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# Self-assembly through hydrogen-bonding and $C-H\cdots\pi$ interactions in metal complexes of *N*-functionalised glycine

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## Abstract

The complex  $[Ni(L1)_2(py)_2]$ . toluene (L1 is *N*-phthaloylglycinato and py is pyridine) was prepared from solid state reaction whereas co-crystals having composition  $2[Ni(L1)_2(py)_3(H_2O)] \cdot [Ni(L1)_2(py)_2(H_2O)_2] \cdot 2py \cdot 2H_2O$  was obtained from solution state reaction. © 2006 Elsevier B.V. All rights reserved.

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Metal directed assembly of molecules is not only governed by coordination mode of metal ion but also directed by various non-covalent forces originating from the structural features of ligand/s of choice [1]. These weak yet reversible and directional interactions such as hydrogenbonding and  $\pi - \pi$  interactions are widely explored to design superstructures with novel properties in the field of inorganic crystal engineering [2]. However, unlike hydrogenbonding, the  $\pi$ - $\pi$  interactions are less directional and hence the structural features of any  $\pi$ -stacked system are less predictable [3]. Moreover the  $\pi$ -interactions are weak in solutions to correlate relative orientations of  $\pi$ -stacked species in solid state with high degree of certainty [4]. Among different metal-organic frameworks the metal carboxylate frameworks have important status for their structural versatility and scope for studying as porous material [5]. In our recent study we have shown the importance of weak interactions in inorganic and organic derivatives of Nphthaloylglycine and in N-phthaloylglycylglycine [6-8]. It would be interesting if these interactions can be guided so that the each of them become competitive and surpass each other to guide the structural features. From our recent experiences and from existing literature on phthaloyl related systems it is felt that the  $\pi$ - $\pi$  and C-H··· $\pi$  interactions may guide structure of self-assembly [9]. In order to study the mutual interplay of hydrogen bonding and  $\pi$ -stacking interactions in metal directed assemblies we have decided to use *N*-phthaloylglycine (L1), 4-carboxy-*N*-phthaloylglycine (L2) and *N*-phthaloylglycylglycine (L3) as ligands for complexation for comparative purpose of which the structure of the ligands L3 [7] and L1 [10] have been reported recently.



The solid-state reaction of *N*-phthaloylglycine (L1) with nickel(II)chloride hydrate in the presence of potassium hydroxide followed by addition of pyridine gave the corresponding carboxylate complex with two pyridine and two aqua-ligands (Eq. (1)). The crystal structure of the complex was determined and is shown in Fig. 1. The compound has a self-assembled structure in which both intra- and intermolecular hydrogen-bonding plays a crucial role. The important bond angles and hydrogen bond geometries are listed in Table 1. The toluene molecules are held in the lattice through  $C-H\cdots\pi$  interactions ( $d_{C\cdots\pi}$  3.74 Å).

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(1)

The visible spectra of the complex have absorption at 637 nm typical of an octahedral geometry and occur due to  ${}^{3}A_{2} \rightarrow {}^{3}T_{1}$  transition.



 $\frac{2[\text{Ni}(\text{L1})_2(\text{py})_3(\text{H}_2\text{O})] \cdot [\text{Ni}(\text{L1})_2(\text{py})_2(\text{H}_2\text{O})_2].2\text{py}.2\text{H}_2\text{O}}{2}$ 

The co-crystals of inorganic complex with another inorganic complex is not common; however, during our study we have observed that when nickel(II)acetate was treated with N-phthaloylglycine, a water insoluble complex was obtained, which on dissolution in pyridine followed by recrystallisation gave a compound (2) having much different composition then the complex that was prepared by solid-state reaction. X-ray diffraction study has revealed



Fig. 1. Hydrogen bonded self-assembly of *bis*-(pyridine)-*bis*(aqua)-*bis*-(*N*-phthaloylglycinato) nickel(II).toluene (1) (30% thermal ellipsoid).

it to be a co-crystal of two molecules of [Ni(L1)<sub>2</sub>- $(py)_3(H_2O)$  with one molecule of  $[Ni(L1)_2(py)_2(H_2O)_2]$ along with two molecules each of pyridine and water. The structure is shown in Fig. 2. We have mentioned about this complex in our earlier report [6], however, without structural details. This complex is interesting for two reasons. Firstly it is a co-crystal containing two independent inorganic complexes having difference in the composition but derived from same set of ligands. Secondly the selfassembly formed has some uncoordinated ligand suggesting it to be an intermediate meta-stable compound. The compound in solid state at room temperature has a very weak ESR signal at 3370 G and in pyridine solution it has a relatively improved signal centering at 3410 G. Thermogravimetry of the compound shows weight loss of 33% at 83-318 °C which corresponds to loss of the pyridine and water molecules. Metastable nature of the compound is revealed from the ESI mass spectra of the compound, in DMF solution it has the highest mass at 483.0; corresponds



Fig. 2. Crystal structure of co-crystals of  $2[Ni(L1)_2(py)_3(H_2O)] \cdot [Ni(L1)_2(py)_2(H_2O)_2] \cdot 2py \cdot 2H_2O$  (the hydrogen atoms are omitted for clarity; 50% thermal ellipsoid).

Table 1		
Hydrogen-bonding interactions	in	1

Hydrogen Bond	$d_{\rm D-H}({ m \AA})$	$d_{\mathrm{A}\cdots\mathrm{H}}(\mathrm{\AA})$	$d_{\mathbf{D}\cdots\mathbf{A}}(\mathbf{\mathring{A}})$	∠D–H…Å (°)
$O(9)-H(9A)\cdots O(2) [1-x,2-y,-z]$	0.81	1.96	2.767(2)	174
$O(9)-H(9B)\cdots O(6)$ (Intramolecular)	0.77	1.89	2.653(3)	172
O(10)-H(10A)···O(2) (Intramolecular)	0.82	1.86	2.623(3)	154
$O(10)-H(10B)\cdots O(4) [1 - x, 2 - y, -z]$	0.69	2.16	2.822(3)	162
C(15)–H(15)···O(8) $[-x, 2 - y, 1 - z]$	0.93	2.49	3.249(5)	139

to a Ni(L1)<sub>2</sub>(H<sub>2</sub>O) cation. The complex 1 and 2 has similar IR spectra but the complex 2 has additional absorptions at 1485, 1476, 1447, 1191, 1217 cm<sup>-1</sup>.

The compound L2 has two carboxylic acid groups, of which one carboxylic acid group is attached to the aromatic ring and other is attached to a methylene group. These carboxylic acid groups of the ligand L2 differ in reactivity [8]. For instance to form the nickel(II) and manganese(II) complexes only one of the acidic hydrogen of carboxylic acid of the ligand L2 gets deprotonated, leaving aside another proton of carboxylic acid group intact. These molecules thus serve as examples for metallo-organic hybrid acids. Reaction of 4-Carboxy *N*-phthaloylglycine (L2) with manganese(II)acetate and nickel(II)acetate is shown in the Eq. (2).

$$HO \xrightarrow{N} OH \xrightarrow{Mn(II)/Ni(II)} M(L2)_2(4H_2O).2H_2O$$

$$HO \xrightarrow{N} OH \xrightarrow{Mn(II)/Ni(II)} M(L2)_2(4H_2O).2H_2O$$

$$M = Mn(II) [3], Ni(II) [4]$$

$$(2)$$

The structure of these two complexes **3** and **4** are determined by X-ray crystallography and found them to be *iso*structural. The structure of the nickel complex is given in Fig. 3a. The nickel centers have octahedral environment with two 4-Carboxy *N*-phthaloylglycinato ligands in *trans*-disposition. The mono-anion of the ligand **L2** is formed through deprotonation of the carboxylic acid at the glycine part. So far, we have not been able to crystallize **L2** in suitable form for crystallographic study. However, the crystal structure of the N-phthaloylglycine is known to have dimeric structure from the H-bonding between two carboxylic acid groups [10]. In the crystal lattice of N-phthaloylglycine the dipoles of the aromatic part is arranged on top of each other, so as to minimise the repulsion from the similar end of dipoles. The packing of the nickel complex of L2 has similar features in the crystal lattice, however, the rings interact with each other through C-H··· $\pi$  [ $d_{C \cdots \pi}$  3.71 Å (complex 3); 3.74 Å (complex 4)] and aromatic  $\pi$ - $\pi$  stacking interactions as depicted in Fig. 3. The  $\pi$ - $\pi$  separation between the aromatic rings in compounds 3 and 4 is 3.37 Å and 3.31 Å, respectively. This is well within the permissible limit for  $\pi$ - $\pi$  stacking [9]. Due to such interactions and the steric reasons the COOH groups attached to the aromatic ring remains free and they also do not self-assemble among themselves but are hydrogen bonded to the lattice water. The structures and the hydrogen-bonding in the lattice resemble similar metallohybrid acid of zinc that we had reported recently [8].



Further to this we have also prepared the cobalt(II) complex of *N*-phthaloylglycylglycinato ligand (Eq. (3)) from the reaction of cobalt(II)acetate with *N*-phthaloylgly-cylglycine in water. The crystal structure of this compound is determined and found to have an octahedral geometry



Fig. 3. Intermolecular aromatic  $\pi$ - $\pi$  stacking interactions between the N-phthaloyl groups in (a) complex 4 and (b) complex 3.



Fig. 4. The ORTEP diagram of (a) tetra-aqua *bis-N*-phthaloylglycylglycinato cobalt(II) (5) (b) the N–H···O interaction leading to  $\beta$  sheet structure (N–H···O 3.048 Å and 160.37 °).

around the cobalt center (Fig. 4). In this compound the *N*-phthaloylglycylglycinato ligands are positioned in *trans*disposition to each other, whereas the four water molecules are in one plane. It is also interesting to note that the presence of phthaloyl group on the ligand adopts a  $\beta$ -pleated sheet structure in the crystal lattice. This complex also has the structural features that are recently reported for zinc and cobalt complexes [7].

Thus, we have demonstrated the supramolecular features of functionalised glycine derivatives are a prominent feature that is to be accounted in their metal complexes. It is also observed that slight structural variation on glycine can result into complexes having different implications such as formation of meta-stable co-crystals, metallo-hybrid acids, and systems having  $\beta$ -pleated structure, adding further insight to the conventional co-ordination chemistry.

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#### Appendix A. Supplementary materials

The synthetic procedures and crystallographic table for the compounds reported is available as supplementary materials. The CIF files of the compounds are deposited to Cambridge Crystallographic database center and have the CCDC numbers 603938, 612371, 612372, 613623 and 613624. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.inoche.2006.07.038.

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