

## Control formation of rigid linear and flexible zig-zig complexes based on Zn(II) and hydroxyquinoline carboxylate ligand system

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### ABSTRACT

Two novel zinc complexes,  $[\text{Zn}(\text{H-hqc})_2(\text{bpy})(\text{H}_2\text{O})_2]$  (**1**) and  $[\text{Zn}(\text{H-hqc})_2(\text{bpe})]\cdot\text{H}_2\text{O}$  (**2**), where  $\text{H}_2\text{-hqc}$  = 2-hydroxyquinoline-4-carboxylic acid,  $\text{bpy}$  = 4,4'-bipyridine and  $\text{bpe}$  = 1,2-bis(4-pyridyl)ethylene, have been prepared under hydrothermal condition. Complex **1** displays a 1D rigid linear chain structure while complex **2** displays 1D flexible zig-zag chain structure. Coordination number of the central Zn ion in complex **1** is six and in complex **2** is four. The structural differences of these complexes suggest the effect of size of the bridging ligands on the construction of metal organic frameworks with the same metal ion under solvothermal conditions.

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Ever-growing interests in the synthesis of metal organic compounds are not only from their potential application in catalysis, sorption, photochemistry, magnetism and numerous other applications, but also from their fascinating architectures and topologies [1–9]. The crystallization is a difficult process and the growth of molecular motifs depends on the combination of several factors, such as the coordination geometry of metal ions, metal–ligand ratio, the structural individuality of ligands, the solvent system, the counter anions, temperature, pH value, templates and so on. Among them, both the suitable choice of a versatile ligand and the selection of suitable N-donor spacer ligands are important to control and adjust the topology of coordination frameworks [10,11]. In addition, a  $d^{10}$  ion generally has no ligand-field stabilization energy and, as a consequence, it can easily attain variable coordination numbers. A systematic and accurate prediction and a total design of coordination compounds are not yet possible. Therefore, with careful selection of ligands and metal centers, it is possible to prepare new complexes. On the other hand,  $d^{10}$  metal complexes are currently of interest in the development of fluorescent materials.

Recently the pyridine, imidazole, pyrazine and triazole based carboxylic acids have been broadly used to build new complexes [12–14]. In this study a new nitrogen containing carboxylate ligand, 2-hydroxyquinoline-4-carboxylic acid ( $\text{H}_2\text{hqc}$ ) is employed, because it has remarkable features as follows: (a) its N atom is a brilliant donor and able to coordinate to varieties of metal ions; (b) it is a rigid ligand which may favor the construction of coordination architectures with high thermal stability; (c) the carboxyl group can adopt

different coordination modes such as monodentate, chelating-bidentate, bridging-bidentate and bridging-multidentate [15] to satisfy the coordination geometric requirement of metal centers; and (d)  $\text{H}_2\text{hqc}$  is a multidentate N- or O-donor ligand that can be deprotonated to produce  $\text{Hhqc}^-$  and  $\text{hqc}^{2-}$  with versatile metal-binding and hydrogen-bonding capabilities. However, the frameworks from quinoline-based carboxylic acid are very uncommon [15–17] and only one report relating to the complexes of  $\text{H}_2\text{hqc}$  with 3d metal ions can be found in the literature [18].

Previously it had been found that use of neutral N-donor auxiliary can afford a wonderful breadth of structural motifs and control of the cavity size and the properties of the metal organic frameworks [10,11]. Herein, we choose the combination of  $\text{H}_2\text{hqc}$  and zinc ion, and focus on the effect of the neutral nitrogen ligands under solvothermal synthesis conditions. With respect to the steric hindrance and electronic effect, the longer (bpe) and shorter (bpy) spacers are employed to construct the structure, respectively. With this strategy, two new coordination polymers,  $[\text{Zn}(\text{H-hqc})_2(\text{bpy})(\text{H}_2\text{O})_2]_n$  (**1**) and  $\{[\text{Zn}(\text{H-hqc})_2(\text{bpe})]\cdot\text{H}_2\text{O}\}_n$  (**2**), have been obtained. Both complexes were synthesized by a solvothermal method in water–DMF solution [19]. Details of X-ray crystallography have discussed in Supporting Information.

Complex **1** crystallizes in a triclinic crystal system with space group of  $P1$  [20]. The crystal structure of **1** consists of infinite  $[\text{Zn}(\text{Hhqc})_2(\text{H}_2\text{O})_2(\text{bpy})]$  chains. As shown in Fig. 1A, the crystallographically unique Zn(II) adopts octahedral coordination,  $\text{ZnN}_2\text{O}_4$ , coordinated by two N atoms from two different 4,4'-bpy, four O atoms from two water and two monodentate  $\text{Hhqc}$  carboxyl groups. The average Zn–O and Zn–N bond distances are 2.130 and 2.155 Å, respectively. The bond angles around the Zn(II) ion are in the range of 86.23(19) to 179.8(3)°. The selected bond distances and angles are

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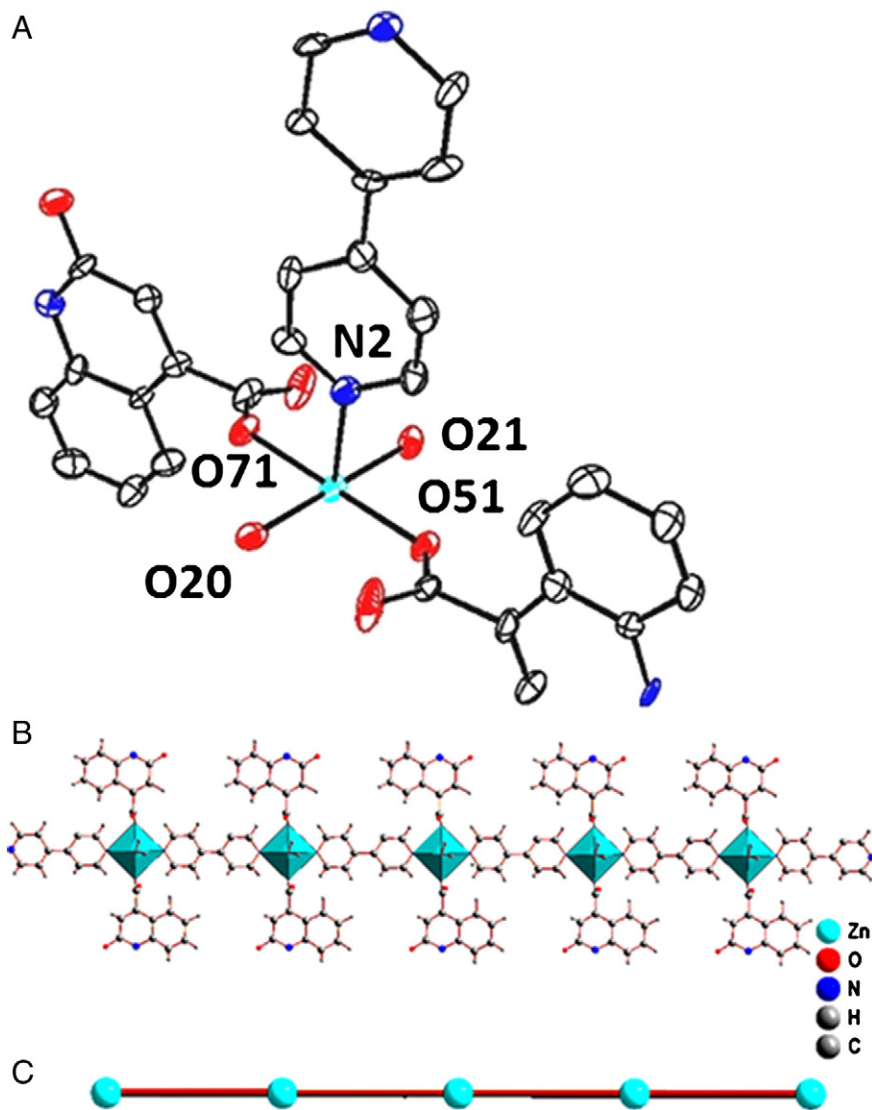


Fig. 1. The asymmetric unit of compound **1**, showing the atomic labeling and displacement ellipsoids at the 50% probability level. b) 1D chain. c) Linear topology.

listed in Table S1 in the Supporting Information. The donor ligand bpy acts as a connector to link two Zn atoms. The monomeric units are connected by bpy bridging ligands and forming the 1D rigid linear chain along (011) direction (Fig. 1B and C). Those chains are held together by strong intermolecular hydrogen bond interactions, ultimately giving rise 3D supramolecular frameworks (Fig. S1). The significant hydrogen bonding parameters are collected in Table S2 in the Supporting Information.

For comparison with compound **1**, when bpy is replaced by a longer spacer ligand, bpe, as an extending bridging linkage, compound **2** displays a flexible 1D coordination network. Complex **2** crystallizes in a triclinic crystal system with space group of *P*-1 [21]. As illustrated in Fig. 2A, the asymmetric unit of **2** contains two Zn(II) ions, four Hhqc<sup>−</sup> anion and two bpe molecules. Zn ions adopt a distorted tetrahedral coordination, ZnN<sub>2</sub>O<sub>2</sub>, coordinated by two N atoms from different bpe, and two O atoms from monodentate Hhqc<sup>−</sup> carboxyl groups.

There are eight carboxylate oxygen atoms for four Hhqc<sup>−</sup> ligands. Among them three oxygen atoms are disordered in O4, O4a; O5, O5a; and O6, O6a. The average Zn–O and Zn–N bond distances are 1.960 and 2.059 Å for Zn1, and 1.9305 and 2.030 Å for Zn2, respectively. For the sake of clarity, only one set of the disordered carboxylate oxygens is shown (Fig. 2A). The bond angles around the Zn(II) are in the range of 93.44(15) to 132.77(16) for Zn1 and 92.9(5) to 118.1(5)° for

Zn2, respectively. The selected bond distances and angles are listed in Table S1 in the Supporting Information. The donor ligand bpe acts as bridging linkage to link two Zn atoms. And finally these dimeric units are connected by bpe ligands forming 1D flexible zig-zig chain (Fig. 2B and C). The one-dimensional chains are further constructed into a three-dimensional supramolecular structure through intermolecular hydrogen bonds (Fig. S2). Details of the hydrogen bonding parameters are given in Table S3 in Supporting Information.

It is well known that divalent Zn ion is a d<sup>10</sup> system and has no crystal field stabilization energy. Zinc ion can easily adopt variable coordination mode: four, five and six. For d<sup>10</sup> system, mainly size of the bridging ligands plays the key role to attain variable geometry. Here, the two complexes are constructed from the same carboxylate and the same metal ion, Zn. Interestingly, nitrogen and hydroxyl group containing carboxylate, H<sub>2</sub>hqc, only acts as a monodentate ligand. Moreover, the solvent system, reaction temperature and reaction time all are the same. Only different auxiliary N-donor bridging ligands are used to synthesize the two complexes. Such results clearly imply that the secondary neutral nitrogen ligands play a major role in determining the structural diversity: length, from short bpy to long bpe, determines the different 1D geometry, i.e. from rigid linear 1D to flexible zig-zag 1D chain. For the flexible ligand, the zig-zag chains form, which may be due to their free rotation. These

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