

## Zinc(II) Complexes Based on *ortho*-Phthalic Acid and Ancillary N-Donor Ligands

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### ABSTRACT

The versatile coordination abilities of *o*-phthalic acid, containing two carboxylic groups in *ortho*-position, allow for a variety of structures ranging from discrete complexes to 1D, 2D and 3D architectures. This review focuses on the synthesis and structural particularities of zinc(II) phthalates with ancillary N-containing ligands such as pyridine, imidazole and their derivatives [3-, 4-methylpyridine, and 1-, 2-methylimidazole], and 2,2', 4,4'-bipyridine. The coordination features manifested by this ligand are analyzed and discussed.

**Keywords:** *o*-Phthalic acid; zinc(II) complexes; carboxylates; coordination polymers; N-donor ligands.

### 1. INTRODUCTION

The design and synthesis of zinc(II) carboxylates are attracting large interest due to their fascinating architectures and remarkable physical and chemical properties such as photoluminescence and nonlinear optical (NLO) properties, catalysis, separation and sorption (see for example Erxleben, 2003; Allendorf et al., 2009; Redshaw et al., 2010; Perry et al., 2011; Wee et al., 2011). Being components of metalloproteins and executing important biochemical functions in living organisms these compounds are often used as artificial and biomimetic models to study biological processes in natural biosystems (Ryde, 1999; Sousa et al., 2007). In the past few years impressive developments have been made in the use of zinc carboxylates in the design of new metal-organic frameworks (MOFs),

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which exhibit high absorption properties and thermal stability (Li et al., 1999; Eddaoudi et al., 2000, 2001; Horike et al., 2011; Zhao et al., 2011). Involving in such systems polyfunctional ligands with two- and more carboxylic groups became an attractive alternative strategy for designing of hybrid materials with advantageous properties. Among these, *ortho*-phthalic acid ( $H_2Pht$ ) is a versatile dicarboxylic ligand and has been widely used in the design of coordination compounds with different metals (Baca et al., 2004a and references therein). There are several reasons for the sustained interest in this ligand. Firstly, for many years, *o*-phthalic acid and its derivatives are of growing interest due to their significant usage in a large variety of substances from dyes, perfumes, and pharmaceuticals to synthetic fibers, plasticizers, gelling agent, lubricants, corrosion inhibitors and others (Ang et al., 2005). Their applications also include building materials, personal care products, detergents, glues and even food products, toys, textiles, and medical devices. Secondly, two carboxylic groups in *ortho*-position (ca.  $60^\circ$ ) promote the variety of bonding of metal centers and result in the formation of diverse topological structures ranging from discrete **mono-** and **polynuclear complexes** (Baca et al., 2005a, 2005b; Brechin et al., 1996, 2000; Canada-Vilalta et al., 2003; Chen et al., 2001; García-Zarracino et al., 2003; Gerbeleu et al., 1999; Johnston et al., 2008; Kato et al., 2006; Kobayashi et al., 2001; Lewinski et al., 1998; Li et al., 2000, 2007c; Ma et al., 2004; Matsumoto et al., 2007; Squire et al., 1995; Solari et al., 1996; Sundberg and Ugglä, 1997; Tang et al., 2004; Tian et al., 2005, 2007b; Wang et al., 2008b; Wu et al., 1998; Xue et al., 1993; Yan et al., 2004; Yang et al., 2005) to **one-dimensional** (Baca et al., 2001, 2003a, 2004a, 2004b, 2005a, 2006; Bakalbassis and Paschalidis, 1998; Braverman et al., 2007; Burke et al., 2003; Burrows et al., 2000; Chen et al., 1998, 2004; Cheng et al., 2004; Cui et al., 2006; Escuer et al., 1997; Filippova et al., 2010; Fu et al., 2006; Gerbeleu et al., 1999; Gong et al., 2007; Hu et al., 2008; Huang et al., 2010b; Kumar et al., 2006; Liet al., 2006a, 2007a, 2007b; Liang et al., 2003; Liu et al., 2007a, 2007b, 2008; Lu et al., 2010; Ma et al., 2004; Padmanabhan et al., 2007; Qi et al., 2008b; Simonov et al., 2001; Song and Yan, 2005a; Song et al., 2005b; Tian et al., 2007a; Thirumurugan and Natarajan, 2004a, 2005a; Thirumurugan and Rao, 2005b; Wan et al., 2003a, 2003b; Wang et al., 2007b, 2008c; Whitcomb and Rogers 1997; Yang et al., 2009a; Yao et al., 2002; Zhang et al., 2000; Zhang and Sun, 2006; Zhao et al., 2009; Zhou, 2007), **two-dimensional** (Askarinejad and Morsali, 2006; Bai et al., 2010; Charushnikova et al., 2007; Chen et al., 1998; Cheng et al., 2007a, 2007b, 2008; Du et al., 2007; Fan et al., 2006; Huang et al., 2010a, 2010b; Kan et al., 2011; Li et al., 2004, 2006b, 2009; Liu et al., 2004; Luo et al., 2010; Ma et al., 2003, 2004; Marandi et al., 2007; Meng et al., 2006; Qi et al., 2008a; Simonov et al., 2004; Song et al., 2010; Stein and Ruschewitz, 2005; Thirumurugan and Natarajan, 2004c; Suresh et al., 2001; Wan et al., 2003b; Wang et al., 2003, 2006, 2007a, 2008a, 2010; Xu et al., 2006; Yang et al., 2003a, 2003b, 2009b; Ye et al., 2005; Zeng et al., 2008; Zhang et al., 2001, 2008a, 2008b, 2008c, 2008d), and **three-dimensional** networks (Bai et al., 2010; Chen et al., 2010; Cheng et al., 2006, 2007a; Gu and Xue, 2006; Li et al., 2008b; Lightfoot and Snedden 1999; Luo et al., 2008; Qi et al., 2008a; Thirumurugan and Natarajan, 2004b; Wang et al., 2005, 2009, 2010). Thirdly, the phthalate ligand can participate in formation of hydrogen bonds as well as  $\pi$ - $\pi$  stacking forces, all interactions playing an important role in the formation of extended architectures (Babb et al., 2003; Baca et al., 2003b, 2005a, 2005b; Braverman et al., 2007; Burke et al., 2003; Burrows et al., 2000, 2004; Chen et al., 1998; Filippova et al., 2010; Fondo et al., 2006; Kumar et al., 2006; Li et al., 2007a, 2008a; Ma et al., 2001; Raj et al., 2003; Sun et al., 2006; Wang et al., 2008a, 2008b, 2008c; Wu et al., 2009; Xuan et al., 2008; Yang et al., 2003c, 2009a, 2009b; Ye et al., 2005; Zhang et al., 2005).

This review focuses on zinc(II) complexes constructed from phthalate and ancillary N-containing ligands and describes our efforts toward the preparation of such zinc(II) phthalates with pyridine (Py), imidazole (Im) and their derivatives [3-methylpyridine ( $\beta$ -Pic),

4-methylpyridine ( $\gamma$ -Pic), 1-methylimidazole (1-Melm), and 2-methylimidazole (2-Melm)], and 2,2'-bipyridine (bpy) and 4,4'-bipyridine (4,4'-bpy). Their synthesis and structural particularities are discussed.

## 2. COORDINATION MODES OF PHTHALATE LIGAND

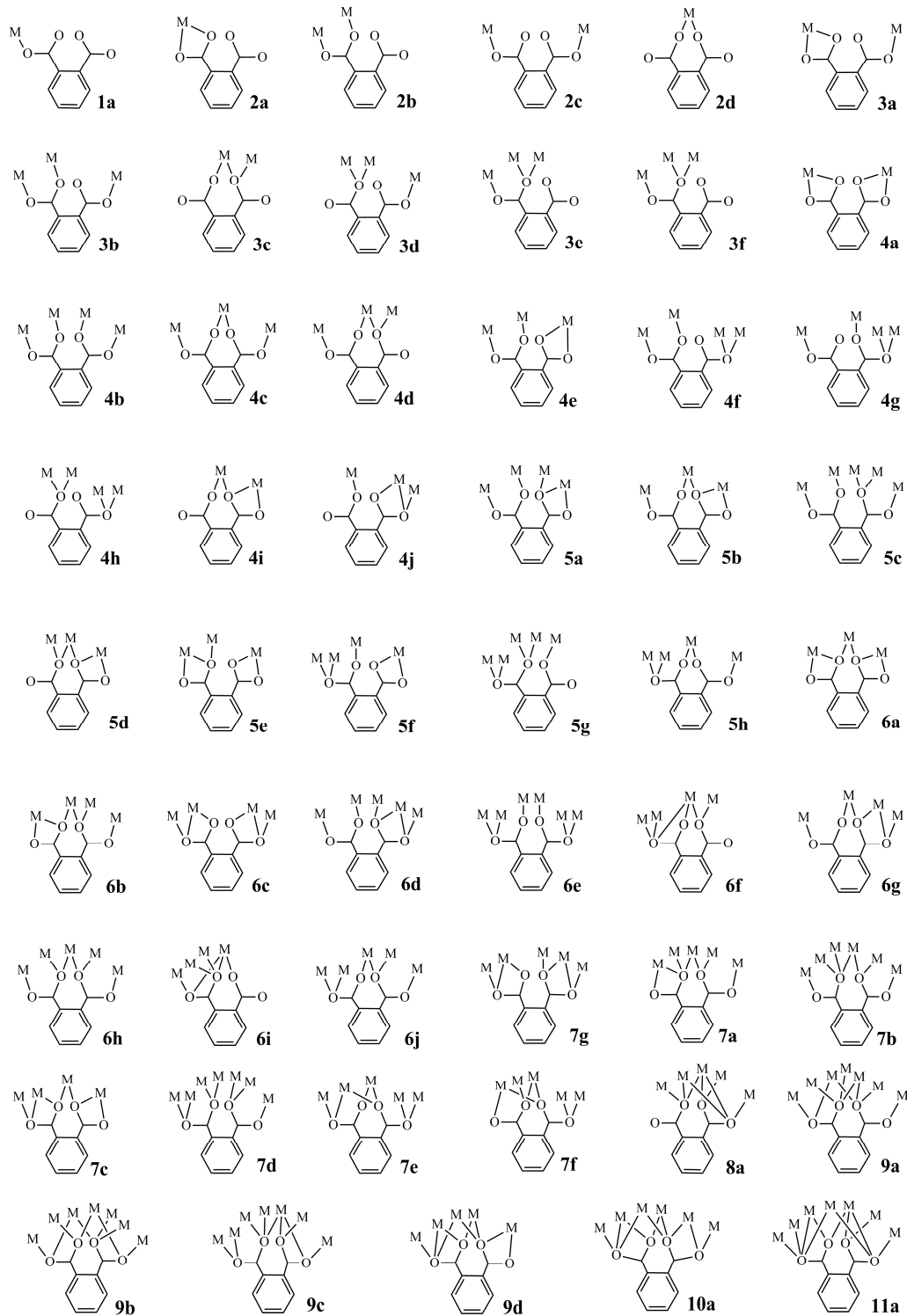
The huge number of metal carboxylates prepared to this day is the result of an extraordinary coordination ability of carboxylic  $\text{COO}^-$  group, which can dentate up to four metal centers and 19 modes (including *anti-anti*, *anti-syn* and *syn-syn* conformations) of metal binding to the carboxylate group were found to exist (Porai-Koshits, 1980). The presence of two carboxylic groups in *ortho*-phthalic acid opened up new opportunities for the preparation of both mononuclear complexes and polynuclear multidimensional systems with this ligand as the number of coordination modes of the metal to two carboxy groups in *ortho*-position is much larger. So far, twenty-six different coordination types, which are summarized on the base of the structural data retrieved from the Cambridge Structural Database (CSD) (Allen, 2002), have been observed in crystal structures of metal complexes containing this ligand and reported by Baca et al. (2004a). After this report, some additional coordination modes of *o*-phthalic acid have been found in structures extracted from CSD (2010 with updates). All coordination features of *o*-phthalic acid are shown in Scheme 1.

In metal complexes the phthalate ligand can coordinate up to seven metal centers at once showing the following connecting features: monodentate (**1a**), 1,3-chelating (**2a**), and 1,6-chelating (**2d**) linking modes, and various bridging modes with combinations of mono-, bi- and tridentate and chelating coordinations (Scheme 1). This coordination ability is influenced and controlled by a large number of different factors such as the nature of the metal ion and ancillary ligands used, the presence of outer sphere cations and anions, reaction conditions, etc. It is noteworthy that 1,6-bridging mode (**2c**), which promotes the formation of coordination polymers, is the most favored (Baca et al., 2004a). Other dominant mode of coordination for the carboxylate groups of the phthalate ligand appeared in its complexes is of type **1a** in Scheme 1, where only one carboxylic group coordinated to a metal ion adopting a  $\mu_1-\eta^1:\eta^0$ -monodentate mode, as well as bidentate chelating **2d** type with carboxylate groups adopting  $\mu_1-\eta^1:\eta^2$ -chelating modes to connect one metal atom, and tridentate (**3a** in Scheme 1) type in which carboxylate groups adopting  $\mu_1-\eta^1:\eta^0$ -monodentate and  $\mu_1-\eta^1:\eta^1$ -chelating modes.

## 3. ZINC(II) PHTHALATES WITH ANCILLARY N-DONOR LIGANDS

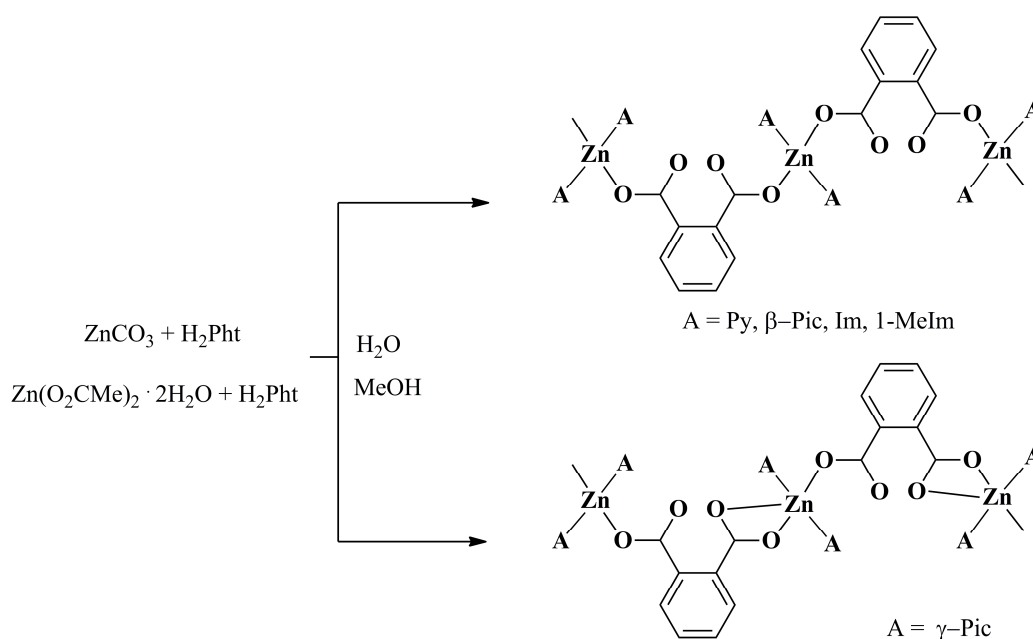
### 3.1 Synthesis of Zinc(II) Phthalates with N-donor Ligands

The design and construction of novel zinc(II) phthalates with an additional ancillary N-containing organic ligand is influenced by factors such as the structural characteristics of used N-donor ligands, the metal-acid-ligand ratio, the reaction conditions, the presence of groups able to form non-covalent interactions such as hydrogen bonds and  $\pi$ - $\pi$  stacking and others. Zinc(II) phthalates with ancillary N-donor ligands such as pyridine or imidazole and their derivatives can be prepared by the addition of *o*-phthalic acid and the corresponding amines in an aqueous or methanolic solution to the aqueous solution of zinc carbonate or zinc acetate salt (Schemes 2-4).



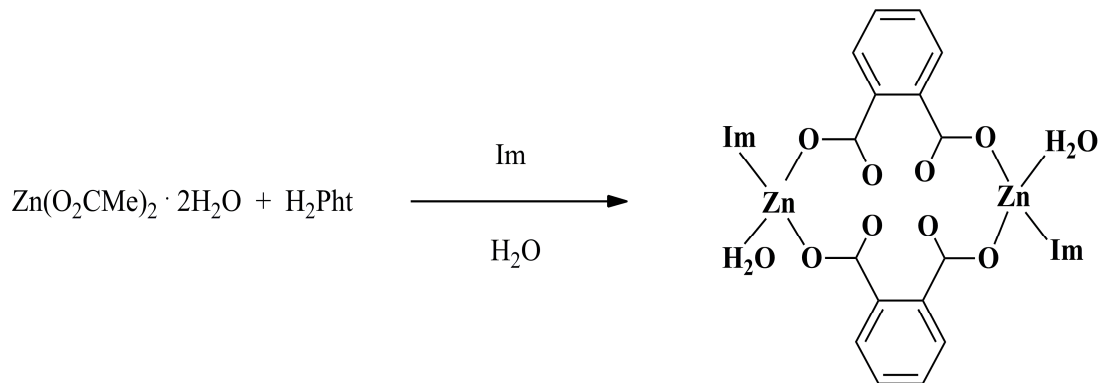
**Scheme 1: Coordination modes of the phthalate ligand in metal complexes**

Depending on the ratio between the starting materials, different products can be formed:  $[\text{Zn}(\text{Pht})\text{A}_2]_n$  (where  $\text{A} = \text{Py}, \beta\text{-Pic}, \gamma\text{-Pic}$  and 1-Melm) and  $[\text{Zn}(\text{Pht})\text{A}]_n$  (where  $\text{A} = \gamma\text{-Pic}$  and 2-Melm). The reaction of zinc(II) carbonate or zinc(II) acetate with pyridine, 3-, 4-methylpyridine and imidazole and *o*-phthalic acid in water in a 1:1:2 ratio under heating leads to crystalline products with the formulae  $[\text{Zn}(\text{Pht})\text{A}_2]_n$  ( $\text{A} = \text{Py}$  (1),  $\beta\text{-Pic}$  (2),  $\gamma\text{-Pic}$  (3), Im (4) (Baca et al., 2001, 2003a) having chain structures as shown in Scheme 2 due to the 1,6-bridging function of the dicarboxylic ligand. In the coordination polymers 1, 2 and 4 both carboxylate groups adopt a  $\mu_1\text{-}\eta^1\text{:}\eta^0$ -monodentate coordination mode (2c type in Scheme 1), whereas in 3 one carboxylate group adopts a  $\mu_1\text{-}\eta^1\text{:}\eta^0$ -monodentate coordination and other  $\mu_1\text{-}\eta^1\text{:}\eta^1$ -chelating mode (3a type in Scheme 1). The reaction of  $\text{Zn}(\text{O}_2\text{CMe})_2 \cdot 2\text{H}_2\text{O}$  with *o*-phthalic acid and an excess of 1-methylimidazole in methanol solution results in  $[\text{Zn}(\text{Pht})(1\text{-Melm})_2]_n$  (5) (Baca et al., 2004a) with the similar chains (Scheme 2).



**Scheme 2: Schematic representation of the synthesis of 1-5 and the connectivity of Pht ligands**

When in the reactions the ratio of initial components was 1:1:1 the following products were formed. In the reaction with imidazole two compounds, coordination polymer  $[\text{Zn}(\text{Pht})(\text{Im})_2]_n$  (4) (Scheme 2) in ca. 40% yield and the 14-membered cyclic dimer  $[\text{Zn}(\text{Pht})(\text{Im})(\text{H}_2\text{O})]_2$  (6, 20% yield) were isolated (Scheme 3). This cyclic dimer was the first example of the dinuclear associate in the family of polymeric Zn(II) complexes with *o*-phthalic acid and amines (Baca et al., 2003a). Two zinc atoms are linked by two phthalate ligands exhibiting a 1,6-bridging function (2c mode) with the formation of a metallocycle.



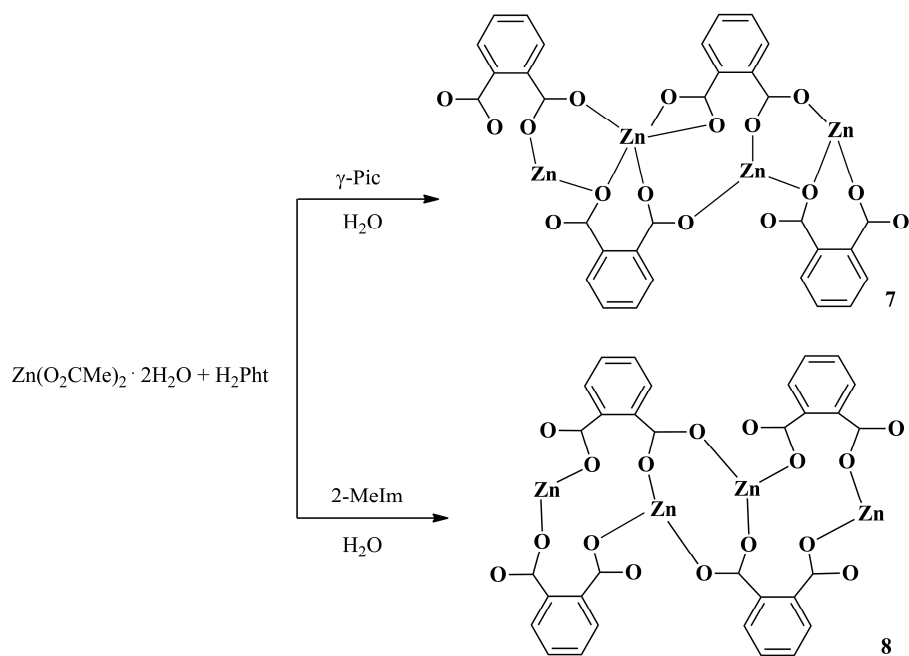
**Scheme 3: Schematic representation of the synthesis of 6 and the connectivity of Pht ligands**

The use of 4-methylpyridine ( $\gamma$ -Pic) and 2-methylimidazole (2-Melm) in the reaction of Zn(II) salt with *o*-phthalic acid in the ratio of 1:1:1 leads to the one-dimensional double-stranded chain coordination polymers  $[\text{Zn}(\text{Pht})(\gamma\text{-Pic})]_n$  (**7**) (Baca et al., 2001) and  $[\text{Zn}(\text{Pht})(2\text{-Melm})]_n$  (**8**) (Baca et al., 2003a) (Scheme 4), in which the *o*-phthalate anion behaves as a tetra- and tridentate ligand, respectively, adopting the different coordination modes. In the coordination polymer **7**, one phthalate ligand has carboxylate groups adopting a  $\mu_1\text{-}\eta^1\text{:}\eta^1$ -chelating and a  $\mu_2\text{-}\eta^1\text{:}\eta^1$ -bridging modes (**4e** type in Scheme 1), whereas other phthalate coordinates in the bridging  $\mu_2\text{-}\eta^2\text{:}\eta^0$  and  $\mu_2\text{-}\eta^1\text{:}\eta^1$  binding modes (**4d** type in Scheme 1). In **8**, the phthalate ligand behaves as a tridentate ligand and adopts the **3b** coordination mode with one carboxylate group exhibiting a  $\mu_1\text{-}\eta^1\text{:}\eta^0$  coordination mode, while the other shows  $\mu_2\text{-}\eta^1\text{:}\eta^1$ -bridging mode.

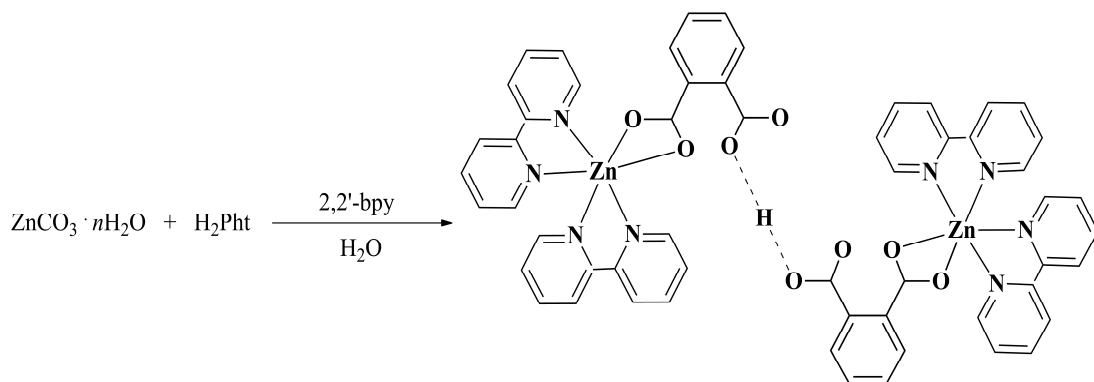
The reaction of *o*-phthalic acid and 2,2'-bipyridine with zinc(II) carbonate resulted in an unusual phthalate dimer  $[(\text{bpy})_2\text{Zn}(\text{Pht})\text{H}(\text{Pht})\text{Zn}(\text{bpy})_2](\text{HPht})(\text{H}_2\text{Pht})] \cdot 2\text{H}_2\text{O}$  (**9**) in ca. 36% yield (Scheme 5) in which  $[\text{Zn}(\text{bpy})_2]$  units are held together via O...H...O interaction between carboxylate groups of two different coordinated phthalate ligands (Baca et al., 2003b). In **9**, the phthalate ligands adopt monodentate coordination mode (**1a**, Scheme 1). Using 4,4'-bipyridine in combination with zinc(II) acetate and hydrophthalate potassium in water solution afforded a coordination polymer  $\{[\text{Zn}(\text{Pht})(4,4'\text{-bpy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**10**) (Simonov et al., 2004) in ca. 68% yield (Scheme 6) consisting of two-dimensional sheets.

### 3.2 Structural Diversity of Zinc(II) Phthalates with Ancillary N-donor Ligands

Zinc(II) complexes with *o*-phthalic acid and ancillary N-containing ligands have a variety of structural features ranging from discrete complexes (Baca et al., 2003a, 2003b; Li et al., 2007c; Wang et al., 2008b) to one-dimensional coordination polymers (Baca et al., 2001, 2003a, 2004a; Gong et al., 2007; Hu et al., 2008; Huang et al., 2010b; Li et al., 2006a, 2007b; Liang et al., 2003; Liu et al., 2008; Lu et al., 2010; Padmanabhan et al., 2007; Song et al., 2005b; Tang et al., 2004; Thirumurugan and Rao, 2005b; Wang et al., 2008c; Yao et al., 2002; Zhang et al., 2005; Zhang and Sun, 2006) and complex two- (Bai et al., 2010; Huang et al., 2010b; Li et al., 2004, 2006b; Simonov et al., 2004; Zhang et al., 2008c) and three-dimensional architectures (Bai et al., 2010; Chen et al., 2010).



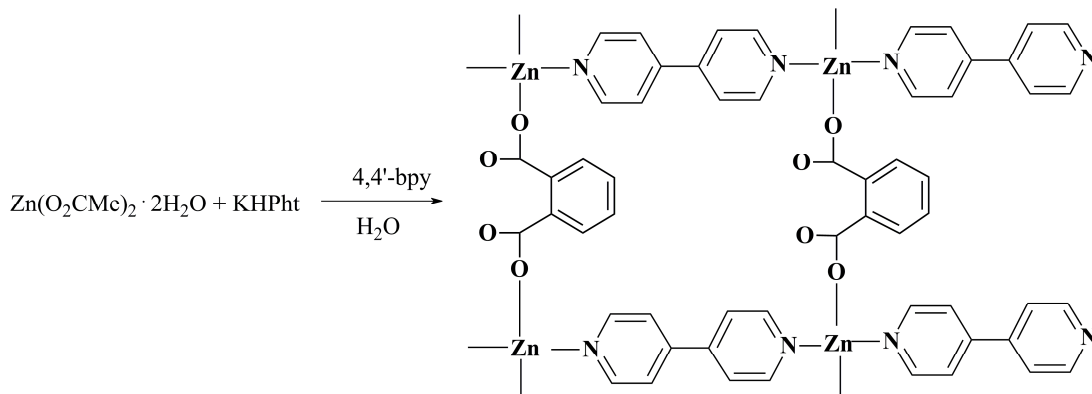
**Scheme 4: Schematic representation of the synthesis of 7 and 8 and the connectivity of Pht ligands**



**Scheme 5: Schematic representation of the synthesis of 9 and the connectivity of Pht ligands**

### 3.2.1 Discrete zero-dimensional (0D) structures

Although, the *o*-phthalate ligand has tendency to form extended polymeric structures adopting a 1,6-bridging coordination mode, some discrete dinuclear complexes have also been obtained. As shown in figure 1, complex  $[\text{Zn}(\text{Pht})(\text{Im})(\text{H}_2\text{O})]_2$  (6) has a dinuclear structure, in which two phthalate ligands are bound to two Zn(II) centers in a 1,6-bridging coordination mode to form a 14-membered macrocycle (Baca et al., 2003a).

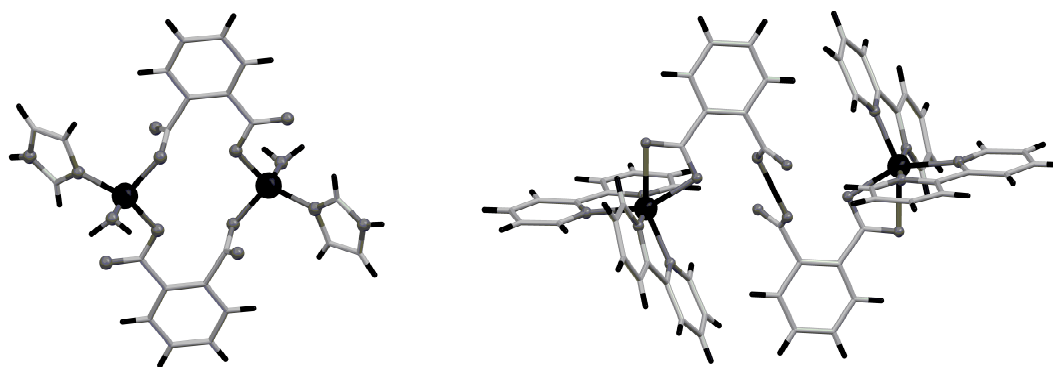


**Scheme 6: Schematic representation of the synthesis of 10 and the connectivity of Pht ligands**

The Zn(II) atoms in **6** are coordinated by two oxygen atoms of the  $\text{Pht}^{2-}$  carboxylate groups [ $\text{Zn}-\text{O}$ , 1.982(1) and 1.935(1) Å], the nitrogen atom of the imidazole molecule [ $\text{Zn}-\text{N}$ , 1.969(1) Å] and the oxygen atom of the water molecule [ $\text{Zn}-\text{O}$ , 1.995(1) Å] with formation of a tetrahedral  $\text{NO}_3$  metal-binding site. The  $\text{Zn}\dots\text{Zn}$  distance in this dimer is 5.369(1) Å, which is slightly longer compared to 5.25 Å for dinuclear complex  $[\text{Zn}(\text{Pht})(\text{L})(\text{H}_2\text{O})]_2$  (where L = dipyrdo[[3,2-d:2',3'-f]quinoxaline]) reported by Wanget al. 2008b. The molecules of **6** form a 3D-network through  $\text{N}-\text{H}\dots\text{O}$  and  $\text{O}-\text{H}\dots\text{O}$  hydrogen bonds between carboxylate groups of  $\text{Pht}^{2-}$ , imidazole and water molecules.

Complex **9**,  $[(\text{bpy})_2\text{Zn}(\text{Pht})\text{H}(\text{Pht})\text{Zn}(\text{bpy})_2](\text{HPht})(\text{H}_2\text{Pht}) \cdot 2\text{H}_2\text{O}$  (Baca et al., 2003b), has a hydrogen-bonded dinuclear structure and consists of a dinuclear cation shown in figure 1,  $\text{HPht}^-$  anion as well as  $\text{H}_2\text{Pht}$  and two water molecules. The Zn(II) atom in **9** has a six-coordinated distorted octahedral  $\text{N}_4\text{O}_2$  geometry with four nitrogen atoms from two 2,2'-bpy ( $\text{Zn}-\text{N}$ , 2.104 – 2.151 Å), and two oxygen atoms from the chelating carboxylate group of the Pht ligand ( $\text{Zn}-\text{O}$ , 2.099 – 2.348 Å). The phthalate ligand coordinates to zinc(II) atom through only one of its two carboxylate groups in a  $\mu_1-\eta^1:\eta^1$ -chelating fashion, while its second carboxylate group forms a very strong  $\text{O}-\text{H}\dots\text{O}$  hydrogen bond of 2.459 Å with the carbonyl group of the phthalate ligand in neighboring cation to generate a hydrogen-bonded zinc(II) dimer. Such formation of hydrogen-bonded dinuclear unit is unprecedented in the metal phthalates and it was the first example of dinuclear associate with  $\text{Pht}\dots\text{H}\dots\text{Pht}$  bridge (Baca et al., 2003b). The hydrogen-bonded dimers are further assembled via hydrogen bonds involving  $\text{HPht}^-$  anions, *o*-phthalic acid and lattice water molecules, into a 3D polymeric network.





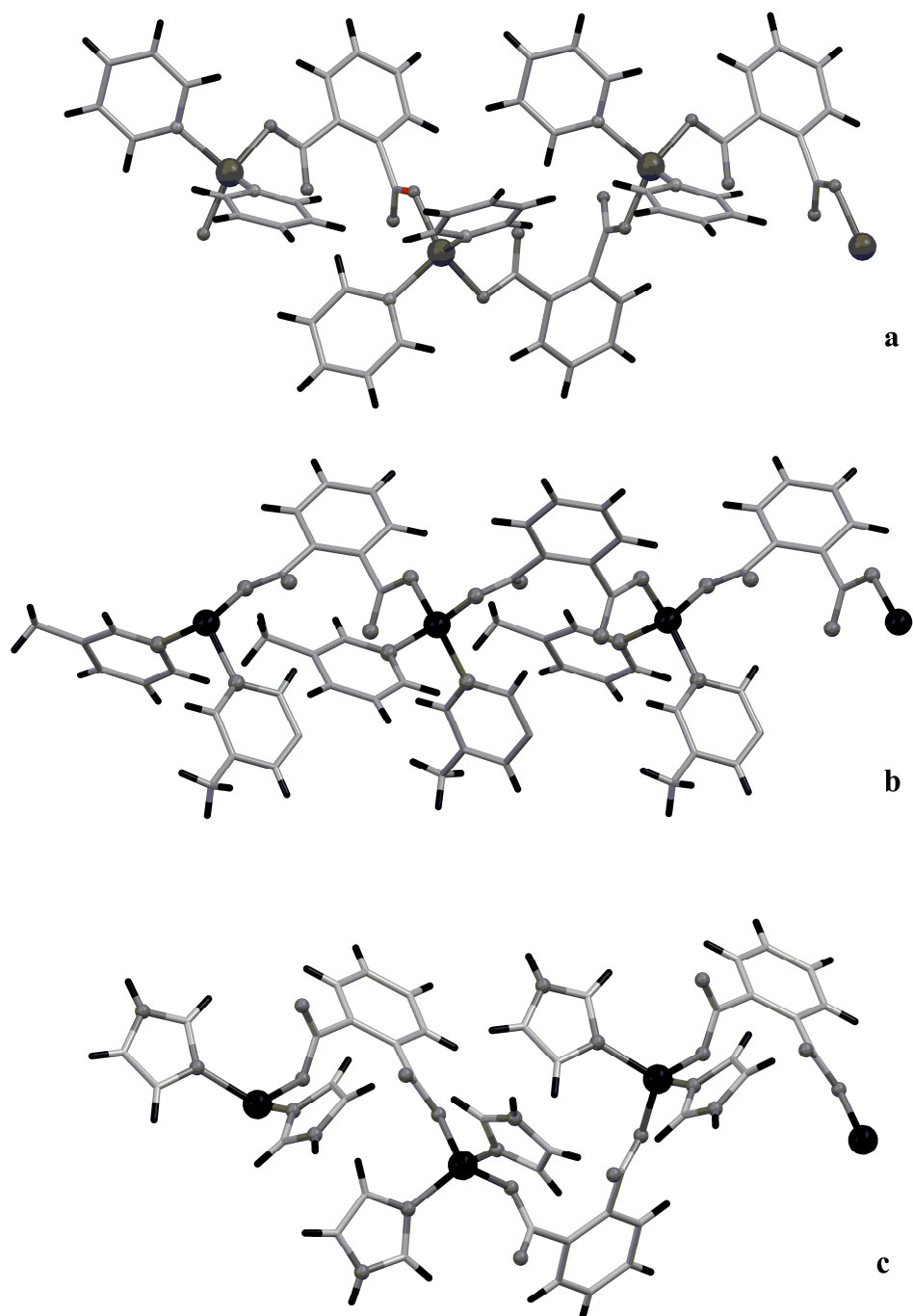
**Figure 1: Molecular/cationic structures of complexes  $[\text{Zn}(\text{Pht})(\text{Im})(\text{H}_2\text{O})]_2$  (left) and  $[(\text{bpy})_2\text{Zn}(\text{Pht})\text{H}(\text{Pht})\text{Zn}(\text{bpy})_2]^+$  (right)**

*Zn atoms, black balls; O and N atoms, dark grey balls;  
C atoms, grey sticks; H atoms, black sticks*

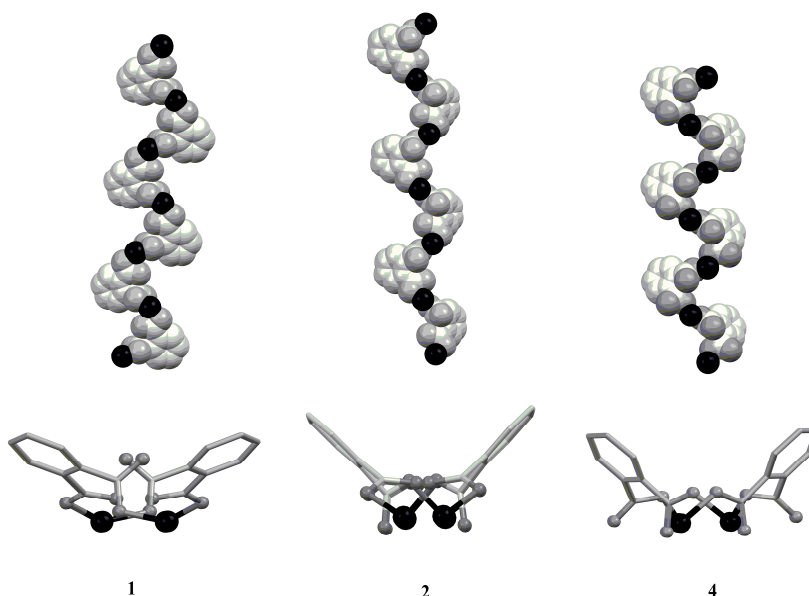
### 3.2.2 One-dimensional (1D) structures

Formation of one-dimensional motif is the most common type of structure formed from the interaction of zinc(II) salts with *o*-phthalic acid and N-containing ligands in a water/alcohol solution. Potentially polydentate phthalate ligand used both carboxyl groups to connect zinc(II) ions into one-dimensional chains with different topologies including zigzag, helical and double-stranded chains. Complexes **1**, **2**, **4** and **5** have similar structures consisting of  $[\text{ZnA}_2]$  building blocks connected by 1,6-phthalate bridges to form infinite chains. However, the one-dimensional motif in complexes **1**, **2** and **4** is zigzag chains as shown in figures 2 and 3, whereas in **5** helical chains are formed (Fig. 4). The Zn...Zn distances in the zigzag chains are at 6.645(1) (**1**), 6.896(2) (**2**) and 6.030(2) Å (**4**) (Fig. 3). Zn(II) ions coordinate to two nitrogen atoms of two pyridine (**1**), 3-methylpyridine (**2**), imidazole (**4**) or 1-methylimidazole (**5**) molecules  $[\text{Zn}-\text{N}, 1.985(4) - 2.073(5) \text{ Å}]$  and two oxygen atoms of two  $\text{Pht}^{2-}$  ligands  $[\text{Zn}-\text{O}, 1.929(2) - 1.987(5) \text{ Å}]$  adopting a tetrahedral  $\text{N}_2\text{O}_2$  environment. All these values agree well with those observed in other  $[\text{Zn}(\text{Pht})\text{L}_2]_n$  zigzag chains, where L = 1-vinylimidazole (Li et al., 2007b). The zigzag chains are further linked through C-H...O (**1** and **2**) and N-H...O (**4**) hydrogen bonds between aromatic and carboxylate groups into a 3D network.

Complex **5**,  $[\text{Zn}(\text{Pht})(1\text{-Melm})_2]_n$  (Baca et al., 2004a), has helical chains as shown in figure 4 with a pitch of 25.7 Å. One helical pitch includes five metal ions, which are separated by 6.943 and 6.985 Å (two independent metal atoms are present in the structure) and four phthalate bridges. Because left-handed and right-handed helical chains are coexisting in the structure, the whole crystal does not show any chirality. Two independent metal atoms are tetrahedrally  $\text{N}_2\text{O}_2$  coordinated to a pair of Pht ligands and a pair of 1-Melm molecules. The helical chains of complexes **5** are connected by C-H...O interactions between the methyl group of 1-Melm and the carboxy oxygen atoms, leading to the formation of a supramolecular 3D structure.

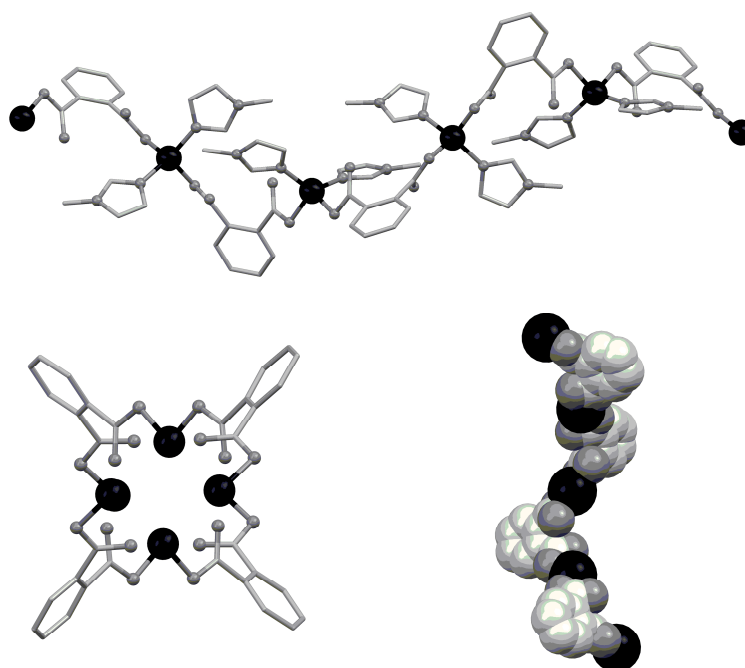


**Figure 2: A view of polymeric chain in  $[\text{Zn}(\text{Pht})(\text{Py})_2]_n$  (a),  $[\text{Zn}(\text{Pht})(\beta\text{-Pic})_2]_n$  (b) and  $[\text{Zn}(\text{Pht})(\text{Im})_2]_n$  (c)**  
*Zn atoms, black balls; O and N atoms, dark grey balls;  
 C atoms, grey sticks; H atoms, black sticks*



**Figure 3: Side (space-filling representation) and top (bottom) view of polymeric chain in 1, 2, and 4**

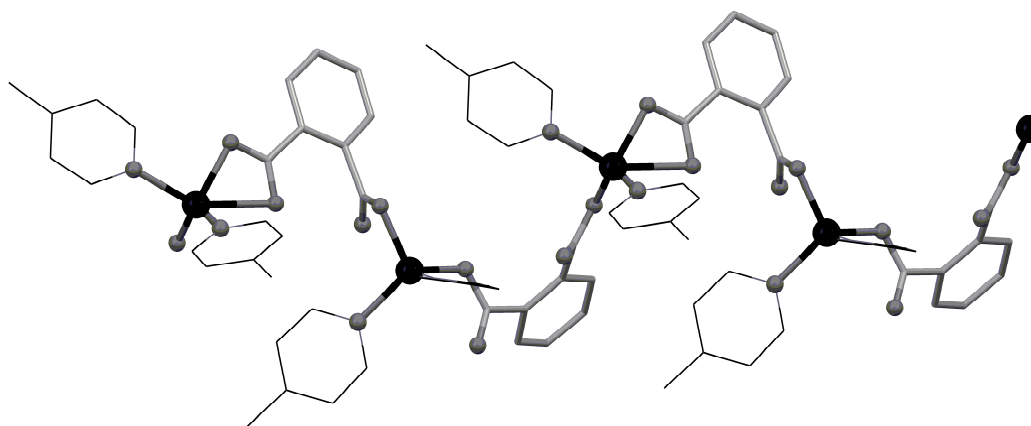
*Hydrogen atoms and N-donor ligands are omitted for clarity.  
Zn atoms, black balls; O atoms, dark grey balls; C atoms, grey sticks*



**Figure 4: Helical chain in  $[Zn(Pht)(1-Melm)_2]_n$  (5) (up) and top and side (space-filling representation) view of the helix (bottom)**

*Hydrogen atoms and N-donor ligands (bottom) are omitted for clarity.  
Zn atoms, black balls; O atoms, dark grey balls; C atoms, grey sticks*

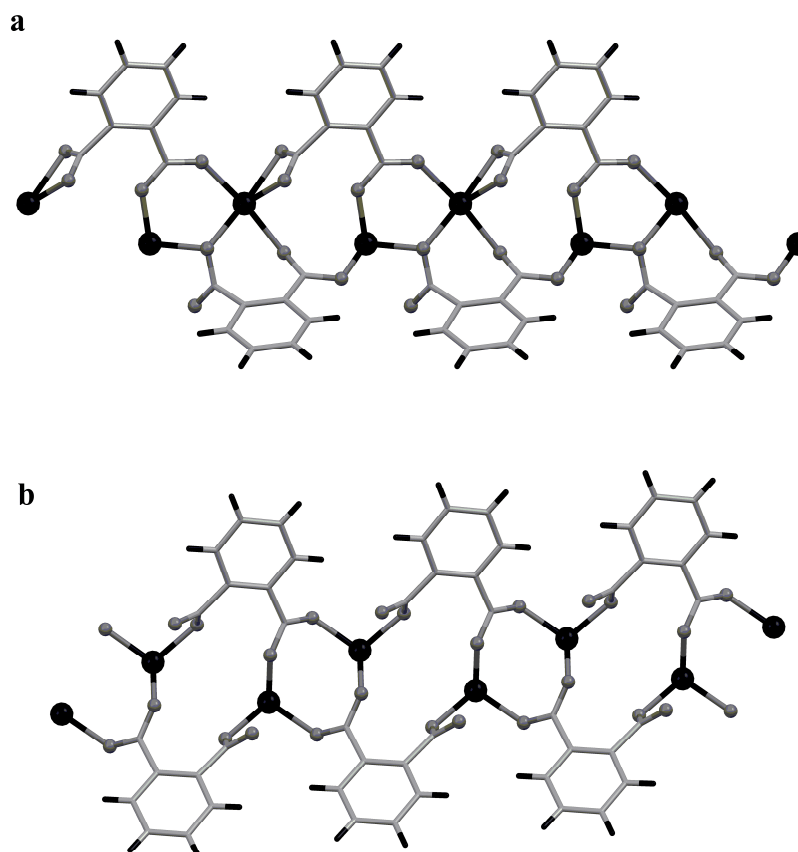
Complex **3**,  $[\text{Zn}(\text{Pht})(\gamma\text{-Pic})_2]_n$  (Baca et al., 2001), has a one-dimensional zigzag chain structure (Fig. 5) with  $[\text{Zn}(\gamma\text{-Pic})_2]$  units connected by the phthalate ligands. One of the acid residues behaves as a bidentate 1,6-bridge, while the other one acts as a tridentate (1,6-bridging and 1,3-chelating) ligand (**3a** type in Scheme 1). As a result, Zn(II) atoms in **3** have two different coordination geometries: tetrahedral  $\text{N}_2\text{O}_2$  comprising two nitrogen atoms of two 4-methylpyridine molecules  $[\text{Zn}-\text{N}, 2.046(4) \text{ and } 2.072(4)\text{\AA}]$  and two oxygen atoms from different phthalate ligands  $[\text{Zn}-\text{O}, 1.921(3) \text{ and } 1.990(3)\text{\AA}]$ , and distorted square-pyramidal  $\text{N}_2\text{O}_3$  environment which is composed of two nitrogen atoms of  $\gamma\text{-Pic}$   $[\text{Zn}-\text{N}, 2.044(4) \text{ and } 2.075(4)\text{\AA}]$  and three oxygen carboxylate atoms  $[\text{Zn}-\text{O}, 1.940(4), 2.047(4) \text{ and } 2.405(4)\text{\AA}]$ . The Zn...Zn intrachain distances are at 6.358 and 6.405 Å, which are shorter than those found in the coordination polymers **1** and **2**, but longer than in **4**. Similar to **1** and **2**, the three-dimensional network in **3** is assembled by C–H...O hydrogen bonds.



**Figure 5: Zigzag chain in  $[\text{Zn}(\text{Pht})(\gamma\text{-Pic})_2]_n$  (**3**)**  
*Zn atoms, black balls; O and N atoms, dark grey balls;  
 C atoms, grey sticks; C atoms of  $\gamma\text{-Pic}$  shown as grey lines*

As the main feature of coordination polymers  $[\text{Zn}(\text{Pht})(\gamma\text{-Pic})]_n$  (**7**) (Baca et al., 2001) and  $[\text{Zn}(\text{Pht})(2\text{-Melm})]_n$  (**8**) (Baca et al., 2003a) there is the formation of 1D double-stranded chains shown in figure 6, in which  $[\text{Zn}(\text{A})]$  ( $\text{A} = \gamma\text{-Pic}, 2\text{-Melm}$ ) units are linked by a pair of Pht ligands to form infinite chains. In these double-stranded chains the  $\text{Pht}^{2-}$  di anion acts as both a tetra- and tridentate ligand, respectively, and exhibits different coordination giving rise to the formation of 6-membered and 11-membered metallocycles in **7**, whereas 8-membered and 14-membered rings are formed in **8**. The double-stranded chain in **7** includes two independent Zn(II) atoms with the different coordination environments. One Zn(II) atom is coordinated by one nitrogen atom of  $\gamma\text{-Pic}$   $[\text{Zn}-\text{N}, 2.002(4) \text{ \AA}]$  and three oxygen carboxylate atoms from three different Pht ligands  $[\text{Zn}-\text{O}, 1.945(3) - 2.031(3) \text{ \AA}]$  to form a  $\text{NO}_3$  tetrahedron, while the coordination environment around the other Zn(II) atom corresponds to a distorted tetragonal bipyramid ( $\text{NO}_5$ ) with one nitrogen atom from  $\gamma\text{-Pic}$  molecule  $[\text{Zn}-\text{N}, 2.072(4) \text{ \AA}]$  and five oxygen atoms from three different carboxylate ligands  $[\text{Zn}-\text{O}, 2.100(3) - 2.240(3) \text{ \AA}]$ . A pair of Pht dianions connects neighboring Zn(II) centers via a  $\mu_2\text{-}\eta^1\text{:}\eta^1$  coordination mode with the formation of a 6-membered metallocycle with the Zn...Zn distance being 3.470(2) Å. Each metal ion is further connected through bridging Pht ligands ( $\mu_2\text{-}\eta^1\text{:}\eta^1$ -bridging and  $\mu_1\text{-}\eta^1\text{:}\eta^1$ -chelating modes) to form an 11-membered ring with Zn atoms being at 4.467(2) Å from each other. As a result, the 1D double-stranded chains with alternation of 6- and 11-membered metallocycles are formed in **7**. In complex **8**,  $[\text{Zn}(\text{Pht})(2\text{-Melm})]_n$

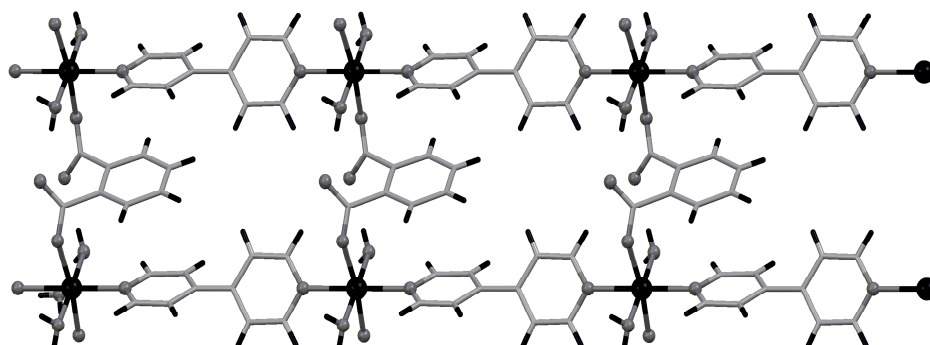
Melm)]<sub>n</sub>, the one-dimensional double-stranded chains are composed of two kinds of rings, the smaller 8-membered ring and the larger 14-membered ring. This double-stranded chains resemble those in {[Zn<sub>2</sub>(Pht)<sub>2</sub>(L)<sub>2</sub>]·H<sub>2</sub>O}<sub>n</sub> (where L = dipyrdo[3,2-d:2',3'-f]quinoxaline) (Wang et al., 2008c). The phthalate ligand is coordinated to the zinc atoms with both bridging and monodentate binding modes: one of the zinc(II) pairs is linked by a 1,6-bridge of two Pht<sup>2-</sup> to form a 14-membered ring with a Zn...Zn distance of 4.195(1) Å, while another zinc(II) pair is held together by 1,3-bridging mode from the same phthalates resulting in smaller 8-membered ring with a shorter Zn...Zn distance of 3.594(1) Å. Each Zn(II) atom in **8** is in a tetrahedral NO<sub>3</sub> environment being coordinated by one nitrogen atom from a 2-Melm [Zn–N, 1.989(3) Å] and three oxygens from three phthalate ligands [Zn–O, 1.971(2) – 1.991(2) Å]. The Zn–O distances are consistent with those for above-mentioned {[Zn<sub>2</sub>(Pht)<sub>2</sub>(L)<sub>2</sub>]·H<sub>2</sub>O}<sub>n</sub> prepared by Wang et al., 2008c, whereas Zn–N distance is shorter than the corresponding values, 2.118(3) – 2.198(3) Å. The ancillary N-donor ligands, 4-methylpyridine in **7** and 2-methylimidazole in **8**, lie on one side of these chains in parallel fashion with strong aromatic π–π stacking interactions at a centroid-centroid distance of 3.583 Å between the γ-Pic pairs and 3.596 and 3.530 Å between 2-Melm heterocycles. The double-stranded chains are further extended through C–H...O hydrogen bonds of 2.41–2.44 Å (**7**) and N–H...O hydrogen bonds of 2.72 Å (**8**) between aromatic groups and carboxylate oxygen atoms into the final 3D and 2D architectures, respectively.



**Figure 6: Double-stranded chain in [Zn(Pht)(γ-Pic)]<sub>n</sub> (a) and [Zn(Pht)(2-Melm)]<sub>n</sub> (b)**  
*N-donor ligands are omitted for clarity. Zn atoms, black balls; O atoms, dark grey balls;  
 C atoms, grey sticks; H atoms, black sticks*

### 3.2.3 Two-dimensional (2D) structures

By using additional bridging linkers, in particular 4,4'-bpy, two-dimensional structures can be generated. In coordination polymer  $\{[\text{Zn}(\text{Pht})(4,4'\text{-bpy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**10**) (Simonov et al., 2004), both ligands, *o*-phthalate and 4,4'-bpy, execute bridging functions. The phthalates act as a 1,6-bridging ligand and connect Zn(II) atoms into 1D chains that are further interlinked through 4,4'-bpy ligands into rectangular grids shown in figure 7. The Zn...Zn distances across the phthalate and 4,4'-bpy linkers are 7.627(2) and 11.302(2) Å, respectively. Each Zn(II) atom is coordinated by two N atoms of different 4,4'-bipyridine molecules [Zn–N, 2.117(3) and 2.131(3) Å], two O atoms of two *o*-phthalic residues [Zn–O, 2.171(2) Å], and two O atoms from two water molecules [Zn–O, 2.129(2) Å] in a distorted octahedral geometry. The complex **10** is isostructural to other reported 2D coordination polymers  $[\text{M}(\text{Pht})(4,4'\text{-bpy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (where M = Co, Cd (Suresh et al., 2001); M = Mn (Ma et al., 2003)). Note, the  $\pi$ – $\pi$  stacking interactions between the phthalic acid residues and the pyridine rings with the centroid-centroid distance being 3.929 Å are observed in the grid layers. The adjacent layers are linked through hydrogen-bonding interactions involving coordinated and lattice water molecules [O–H...O, 2.694(2) – 2.818(3) Å] into a 3D network.



**Figure 7: Two-dimensional layer in  $\{[\text{Zn}(\text{Pht})(4,4'\text{-bpy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**10**)**

*Zn atoms, black balls; O and N atoms, dark grey balls;  
C atoms, grey sticks; H atoms, black sticks*

## 4. CONCLUSION

Simple synthetic approach to a series of discrete complexes and coordination polymers with chain and layer structures by using Zn(II) ions, *o*-phthalate bridging ligand and the different co-ligands like pyridine, imidazole and its derivatives, and 2,2', 4,4'-bipyridine was developed. The strategy is to use multi-bridging ligand and  $[\text{Zn}(\text{amine})_n]^{2+}$  ( $n = 1, 2$ ) blocks as the key elements. These studies revealed that using of the different N-donor ligands leads to the formation of dinuclear complexes and one-, two-dimensional coordination polymers with different topologies including zigzag, helical and double-stranded chains, and rectangular grid-like layers. The chains and two-dimensional sheets are held together by strong or weak hydrogen bonds and/or aromatic-aromatic interactions, to generate 2D or 3D networks.

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## COMPETING INTERESTS

Author has declared that no competing interests exist.

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