

*A recurrent Motive in the Supramolecular Assembly of Coordination Compounds with 2,6-bis(Benzimidazol-2-yl)pyridine (Bzimpy) and Two Identical H-bond Acceptor Co-ligands: [Cd(Ac)<sub>2</sub>(Bzimpy)], [Zn(Ac)<sub>2</sub>(Bzimpy)]·H<sub>2</sub>O (Ac:acetato) and Related Compounds*

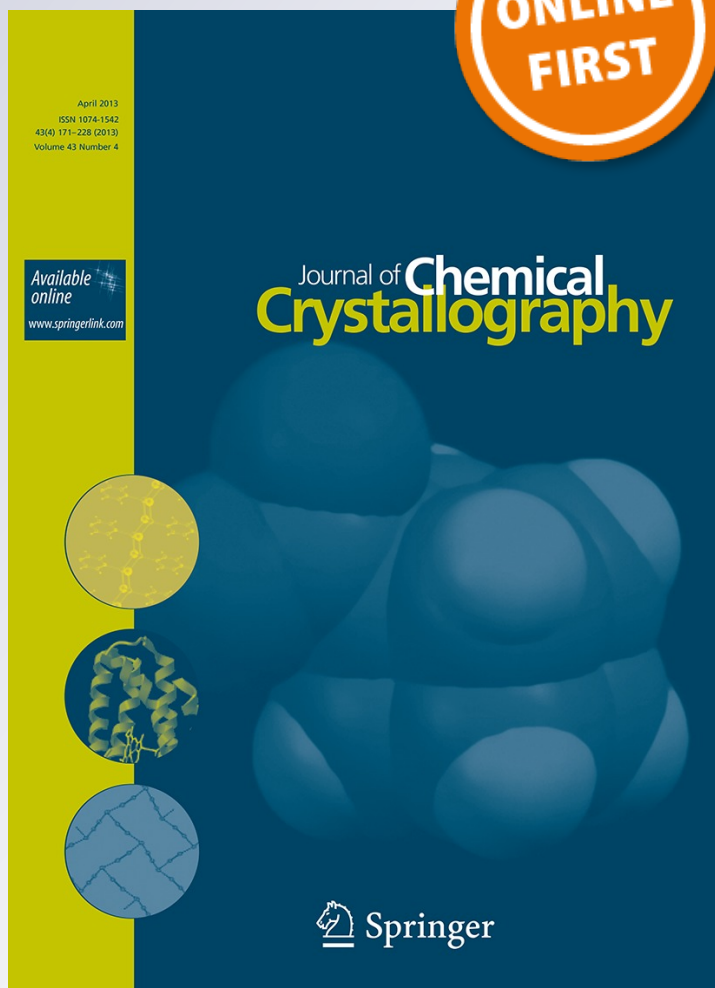
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# A recurrent Motive in the Supramolecular Assembly of Coordination Compounds with 2,6-bis(Benzimidazol-2-yl)pyridine (Bzimpy) and Two Identical H-bond Acceptor Co-ligands: $[\text{Cd}(\text{Ac})_2(\text{Bzimpy})]$ , $[\text{Zn}(\text{Ac})_2(\text{Bzimpy})]\cdot\text{H}_2\text{O}$ (Ac:acetato) and Related Compounds

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**Abstract** We report the crystal structures of two novel coordination compounds with similar complex composition:  $[\text{Cd}(\text{Ac})_2(\text{Bzimpy})]$  (**I**) and  $[\text{Zn}(\text{Ac})_2(\text{Bzimpy})]\cdot\text{H}_2\text{O}$  (**II**). Both compounds are monomeric. Compound **I** consists of a Cd(II) center heptacoordinated with three N atoms from a Bzimpy molecule and four O atoms from two bidentate acetato molecules. Compound **II** consists of a Zn(II) center pentacoordinated with three N atoms from a Bzimpy molecule and two O atoms from two monodentate acetato molecules. A non-coordinated water molecule completes the formula. In addition, we highlight some common features in the supramolecular assembly of both compounds and with similar structures deposited in the version 5.33 of the CSD. This assembly occur through H-bridges and  $\pi$ - $\pi$  offset stacked interactions, giving rise to the formation of what we call “directed ring” of two types: two molecular components  $^2\text{R}_d$  and three molecular components  $^3\text{R}_d$ . Structures are viewed as composed of well defined substructures in order to analyze them.

**Keywords** 2,6-bis(benzimidazol-2-yl)pyridine coordination compounds · Supramolecular architecture · Supramolecular synthons

## Introduction

As was pointed out by Boča et al., [1] the ligand Bzimpy (Scheme 1) is very versatile in three aspects of its coordination chemistry: (1) it can coordinate with different numbers of N-atoms, (2) it can have different grades of protonation or deprotonation of its imidazolic N-atoms and (3) it can participate in a great variety of strong ( $\text{N}_{\text{imid}}\text{H}\cdots\text{X}$  or  $\text{X}\text{H}\cdots\text{N}_{\text{imid}}$ ) (imid:imidazolic) and/or weak ( $\text{C}\text{H}\cdots\text{X}$ ) H-bridges. On the other hand, there is a very rich literature on its wide application in a variety of biochemical, scientific and technological areas (see Review [1] and references therein).

A search in the version 5.33 of the Cambridge Structural Database (CSD). [2] gave 53 different coordination compounds of neutral, protonated or deprotonated, non-substituted Bzimpy with transition metals. Only 12 of them are of group XII metal ions, which are of particular interest for us because of the special characteristics of their closed *d* shell structures.

## Experimental

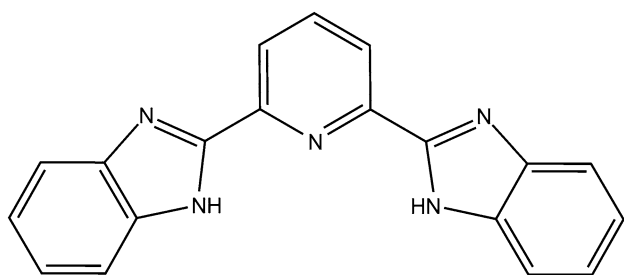
### Synthesis

We have synthesized compounds **I** and **II** serendipitously, in an attempt to obtain the respective tetrathionates. An aqueous solution of cadmium/cinc acetate dihydrate and potassium tetrathionate was allowed to diffuse in a solution of Bzimpy in DMF, being all solutions equimolar (0.080 final molarity).

During the first day some solid conglomerates precipitate in both systems. After spontaneous resolubilization and recrystallization each system was disassembled and allowed

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**Scheme 1** Schematic view of the ligand Bzimpy, IUPAC name 2,2'-Pyridine-2,6-diylbis(1H-benzimidazole)

to evaporate. Finally, near twenty days later, crystals with two (Cd system) and three (Zn system) different habits were identified, from which colorless prisms of **I** and colorless needles of **II** were isolated. Due to the great variety of products and the difficulties in its fractionation, we were not able to establish the yield in each synthesis.

#### Elemental Analysis

The formulation of each one of the two compounds was supported by elemental analysis (C, H, N) performed on a Carlo Erba EA 1108 instrument and, ultimately, by the structure determination by single crystal X-ray diffraction.

#### Compound **I**:

Required (%): C 50.98; H 3.53; N 12.93.  
Measured (%): C 51.2; H 3.5; N 13.1

#### Compound **II**:

Required (%): C 53.87; H 4.13; N 13.66.  
Measured (%): C 54.0; H 4.1; N 13.9

#### Structure Determination

A room temperature data set was collected for each structure on a four circle Oxford Diffraction Gemini CCD S Ultra diffractometer using a graphite monochromated Mo K $\alpha$  source ( $\lambda = 0.71073$  Å for **I** and 0.71069 for **II**). Measurements yielded 5074 (**I**) and 5502 (**II**) independent reflections of which 3810 (**I**) and 3018 (**II**) were considered observed [ $I > 2\sigma(I)$ ], with an internal consistency  $R_{\text{int}} = 0.0252$  for **I** and 0.1315 for **II**. We were not able to achieve neither better diffraction measurements nor better crystals. Both structure determinations were achieved routinely by direct methods and difference Fourier. Both structures were refined by least squares on  $F^2$ , with anisotropic displacement parameters for non-H atoms. Hydrogen atoms unambiguously defined by the stereochemistry (C–H's and N–H's) were placed at their

calculated positions and allowed to ride on their host carbon or nitrogen atoms with respect to both their coordinates and their thermal parameters. Those corresponding to water molecule in **II** were located in a late Fourier map with the help of potential H-acceptor atoms and refined with geometrical restraints (O–H: 0.82(1) Å and H–H: 1.30(1) Å). All calculations to solve and refine the structures and to obtain some derived results were carried out with the computer programs SHELXS97 [3], SHELXL97 [3] and SHELXTL/PC [3]. MERCURY [4] was used to draw molecular views and derive further results. Full use of the CCDC package was also made for searching in the CSD Database [2]. Pertinent results are given in Table 1.

CCDC 90197/58 & 901959/60 contains the supplementary crystallographic data for this paper. 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) by e-mailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting.

The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44(0)1223-336033.

## Results and Discussion

Note: there being no general agreement on the limiting values of the geometric parameters that characterize D–H...A non-covalent bonding interactions, we use the following conditions while accepting a D–H...O geometry as a hydrogen bridge:  $O/N-H...O \geq 90^\circ$ ,  $C-H...O \geq 120^\circ$ ; intramolecular: donor and acceptor separated by  $>3$  bonds; unquestionable directionality towards an acceptor lone pair or towards the middle of two acceptor lone pairs. Having these type of interaction a high electrostatic component, we privilege topological considerations over geometrical ones on limiting the H...O distance. On this basis and in order to select the H-bridges, we assign a limiting value of 3.0 Å to these distances but we accept values barely higher when an interaction seems to exist from the topological point of view.

#### Molecular Structures Analysis

$[Cd(C_2H_3O_2)_2(C_{19}H_{13}N_5)]$ , (**I**), is monomeric with a Cd(II) heptacoordinated center (Fig. 1). The coordination sphere is formed by three nitrogen atoms from one Bzimpy molecule and four oxygen atoms from two bidentate acetato ligands, with metal–N/O distances in the range 2.292(2)–2.468(2) Å (Table 2). It is remarkable the fact that the central N–Cd bond of the Bzimpy molecule is somewhat shorter than the lateral ones. This is not the case in the four structures in the version 5.33 of the CSD [2] containing the Bzimpy molecule coordinated to one Cd center, in which

**Table 1** Crystal data and structure refinement for **I** and **II**

| Empirical formula                           | C <sub>23</sub> H <sub>19</sub> CdN <sub>5</sub> O <sub>4</sub> ( <b>I</b> )   | C <sub>23</sub> H <sub>19</sub> N <sub>5</sub> O <sub>4</sub> Zn·H <sub>2</sub> O ( <b>II</b> )         |
|---|--|---|
| Formula weight                              | 541.84   | 512.84  |
| T/°K  | 298  | 298   |
| Radiation, k/Å°                             | 0.71073  | 0.71073   |
| Crystal system, Space group                 | Triclinic, <i>P</i> -1   | Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>  |
| Unit cell dimensions/<br>Å° and °           | <i>a</i> = 9.8900 (5) Å<br><i>b</i> = 10.0376 (3) Å<br><i>c</i> = 11.6432 (6) Å<br>$\alpha$ = 81.445 (3)°<br>$\beta$ = 84.867 (4)°<br>$\gamma$ = 78.938 (4)° | <i>a</i> = 10.480 (5) Å<br><i>b</i> = 24.007 (5) Å<br><i>c</i> = 10.117 (5) Å<br>$\beta$ = 115.425 (5)° |
| Volume/Å° <sup>3</sup>                      | 1119.53 (9)  | 2298.8 (17)   |
| Z   | 2  | 4   |
| Calculated density/<br>g cm <sup>-3</sup>   | 1.607  | 1.482   |
| Absorption coefficient/<br>mm <sup>-1</sup> | 1.01   | 1.11  |
| F(000)                                      |  |   |
| Crystal size/mm                             | 0.44 × 0.29 × 0.15   | 0.5 × 0.1 × 0.05  |
| Description                                 | Prism, colourless  | Prism, colourless   |
| Theta range/°                               | 3.8 to 29.1  | 3.5 to 28.8   |
| Index ranges                                | -12 ≤ <i>h</i> ≤ 13,<br>-12 ≤ <i>k</i> ≤ 13,<br>-15 ≤ <i>l</i> ≤ 15  | -12 ≤ <i>h</i> ≤ 13,<br>-30 ≤ <i>k</i> ≤ 31,<br>-13 ≤ <i>l</i> ≤ 13                                     |
| Reflections collected                       | 9118   | 34370   |
| Independent reflections                     | 5074<br>[ <i>R</i> <sub>(int)</sub> = 0.025]   | 5502 [ <i>R</i> <sub>(int)</sub> = 0.132]   |
| Max. and min. transmission                  | 1.000 and 0.870  | 0.984 and 0.894   |
| Observed data/<br>restraints/parameters     | 5074/0/306   | 5502/3/315  |

the central bond is in general longer than the lateral ones. Two intramolecular C–H...O hydrogen bridges contribute to the stabilization of the structure (Table 3, entries 1 and 2, and Fig. 1). The molecule has a pseudo two-fold axis that bisect the Bzimpy ligand.

The coordination polyhedron is a pentagonal bipyramid strongly distorted because of the steric restrictions imposed by the chelate ligands, with angles in the range 67.87(6)°–86.40(6)° for those corresponding to the ideal value of 72°, in the range 54.08(6)°–117.72(7)° for those corresponding to the ideal value of 90° and 167.28(6)° for that corresponding to an expected 180°. However, the coordination geometry can be elegantly described through the ligand bond valence vectors (BVV) geometry, [5] which in the present case (three ligands) is a trigonal planar one, with a sum of angles of 359.9° (ideal 360°). Excellent agreements are found for the classical bond valence scalar sum [6] on the metal ion (experimental  $\Sigma s_i = 1.97$  v.u.; ideal: 2.00

v.u.). The departure of the bond valence vector sum [5] ( $\Sigma s_i = 0.12$  v.u.) from the ideal value of 0.00 is reasonable for a coordination sphere with three chelate ligands.

The Bzimpy molecule is not planar, being the mean planes of both benzimidazole groups displaced and torsioned towards opposite sides with respect to the central ring. Angles between each benzimidazole mean-plane and the central pyridine mean-plane are 6.6° and 7.0° respectively.

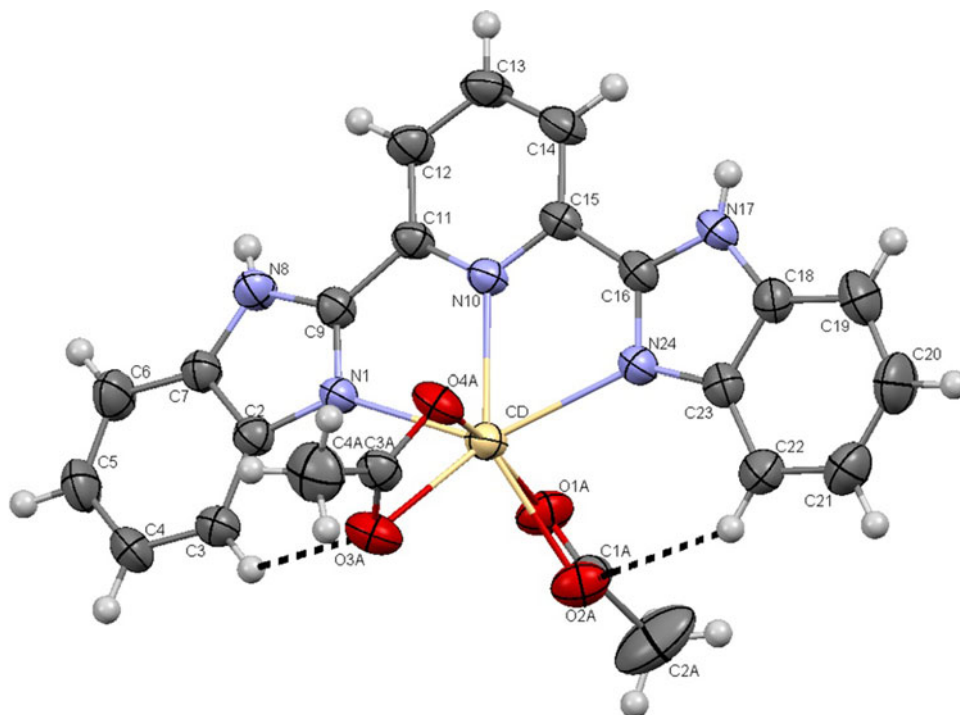
Mean planes C–O–Cd–O' in both acetato molecules subtend a dihedral angle of 72.20°. One of the bond in each acetato molecule belong to the ecuatorial plane of the distorted coordination polyhedra whilst the other form the axis.

[Zn(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>19</sub>H<sub>13</sub>N<sub>5</sub>)]·H<sub>2</sub>O, (**II**), is monomeric with a Zn(II) pentacoordinated center (Fig. 2). The coordination sphere is formed by three nitrogen atoms from one Bzimpy molecule and two oxygen atoms from two monodentate acetato ligands, with metal–N/O distances in the range 1.960(3)–2.197(3) Å (Table 2). Like in the Cd complex **I**, in **II** the central N–Zn bond is somewhat shorter than the lateral ones, but unlike in **I** this is the common behaviour in the four compounds with one Bzimpy molecule coordinated to one Zn center deposited in the version 5.33 of the CSD. A non-coordinated water molecule completes the formula, fulfilling an important role in the stabilization of the structure through the formation of H-bridges in which it acts both as donor and acceptor (Table 3, entries 13, 15 and 16). Greater displacement ellipsoids in **II** as compared with those in **I** can be explained by different facts: (i) while in **I** the four oxygen atoms from the two acetato groups are coordinated to Cd, in **II** only two of them are coordinated to the Zn centre; (ii) the crystal quality in **II** is lower than in **I**, as it can be seen by the higher value of *R*<sub>int</sub> in the first compound; (iii) the overall H-bridges strength in **I** seems to be greater than those in **II**; (iv)  $\pi$ – $\pi$  interactions in **II** are weaker than in **I**, due to a much lower overlap of arene groups between neighboring ligand molecules.

The coordination polyhedron is a trigonal bipyramid, distorted because of the steric restrictions imposed by the chelate Bzimpy and, perhaps, under the influence of the hydration water molecule that strongly H-bridges two non-coordinated oxygen atoms from different acetato groups of two translationally related complex molecules. Angle ranges: 74.73(12)°–102.84(13)° for those corresponding to the ideal value of 90°, 95.23(14)°–141.93(12)° for those corresponding to the ideal value of 120° and 149.15(12)° for that corresponding to an expected 180°. Some departure from ideal values are found both for the classical bond valence **scalar** sum [6] on the metal ion (experimental  $\Sigma s_i = 1.87$  v.u.; ideal: 2.00 v.u.) as well as for the bond valence **vector** sum [5] (experimental  $\Sigma s_i = 0.19$  v.u.; ideal: 0.00 v.u.). Being both acetato groups in **II** monodentates it seems that the cause of this distortion, greater



**Fig. 1** The asymmetric unit of  $[\text{Cd}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_{19}\text{H}_{13}\text{N}_5)]$  with labelling except for H atoms for clarity. Thermal ellipsoids are drawn at the 50 % probability level. Intramolecular H-bridges are shown as *dotted line*



**Table 2** Selected bond distances (Å) and bond angles (°) for the title compounds

| Compound (I)  |             |                   |            |
|---------------|-------------|-------------------|------------|
| Cd–N(1)       | 2.4195 (19) | N(10)–Cd–N(1)     | 67.87(6)   |
| Cd–N(10)      | 2.4129 (18) | N(10)–Cd–N(24)    | 67.98(6)   |
| Cd–N(24)      | 2.437 (2)   | O(1A)–Cd–N(24)    | 91.62(7)   |
| Cd–O(1A)      | 2.357 (2)   | O(1A)–Cd–O(2A)    | 54.08(6)   |
| Cd–O(2A)      | 2.4180 (19) | O(4A)–Cd–O(2A)    | 113.51(6)  |
| Cd–O(3A)      | 2.4675 (18) | O(4A)–Cd–O(1A)    | 167.28(6)  |
| Cd–O(4A)      | 2.2921 (18) | O(4A)–Cd–N(1)     | 95.20(7)   |
| Compound (II) |             |                   |            |
| Zn1–N1        | 2.197 (3)   | N(10)–Zn(1)–N(1)  | 74.46(11)  |
| Zn1–N10       | 2.132 (3)   | N(10)–Zn(1)–N(24) | 74.73(12)  |
| Zn1–N24       | 2.174 (3)   | N(24)–Zn(1)–N(1)  | 149.15(12) |
| Zn1–O2A       | 1.960 (3)   | O(2A)–Zn(1)–N(24) | 102.84(13) |
| Zn1–O3A       | 1.984 (3)   | O(2A)–Zn(1)–O(3A) | 95.23(14)  |

than that in **I** where the anion molecules act as bidentate, are the strong H-bridges that the non-coordinated water molecule subtend with both acetato groups.

Like in **I**, Bzimpy molecule is not planar, with dihedral angles between each benzimidazole group and the central pyridine ring being 2.0° and 7.3°. The molecule coordinates in a slightly slanted way.

Acetato groups behave very different in **II** with respect to **I**, being the dihedral angle between both C–O–Zn–O' mean planes 24.7°. Also, unlike **I** both O–Zn bonds belong to the equatorial plane of the coordination polyhedra.

### 3-D construction analysis

Despite the differences in the molecular structures of the title compounds, both of them 0-D, some outstanding similarities can be observed in the 3-D construction in both structures. To best see them one can imagine a step-by-step construction of the crystal structure. In order to do this one must first identify the set of molecules which interact among them with the same and overall strongest set of intermolecular interactions. This supramolecular assembly defines a *first-level substructure* in the crystal structure, that can be a *j*-dimensional one (*j*: 0, 1, 2 or 3), unless this assembly be the global crystal structure. Proceeding in the same way while looking for associations of the *first-level substructures*, will bring to light the presence of even *higher level (second, etc.) substructures*. Going on with this procedure the crystal structure will be completely analysed. Interactions of the same type but with somewhat different geometries and those with slightly different strengths (e.g. C–H···O and C–H···π) will be considered as similar in this work.

Following the described procedure in both title crystal structures, similarities and differences in the 3-D construction clearly become visible.

#### First-level substructures

Both in **I** and **II** can be distinguished a *chain* as a first-level substructure, in which molecules join together by strong

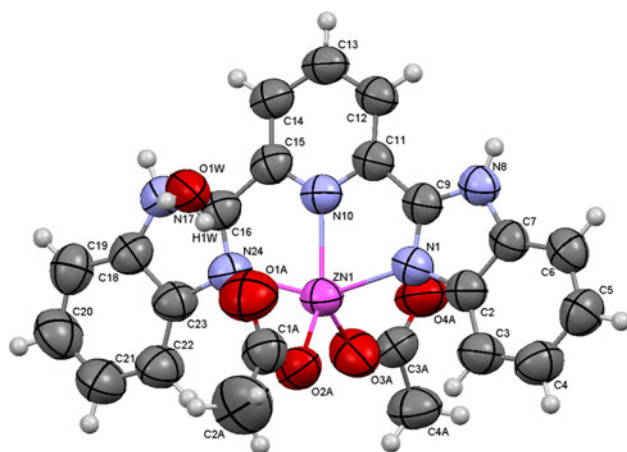
**Table 3** Hydrogen-bridge geometry (Å, °)

| D–H...A                                | D–H       | H...A   | D...A    | D–H...A |
|--|-----------|---------|----------|---------|
| Compound ( <b>I</b> ) <sup>a</sup>     |           |         |          |         |
| Intramolecular                         |           |         |          |         |
| C3–H3...O3A                            | 0.93      | 2.71    | 3.372(3) | 28.6    |
| C22–H22...O2A                          | 0.93      | 2.68    | 3.407(3) | 135.8   |
| Intermolecular. 1st level substructure |           |         |          |         |
| N8–H8...O1A <sup>i</sup>               | 0.77(2)   | 1.97(3) | 2.734(3) | 171(3)  |
| C12–H12...O1A <sup>i</sup>             | 0.93      | 2.64    | 3.441(3) | 144.9   |
| N17–H17...O4A <sup>ii</sup>            | 0.80(2)   | 1.90(3) | 2.690(3) | 165(3)  |
| C14–H14...O4A <sup>ii</sup>            | 0.93      | 2.75    | 3.549(3) | 144.3   |
| Intermolecular. 3rd dimension          |           |         |          |         |
| C13–H13...O3A <sup>iii</sup>           | 0.93      | 2.80    | 3.384(3) | 122.3   |
| C14–H14...O3A <sup>iii</sup>           | 0.93      | 2.78    | 3.370(3) | 122.2   |
| C21–H21...O2A <sup>iv</sup>            | 0.93      | 2.95    | 3.873(3) | 172.0   |
| C2A–H1A... $\pi^b$                     | 0.96      | 3.00    | 3.68     | 128.9   |
| Compound ( <b>II</b> ) <sup>c</sup>    |           |         |          |         |
| Intermolecular. 1st level substructure |           |         |          |         |
| N8–H8...O4A <sup>i</sup>               | 0.86      | 1.86    | 2.697(5) | 165.5   |
| C12–H12...O4A <sup>i</sup>             | 0.93      | 2.98    | 3.809(6) | 148.6   |
| N17–H17...O1 W <sup>ii</sup>           | 0.86      | 1.88    | 2.733(5) | 170.3   |
| C14–H14...O1A <sup>ii</sup>            | 0.93      | 2.52    | 3.364(6) | 150.6   |
| O1 W–H1 W...O1A                        | 0.788(19) | 1.86(2) | 2.649(6) | 176(5)  |
| Intermolecular. 2nd level substructure |           |         |          |         |
| O1W–H2 W...O4A <sup>iii</sup>          | 0.833(19) | 1.99(3) | 2.796(6) | 162(7)  |
| Intermolecular. 3rd dimension          |           |         |          |         |
| C21–H21...O2A <sup>iv</sup>            | 0.93      | 2.86    | 3.479(7) | 125.2   |

<sup>a</sup> Symmetry codes: (i)  $-x, -y + 1, -z + 1$ ; (ii)  $-x, -y + 1, -z + 2$ ; (iii)  $x, y + 1, z$ ; (iv)  $-x + 1, -y, -z$

<sup>b</sup> Benzene ring C2 to C7. A in the column headings refers to the ring centroid

<sup>c</sup> Symmetry codes: (i)  $x, -y + 1/2, z + 1/2$ ; (ii)  $x, -y + 1/2, z - 1/2$ ; (iii)  $x - 1, y, z$ ; (iv)  $-x + 1, -y, -z$



**Fig. 2** The asymmetric unit of  $[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_{19}\text{H}_{13}\text{N}_5)]$  with labelling except for H atoms for clarity. Thermal ellipsoids are drawn at the 50 % probability level

N/O–H...O and weak C–H...O bridges (Table 3, entries 3 to 6 for **I** and 11 to 15 for **II**) and  $\pi$ – $\pi$  offset stacked interactions between half of each symmetry related molecules of Bzimpy. In **I** the nearer arene–arene contacts occur between the central pyridine group of one molecule and the benzene ring of the other, with MP–MP' distances 3.503 and 3.577 Å and Cg–Cg' distances range 3.530 to 3.759 Å (MP: mean plain of interacting half of each molecule; Cg: centroid of each interacting ring). In **II**, instead, the nearer contacts occur between the central pyridine group of one molecule and the imidazole ring of the other, subtending the two mean planes of interacting groups an angle of 6.15°, with Cg–Cg' distances range 3.512 to 3.625 Å. All these values are among those found in literature [7].

What is relevant in the first-level substructure of the Cd crystal structure (**I**) is the selfcomplementarity of intermolecular H-bridges, assisted both by  $\pi$ – $\pi$  stacking interactions and by the molecular shape. This assembly of two complex molecules give rise to what we call a “directed” two membered ring motive, since each intermolecular H-bridge travel the ring only in one direction, no matter which or how many the hydrogen bridges are. We are not interested in how many atoms form the ring either, so we symbolize herein this ring as  ${}^2\text{R}_d$  (left-hand superscript stands for the number of molecular components of the ring, right-hand subscript stands for “directed”). Each complex molecule participates in two such rings, one with each neighbour through the corresponding  $\pi$ – $\pi$  stacked half of the Bzimpy ligand.

In the first-level substructure of the Zn crystal structure (**II**),  ${}^2\text{R}_d$  is also formed by each complex molecule with one of its two neighbours, but a new kind of ring is generated with the other, in which the water molecule plays a bridging role between one of the Bzimpy nitrogen atoms acting as donor and one O<sub>Ac</sub> as acceptor. We symbolize this directed three-membered ring as  ${}^3\text{R}_d$ .

In order to know if these two kinds of directed rings are common in similar structures, we made a search in the version 5.33 of the CSD [2] for coordination compounds containing (i) any transition metal center, (ii) one neutral, non-substituted Bzimpy molecule as ligand and (iii) two identical molecules of a co-ligand that have an H-bridge acceptor atom within or near the coordination sphere of the metal and that does not have a strong H-bridge donor. When more than one entry for the same compound was found, the one with no disorder and/or the best R index was selected. The search gave as a result 9 compounds, out of which 3 have no solvent molecules as in the Cd compound **I**, 5 have one solvent molecule that can act both as donor and acceptor (in all cases dimethylformamide, DMF) as in the Zn compound **II** and 1 has two solvent molecules (also DMF). Six out of the nine compounds have group XII metal centers, just half the total amount of coordination

compounds of neutral, protonated or deprotonated, non-substituted Bzimpy with transition metals deposited in the CSD.

The three structures from the CSD without solvent molecules: catena-[( $\mu_2$ -4-Carboxylato-phenoxyacetato)-(2,6-bis(benzimidazolyl)pyridine)-zinc(ii)], ( $C_{28} H_{19} N_5 O_5 Zn_1$ )<sub>n</sub> [8], Refcode SIKTAI; catena-(bis( $\mu_2$ -2,2'-(p-phenylenedioxy)bis(acetato-O))-bis(2,6-bis(benzimidazol-2-yl)pyridine)-di-zinc(ii)), ( $C_{58} H_{42} N_{10} O_{12} Zn_2$ )<sub>n</sub> [9], Refcode XOBXUI and catena-(( $\mu_2$ -benzene-1,4-dioxydiacetato)-(2,6-bis(benzimidazol-2-yl)pyridine-N,N',N'')-cadmium(ii)), ( $C_{29} H_{21} Cd_1 N_5 O_6$ )<sub>n</sub> [10], Refcode XONHEO, are polymeric with the anion, a big dicarboxylate in each case, bridging two metal centers. However and despite of this, all of them display the same  ${}^2R_d$  motive as in the title structures (in XONHEO the C–H...O distance is noticeably higher than the 3.0 Å imposed as limit in this work and therefore not considered an H-bridge).

The five structures from the CSD with one solvent molecule as **I** in this work: Dichloro-(2,6-bis(2-benzimidazolyl)pyridine-N,N',N'')-copper(ii) bdimethylformamide solvate,  $C_{19} H_{13} Cl_2 Cu_1 N_5 C_3 H_7 N_1 O_1$  [11], Refcode SICPUP; Dichloro-(2,2'-(pyridine-2,6-diyl)bis-1H-benzimidazole)-cobalt N,N-dimethylformamide solvate,  $C_{19} H_{13} Cl_2 Co_1 N_5 C_3 H_7 N_1 O_1$  [12], Refcode WAKJID; Dichloro-(2,6-bis(benzimidazol-2-yl)pyridine)-cadmium(ii) dimethylformamide solvate,  $C_{19} H_{13} Cd_1 Cl_2 N_5 C_3 H_7 N_1 O_1$  [13], Refcode IBEWIW; Dichloro-(2,6-bis(1H-benzimidazol-2-yl)pyridine)-zinc dimethylformamide solvate,  $C_{19} H_{13} Cl_2 N_5 Zn_1 C_3 H_7 N_1 O_1$  [14], Refcode MAHWIC01 and (2,6-bis(Benzimidazole-2'-yl)pyridine-N,N',N'')-dichloro-manganese(ii) dimethylformamide solvate,  $C_{19} H_{13} Cl_2 Mn_1 N_5 C_3 H_7 N_1 O_1$  [15], Refcode VURZIR also display the  ${}^2R_d$  motive and, unlike that of **II**, none of them display the  ${}^3R_d$  motive. Unlike the crystal structure of the title compounds, in these five structures the complex molecule participates in only one ring with half the Bzimpy molecule.

Finally, in the structure with two solvent molecules Dichloro-(2,6-bis(1H-benzimidazol-2-yl)pyridine)-mercury(ii) dimethylformamide solvate,  $C_{19} H_{13} Cl_2 Hg_1 N_5 2(C_3 H_7 N_1 O_1)$  [16], Refcode DIXNUU, again each Bzimpy molecule form two rings, but this time both of the type  ${}^3R_d$  as in **II**.

The number of available structures similar to that of the title compounds is not enough to draw definitive conclusions about the tendency to form the directed rings motives here discussed, both having in common the synergistic interplay of H-bridge and  $\pi$ - $\pi$  stacking interactions. However, the  ${}^2R_d$  ring motive is a good candidate to be a supramolecular homomeric synthon with variable metal centre (M) and coligand, the only requirement for the last being to have the H-bridge acceptor atom within or near the coordination sphere of M, to meet geometrical

requirements. Two structures that not meet the search criteria given above encourage us in this proposal:

(1) ( $\mu_2$ -Acetato-O,O,O')-(acetato-O,O')-(acetato-O)-bis(2,6-bis(benzimidazol-2-yl)pyridine)-di-cadmium hemikis(peroxodisulfate)dihydrate,  $C_{44} H_{35} Cd_2 N_{10} O_6^{1+} \cdot 0.5(O_8 S_2^{2-}) \cdot 2(H_2 O_1)$  [17], Refcode XAMFEX in the CSD have a dinuclear complex cation in which three acetato groups coordinate in different manner: (i) monodentate, (ii) O,O'-bidentate, O-bridging and (iii) bidentate. In spite of the complexity of this molecule, it also forms chains in which molecules bind by H-bridges and  $\pi$ - $\pi$  stacking exactly as in **I**.

(2) (2-(6-(1H-Benzimidazol-2-yl- $\kappa N^3$ ))-2-pyridyl- $\kappa N$ )benzimidazolato- $\kappa N$ )-(dicyanamido- $\kappa N$ )-(methanol- $\kappa O$ )-copper(ii),  $C_{22} H_{16} Cu_1 N_8 O_1$  [18], Refcode QAHTAW in the CSD is a complex in which Bzimpy is monodeprotonated and ethanol is one of the two different co-ligand molecules. This molecule meets the geometric and chemical requirements to establish the same kinds of H-bridges and  $\pi$ - $\pi$  interactions as in **I**. Thus, two complex molecules form the  ${}^2R_d$  motive, but this time with a small difference: the H-bridge that involves the imidazolic N travels the ring in opposite direction with respect to that in **I**.

## Second-level substructure in **II**

At this point both structures clearly differentiate. In compound **I** no higher order substructure can be identified, while in compound **II** chains are H-bridged through the water molecules from one of them acting as donors and the acetato groups of the other as acceptors (Table 3, entry 16) and, at the same time, bound by weak arene-arene interactions between almost parallel benzene rings (C2-C7 and C18-C23), with centroid to centroid distance of 3.862 Å (Fig. 3). These interactions give rise to a *sheet* as a second-level substructure in **II**.

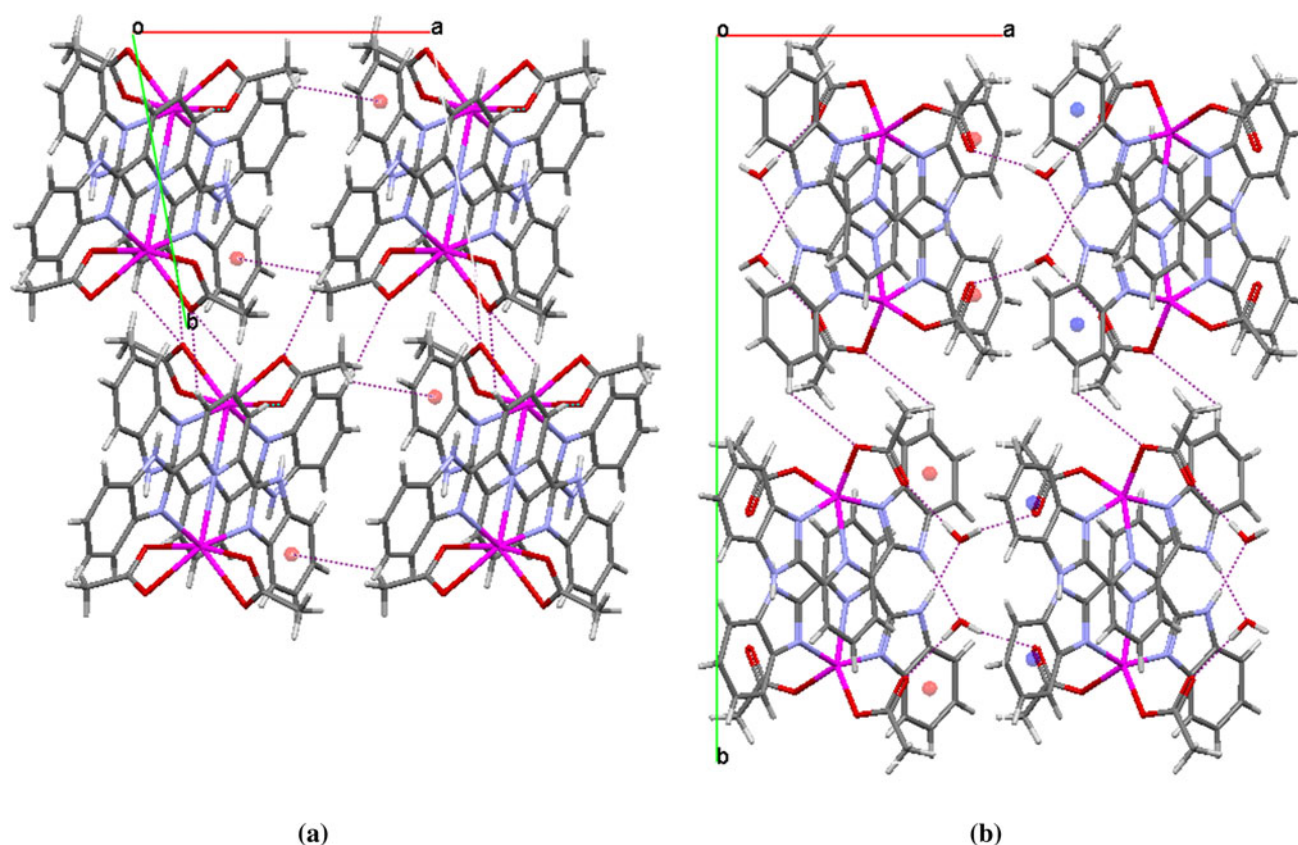
## Final 3-D construction

In (**I**) each *chain* interacts with six neighbours through weak  $C_{ar}-H \cdots O_{Ac}$  and  $C-H \cdots \pi$  bridges (Fig. 3 and Table 3, entries 7 to 10). In (**II**) *sheets* are H-bridged by weak  $C_{ar}-H \cdots O_{Ac}$  interactions (Fig. 3 and Table 3, entry 17).

## Conclusions

Both title compounds display a remarkable similarity in the construction of the crystal structure: the formation of a *chain* as a first-level substructure through the synergistic interplay of H-bridges and  $\pi$ - $\pi$  interactions, which jointly can be considered a single entity.





**Fig. 3** View along *chains* of the crystal structures of compound **I** (a) and compound **II** (b). H-bridges as *dotted lines* (only the relevant ones; some of those involved in the chain construction omitted for

clarity). Rings involved in  $\pi$ - $\pi$  and  $C_{Me}-H \cdots \pi$  interactions identified with the respective centroids. Note the *second-level substructure(sheet)* in **II** parallel to the *B* face

Based on the research on the version 5.33 of the CSD [2], we sustain the hypothesis that the ring motive  ${}^2R_d$  is a supramolecular homomeric synthon in species containing (i) one transition metal center, (ii) one protonated and non-substituted Bzimp molecule as ligand and (iii) two identical co-ligand molecules with at least one H-bridge acceptor atom within or near the coordination sphere of the metal atom.

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**Conflict of interest** The authors declare that they have no conflict of interest.

## References

- Bocă M, Jameson RF, Linert W (2011) *Coordin Chem Rev* 255:290
- Allen FH (2002) *Acta Cryst B* 58:380
- Sheldrick GM (2008) *Acta Cryst A* 64:112
- Macrae CF, Edgington PR, McCabe P, Pidcock E, Shields GP, Taylor R, Towler M (2006) *J Appl Cryst* 39:453
- Harvey MA, Baggio S, Baggio R (2006) *Acta Cryst B* 62:1038
- Brown ID (1994) Bond-length-bond-valence relationships in inorganic solids. In: Bürgi H-B, Dunitz JD (eds) *Structure correlation*, vol 2. VCH, Weinheim, New York, pp 405–429
- Malathy Sony SM, Ponnuswamy MN (2006) *Cryst Growth Des* 6:736
- Yang Y, Zeng MH, Zhang SH, Liang H (2007) *Wuji Huaxue Xuebao (Chin) (Chin J Inorg Chem)* 23:1435
- Yang Y, Zeng M-H, Zhang L-J, Liang H (2008) *Jiegou Huaxue (Chin J Struct Chem)* 27:749
- Yang Y, Zeng M-H, Zhang S-H, Liang H (2007) *Chin J Chem* 26:1121
- Bernardinelli G, Hopfgartner G, Williams AF (1990) *Acta Cryst C* 46:1642
- Cariou R, Chirinos JJ, Gibson VC, Jacobsen G, Tomov AK, Britovsek GJP, White AJP (2010) *Dalton Trans* 39:9039
- Liu S-G, Zuo J-L, Li Y-Z, You X-Z (2004) *J Mol Struct* 705:153
- Liu SG, Zuo J-L, Wang Y, Li Y-Z, You XZ (2005) *J Phys Chem Solids* 66:735
- Wang S, Zhu Y, Zhang F, Wang Q, Wang L (1992) *Polyhedron* 11:1909
- Liu X-m, Mu X-y, Xia H, Su Q, Ye L, Chen C, Gao W, Mu Y (2007) *Chem Res Chin Univ* 23:159
- Harvey MA, Baggio S, Garland MT, Baggio R (2005) *J Coord Chem* 58:243
- Hu J, Zhang J, Zhang W, Zhang C (2011) *Acta Cryst E* 67:m61