

Scientific paper

# Two New Zinc(II) Acetates with 3- and 4-Aminopyridine: Syntheses and Structural Properties

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Received: 06-10-2014

Dedicated to the memory of Prof. Dr. Jurij V. Brenčič.

## Abstract

The synthesis and characterization of two new zinc(II) coordination compounds with 3- and 4-aminopyridine are reported. They were obtained after adding a water solution of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  or dissolving solid  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  in methanol solutions of 3- and 4-aminopyridine. The products were characterized structurally by single-crystal X-ray diffraction analysis. Colourless crystals of the compound synthesized by the reaction of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and 3-aminopyridine (3-apy), are built of trinuclear complex molecules with the formula  $[\text{Zn}_3(\text{O}_2\text{CCH}_3)_6(3\text{-apy})_2(\text{H}_2\text{O})_2](1)$ . The molecules consists of two terminal Zn atoms, coordinated tetrahedrally, and one central Zn atom, coordinated octahedrally. Colourless crystals, obtained by the reaction of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  with 4-aminopyridine (4-apy), consist of a mononuclear complex  $[\text{Zn}(\text{O}_2\text{CCH}_3)_2(4\text{-apy})_2](2)$ . Hydrogen-bonding interactions in the crystal structures of both complexes are reported.

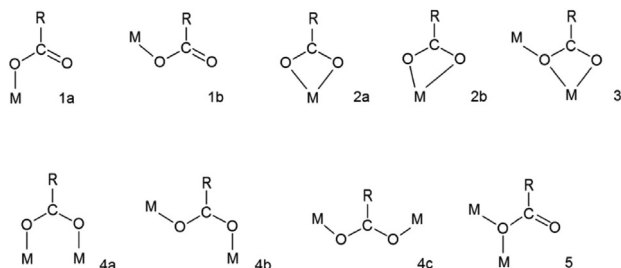
**Keywords:** Zinc(II) acetate dihydrate; Aminopyridine; X-ray crystal structure; Hydrogen bonds.

## 1. Introduction

Zinc is an important trace element in human body, second only to iron among elements for which human nutritional requirement has been established. The biologic role of Zn is recognized in structure and function of proteins, including enzymes, as well as in DNA and RNA metabolism.<sup>1</sup> Nutritional deficiency of zinc is very prevalent in the developing world and is associated with many diseases. Zinc supplementation has a significant effect on growth and body weight gain in children and results in decreased child mortality.<sup>2</sup> Zinc coordination compounds have been successfully tested for treatment of diabetes<sup>3</sup> whilst other papers report their excellent antibacterial,<sup>4,5</sup> antifungal,<sup>5,6</sup> anti-inflammatory,<sup>7</sup> and antioxidant<sup>8</sup> activities, including their use as anti-tumor antibiotics<sup>9</sup> and antihypertensive drug.<sup>10</sup> Most studies indicate that zinc coordination compounds exhibit greater antimicrobial activity than the parent ligands.<sup>5,6</sup>

Zinc carboxylates containing Lewis bases as ligands have been studied in last two decades especially because of their structural properties, different geometry, coordination propensity and spectroscopic properties. Zinc coordination compounds with carboxylate ligands are important as building modes for metal organic frameworks (MOFs),<sup>11–15</sup> *i.e.* compounds consisting of metal ions coordinated to organic molecules to form supramolecular structures. Such materials have been studied for many applications, including hydrogen storage, catalysis, and non-linear optics.<sup>16,17</sup> Carboxylate ligands are among the common ligands in preparation of MOFs, while recently, N-donor ligands have also attracted increasing attention in preparation of interesting supramolecular complexes.<sup>17</sup> As a  $d^{10}$  metal ion,  $\text{Zn}^{2+}$  is particularly suited for the construction of coordination networks.<sup>18,19</sup> Carboxylate ligands can coordinate to metals in many ways: as monodentate, chelate, bidentate bridging in a *syn-syn*, *syn-anti* or *anti-*

*anti* configuration, monoatomic alone or additional bridging and chelating bridging<sup>20,21</sup> (Figure 1), which is one of the reasons for the existence of a huge number of metal acetates. Coordination varieties depend on many factors such as nature of the ligands, preparation methods, used solvents and temperature of the reacting system.<sup>22–25</sup>



**Figure 1.** Various carboxylate coordination modes: *syn* monodentate (1a), *anti* monodentate (1b), *syn-syn* symmetric chelate (2a), *syn-syn* asymmetric chelate (2b), chelating bridging (3), *syn-syn* asymmetric bridging (4a), *syn-anti* bridging (4b), *anti-anti* bridging (4c), monoatomic bridging (5).

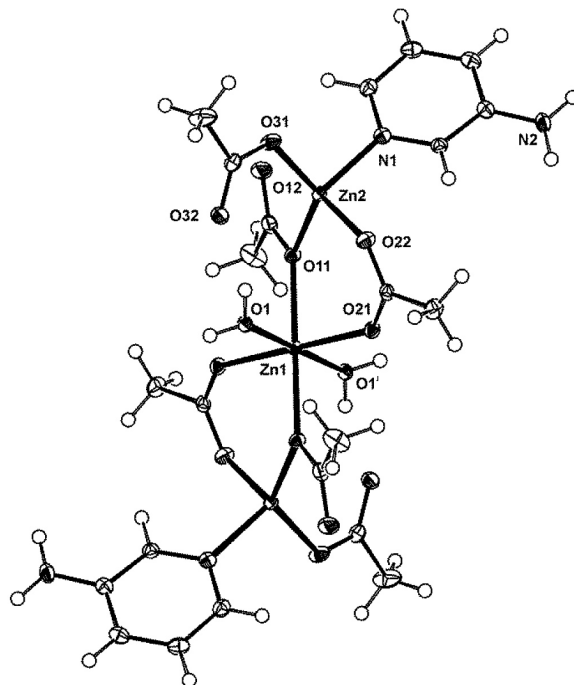
Among the great number of structurally characterized carboxylate coordinated zinc complexes, there are also a few examples of acetato coordinated compounds of Zn(II) with 2-aminopyridine.<sup>26–29</sup> Since we have not found any complexes of zinc and 3-aminopyridine ligands and because there is a huge amount of carboxylate coordinated compounds of Zn(II) with pyridine derivatives<sup>22,23,30–32</sup> we decided to investigate zinc compounds with carboxylate and *meta*-substituted pyridine derivative ligands. In here acetato ligands are coordinated monodentately, monodentately bridging and bidentately bridging,<sup>22</sup> pivalate monodentately and bidentately bridging,<sup>23</sup> benzoate monodentately bridging and bidentately bridging<sup>30,32</sup> and 2-benzoylbenzoate ligand bidentately bridging.<sup>31</sup>

There seem to be no published reports of zinc carboxylates with 4-aminopyridine ligands. Nevertheless, we found some mononuclear compounds of Zn carboxylates with *para*-substituted pyridine derivative ligands, like 4-(dimethylamino)pyridine,<sup>33–35</sup> 4,4'-dipyridylamine,<sup>36,37</sup> 4,4'-azopyridine,<sup>38</sup> N-(9-anthracenyl)-N'-(4-pyridyl)urea,<sup>39</sup> 4-pyridylbenzamide<sup>40</sup> and 4-pyridinylnicotinamide<sup>41</sup> and different carboxylates: pivalate,<sup>33</sup> 1,3,5-benzenetricarboxylate,<sup>36</sup> naphthalene-2,3-dicarboxylate,<sup>38</sup> acetate,<sup>39,40</sup> malonate,<sup>41</sup> 4,4'-biphenyldicarboxylate,<sup>37</sup> salicylate,<sup>34</sup> and trifluoroacetate.<sup>35</sup>

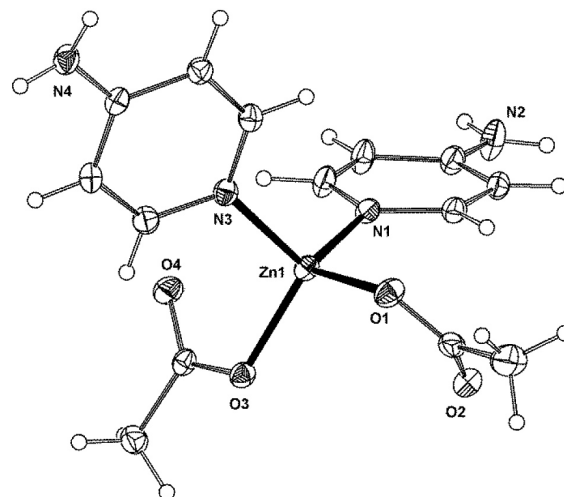
In the present paper, we report a study of two new zinc(II) coordination compounds with 3- and 4-aminopyridine and acetate ligands, analogous to some cobalt(II) and nickel(II) complexes that we have recently prepared and reported.<sup>42–44</sup> We present metal-ligand coordination and the hydrogen bonding interactions in both new compounds.

## 2. Results and Discussion

We synthesized and characterized two new coordination compounds:  $[\text{Zn}_3(\text{O}_2\text{CCH}_3)_6(3\text{-apy})_2(\text{H}_2\text{O})_2](\mathbf{1})$  and  $[\text{Zn}(\text{O}_2\text{CCH}_3)_2(4\text{-apy})_2](\mathbf{2})$  by the reactions of corresponding aminopyridine (apy) with  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , respectively. The molecular structures of both compounds are shown in Figures 2 and 3. Selected bond distances and angles are displayed in Table 1. The reactions were performed at different conditions (temperature, solvent, amounts of the reagents).



**Figure 2.** A view of **1** showing the atom-labelling scheme for non C and H atoms. Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .



**Figure 3.** A view of **2** showing the atom-labelling scheme for non C and H atoms.

**Table 1.** Selected bond lengths (Å) and angles (°) for **1** and **2**.

<b>1</b>			
Zn1–O1	2.0910(13)	O1–Zn1–O11	88.12(5)
Zn1–O21	2.0581(13)	O1–Zn1–O21	90.23(5)
Zn1–O11	2.1736(13)	O1–Zn1–O1 <sup>i</sup>	180
Zn2–N1	2.0378(16)	O11–Zn2–N1	116.15(6)
Zn2–O11	1.9963(13)	O11–Zn2–O22	100.46(6)
Zn2–O22	1.9682(13)	O11–Zn2–O31	128.53(6)
Zn2–O31	1.9458(14)	Zn1–O11–Zn2	137.23(12)
<b>2</b>			
Zn1–N1	2.004(2)	N1–Zn1–O1	109.23(9)
Zn1–N3	2.010(2)	N1–Zn1–O3	116.95(9)
Zn1–O1	1.971(2)	N1–Zn1–N3	115.19(9)
Zn1–O3	1.984(2)	O1–Zn1–O3	108.55(8)

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ .

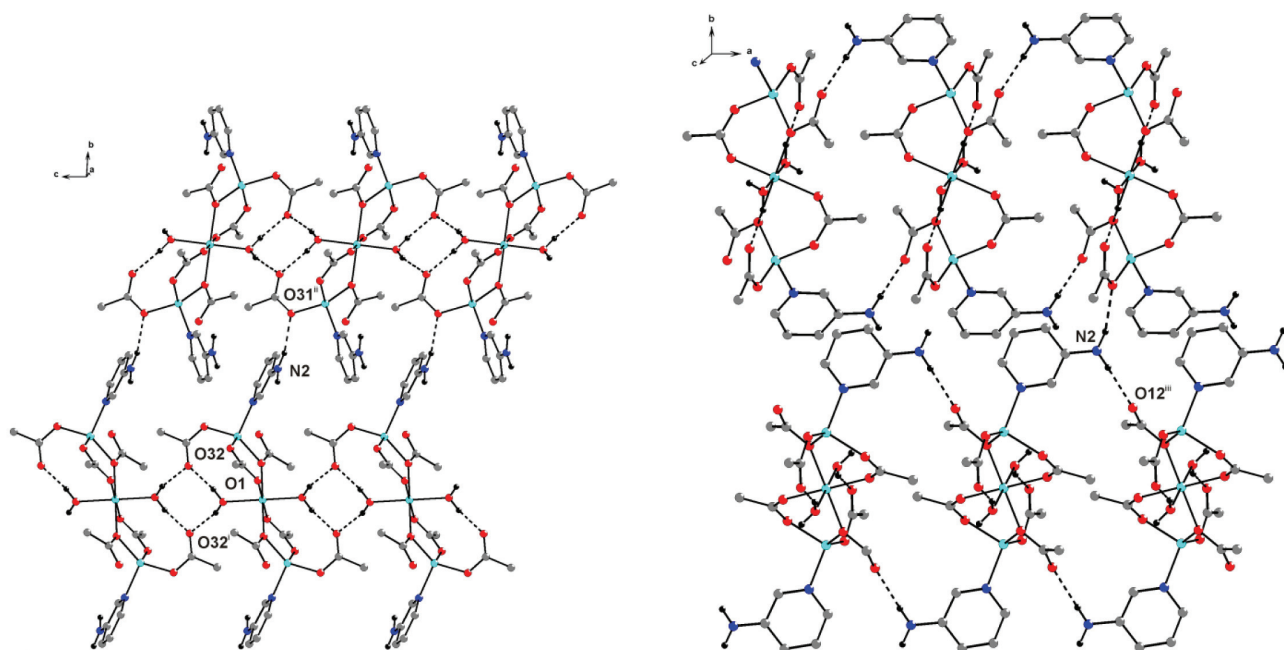
## 2. 1. Description of the Structures

A trinuclear complex molecules of compound **1** consists of three zinc(II) cations, six acetate anions, two 3-aminopyridine ligands and two water molecules (Figure 2). Two of those zinc(II) ions are terminal and one is a central. The separation between the central and terminal zinc ions is 3.5805(2) Å. The complex possesses three different acetate coordination modes. Each terminal ion is coordinated by one 3-aminopyridine ligand, one monodentate acetato ligand, one bridging bidentate acetato ligand and a bridging monoatomic acetato ligand. The geometry around the terminal zinc ion is distorted tetrahedral. The central zinc ion lies on an inversion centre and is oc-

tahedrally coordinated by two bridging bidentate acetato ligands, two water molecules and two bridging monodentate acetato ligands. The water molecules are donors of intramolecular O1–H11...O32 hydrogen bonds. They also connect the complex molecules by intermolecular O1–H12...O32<sup>i</sup> hydrogen bonds into chains parallel to the *c*-axis (Figure 4, left). These chains are interconnected by hydrogen bonds donated by the NH<sub>2</sub> groups creating first a two-dimensional layer (via N2–H21...O31<sup>ii</sup>, Figure 4, left) and then a three-dimensional network (via N2–H22...O12<sup>iii</sup> H-bonds, Figure 4, right).

The geometry of hydrogen bonds is presented in Table 2. The distortions of angles from ideal 109° are probably due to the steric hindrance between aromatic ring and acetato ligands and in the case of the complex **1** also due to the bridging role of acetato ligands in the trinuclear molecules. Nevertheless, intra- and intermolecular hydrogen bonds could also be the reason of the distorted geometry around the zinc ions. O21–Zn1–O1, O21–Zn1–O11 and O1–Zn1–O11 angles of 90.23(5)°, 88.27(5)° and 88.12(5)° around the central zinc ion with small deviations from ideal 90° and angles around the terminal zinc ion, especially O31–Zn2–O11 (128.53(6)°), with large deviation from ideal 109° are comparable to those in the similar compound [Zn<sub>3</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(3,5-lutidine)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].<sup>22</sup> Moreover, the distances central/terminal zinc atom–ligands in the compound **1** are also comparable with those in the compound [Zn<sub>3</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(3,5-lutidine)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].<sup>22</sup>

The crystal structure of the compound **2** is made up of mononuclear [Zn(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(4-apy)<sub>2</sub>] molecules. The



**Figure 4.** Hydrogen-bonding interactions in **1**. Formation of chains and layers (left) and arrangement the layers into 3D network (right). Symmetry codes: (i)  $-x + 1, -y + 1, -z + 2$ ; (ii)  $x + 1/2, -y + 3/2, z - 1/2$ ; (iii)  $x + 1, y, z$ .

Table 2. Hydrogen bonding geometry for **1** and **2**.

D–H...A	<i>d</i> (D–H)/ Å	<i>d</i> (H...A)/ Å	<i>d</i> (D...A)/ Å	∠(DHA)/ °	Symmetry codes for acceptors
<b>1</b>					
O1–H11...O32	0.84	1.91	2.7198(19)	162.5	
O1–H12...O32	0.84	1.97	2.7881(19)	162.9	$-x + 1, -y + 1, -z + 2$
N2–H21...O31	0.91	2.12	2.993(2)	160.5	$x + 1/2, -y + 3/2, z - 1/2$
N2–H22...O12	0.91	2.10	3.011(2)	176.0	$x + 1, y, z$
<b>2</b>					
N2–H1N...O2	0.880(19)	2.17(2)	3.020(4)	163(4)	$-x + 1/2, y + 1/2, -z + 1/2$
N2–H2N...O4	0.862(19)	2.02(2)	2.853(3)	162(4)	$-x + 1/2, y - 1/2, -z + 1/2$
N4–H3N...O3	0.894(18)	2.067(19)	2.957(3)	173(3)	$-x + 1/2, y + 1/2, -z - 1/2$
N4–H4N...O2	0.892(18)	2.03(2)	2.885(3)	159(3)	$x - 1/2, -y + 1/2, z - 1/2$

zinc(II) ion is four-coordinated by two aromatic N atoms of 4-aminopyridine ligands and two oxygen atoms from two monodentate acetato ligands (Figure 3). The bond angles around the zinc atom range from 98.90(9)° to 116.95(9)°, indicating a distorted tetrahedral geometry around the metal centre, which could be explained by hydrogen bonds in the crystal. The Zn–O acetate bond lengths are close to those found in the compound of bis(acetato-*O*)bis(2-aminopyridine-*N*)zinc(II)<sup>30</sup> (1.9614(17) and 1.9865(17) Å, respectively), while Zn–N bond distances are longer in the comparable compound (2.0643(19) and 2.0697(19)).<sup>30</sup> Amino nitrogen atoms of both coordinated 4-apy groups in **2** are donor of four hydrogen bonds to coordinated or non-coordinated acetate oxygen atoms forming a three-dimensional network (Figure 5, Table 2).

Both uncoordinated (O2, O4) and one coordinated (O3) oxygen atoms are bi- (O2) and monofurcated (O3, O4) acceptors of these bonds.

In the crystal structures of both compounds **1** and **2** no significant stacking effects between aromatic rings have been observed.

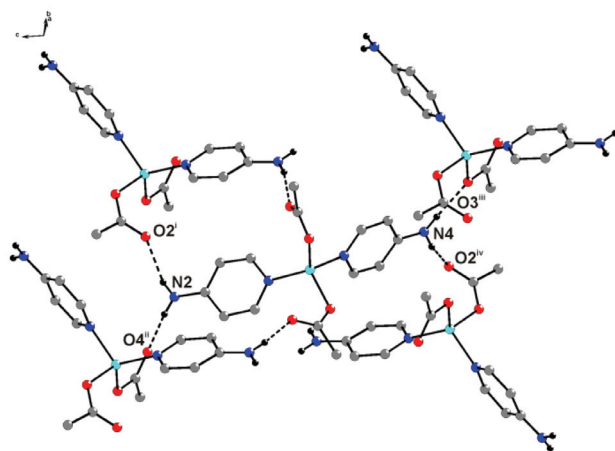


Figure 5. Hydrogen-bonding interactions in **2**. Symmetry codes: (i)  $-x + 1/2, y + 1/2, -z + 1/2$ ; (ii)  $-x + 1/2, y - 1/2, -z + 1/2$ ; (iii)  $-x + 1/2, y + 1/2, -z - 1/2$ ; (iv)  $x - 1/2, -y + 1/2, z - 1/2$ .

## 3. Experimental

### 3.1. General Experimental Procedures

All starting compounds and solvents were used as purchased. Elemental analyses were carried out on a PerkinElmer 2400 series II CHNS/O elemental analyzer at the University of Ljubljana.

### 3.2. Synthesis of bis[( $\mu_2$ -acetato-*O, O'*)( $\mu_2$ -acetato-*O, O*)(acetato-*O*)]diaquabis(3-aminopyridine-*N*)trizinc(II) (**1**)

The water solution of 3-aminopyridine (0.376 g; 4.0 mmol) was added to a methanol solution of zinc(II) acetate dihydrate (1.317 g; 6.0 mmol). The solution was refluxed for about 2 hours. After filtration and slow cooling, the solution was left in the air till most of the solvent was evaporated. The sample was left for 2 days at 277 K in the fridge. Dark red oily mass with some colourless crystals was obtained. The product was dried in a desiccator above KOH. Yield: 0.873 g (56.3%). Anal. Calc. for C<sub>22</sub>H<sub>34</sub>N<sub>4</sub>O<sub>14</sub>Zn<sub>3</sub> (*M<sub>r</sub>* = 774.64): C 34.11; H, 4.42; N, 7.23. Found: C, 33.6; H, 4.66; N, 7.29.

### 3.3. Synthesis of bis(acetato-*O*)bis(4-aminopyridine-*N*)zinc(II) (**2**)

Solid zinc acetate dihydrate (0.329 g; 1.5 mmol) was added to a methanol solution of 4-aminopyridine (0.282 g; 3.0 mmol). The obtained solution was heated and stirred at about 60 °C for 2 hours. After filtration, the solution was put on air and crystalline product was grown in one day. The crystals of **2** were dried in desiccator above KOH. Yield: 0.388 g (64.5%). Anal. Calc. for C<sub>14</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>Zn (*M<sub>r</sub>* = 371.70): C, 45.24; H, 4.88; N, 15.07. Found: C, 44.96; H, 4.79; N, 14.31.

### 3.4. X-ray Crystallography

The crystal structures of complexes **1** and **2** were determined by single-crystal X-ray diffraction methods.

Crystallographic data and refinement details are given in Table 3.

X-ray diffraction data for **1** were collected on a Bruker APEX-II CCD diffractometer with graphite-monochromated Mo  $K_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 100 K. The structure was solved by direct methods (SHELXS-97)<sup>45</sup> and refined by full-matrix least-squares techniques against  $F^2$  (SHELXL-97).<sup>45</sup> The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98 Å. The positions of the H atoms of the water molecule were taken from a difference Fourier map, the O–H distances were fixed to 0.84 Å, and the H atoms were refined with common isotropic displacement parameters without any constraints to the bond angles. The H atoms of the NH<sub>2</sub> group were treated analogously, but the N–H distances were fixed to 0.91 Å.

X-ray diffraction data for **2** were collected on a No-nius Kappa CCD diffractometer with graphite-monochromated Mo  $K_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 150 K. The structure was solved by direct methods (SIR-92)<sup>46</sup> and refined by full-matrix least-squares techniques against  $F^2$

(SHELXL-97)<sup>45</sup>. All of the non-hydrogen atoms were refined anisotropically. All of the C–H hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The hydrogen atoms of the NH<sub>2</sub> group were visible in the last stages of the refinement process and were refined with the constrained bond length and isotropic thermal parameters (1.2 times the thermal parameter of the attached nitrogen atom). Two peaks higher than  $1 \text{ e \AA}^{-3}$  observed in the structure of **2** were unrefineable, with no chemical meaning. They indicate the possible disordered solvent in the crystal structure.

CCDC-1026742 and 1024140 contains the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## 4. Conclusions

The present work describes the synthesis and characterization of two new coordination compounds of zinc(II) acetate and aminopyridines. The compound of zinc acetate with 3-aminopyridine is a trinuclear compound where terminal zinc ions are tetrahedrally coordi-

**Table 3.** Crystallographic data for the X-ray diffraction studies on compounds **1** and **2**.

	<b>1</b>	<b>2</b>
formula	C <sub>22</sub> H <sub>34</sub> N <sub>4</sub> O <sub>14</sub> Zn <sub>3</sub>	C <sub>14</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> Zn
Fw (g mol <sup>-1</sup> )	774.64	371.69
crystal size (mm)	0.32 × 0.28 × 0.12	0.10 × 0.05 × 0.05
crystal color	colourless	colourless
crystal system	monoclinic	monoclinic
space group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> (Å)	7.6626(3)	13.1446(3)
<i>b</i> (Å)	25.9933(10)	10.2806(2)
<i>c</i> (Å)	8.1529(3)	14.0935(3)
$\beta$ (°)	114.2820(10)	112.8859(11)
<i>V</i> (Å <sup>3</sup> )	1480.20(10)	1754.59(7)
<i>Z</i>	2	4
calcd density (g cm <sup>-3</sup> )	1.738	1.407
<i>F</i> (000)	792	768
<i>T</i> (K)	100(2)	150(2)
no. of collected rflns	13077	7628
no. of independent rflns	3561	4001
<i>R</i> <sub>int</sub>	0.0329	0.0320
no. of rflns observed	3111	3339
no. parameters	205	222
$R[I > 2\sigma(I)]$	0.0264	0.0402
$wR_2$ (all data) <sup>b</sup>	0.0654	0.1242
<i>Goof</i> , <i>S</i> <sup>c</sup>	1.053	1.042
maximum/minimum residual	+0.59/−0.41	+2.23/−0.28
electron density (e Å <sup>-3</sup> )		

<sup>a</sup>  $R = \sum |F_o| - |F_c| / \sum |F_o|$ . <sup>b</sup>  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ . <sup>c</sup>  $S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n/p) \}^{1/2}$  where *n* is the number of reflections and *p* is the total number of parameters refined.

nated while the central ion is octahedrally coordinated. The compound of zinc acetate with 4-aminopyridine is a mononuclear complex with the tetrahedral geometry around the zinc ion. There are intramolecular hydrogen bonds in the trinuclear compound and intermolecular hydrogen bonds in both complexes. Acetato ligands in the trinuclear compound possess different coordination to the central ions. They are monodentately, monodentately bridging or bidentately bridging coordinated.

## 5. Acknowledgement

This work was partly supported by the Grant P1-0175-103 from the Ministry of Education, Science and Sport, Republic of Slovenia.

## 6. References

1. K. M. Hambidge, N. F. Krebs, *J. Nutr.* **2007**, *137*, 1101–1105. <http://dx.doi.org/10.1136/bmj.326.7386.409>
2. A. S. Prasad, *Br. Med. J.* **2003**, *326*, 409–410.
3. Y. Yoshikawa, H. Yasui, *Curr. Top. Med. Chem.* **2012**, *12*, 210–218. <http://dx.doi.org/10.2174/156802612799078874>
4. J. Qin, F.-X. Li, L. Xue, N. Lei, Q.-L. Ren, D.-Y. Wang, H.-L. Zhu, *Acta Chim. Slov.* **2014**, *61*, 170–176.
5. M. Hanif, Z. H. Chohan, J. Y. Winum, J. Akhtar, *J. Enzyme Inhib. Med. Chem.* **2014**, *29*, 517–526. <http://dx.doi.org/10.3109/14756366.2013.815178>
6. B. Manjula, S. A. Antony, C. J. Dhanaraj, *Spectrosc. Lett.* **2014**, *47*, 518–526. <http://dx.doi.org/10.1080/00387010.2013.820196>
7. A. Tarushi, X. Totta, C. P. Raptopoulou, V. Psycharis, G. Psomas, D. P. Kessissoglou, *Dalton Trans.* **2012**, *41*, 7082–7091.
8. E. Pienązek, J. Kalemkiewicz, M. Dranka, E. Woźnicka, *J. Inorg. Biochem.* **2014**, *141*, 180–187. <http://dx.doi.org/10.1016/j.jinorgbio.2014.09.005>
9. A. Galani, E. K. Efthimiadou, T. Theodosiou, G. Kordas, A. Karaliota, *Inorg. Chim. Acta* **2014**, *423*, 52–59. <http://dx.doi.org/10.1016/j.ica.2014.09.034>
10. M. C. de Souza, C. H. J. Franco, C. B. Pinheiro, R. Diniz, *Polyhedron* **2014**, *81*, 290–297. <http://dx.doi.org/10.1016/j.poly.2014.06.025>
11. A. D. Burrows, C. G. Frost, M. F. Mahon, C. Richardson, *Angew. Chem. Int. Ed.* **2008**, *47*, 8482–8486. <http://dx.doi.org/10.1002/anie.200802908>
12. B. S. Luisi, Z. Ma, B. J. Moulton, *J. Chem. Crystallogr.* **2007**, *37*, 743–747. <http://dx.doi.org/10.1007/s10870-007-9244-3>
13. C. A. Williams, A. J. Blake, P. Hubberstey, M. Schroder, *Chem. Commun.* **2005**, *43*, 5435–5437. <http://dx.doi.org/10.1039/b509929c>
14. A. Erxleben, *Coord. Chem. Rev.* **2003**, *246*, 203–228. [http://dx.doi.org/10.1016/S0010-8545\(03\)00117-6](http://dx.doi.org/10.1016/S0010-8545(03)00117-6)
15. M. T. Ng, T. C. Deivaraj, J. J. Vittal, *Inorg. Chim. Acta* **2003**, *348*, 173–178. [http://dx.doi.org/10.1016/S0020-1693\(02\)01488-3](http://dx.doi.org/10.1016/S0020-1693(02)01488-3)
16. Z. Ni, R. I. Masel, *J. Am. Chem. Soc.* **2006**, *128*, 12394–12395. <http://dx.doi.org/10.1021/ja0635231>
17. M. D. Yang, W. G. Xi, J. Zheng, X. Z. Zhang, H. P. Zhou, Z. C. Wu, J. Y. Wu, Y. P. Tian, *Russ. J. Coord. Chem.* **2014**, *40*, 558–593. <http://dx.doi.org/10.1134/S1070328414080028>
18. F. Marandi, S. Teimouri, H.-K. Fun, *Acta Chim. Slov.* **2013**, *60*, 328–334.
19. Y.-F. Xiao, T.-T. Wang, H.-P. Zeng, *J. Mol. Struct.* **2014**, *1074*, 330–338. <http://dx.doi.org/10.1016/j.molstruc.2014.06.018>
20. G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **1980**, *3*, 227–250. [http://dx.doi.org/10.1016/S0010-8545\(00\)80455-5](http://dx.doi.org/10.1016/S0010-8545(00)80455-5)
21. R. J. Deeth, *Inorg. Chem.* **2008**, *47*, 6711–6725. <http://dx.doi.org/10.1021/ic800313s>
22. U. Kumar, J. Thomas, N. Thirupathi, *Inorg. Chem.* **2010**, *49*, 62–72. <http://dx.doi.org/10.1021/ic901100z>
23. U. Kumar, J. Thomas, M. Agarwal, N. Thirupathi, *Inorg. Chim. Acta* **2010**, *370*, 122–131. <http://dx.doi.org/10.1016/j.ica.2011.01.040>
24. W. Clegg, I. R. Little, B. P. Straughan, *J. Chem. Soc., Dalton Trans* **1986**, *6*, 1283–1288. <http://dx.doi.org/10.1039/dt9860001283>
25. W. Clegg, I. R. Little, B. P. Straughan, *J. Chem. Soc., Chem. Commun.* **1985**, *2*, 73–74. <http://dx.doi.org/10.1039/c39850000073>
26. R. Y. Li, F.-L. Bei, X.-J. Yang, L.-D. Lu, X. Wang, W. H. Xuebao, *Chin. J. Inorg. Chem.* **2003**, *19*, 543–546.
27. L. Mei, T. H. Ming, *Asian J. Chem.* **2008**, *20*, 6589–6593.
28. L. Mei, T. H. Ming, L. Q. Rong, S. Jie, Y. S. Zhong, L. X. Liang, *J. Chem. Sci.* **2009**, *121*, 435–440. <http://dx.doi.org/10.1007/s12039-009-0051-6>
29. H.-L. Zhu, J.-L. Ma, D.-Q. Wang, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1317–1320. <http://dx.doi.org/10.1002/zaac.200400031>
30. V. Zelenak, M. Sabo, W. Massa, P. Llewellyn, *Inorg. Chim. Acta* **2004**, *357*, 2049–2059. <http://dx.doi.org/10.1016/j.ica.2004.01.016>
31. S. Caglar, Z. Heren, M. H. Yildirim, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2011**, *41*, 1022–1027.
32. K. F. Konidaris, M. Kaplanis, C. P. Raptopoulou, S. P. Perlepes, E. Manessi-Zoupa, E. Katsoulakou, *Polyhedron* **2009**, *28*, 3243–3250. <http://dx.doi.org/10.1016/j.poly.2009.05.076>
33. U. Kumar, M. Singh, N. Thirupathi, *Polyhedron* **2013**, *55*, 233–240. <http://dx.doi.org/10.1016/j.poly.2013.02.081>
34. K.-H. Lin, F.-F. Zhang, Z.-Y. Yu, S. Min, *Acta Crystallogr.* **2007**, *E63*, m1930.
35. W. Tyrra, D. Naumann, I. Pantenburg, *J. Fluorine Chem.* **2003**, *120*, 13–19. [http://dx.doi.org/10.1016/S0022-1139\(02\)00277-4](http://dx.doi.org/10.1016/S0022-1139(02)00277-4)
36. M. A. Braverman, R. M. Supkowski, R. L. LaDuca, *J. Solid State Chem.* **2007**, *180*, 1852–1862. <http://dx.doi.org/10.1016/j.jssc.2007.04.010>

37. M. Hu, R. Wang, Z. *Kristallogr.-New Cryst. Struct.* **2010**, 225, 265–266.
38. Q. Zhao, X.-J. Yang, C. Jia, B. Wu, *Inorg. Chem. Commun.* **2010**, 13, 873–877.  
<http://dx.doi.org/10.1016/j.inoche.2010.04.018>
39. J. C. Noveron, M. S. Lah, R. E. Del Sesto, A. M. Arif, J. S. Miller, P. J. Stang, *J. Am. Chem. Soc.* **2002**, 124, 6613–6625.  
<http://dx.doi.org/10.1021/ja0200241>
40. D. K. Kumar, *Inorg. Chim. Acta* **2009**, 362, 1767–1771.  
<http://dx.doi.org/10.1016/j.ica.2008.08.033>
41. M. R. Montney, R. M. Supkowski, R. L. LaDuca, *CrystEng-Comm.* **2008**, 10, 111–116.  
<http://dx.doi.org/10.1039/B705987F>
42. B. Dojer, A. Pevec, P. Šegedin, Z. Jagličič, C. Stropnik, M. Kristl, M. Drogenik, *Inorg. Chim. Acta* **2010**, 363, 1343–1347. <http://dx.doi.org/10.1016/j.ica.2009.12.052>
43. B. Dojer, A. Pevec, M. Jagodič, M. Kristl, M. Drogenik, *Inorg. Chim. Acta* **2012**, 383, 98–104.  
<http://dx.doi.org/10.1016/j.ica.2011.10.056>
44. B. Dojer, A. Golobič, Z. Jagličič, M. Kristl, M. Drogenik, *Monatsh. Chem.* **2012**, 143, 73–78.  
<http://dx.doi.org/10.1007/s00706-011-0578-3>
45. G. M. Sheldrick, *Acta Cryst.* **2008**, A64, 112–122.  
<http://dx.doi.org/10.1107/S0108767307043930>
46. A. Altomare, M. C. Burla, M. Camalli, G. L. Casciarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* **1999**, 32, 115–119.  
<http://dx.doi.org/10.1107/S0021889898007717>

## Povzetek

Sintetizirali in karakterizirali smo novi cinkovi koordinacijski spojin s 3- in 4-aminopiridinom. Dobili smo ju z dodajanjem metanolne raztopine  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  v vodno raztopino 3-aminopiridina oziroma raztapljanjem  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  v metanolni raztopini 4-aminopiridina. Produkta sta bila okarakterizirana z rentgensko strukturalno analizo monokristalov. Brezbarvni kristali, pridobljeni z reakcijo med  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  in 3-aminopiridinom, so zgrajeni iz trijedrnih koordinacijskih molekul s kemijsko formulo  $[\text{Zn}_3(\text{O}_2\text{CCH}_3)_6(3\text{-apy})_2(\text{H}_2\text{O})_2](\mathbf{1})$ . Molekula je sestavljena iz dveh terminalnih cinkovih ionov, ki sta tetraedično koordinirana, in enega centralnega iona, ki je oktaedrično koordiniran. Brezbarvni kristali, dobljeni z reakcijo med  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  in 4-aminopiridinom, sestojijo iz enojedrnih koordinacijskih molekul s kemijsko formulo  $[\text{Zn}(\text{O}_2\text{CCH}_3)_2(4\text{-apy})_2](\mathbf{2})$ . Poročamo tudi o vodikovih vezeh v kristalnih strukturah obeh spojin.