dichlorobis(L-proline)zinc(II) **2**, the differing stereochemical requirements of the bivalent metal ions Cd and Zn, makes it impossible to incorporate Zn(II) ions into the crystal structure of compound **1**. Hence, the paper by Vetrivel *et al* [6] reporting growth of the „so called“ zinc doped L-PCCM crystals namely $\text{Zn}_{(0.4\text{mol})}$:LPCCM **3** and $\text{Zn}_{(0.2\text{mol})}$:LPCCM **4**, is completely erroneous.

Footnotes:

¹In this report, compounds are referred to by numbers instead of non standard abbreviations.

²This relevant paper is not cited by authors of [6].

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