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### Two new dinuclear complexes with dipicolinate and bridging 2-aminopyrazine ligands: preparation, structural, spectroscopic, and thermal characterizations

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## Two new dinuclear complexes with dipicolinate and bridging 2-aminopyrazine ligands: preparation, structural, spectroscopic, and thermal characterizations

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Treatment of an aqueous solution of dipicolinic acid (dipicH<sub>2</sub>) and 2-aminopyrazine (apyz) with Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O or ZnCl<sub>2</sub> (in molar ratio 1:1:1) led to formation of dinuclear complexes, [M<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(dipic)<sub>2</sub>(μ-apyz)] (M = Cu (**1**) and Zn (**2**)). Both complexes were characterized by elemental analyses, IR, and UV-Vis spectroscopy. Their molecular and crystal structures were determined by X-ray crystal structure analysis and their thermal stabilities were confirmed by TGA/DTA methods. Complex **1** crystallizes in the triclinic *P*-1 space group, while **2** crystallizes in the monoclinic *P*<sub>2</sub><sub>1</sub>/*c* space group. The dinuclear complexes are analogous and composed of two metal ions bridged by 2-aminopyrazine. Each M(II) is coordinated by one nitrogen atom and two oxygen atoms of tridentate dipicolinate, one heterocyclic nitrogen of 2-aminopyrazine, and two coordinated water molecules. The resulting geometry for the MN<sub>2</sub>O<sub>4</sub> coordination environment can be described as distorted octahedral. Extensive hydrogen-bonding interactions involving all water ligands, dipicolinate oxygen atoms, and amino groups further stabilize the complex units by linking them to form 3-D networks for **1** and **2**.

**Keywords:** Dinuclear complex; Copper complex; Zinc complex; Dipicolinic acid; 2-Aminopyrazine

### 1. Introduction

Binuclear complexes have potential applications as magnetic materials and in catalytic and electron-transfer reactions. Bi- or multidentate bridging ligands containing N- or O-donors influence the structures of coordination compounds. Polycarboxylates and

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polynitrogen-containing ligands, two excellent classes of bridging ligands, are used to generate a number of bi- or multinuclear metal complexes. Among polycarboxylic acids, pyridine-2,6-dicarboxylic acid (pydcH<sub>2</sub>) has attracted much interest in coordination chemistry and one we utilized widely in our studies [1–7]. Dinuclear dipicolinate complexes, with pyrazine [8, 9] or 4,4-bipyridine [10, 11] as bridging molecules, are known but rather rare. Metal ions found in these complexes are nickel(II) [8] and copper(II) [9] in the case of pyrazine and just copper(II) in the case of 4,4-bipyridine [10, 11]. Several transition metal complexes containing dipicolinate bound in a tridentate-*N,O,O'* fashion are also known [4, 6, 7, 12, 13]. In continuation of earlier work on metal complexes with dipicolinate in the presence of some amino compounds, we reported the first example of a cobalt(II) complex with tridentate-*N,O,O'* pyridine-2,6-dicarboxylate and bridging 2-aminopyrazine [14]. Here, we present the preparation, spectroscopic characterization, thermal properties, and crystal structure of two dinuclear M(II) complexes, [M<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(dipic)<sub>2</sub>(μ-apyz)] (M = Cu (**1**) and Zn (**2**)). A variety of zinc and copper complexes containing 2-aminopyrazine as terminal or bridging ligand have been reported [15–19]. Formate, acetate, propionate, malonate, and succinate have been used to construct several copper coordination polymers containing 2-aminopyrazine spacer together with carboxylato bridges [20]. Our complexes are new examples of dinuclear copper(II) and zinc(II) complexes with the bridging 2-aminopyrazine. The dipicolinate hampers the formation of polymeric structures in our complexes.

## 2. Experimental

### 2.1. Materials and instrumentation

All purchased chemicals were of reagent grade and used without purification. IR spectra were recorded using an FTIR Spectra Bruker Tensor 27 spectrometer (KBr pellets, 4000–400 cm<sup>-1</sup>). Absorption spectra were recorded on a Shimadzu Model 160-A UV-VIS spectrophotometer with a 1-cm quartz cell. The thermogravimetric analysis (TGA/DTA) measurements were performed at 10°C min<sup>-1</sup> from 25°C to 800°C under argon flow of 20 mL min<sup>-1</sup> on a Rheometrics STA 1500. Elemental analyses were performed using a Costech ECS 4010 CHNS analyzer.

### 2.2. Synthesis of complex

Preparation of [M<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(dipic)<sub>2</sub>(μ-apyz)] (**1**) and (**2**): Pyridine-2,6-dicarboxylic acid (0.334 g, 2 mmol) and NaOH (0.16 g, 4 mmol) were dissolved in deionized water (20 mL) and the mixture was stirred for 30 min at room temperature. Then an aqueous solution of metal salt Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O (0.483 g, 2 mmol) for **1** and ZnCl<sub>2</sub> (0.272 g, 2 mmol) for **2** and 2-aminopyrazine (0.190 g, 2 mmol) was added. The reaction mixtures were placed in a Parr Teflon-lined stainless-steel vessel, sealed and heated at 130°C for 8 h. Solution of **1** was kept at 4°C. The green-blue crystals of **1** were obtained after a few days. White precipitate was filtered from the reaction mixture of **2** and the clear solutions were kept at 4°C until colorless crystals of **2** suitable for X-ray diffraction were obtained.

[Cu<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(dipic)<sub>2</sub>(μ-apyz)] (**1**): IR (KBr) ( $\tilde{\nu}$ , cm<sup>-1</sup>): 3500–3050 (b), 1649 (s), 1615 (s), 1590 (s), 1542 (s), 1431 (s), 1377 (s), 1355 (s), 1276 (m), 1223 (m), 1089 (s), 1026 (s),

912 (m), 825 (m), 768 (m), 736 (m), 686 (m), 597 (m), 562 (w), 483 (w), 437 (w). Anal. Calcd for  $C_{18}H_{19}Cu_2N_5O_{12}$  ( $M = 624.46$ ) (%): C, 34.59; H, 3.04; N, 11.21. Found (%): C, 34.19; H, 3.08; N, 11.08.

$[Zn_2(H_2O)_4(dipic)_2(\mu\text{-apyz})]$  (**2**): IR (KBr) ( $\tilde{\nu}$ ,  $cm^{-1}$ ): 3410–3296 (b), 3170 (s), 1665 (s), 1617 (s), 1592 (s), 1458 (s), 1397 (s), 1303 (m), 1074 (s), 1032 (m), 921 (s), 835 (m), 758 (s), 690 (s), 599 (s), 427 (w). Anal. Calcd for  $C_{18}H_{19}Cu_2N_5O_{12}Zn_2$  ( $M = 628.12$ ) (%): C, 33.39; H, 3.02; N, 11.50. Found (%): C, 33.20; H, 3.16; N, 11.39.

### 2.3. Single-crystal structure determination

The diffraction intensities of **1** were collected on a Stoe IPDS I diffractometer (Mo-K $\alpha$  radiation;  $\lambda = 71.073$  pm, graphite-monochromated), while those of **2** were on an Oxford Diffraction Xcalibur nova R, with microfocusing Cu tube ( $\lambda = 154.179$  pm). The intensities were corrected for Lorentz and polarization effects and a multiscan absorption correction was applied.

Both structures were solved by direct methods (SIR-92 [21], SHELXS-97 [22]) and refined against  $F^2$  by full-matrix least-squares using SHELXL-97 [22]. Molecular graphics were produced with PLATON [23] and MERCURY (version 2.4) [24]. The crystal parameters, data collection and refinement results for **1** and **2** are summarized in table 1.

Table 1. Crystal data and details of the structure determination for **1** and **2**.

Empirical formula	$C_{18}H_{19}Cu_2N_5O_{12}$	$C_{18}H_{19}Zn_2N_5O_{12}$
Formula weight	624.46	628.12
Color and habit	Green-blue	Colorless
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Crystal size ( $mm^3$ )	$0.26 \times 0.12 \times 0.04$	$0.20 \times 0.15 \times 0.10$
Unit cell dimensions ( $\text{\AA}$ , $^\circ$ )		
$a$	6.370(1)	7.3668(4)
$b$	7.014(1)	39.643(2)
$c$	13.506(2)	7.5249(5)
$\alpha$	88.32(2)	90
$\beta$	76.84(2)	96.136(5)
$\gamma$	71.66(2)	90
Volume ( $\text{\AA}^3$ ), $Z$	557.2(4), 1	2185.0(2), 4
Calculated density ( $g\ cm^{-3}$ )	1.86	1.91
Absorption coefficient ( $mm^{-1}$ )	1.986	3.428
$\theta$ range for data collection ( $^\circ$ )	3.06–26.00	4.46–76.12
Limiting indices	$-7 \leq h \leq 7$ ; $-8 \leq k \leq 8$ ; $-16 \leq l \leq 16$	$-8 \leq h \leq 8$ ; $-34 \leq k \leq 49$ ; $-9 \leq l \leq 8$
Scan type	$\varphi$	$\omega$ , $\varphi$
Reflections collected	4417	6423
Independent reflections	2080 [ $R(\text{int}) = 0.0330$ ]	3721 [ $R(\text{int}) = 0.0966$ ]
Observed reflections [ $I \geq 2\sigma(I)$ ]	1579	3151
Refined parameters	179	366
$R^a$ , $wR^b$ [ $I \geq 2\sigma(I)$ ]	0.0432, 0.1089	0.0525, 0.0675
$R$ , $wR$ (all data)	0.0574, 0.1147	0.1597, 0.1597
Goodness of fit on $F^2$ , $S^c$	0.985	1.053
Max. and min. electron density ( $e\ \text{\AA}^{-3}$ )	1.853 and $-0.523$	0.472 and $-0.677$

<sup>a</sup> $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ; <sup>b</sup> $wR = [\sum (F_o^2 - F_c^2) / \sum w(F_o^2)^2]^{1/2}$ ; <sup>c</sup> $S = \sum [w(F_o^2 - F_c^2)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$ .

### 3. Results and discussion

Treatment of  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{ZnCl}_2$  with pyridine-2,6-dicarboxylic acid in the presence of 2-aminopyrazine in 1 : 1 : 1 molar ratio gave **1** or **2**. Complex **1** is green-blue and **2** colorless blocks; both complexes are stable in air and soluble in water.

#### 3.1. Crystal structure

The molecular structures of **1** and **2** are depicted in figures 1 and 2, respectively. Some selected bond lengths and angles are listed in table 2 and hydrogen-bond data in table 3. The 2-aminopyrazine is a bridge between adjacent metal centers with  $\text{M} \cdots \text{M}$  separations of 6.752 and 6.961 Å in **1** and **2**, respectively.  $\text{Cu} \cdots \text{Cu}$  separation agrees well with those reported for a series of copper(II) coordination polymers containing aminopyrazine and different carboxylate bridges [20]. In comparison to the latest reported Co(II) complex with pyridine-2,6-dicarboxylate and bridging 2-aminopyrazine ( $[\text{Co}_2(\text{H}_2\text{O})_4(\text{dipic})_2(\mu\text{-apyz})]$ ) [14], the Zn complex is isostructural. The imposed

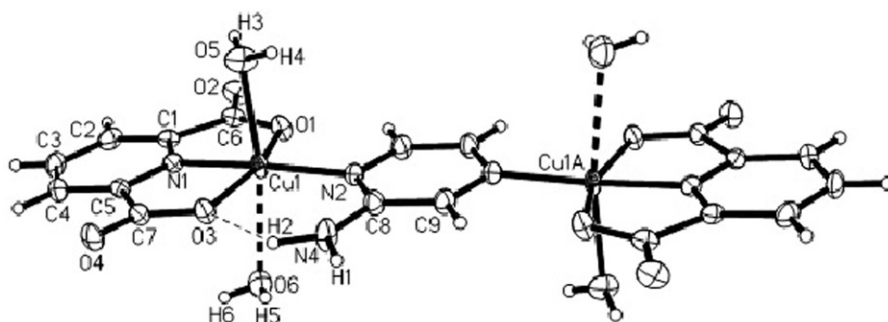


Figure 1. Molecular structure of **1**, thermal ellipsoids drawn at 40% probability level (2-aminopyrazine is disordered around a center of symmetry; only one position is drawn).

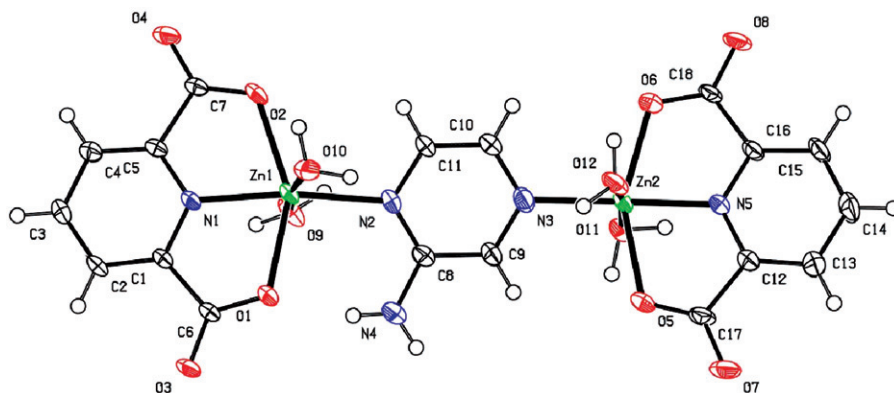


Figure 2. Molecular structure of **2** (thermal ellipsoids drawn at 50% probability level).

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

<b>1</b>			
Cu1–O1	2.034(3)	N1–Cu1–N2	175.2(2)
Cu1–O3	2.029(3)	N1–Cu1–O3	80.7(1)
Cu1–O5	2.308(3)	N2–Cu1–O3	100.8(1)
Cu1–N1	1.906(3)	N1–Cu1–O1	80.4(1)
Cu1–N2	1.988(4)	N2–Cu1–O1	97.8(1)
Cu1–O6	2.688(3)	N1–Cu1–O5	90.0(1)
		N2–Cu1–O5	94.6(1)
		O3–Cu1–O1	160.7(1)
		O3–Cu1–O5	90.1(1)
		N1–Cu1–O5	93.6(1)
		N1–Cu1–O6	82.0(1)
		N2–Cu1–O6	93.5(1)
		O1–Cu1–O6	88.2(1)
		O3–Cu1–O6	85.4(1)
		O5–Cu1–O6	171.4(1)
<b>2</b>			
Zn1–N1	2.053(3)	N1–Zn1–O9	89.1(1)
Zn1–O9	2.108(3)	N1–Zn1–O10	102.6(1)
Zn1–O10	2.115(3)	O9–Zn1–O10	168.0(1)
Zn1–N2	2.130(4)	N1–Zn1–N2	170.1(1)
Zn1–O1	2.211(3)	O9–Zn1–N2	83.3(1)
Zn1–O2	2.222(3)	O10–Zn1–N2	85.4(1)
Zn2–N5	2.017(3)	N1–Zn1–O1	75.3(1)
Zn2–N3	2.065(3)	O9–Zn1–O1	92.8(1)
Zn2–O11	2.166(3)	O10–Zn1–O1	93.1(1)
Zn2–O6	2.168(3)	N1–Zn1–O2	75.6(1)
Zn2–O5	2.181(3)	O9–Zn1–O2	90.7(1)
Zn2–O12	2.199(3)	O10–Zn1–O2	89.3(1)
		N2–Zn1–O2	110.9(1)
		O1–Zn1–O2	150.6(1)
		N2–Zn1–O1	98.5(1)
		N5–Zn2–N3	177.2(1)
		N5–Zn2–O11	93.3(1)
		N3–Zn2–O11	89.3(1)
		N5–Zn2–O6	76.6(1)
		N3–Zn2–O6	104.3(1)
		O11–Zn2–O6	94.7(1)
		N5–Zn2–O5	77.0(1)
		N3–Zn2–O5	102.0(1)
		O11–Zn2–O5	87.9(1)
		O6–Zn2–O5	153.5(1)
		N5–Zn2–O12	92.2(1)
		N3–Zn2–O12	85.2(1)
		O11–Zn2–O12	172.2(1)
		O5–Zn2–O12	87.8(1)
		O6–Zn2–O12	92.1(1)

crystallographic centrosymmetric arrangement of **1** leads to a disordered 2-aminopyrazine (figure 1).

Zn and Cu ions are coordinated by an *O,N,O'*-tridentate dipicolinate (bound *via* the pyridine and two carboxylate oxygen atoms and forming two five-membered chelate rings) and by the heterocyclic pyrazine (from 2-aminopyrazine). Coordinated pyridine from dipicolinate and 2-aminopyrazine are *trans* [ $\angle$ N1–Cu1–N2, 175.2(2)°;  $\angle$ N1–Zn1–N2, 170.0(1)°, and  $\angle$ N5–Zn2–N3, 177.2(1)°]. The Cu–N, Cu–O, Zn–N, and

Table 3. Hydrogen-bond 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)	∠(D–H...A) (°)	Symmetry code on A
<b>1</b>					
N4–H1...O6a	1.06	1.95	2.958(10)	157	<i>x</i> , 1 + <i>y</i> , <i>z</i>
N4–H2...O3	1.01	1.86	2.649(9)	133	
O6–H5...O6c	0.77	2.44	2.797(6)	110	1 – <i>x</i> , – <i>y</i> , – <i>z</i>
O6–H6...O2d	0.78	2.12	2.851(5)	155	1 + <i>x</i> , <i>y</i> , <i>z</i>
O5–H3...O4	0.82(7)	1.93(7)	2.745(5)	172(6)	–1 + <i>x</i> , <i>y</i> , <i>z</i>
O5–H4...O2	0.87(7)	1.92(6)	2.780	173(6)	<i>x</i> , 1 + <i>y</i> , <i>z</i>
<b>2</b>					
N4–H4A...O1	0.86	1.97	2.788(5)	158	
N4–H4B...O3	0.86	2.11	2.902(5)	152	1 – <i>x</i> , – <i>y</i> , 1 – <i>z</i>
O9–H9A...O3	0.92(4)	1.80(4)	2.705(4)	166(4)	1 – <i>x</i> , – <i>y</i> , 2 – <i>z</i>
O9–H9B...O5	0.93(5)	1.76(4)	2.668(4)	164(6)	<i>x</i> , <i>y</i> , 1 + <i>z</i>
O10–H10A...O7	0.94(5)	1.72(5)	2.603(5)	157(5)	1 + <i>x</i> , <i>y</i> , 1 + <i>z</i>
O10–H10B...O4	0.95(4)	2.01(4)	2.963(5)	176(7)	<i>x</i> , <i>y</i> , –1 + <i>z</i>
O11–H11A...O4	0.94(4)	1.91(4)	2.825(4)	164(7)	–1 + <i>x</i> , <i>y</i> , –1 + <i>z</i>
O11–H11B...O8	0.95(6)	1.80(7)	2.726(4)	162(7)	1/2 + <i>x</i> , 1/2 – <i>y</i> , <i>z</i>
O12–H12A...O8	0.93(5)	1.80(5)	2.720(4)	169(7)	1/2 + <i>x</i> , 1/2 – <i>y</i> , <i>z</i>
O12–H12B...O2	0.92(4)	1.87(3)	2.784(4)	172(6)	<i>x</i> , <i>y</i> , –1 + <i>z</i>

Zn–O bond lengths (N, O from dipicolinate) in **1** and **2** (table 2) are in accord with values reported in complexes containing dipicolinate bound to Cu(II) and Zn(II) ions in a tridentate-*N,O,O'* fashion [5–7]. The Cu–N2 distance in **1** (1.988(4) Å) is shorter than the distances in reported copper complex with bridging 2-aminopyrimidine [18]. The water molecules are in axial positions. The O(water)–M–O(water) angles are 171.4(1)° (O5–Cu1–O6) for **1** and 168.9(1)° (O9–Zn1–O10) and 172.2(1)° (O11–Zn2–O12) for **2**. The Cu1–O6 bond length (2.688(3) Å) in **1** is longer than all Cu–O bond lengths but is clearly shorter than the sum of van der Waals radii of copper and oxygen (1.40 + 1.52 = 2.92 pm) [25]. This high value may be due to crystal packing requirements and H-bonds of O6. The coordination around copper can be described as 5 + 1. Together with the distance Cu1–O5 (water) of 2.308(3) Å the Jahn–Teller distortion is asymmetrical.

The dihedral angle between the planes of the pyridine and pyrazine rings in **1** is 3.6(2)°, indicating that pyrazine is approximately coplanar with pyridine rings. In **2**, the bridging pyrazine is not coplanar with the pyridine rings of both dipicolinate ligands, with dihedral angles between the pyrazine and pyridine rings N1 and N5 being 21.4(2)° and 22.3(2)°, respectively.

There are O–H...O, N–H...O, and C–H...O hydrogen bonds in the crystal structures of **1** and **2** (table 3). Generally, coordinated water and amino are double proton donors, while coordinated and uncoordinated carboxylate participate in hydrogen-bonding as proton acceptors, some as double proton acceptors. A rather extensive hydrogen-bond network assembles [Cu<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(dipic)<sub>2</sub>(μ-apyz)] and [Zn<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(dipic)<sub>2</sub>(μ-apyz)] into 3-D structures (figures 3 and 4). The packing in **1** is stabilized by π–π stacking interactions between pyridine ring N1/C1/C2/C3/C4/C5 and its symmetry related at –*x*, –*y*, 1 – *z* [centroid–centroid distance 3.822(2) Å, angle between the planes 0°; perpendicular distance between the planes 3.382(2) Å; slippage 1.781 Å] and in **2** between N1/C1/C2/C3/C4/C5 and its symmetry related at 2 – *x*, –*y*, 2 – *z* [corresponding values are: 3.803(2) Å, 0°; 3.299(2) Å; 1.892 Å].



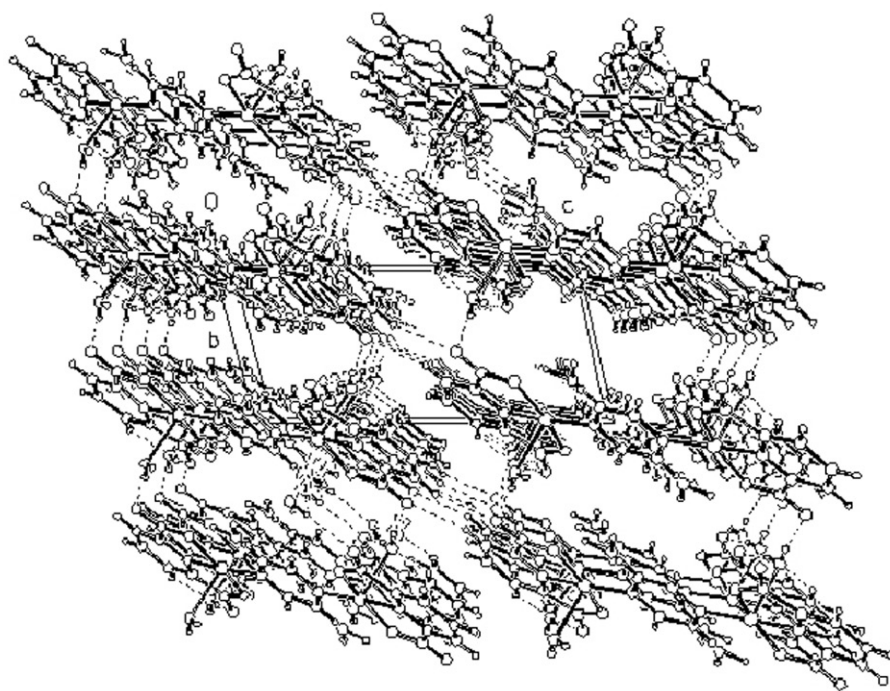


Figure 3. A view of the crystal structure of **1** projected onto (100). Molecules of  $[\text{Cu}_2(\text{H}_2\text{O})_4(\text{dipic})_2(\mu\text{-apyz})]$  are linked by  $\text{O-H}\cdots\text{O}$  and  $\text{N-H}\cdots\text{O}$  hydrogen bonds (represented by dotted lines) into a 3-D structure.

### 3.2. Infrared spectra

Patterns of IR spectra are exactly the same and show two sets of vibrations due to water and dipicolinate ligands. The similarity of IR data supports the idea that these compounds are analogs. In spectra of **1** and **2**, the antisymmetric stretch,  $\nu_{\text{as}}(-\text{COO})$ , is at  $1649\text{ cm}^{-1}$  (**1**) and  $1665\text{ cm}^{-1}$  (**2**) together with  $\nu_{\text{s}}(-\text{COO})$  at  $1377\text{ cm}^{-1}$  (**1**) and  $1397\text{ cm}^{-1}$  (**2**). The value of  $\Delta(\nu_{\text{as}}(-\text{COO}) - \nu_{\text{s}}(-\text{COO}))$  of  $272\text{ cm}^{-1}$  and  $268\text{ cm}^{-1}$  for **1** and **2** indicate the presence of carboxylate coordinated unidentate to metal ions [26–28], in agreement with the crystal structure. Broad and strong bands at  $3450\text{--}3050\text{ cm}^{-1}$  can be assigned to O–H and N–H stretches of  $\text{O-H}\cdots\text{O}$  and  $\text{N-H}\cdots\text{O}$  hydrogen-bonded groups. Aromatic C–H stretching vibrations of dipic and  $\text{atrH}^+$  should also occur at  $3100\text{--}3000\text{ cm}^{-1}$  [29, 30].

### 3.3. Thermal analysis

The TGA/DTA curves for **1** and **2** show that the first weight loss at  $112^\circ\text{C}$  for **1** and at  $142^\circ\text{C}$  for **2** correspond to removal of four coordinated water molecules (experimental value  $10.1\%$  (for **1**) and  $9.8\%$  (for **2**) and calculated value  $11.6\%$  (for **1**) and  $11.5\%$  (for **2**)). Further exothermic decomposition began at  $400^\circ\text{C}$  for **1** and at  $350^\circ\text{C}$  for **2** and finished at  $800^\circ\text{C}$  and  $750^\circ\text{C}$ , indicating complete removal of organic part of the complex. The residual value of **1** is  $20.9\%$ , assigned to  $\text{CuCO}_3$  as product (theoretical

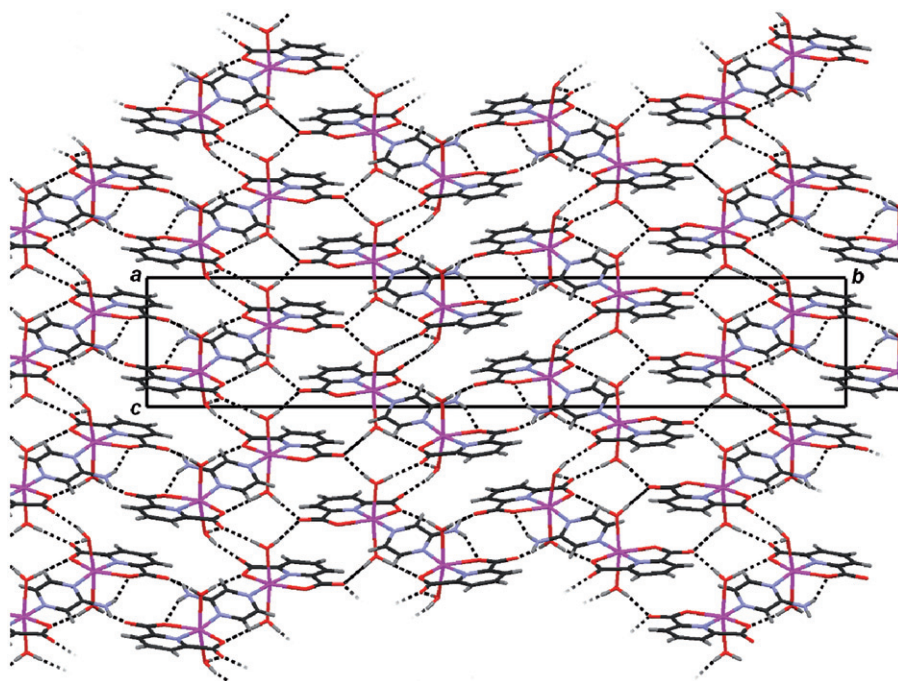


Figure 4. A view of the crystal structure of **2** projected onto (100). Molecules of  $[\text{Zn}_2(\text{H}_2\text{O})_4(\text{dipic})_2(\mu\text{-apyz})]$  are linked by  $\text{O-H}\cdots\text{O}$  and  $\text{N-H}\cdots\text{O}$  hydrogen bonds (represented by dotted lines) into a 3-D structure.

residual value, 19.8%). The main product is ZnO with residual value of 14.3% for **2** (theoretical residual value, 13.0%, respectively).

#### 4. Conclusion

Preparation, spectroscopic characterization, thermal properties, and crystal structure analysis of  $[\text{M}_2(\text{H}_2\text{O})_4(\text{dipic})_2(\mu\text{-apyz})]$  ( $\text{M} = \text{Cu}, \text{Zn}$ ) are presented. Complexes are new examples of dinuclear Cu(II) and Zn(II) complexes with bridging 2-aminopyrazine. A similar complex was previously prepared with Co(II) ion that is isostructural with the Zn(II) complex. In **1**, 2-aminopyrazine is disordered around an inversion center. The amino group and water significantly influence the formation of a complicated hydrogen-bond network. In continuation of our research, we wish to prepare similar dinuclear complexes with mixed transition metals and differently substituted pyrazines.

#### Supplementary material

CCDC 860766 and 860767 contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) from The Cambridge Crystallographic Data Centre (CCDC).

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