

## Structure and thermal reactivity of Zn(II) salts of isocinchomeric acid (2,5-pyridinedicarboxylic acid)

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**Abstract** The synthesis, an improved refined crystal and molecular structure re-determination, and the thermal decomposition behavior of two Zn(II) derivatives of isocinchomeric acid (2,5-pyridinedicarboxylic acid or H<sub>2</sub>2,5-pydc) are presented. [Zn(2,5-pydc)(H<sub>2</sub>O)<sub>3</sub>Zn(2,5-pydc)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> (**1**) crystallizes in the triclinic P-1 space group with  $a = 7.106(2)$ ,  $b = 11.450(2)$ ,  $c = 11.869(1)$  Å,  $\alpha = 107.29(1)$ ,  $\beta = 104.08(1)$ ,  $\gamma = 90.32(2)^\circ$ , and  $Z = 2$ . [Zn(2,5-pydc)(H<sub>2</sub>O)<sub>2</sub>] · H<sub>2</sub>O (**2**) is orthorhombic (P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> space group), with  $a = 7.342(1)$ ,  $b = 9.430(1)$ ,  $c = 13.834(2)$  Å, and  $Z = 4$ . The structures were refined to agreement  $R_1$ -factors of 0.0315 (**1**) and 0.0336 (**2**). Complex (**1**) is arranged as molecular Zn<sub>4</sub>(2,5-pydc)<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub> tetramers, the cages of which define channels that remain unblocked by anions. Compound (**2**) is polymeric with Zn(2,5-pydc)(H<sub>2</sub>O)<sub>2</sub> and Zn(2,5-pydc)(H<sub>2</sub>O)<sub>3</sub> units linked through bridging ligands. Both compounds were synthesized

under mild conditions in aqueous media, without need to resort to hydrothermal media. Changing the pH from 4.51 to 5.75 suffices to direct the chemical processes toward the orthorhombic compound rather than to the triclinic one.

**Keywords** 2,5-Pyridinedicarboxylate · Isocinchomeronate · Zinc · Structure · Thermal properties

### Introduction

During the last decade the series of metal complexes formed by the pyridine-dicarboxylic acids have drawn considerable interest because these ligands are able to form compounds of large structural diversity. All the anionic isomers (2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dicarboxylates) present several potential donor sites: the oxygen atoms of the carboxylic groups and the nitrogen atom in the aromatic ring. Depending on the relative position of the donor sites (angles and distances), the solid complexes formed by these ligands may be molecular solids, as in the case of 2,6- and 2,4-pydc derivatives [1–3], or may contain chains [4] or complex three-dimensional structures [5] hence giving rise to a variety of materials with properties useful for potential applications. In particular, discrete macro-cyclic metal complexes may be tailored to form cavities, porous materials or channels that behave as hosts for small molecule guests. The synthesis of these open molecular frameworks has received much attention [6–10].

The structure of the isocinchomeric acid (H<sub>2</sub>2,5-pydc) makes this ligand suitable for the synthesis of cage materials because the two carboxylate groups in the 2- and 5- ring positions may easily coordinate to different metal centers, and the relative position of the coordinative moieties is adequate to form supramolecular structures of varied

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structural features. The carboxylic groups also stabilize the 3-D structure acting as proton donors and H-acceptors as each carboxylate can accept up to four hydrogen bonds [11, 12]. The formation of mono-dentate and/or multi-dentate M–O and M–N metal–ligand bonds [13] may also change the crystal properties. H<sub>2</sub>,5-pydc complexes of first transition metal (II) ions having 1:1 ratio have been reported to be molecular, as in [Ni(2,5-pydc)(H<sub>2</sub>O)<sub>4</sub>] · 2H<sub>2</sub>O [14], 1-D polymeric, as in Cu(2,5-pydc)(H<sub>2</sub>O) [15], 2D- polymeric, as in [Me(2,5-pydc)(H<sub>2</sub>O)<sub>2</sub> · H<sub>2</sub>O] (Me: Co [16, 17], Zn [18] and Ni [19]), and 3-D polymeric, as in [Fe(2,5-pydc)(H<sub>2</sub>O)] [20]. A supramolecular structure has also been reported by Liang et al. [21], by Wang et al. [22] and by Mahata et al. [23]: the compound with stoichiometry Zn(2,5pydc)(H<sub>2</sub>O)<sub>2</sub> contains the discrete entity Zn<sub>4</sub>(2,5pydc)<sub>4</sub>(H<sub>2</sub>O)<sub>8</sub> where the four penta-coordinated Zn atoms are connected by four 2,5-pydc ligands through bridges forming a rectangular structure. Stacking of the tetramers leads to the formation of channels.

We report here the synthesis, a more precise structure refinement and the thermal decomposition behavior of a complex containing Zn(2,5-pydc) tetramers (**1**) in which the channels remain unblocked by anions. After our own X-ray diffraction measurements were completed, the crystal structure of this compound was reported by Wei [24] with a rather limited crystallographic agreement factor ( $R = 0.0812$ ). As the crystal structure of the coordination compounds depends also on the electronic configuration of the metal site, we chose Zn(II) as the metallic center because of its structural flexibility to adopt various coordination polyhedra. The supramolecular structure shown by the Zn(II) derivative is unusual and defined by hexa- and penta-coordinated zinc ions, conformational features that suggest the potential use of this material to host for small guests.

We also report the synthesis, structural and thermal study of another complex with stoichiometry Zn(C<sub>7</sub>H<sub>3</sub>O<sub>4</sub>N)(H<sub>2</sub>O)<sub>3</sub> (**2**). There are previous references to this compound in the literature [16–18], but only cell parameters are reported along with data for the isostructural Co and Ni compounds.

In this paper we show that adequate choice of pH during the preparation procedure provides a powerful tool to tailor the material's properties, not only because the protonation or deprotonation of the ligand may determine the possibility of obtaining 1:1 or 1:2 compounds, but also because the incorporation of water in the solid framework can be modulated by the pH.

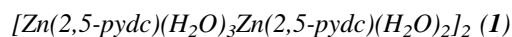
## Experimental

### Materials and methods

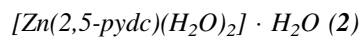
All chemicals were reagent grade and have been used as provided. The metal content of the solid was determined at

INQUIMAE, Universidad de Buenos Aires, with a Varian Techrom A-A5R atomic absorption spectrometer. Elemental analyses were performed in a Carlo Erba EA 1108 microanalyzer. The X-ray diffraction data were collected on an Enral-Nonius CAD-4 diffractometer working in the  $\omega$ - $2\theta$  scanning mode. Thermal analyses were performed in a Shimadzu TGA-51 and DTA-50 thermal analyzers, under a nitrogen atmosphere, at a heating rate of 6 °C min<sup>-1</sup>. PXRD patterns were recorded in a Siemens D5000 diffractometer with a Bragg-Brentano geometry, using the Cu K $\alpha$  radiation and a curved graphite-monochromator.

### Synthesis of the solids



ZnSO<sub>4</sub> · 7H<sub>2</sub>O (0.287 g, 1 × 10<sup>-3</sup> mol) was added to 200 mL of an aqueous suspension of 2,5-pydc acid (0.175 g, 1 × 10<sup>-3</sup> mol). A NaOH solution (0.1 N) was added until final pH 4.51. The solid was obtained by slow evaporation at 298 K. The crystals formed were collected by filtration and washed twice with bidistilled water. Calc. for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>13</sub>Zn<sub>2</sub>: C, 30.5; H, 2.9; N, 5.1; Zn, 23.7. Found: C, 30.2; H, 2.8; N, 5.1; Zn, 23.8.



The same procedure was used, but NaOH was added until pH 5.75 was reached. The crystals obtained were pale yellow and the chemical analyses indicated the empirical formula Zn(C<sub>7</sub>H<sub>3</sub>O<sub>4</sub>N)(H<sub>2</sub>O)<sub>3</sub>. Calc. for C<sub>7</sub>H<sub>9</sub>NO<sub>7</sub>Zn: C, 29.8; H, 3.2; N, 4.3; Zn, 23.1. Found: C, 29.7; H, 3.5; N, 4.2; Zn, 23.0.

### Data collection and processing

Crystal data, data collection procedure, structure determination methods, and refinement results for the two complexes are summarized in Table 1 [25–29]. In **1**, the hydrogen atoms of the 2,5-pydc group were positioned stereo-chemically while the ones of the water molecules located in a difference Fourier map. All H-atoms were refined with a common isotropic displacement parameter (which converged to 0.050(3) Å<sup>2</sup>), the former riding on the corresponding carbon atom and the latter kept fixed at their found positions.

In **2**, the H-atoms of the 2,5-pydc ligand were positioned on stereo-chemical basis and refined with the riding model. The water H-atoms were found in a difference Fourier map and refined isotropically with O–H and O···O distances constrained to target values of 0.86(1) and 1.36(1) Å, respectively.

**Table 1** Crystal data and structure solution methods and refinement results for [Zn(2,5-pydc)(H<sub>2</sub>O)<sub>3</sub>Zn(2,5-pydc)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> (**1**) and Zn(2,5-pydc)(H<sub>2</sub>O)<sub>2</sub>·H<sub>2</sub>O (**2**)

	Compound 1	Compound 2
Empirical formula	C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> O <sub>13</sub> Zn <sub>2</sub>	C <sub>7</sub> H <sub>9</sub> NO <sub>7</sub> Zn
Formula weight	551.03	284.52
Temperature (K)	294(2)	294(2)
Crystal system	triclinic	orthorhombic
Space group	P-1	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	7.106(2)	7.342(1)
<i>b</i> (Å)	11.450(2)	9.430(1)
<i>c</i> (Å)	11.869(1)	13.834(2)
$\alpha$ (°)	107.29(1)	90.00
$\beta$ (°)	104.08(1)	90.00
$\gamma$ (°)	90.32(2)	90.00
Volume (Å <sup>3</sup> )	891.2(3)	957.8(2)
Z, calc. density (Mg/m <sup>3</sup> )	2, 2.053	4, 1.973
Absorpt.coef. (mm <sup>-1</sup> )	4.073	3.853
Crystal color/shape	yellow/prism	yellow/prism
Diffractionmeter/scan	Enraf-Nonius CAD4/ $\omega$ – 2 $\theta$	
$\lambda$ (Å)	1.54184	
Reflections collected/unique	3482/3319	1141/1116
<i>R</i> (int)	0.0175	0.0461
Obs. Reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	3177	1082
Data collection	COLLECT [25]	
Data reduc and correc <sup>a</sup>	XCAD4 [26]	
Absorption correction	PLATON [27]	
Structure solution <sup>b</sup> and Refinement <sup>c</sup> programs	SHELXS-97 [28] SHELXL-97 [29]	
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.189	1.063
Final <i>R</i> -index [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0315, <i>wR</i> <sub>2</sub> = 0.0909	<i>R</i> <sub>1</sub> = 0.0336, <i>wR</i> <sub>2</sub> = 0.0911
<i>R</i> indices (all data) <sup>d</sup>	<i>R</i> <sub>1</sub> = 0.0331, <i>wR</i> <sub>2</sub> = 0.0925	<i>R</i> <sub>1</sub> = 0.0345, <i>wR</i> <sub>2</sub> = 0.0925
Largest peak and hole(e·Å <sup>-3</sup> )	0.562 and –0.525	0.565 and –0.395

<sup>a</sup> Corrections: Lorentz and polarization

<sup>b</sup> Structure solved by direct and Fourier methods

<sup>c</sup> Neutral scattering factors and anomalous dispersion corrections. Final molecular model obtained by anisotropic full-matrix least-squares refinement of the non-hydrogen atoms

<sup>d</sup> *R*-indices defined as:  
 $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ ,  
 $wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^{1/2}}$

## Results and discussion

Description of the structure of [Zn(2,5-pydc)(H<sub>2</sub>O)<sub>3</sub>Zn(2,5-pydc)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> (**1**)

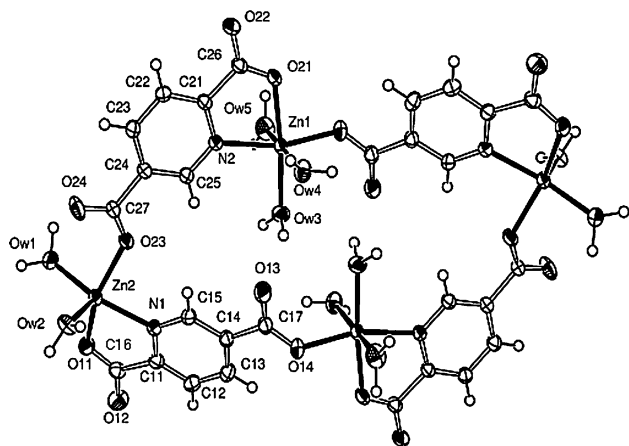
The compound contains discrete [Zn<sub>4</sub>(pydc)<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>] molecules, in which the four coplanar Zn atoms are connected by four 2,5-pydc ligands through bridges forming a centrosymmetric structure. The four Zn atoms define a parallelogram. Figure 1 shows the ORTEP [30] plot and the labeling scheme of the tetrameric complex. Selected bond distances and angles are shown in Table 2.

Atoms Zn(1) and Zn(2) are related to atoms Zn(1') and Zn(2') through the inversion symmetry operation 1 – *x*, –*y* + 1, –*z*. Zn(1) is coordinated to a 2,5-pydc group acting as a bidentating ligand through N(2) and one oxygen atom in the carboxylate 2-position of the pyridinic ring (ring (II)) [distances Zn(1)–N(2) = 2.170(2) and Zn(1)–O(21) = 2.129(2) Å]. Zn(1) is also bounded to three water

molecules (distances Zn(1)–OW(3) = 2.037(2), Zn(1)–OW(4) = 2.177(2), and Zn(1)–OW(5) = 2.122(2) Å). The hexacoordination is achieved by bonding to O(14) from carboxylate in 5-position in 2,5-pydc (ring I) [distance Zn(1)–O(14') = 2.014(2) Å]. Because of ligand constrain the smaller angle around Zn(1) is formed with the bidentating ligand (O(21)–Zn(1)–N(2) = 75.85(8)°), all other angles in the Zn(1) polyhedron are larger (range 88.5–95.97(9)°).

In the carboxylate groups the shorter distances are found in the non-coordinating O atom, indicating a double bond C=O. In ring (I), distances C(16)–O(12), C(16)–O(11), C(17)–O(13), and C(17)–O(14) are 1.233(4), 1.272(4), 1.244(4), and 1.258(4) Å, respectively. The same feature is observed in ring (II) (see Table 2).

Zn(2) is penta-coordinated, the metal is chelated by atoms N(1) and O(11) from ring (I) [distances Zn(2)–N(1) = 2.086(2), Zn(2)–O(11) = 2.069(2) Å], and is also coordinated to two water molecules OW(1) and OW(2) and to carboxylate



**Fig. 1** Molecular plot of the centrosymmetric crown-like  $[\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_3\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_2]_2$  complex showing the labeling of the non-H atoms and their displacement ellipsoids at the 50% probability level. Metal–ligand bonds are indicated by full lines

**Table 2** Selected bond distances (Å) and angles ( $^\circ$ ) around Zn(II) in  $[\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_3\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_2]_2^a$

Bond	Distance	Bond	Distance
Zn(1)–O(14')	2.014(2)	Zn(2)–O(23)	2.010(2)
Zn(1)–OW3	2.037(2)	Zn(2)–OW2	1.990(2)
Zn(1)–OW5	2.122(2)	Zn(2)–OW1	2.048(2)
Zn(1)–O(21)	2.129(2)	Zn(2)–O(11)	2.069(2)
Zn(1)–N(2)	2.170(2)	Zn(2)–N(1)	2.086(2)
Zn(1)–OW4	2.177(2)		
C(16)–O(12)	1.233(4)	C(26)–O(22)	1.239(4)
C(16)–O(11)	1.272(4)	C(26)–O(21)	1.262(4)
C(17)–O(13)	1.244(4)	C(27)–O(24)	1.235(4)
C(17)–O(14)	1.258(4)	C(27)–O(23)	1.255(4)
<b>Angle</b>			
O(14')–Zn(1)–OW5	88.5(1)	O(11)–Zn(2)–N(1)	79.16(9)
O(14')–Zn(1)–OW4	87.9(1)	OW1–Zn(2)–O(11)	88.38(9)
N(2)–Zn(1)–OW4	91.55(9)	OW2–Zn(2)–OW1	105.1(1)
O(14')–Zn(1)–OW3	100.6(1)	OW2–Zn(2)–N(1)	103.9(1)

<sup>a</sup> Primed atoms are related to the unprimed ones through the inversion symmetry operation  $1 - x, -y + 1, -z$

O(23) from ring (II) [distances Zn(2)–OW(1) = 2.048(2), Zn(2)–OW(2) = 1.990(2), Zn(2)–O(23) = 2.010(2) Å]. These values are slightly shorter than those reported earlier by Wei et al. [24] with an appreciably higher error ( $R_1 = 0.0812$ ,  $wR_2 = 0.2194$ ). Again, the smaller angle around Zn(2) is displayed by the bidentating 2,5-pydc [angle O(11)–Zn(2)–N(1) = 79.16(9)], all other angles differ greatly from symmetric coordination values indicating an angular distorted coordination [angles in the range 85.87(9)–107.66(9) $^\circ$ ].

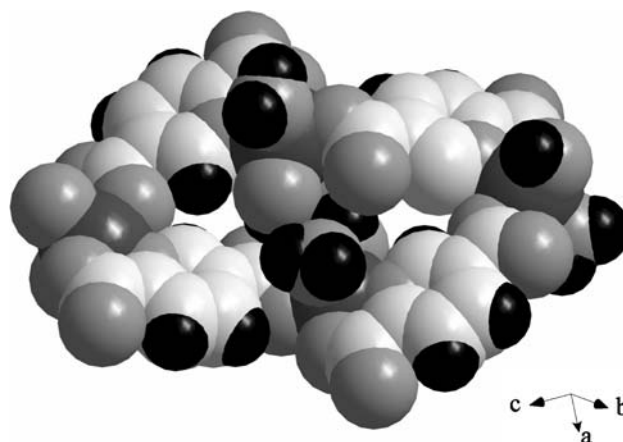
Ring (I) is almost planar and angles between the pyridinic ring and the carboxylate groups in 2- and 5-positions are 2.6 $^\circ$  (1.5 $^\circ$ ) and 2.4 (1.7). The pyridinic ring (II) departs from planarity, the carboxylates O(11)–C(16)–O(12) bonded to Zn(2) and O(13)–C(17)–(14) bonded to Zn(1) are rotated 2.2(1.1) $^\circ$  and 10.8 $^\circ$ (2) $^\circ$ , from the pyridine ring plane (angle between groups in 2- and 5- is 9.5 $^\circ$ (3)). The angle formed by the two aromatic rings is 34.0 $^\circ$ . The non-restrained angular position in the 5-carboxylate in ring (II) facilitates the bond to Zn(1) and Zn(2) forming a four-member crown, with two pairs of equivalent metal centers.

As stated above, the four Zn atoms define a parallelogram with Zn(1)–Zn(2) and Zn(2)–Zn(1') sides of 8.440(6) and 7.429(5) Å and long and short diagonals dimensions of 14.732(6) and 5.983(6) Å. The symmetry related OW(3) and OW(3') water molecules are directed toward the center of the crown along the short diagonal hence partitioning the parallelogram into two adjacent triangular sections. Taking into account the van der Waals radii of the surrounding atoms, each section encloses a cavity with transversal dimensions of about 3.20  $\times$  5.66 Å (cf. Fig. 2).

The aromatic rings are stacked by  $\pi$ – $\pi$  interactions (distance 3.280 Å) forming layers approximately parallel to crystallographic plane bc. The lattice is stabilized by a network of OW–H $\cdots$ O and OW–H $\cdots$ OW hydrogen bonds involving water molecules OW(1), OW(2), OW(3), OW(4), and OW(5). These molecules bind consecutive layers by forming intermolecular hydrogen bridges with oxygen atoms of carboxylate groups.

OW(3) also forms very weak intramolecular H-bridges through the center of the crown (calculated distances are [HW(31) $\cdots$ OW(3) = 2.5069 Å (D $\cdots$ A = 2.979 Å) and HW(52) $\cdots$ OW(4) = 2.373 Å (D $\cdots$ A) = 3.283 Å]).

This structure differs from the one found for  $[\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_2]_{4n}$  [21–23] that contains one water molecule



**Fig. 2** Space filling model showing the two channels formed by the Ow(3) and Ow(3') water molecules directed toward the center of the crown. Oxygen atoms from water molecules are shown in black

less per tetramer. In particular, the cell volume of  $[\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_3\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_2]_2$  is larger than that of  $[\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_2]_4$  (compare 891.2(3) and 859.1(3) Å<sup>3</sup>). The dimensions of the cage are however similar, with small differences in shape. The ratios of the longer to the shorter diagonal dimensions are 11.952: 3.203 for the compound reported here and 12.254: 2.579 for the one reported in references 21–23. The additional water molecule in  $[\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_3\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_2]_2$  (OW(4) or OW(5), see above) acts as a spacer between cages, and the robustness of the basic Zn tetramer opens the possibility to tailor other materials by introducing new spacers.

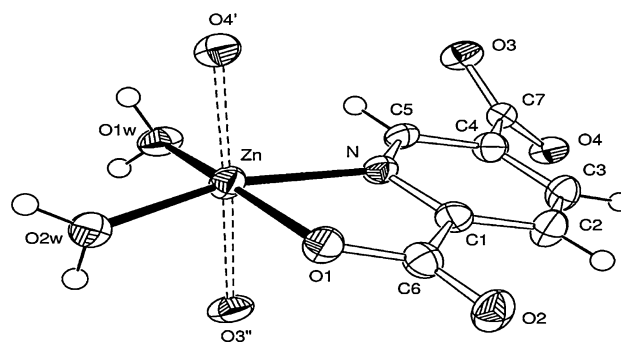
As can be seen, different preparative techniques may lead to different solids. In hydrothermal media, one water molecule may be removed [21–23] or not [24], depending on the concentration of the reagents. High concentrations and slightly higher temperatures lead to the less hydrated material. At the concentrations used in our work, in hydrothermal media the weaker Zn–OW(4) or Zn–OW(5) bond is broken, and all the Zn atoms become penta-coordinated [21]; as stated, Zn–OW(3) bond is unaffected, reflecting a large stability of the water molecule protruding into the cavity.

Also in hydrothermal media, hexa-coordinated Zn(1) can only be prepared at much lower concentrations (tenfold decrease in Zn and ligand concentrations) [24]. Hence, it is concluded that the use of hydrothermal conditions favor the dehydration, although several other experimental conditions differ: the starting Zn salt and, very especially, the pH, which was very low in Liang's synthesis. Indeed, even in our experimental conditions, raising the pH to 5.75 leads to the formation of orthorhombic  $\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ , to be described next.

#### Description of the structure of $[\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (2)

The compound is orthorhombic (space group  $P2_12_12_1$ ),  $a = 7.3418(10)$  Å,  $b = 9.4297(10)$  Å, and  $c = 13.834(2)$  Å. There is an earlier mention about this compound by Zhang et al. [18], and the structures of the isostructural Co and Ni compounds have been reported [16, 17]. The coordination polyhedron around Zn is a distorted octahedron, as shown in Fig. 3 and Table 3.

The equatorial plane is defined by N and O(1) from the carboxylate in 2-position, and two water molecules (OW(1) and OW(2)) slightly protruding above and below the plane. The aromatic ring is slightly tilted from the equatorial plane ( $18.35(8)^\circ$ ). The axial positions are covered by O(3'') and O(4') from 5-positioned carboxylate groups belonging to different ligands. The interaction of O(3) and O(4) with other Zn atoms is responsible for an appreciable deviation of the carboxylate plane for the ring plane



**Fig. 3** Molecular plot of  $[\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_2]$  complex showing the axial coordination of the metal (in double dashed line) to the terminal carboxylic oxygen atoms of neighboring ligand groups in the lattice. The primed oxygen atom is obtained through a unit translation along the crystal  $a$ -axis, the double primed one by the screw-rotation  $1 - x, -0.5 + y, 0.5 - z$  around the  $b$ -axis

**Table 3** Selected bond distances (Å) and angles ( $^\circ$ ) around Zn(II) in  $[\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (2)

Bond	Distance	Bond	Distance
Zn–OW1	2.034(3)	Zn–OW2	2.038(3)
Zn–O(1)	2.074(3)	Zn–O(4')	2.117(3)
Zn–N	2.135(3)	Zn–O(3'')	2.275(3)
Angle			
OW1–Zn–OW2	99.52(14)	OW2–Zn–O(1)	86.91(12)
O(1)–Zn–O(4')	100.16(11)	OW1–Zn–N	94.40(12)
O(1)–Zn–N	77.74(11)	O(4')–Zn–N	95.35(11)
O(4')–Zn–O(3'')	173.35(10)	N–Zn–O(3'')	84.56(11)

aPrimed atoms are obtained from the unprimed ones through the translation symmetry operation  $x + 1, y, z$ ; double primed atoms are obtained through the screw-rotation parallel to the  $b$ -axis  $-x + 1, y - 1/2, -z + 1/2$

( $34.03(13)^\circ$ ). This deviation is typical of 2,5-pydc compounds, as opposed, for instance to 2,6-pydc compounds featuring one or two ligands bound to one central metal ion [1–3].

The lack of coplanarity of the carboxylate in the 5-position determines in turn a three-dimensional structure that differs appreciably from that of 2,6-pydc compounds. The third water molecule is interstitial water, located between layers.

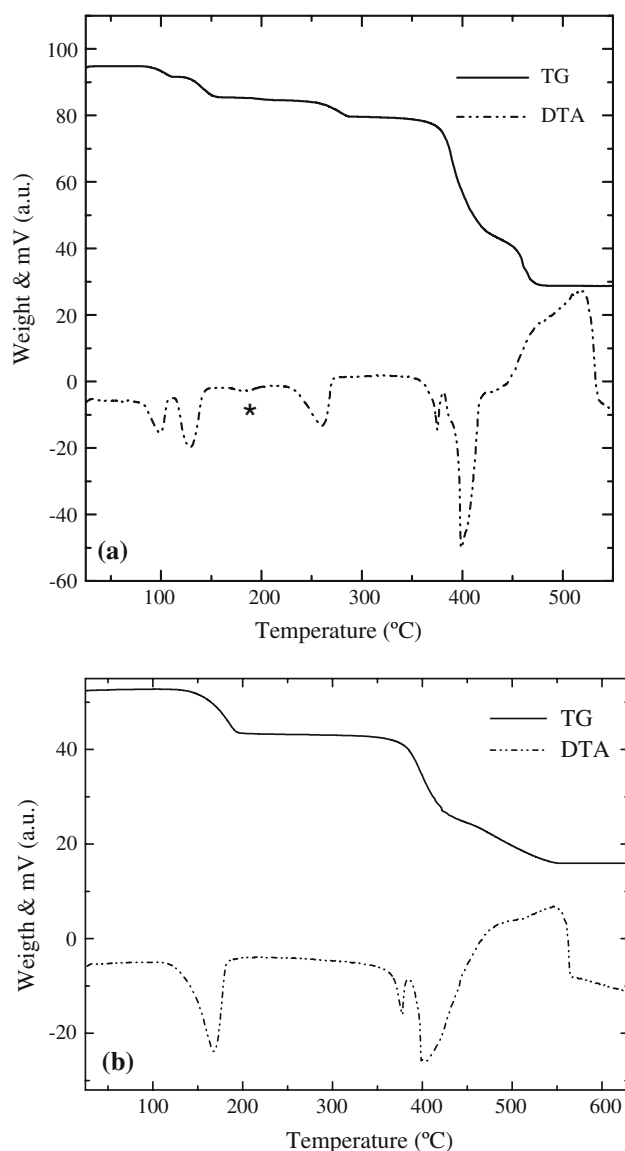
Alternate anion and cation polymeric layers are defined approximately along the  $a$ - (bidentate ring and O(4)) and  $b$ -axis (O(3)). Tian et al. [17] have shown that the isostructural Co(II) derivative corresponds to a chiral coordination polymer containing interconnected right-handed and left-handed helical chains; thus, the compound exhibits strong signals in vibrational circular dichroism spectra.

Distances Zn–O(3'') (2.275(3) Å) and Zn–O(4') (2.117(3) Å) are longer than the equatorial Zn–(O) distances

(2.0174 and 2.038(3) Å) and thus the compound may be viewed as formed from discrete monomers. There is an extensive hydrogen bonding network within each layer and between layers, linking coordinated water (OW(1) and OW(2)) with carboxylate groups (O(1) and O(2) for OW(1), and O(4) for OW(2)). Interstitial water (OW(3)) also links coordinated water (OW(2)), and carboxylate group (O(3)), forming further weak hydrogen bonds with the polymeric layers.

#### Thermal properties

Figure 4a shows the TG and DTA traces obtained for (1). Five well-defined weight losses are seen. The first

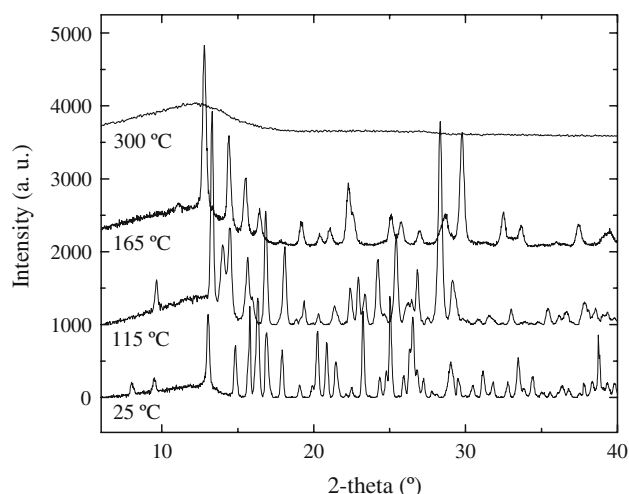


**Fig. 4** TG and DTA traces for [Zn(2,5-pydc)(H<sub>2</sub>O)<sub>3</sub>Zn(2,5-pydc)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> (a) and for [Zn(2,5-pydc)(H<sub>2</sub>O)<sub>2</sub>] (b). The asterisk in (a) shows the small endothermic peak

endothermic step centered at 106.6 °C (weight loss 3.3 %) accounts for the release of two water molecules. Both the second and third endothermic steps (centered at 142.1 °C and 280.5 °C) correspond to the release of approximately four water molecules each (weight losses are 6.6% and 6.3 %). Decomposition of the organic moiety takes place in the third and fourth steps centered at 390.2 °C and 458.6 °C. The DTA trace shows that the third step embodies two endothermic peaks at 372.7 °C and 397.0 °C. At 478 °C the weight stabilizes; however, the DTA trace shows an exothermic peak that may be attributed to the crystallization of ZnO as determined by PXRD (PDF file: 36–1451) in the residue obtained at 560.0 °C. Although no weight loss is detected in the range 171.0–249.0 °C, a weak endothermic peak is found at 189 °C. This DTA may be attributed to a phase change. These results contrast with the gradual featureless weight loss reported by Wei et al. between 68 °C and 489 °C.

The PXRD diagrams of (1) heated at 115 °C, 165 °C, and 300 °C are shown in Fig. 5. The diagram obtained at 115 °C was compared with the simulated diffractogram of Zn<sub>4</sub>(2,5-pydc)<sub>4</sub>(H<sub>2</sub>O)<sub>8</sub>. Both diagrams are identical indicating that in the first step of dehydration each of the two octahedrally coordinated Zn ions in [Zn(2,5-pydc)(H<sub>2</sub>O)<sub>3</sub>Zn(2,5-pydc)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> lose one water molecule to give Zn<sub>4</sub>(2,5-pydc)<sub>4</sub>(H<sub>2</sub>O)<sub>8</sub>, retaining the cage structure.

At 165 °C, after the loss of four additional water molecules, the PXRD indicates the formation of a new crystallographic phase, probably containing tetra-coordinated Zn. This new phase does not correspond to any of the reported Zn 2,5-dipicolinate complexes. It is interesting to note that in hydrothermal media, (1) is stable at this temperature. The amorphous precursor of crystalline ZnO is seen in the PXRD of the solid formed at 300 °C.



**Fig. 5** PXRD diagrams of (1) at 25 °C and heated at 115 °C, 165 °C, and 300 °C

The TG and DTA traces for  $[\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (**2**) are shown in Fig. 4b. Only one endothermic dehydration step is found at 166.8 °C, with a weight loss (18.7%) corresponding to the three water molecules. The organic ligand decomposes in one endothermic step characterized by two DTA peaks (376.4 °C and 402.0 °C, weight loss (31.2%), and by an exothermic step at 490.0 °C (weight loss 20.2 %). At 543.0 °C a new exothermic peak is detected. The final product at 650 °C is also ZnO.

## Conclusions

The tetramer  $[\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_n\text{Zn}(2,5\text{-pydc})(\text{H}_2\text{O})_2]_2$  is a robust entity that constitutes the basic structural unit of two different compounds with  $n = 2$  or 3. The thermal treatment of the more hydrated solid leads to the less hydrated one, with retention of the cage structure. Further loss of water at higher temperatures is accompanied with the destruction of the cage. The decomposition of (**1**) when heated in dry atmosphere also indicates that the thermodynamic stability of the phase is not very large at a relatively high temperature.

The syntheses of the tetrameric material ( $n = 2$ ) [21, 24] is achieved if no base is added to the system. The formation of the Zn salt is therefore attended by strong acidification that compensates the increased rates of chemical reactions, and the tetramer forms.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC–271469 for (**1**) and CCDC–271470 for (**2**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: 1 44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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