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Reactivity of Pyridine-2,4,6-tricarboxylic Acid toward Zn(II) Salts under Different Reaction Conditions

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Pyridine-2,4,6-tricarboxylic acid (ptcH$_3$) readily reacts with a Zn(II) salt at room temperature to form different products depending upon the presence or absence of pyridine in the reaction mixture. In the presence of pyridine, the ligand breaks to form infinitely zigzag coordination polymers with the empirical formula $\{Zn(Ox)(py)_2\}_n$ (Ox = oxalate, py = pyridine). The backbone is formed from Zn(II)–oxalate where two pyridine molecules are coordinated to each Zn(II) ion giving it hexacoordination. The orientation of the bound pyridines is slightly different when Zn(II)–nitrate is used compared to that when Zn(II)–sulfate (or acetate) salt is used. In absence of pyridine, the ligand remains intact and forms a mixture of a carboxylate-bridged coordination polymer and a discrete carboxylate-bridged 12-membered metallomacrocycle.

Synthesis of metal organic framework (MOF) structures by the modular approach is an area of intense research activity as potential zeolitic, optoelectronic, magnetic, and conducting materials.[1−5] While most of these structures have been generated utilizing hydro(solvo)thermal techniques, a substantial number of compounds are also synthesized at room temperature. This modular route utilizes the coordination tendencies of the metal ions toward multidentate organic ligands. Success in producing such structures will depend on understanding and controlling the topological and geometrical relationships between molecular modules along with the coordination characteristics of the metal ions. It has been observed[6−8] occasionally that unexpected reactions such as ligand oxidative coupling, hydrolysis, and substitution can occur under hydro(solvo)thermal conditions. Although such reactions are difficult to predict, they provide a new route for the construction of novel open framework structures. Here, we wish to report that pyridine-2,4,6-tricarboxylic acid (ptcH$_3$)[9] reacts with a Zn(II) salt differently depending upon the presence/absence of pyridine.

Reaction[10] of a Zn(II) salt with pyridine-2,4,6-tricarboxylic acid at room temperature in the presence of pyridine affords $\{Zn(ox)(py)_2{\cdot}H_2O\}_n$ (**1**) or $\{Zn(ox)(py)_2{\cdot}H_2O\}_n$ (**2**) in the form of a zigzag Zn(II)−oxalate coordination polymer. Although **1** and **2** have the same empirical formula, they are structurally different. A similar zigzag Zn(II)−oxalate coordination polymer is known[11] to form when $Zn(NO_3)_2{\cdot}6H_2O$, pyridine, and ethanol are allowed to react under hydrothermal conditions. In the absence of pyridine, however, ptcH$_3$ remains intact and forms a mixture of $\{Zn_{1.5}(2,4,6\text{-}ptc)(H_2O)_6\}_n$ (**3**) and $\{Zn(2,4,6\text{-}ptcH)(H_2O)_{4.33}\}_3$ (**4**). All compounds are characterized by elemental analysis and X-ray crystallography.[12]

Once formed, the compounds are stable in air and insoluble in water or in common organic solvents. High yields of the products indicate that they are thermodynamically stable under the prevailing reaction conditions. The counteranion does not play any role in this transformation as either **1** or

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(10) Synthesis of **1**: Reaction of $Zn(NO_3)_2{\cdot}6H_2O$ and ptcH$_3$ in 2:1 molar ratio at room temperature in the presence of excess pyridine affords. in 2 h, colorless crystals of **1** in ∼50% yield. The same crystalline product can be obtained when acetate or perchlorate salt of Zn(II) is used in place of the nitrate salt. Anal. Calcd for $C_{12}H_{12}N_2O_5Zn$: C, 43.73; H, 3.67; N, 8.50%. Found: C, 43.64; H, 3.42; N, 8.47%. Synthesis for **2**: When $Zn(SO_4)_2{\cdot}xH_2O$ is used in place of the nitrate salt, **2** is formed in 2 h in ∼60% yield. Anal. Calcd for $C_{12}H_{12}N_2O_5Zn$: C, 43.73; H, 3.67; N, 8.50%. Found: C, 44.01; H, 3.64; N, 8.59%. When an aqueous solution of $Zn(OAc)_2{\cdot}6H_2O$ is added to an aqueous solution of ptcH$_3$ in 2:1 molar ratio at room temperature, **3** is formed as needle-shaped crystals within 15 min in ∼45% yield. Anal. Calcd for $C_8H_{14}NO_{12}Zn_{1.5}$: C, 23.19; H, 3.41; N, 3.38%. Found: C, 22.84; H, 3.28; N, 3.47%. The filtrate from the reaction of $Zn(OAc)_2{\cdot}6H_2O$ and ptcH$_3$ on further evaporation affords **4** as colorless hexagonal-shaped crystals in ∼15% yield. Anal. Calcd for $C_8H_{11.67}NO_{10.33}Zn$: C, 27.26; H, 3.34; N, 3.97%. Found: C, 26.94; H, 3.48; N, 3.90%.

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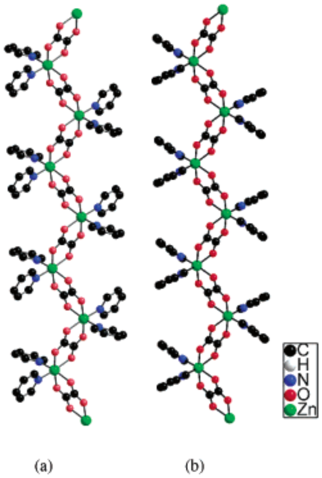

Figure 1. Zigzag chain structure of **1** (a) and **2** (b). The hydrogen atoms are omitted for clarity.

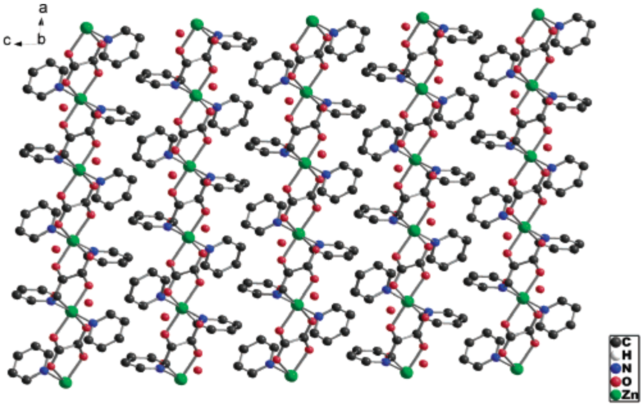

Figure 2. Packing of the zigzag chains through interchain interdigitization of pyridine molecules in **1**.

2 is obtained using different Zn(II) salts, such as nitrate, sulfate, perchlorate, or acetate. No crystalline product can be isolated when either nitrate or perchlorate salt of Zn(II) is treated with the ligand in absence of pyridine. Both Zn(II)−acetate and −sulfate afford **3** as the primary product in the absence of pyridine or in the presence of a base other than pyridine such as triethylamine or hexamethylenetetramine. Compound **4** is obtained as a minor product in these cases on further evaporation of the filtrate after isolating compound **3**. A Zn(II)−halide salt does not afford a crystalline product under any condition, due to immediate precipitation. Therefore, it is evident that in the presence of pyridine, the ligand breaks down at room temperature by Zn(II). Stability of the product and its insolubility in the reaction medium are mostly responsible for the breakage of the ligand and drive the reaction forward. Presence of a base other than pyridine does not lead to the breakage of the ligand showing that a base probably has no role to play in these reactions. It has been reported[11] that when $Zn(NO_3)_2 \cdot 6H_2O$ and pyridine are allowed to react in ethanol under solvothermal conditions at 140 °C for 14 days, a structure very similar to that of **1** is formed. This was suggested as due to oxidation of ethanol under the reaction conditions, and the product is driven due to stability of the zigzag chain structure. Interestingly, in our case, the reaction is almost instantaneous at room temperature, and colorless crystals can be seen with the naked eye in about 60 min. The IR spectra of **1** and **2** are similar, each showing strong absorption bands between 1350 and 1550 cm^{-1} that are diagnostic[13] of coordinated oxalate with D_{2h} symmetry. Compounds **3** and **4** also exhibit strong peaks between 1350 and 1550 cm^{-1} attributable[14] to coordinated carboxylates.

The structure of **1** consists of infinite 1D zigzag chains where each metal ion is coordinated to two oxalate groups and two pyridine molecules showing hexacoordination with O_4N_2 donor set (Figure 1a). Coordination geometry around each metal center can be described as slightly distorted octahedral. The two pyridine molecules are similarly oriented with respect to the Zn−oxalate backbone. These infinite zigzag chains pack in the lattice through interdigitization involving the pyridine molecules (Figure 2). The water molecules present in the lattice are hydrogen-bonded to the π ring of the nearby pyridine molecule.

The Zn−O bond distances lies in the narrow range 2.13−2.09 Å, signifying that the oxalate group is almost symmetrically bound to the metal. The Zn(II)−N(pyridine) distance of 2.14 Å is slightly longer compared to other Zn−pyridine complexes.[15]

Compound **2** has the same empirical formula as **1**, but there are subtle differences in the structure due to different orientation of the pyridine rings with respect to the Zn(II)−oxalate backbone (Figure 1b). Like in the case of **1**, coordination geometry (Table 1, Supporting Information) around each metal center is distorted octahedral, the infinite zigzag chains pack with an interdigitization of the pyridines, and the water molecules present in the lattice are hydrogen-bonded to the π ring of the nearby pyridine molecule. All bond distances and bond angles involving the metal ion are similar to the ones found in **1**.

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(12) Crystal data for **1**: $C_{12}H_{12}N_2O_5Zn$; $M = 329.61$, rectangular parallelopiped, colorless crystals, $0.18 \times 0.15 \times 0.11$ mm^3, monoclinic space group $P2_1/n$, $a = 9.444(3)$ Å, $b = 9.162(3)$ Å, $c = 14.979(2)$ Å, $\beta = 94.724(5)°$, $V = 1291.7(11)$ Å^3, $R1 = 0.042$, $wR2 = 0.1146$, $S = 0.848$, $T = 100$ K, $Z = 4$, $\mu(\text{Mo K}\alpha) = 1.922$ mm^{-1}, 8473 reflections measured, 2681 ($I \geq 2\sigma(I)$) unique reflections were used in all calculations. Crystal data for **2**: $C_{12}H_{12}N_2O_5Zn$; $M = 329.61$, rectangular parallelopiped, colorless crystals, $0.17 \times 0.15 \times 0.11$ mm^3, monoclinic space group $P2_1/c$, $a = 9.444(2)$ Å, $b = 8.827(2)$ Å, $c = 15.397(3)$ Å, $\beta = 91.806(5)°$, $V = 1282.9(11)$ Å^3, $Z = 4$, $R1 = 0.0518$, $wR2 = 0.1290$, $S = 1.068$, $T = 100$ K, $Z = 4$, $\mu(\text{Mo K}\alpha) = 1.935$ mm^{-1}, 8324 reflections measured, 2683 ($I \geq 2\sigma(I)$) unique reflections were used in all calculations. Crystal data for **3**: $C_8H_{14}NO_{12}Zn_{1.5}$; $M = 414.26$, colorless needles, $0.16 \times 0.14 \times 0.10$ mm^3, monoclinic space group $P2_1/c$, $a = 7.091(2)$ Å, $b = 18.493(3)$ Å, $c = 10.839(2)$ Å, $\beta = 103.879(5)°$, $V = 1379.9(12)$ Å^3, $Z = 4$, $R1 = 0.0317$, $wR2 = 0.0718$, $S = 1.043$, $T = 100$ K, $\mu(\text{Mo K}\alpha) = 2.696$ mm^{-1}, 9134 reflections measured, 2918 ($I \geq 2\sigma(I)$) unique reflections were used in all calculations. Crystal data for **4**: $C_8H_{11.67}NO_{10.33}Zn$; $M = 352.55$, hexagonal colorless crystals, $0.18 \times 0.15 \times 0.11$ mm^3, trigonal space group $R3$, $a = 17.158(2)$ Å, $b = 17.158(2)$ Å, $c = 10.431(1)$ Å, $V = 2659.4(4)$ Å^3, $Z = 3$, $R1 = 0.0960$, $wR2 = 0.2529$, $S = 1.084$, $T = 100$ K, $\mu(\text{Mo K}\alpha) = 0.715$ mm^{-1}, 2842 reflections measured, 2377 ($I \geq 2\sigma(I)$) unique reflections were used in all calculations.

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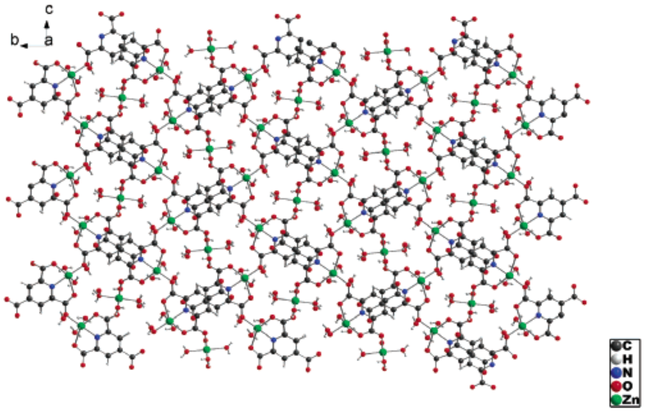

Figure 3. Packing diagram of **3** viewed in the *bc* plane.

Compounds **3** and **4** are obtained when pyridine is not added to the reaction mixture. This clearly demonstrates that thermodynamic stability of the zigzag coordination polymer $\{Zn(ox)(py)_2{\bullet}H_2O\}_n$ is the driving force behind cleaving the ligand in the case of **1** and **2**. The structure of **3** consists of two Zn(II) ions, one ligand, and six water molecules in the asymmetric unit. Here, Zn(1) is bonded equatorially to the ligand at the pyridine-2,6-dicarboxylate position (NO_2 donor set) and an O atom of the carboxylate from a neighboring ligand that propagates the coordination polymeric chain. The axial sites are occupied by two water molecules. The Zn(2) position is coincident with crystallographic inversion symmetry. It is equatorially bonded to two carboxylate O atoms from two neighboring Zn(1) centers and two water molecules (Figure 3) while two water molecules are bound axially. All Zn−O and Zn−N bond distances are within normal ranges found in other Zn(II) structures.[16] An interesting aspect of this structure is the presence of an almost linear water dimer (Ow2···Ow3) in the lattice. This dimer is involved in hydrogen bonding interactions with water molecules bound to different metal ions (Figure 4).

The structure of **4** consists of one Zn(II), one ligand, and five water molecules in the asymmetric unit. The molecule forms a discrete 12-membered macrocycle containing three Zn(II) ions and three bridging carboxylates (Figure 5). Each metal ion is bonded equatorially to one ligand at the pyridine-2,6-position and a bridging carboxylate O from one of its neighbors (NO_3 donor set). Two water molecules are bonded axially to each metal giving it octahedral coordination. The center of the macrocyclic ring coincides with the crystallographic 3-fold axis making the 12-membered ring perfectly planar. The distance between any two Zn(II) ions is 4.93 Å describing an equilateral triangle. The three water molecules on one side of the ring are tilted toward the center (Ow···Ow, 4.25 Å) while the three on the other side are tilted slightly away from the center (Ow···Ow, 5.24 Å). The carboxylic acid group at the 4-position remains protonated and uncoordinated. The remaining water molecules are present in the lattice; one of them is present at the center of the macrocycle with disordered H atom positions. Also, several disordered water molecules with partial occupancy could be located in the difference maps which were ignored.

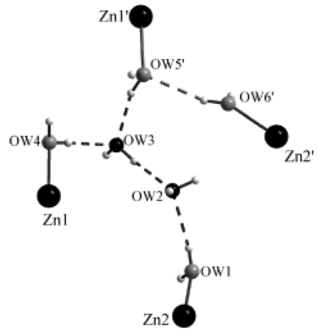

Figure 4. Hydrogen bonding scheme for the water molecules in **3**.

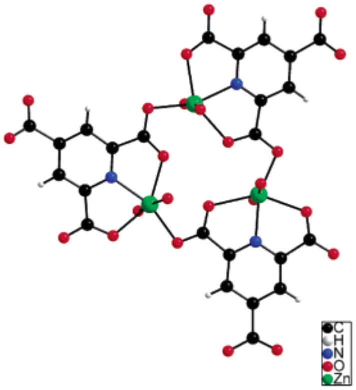

Figure 5. A perspective view of **4** showing the 12-membered metallomacrocycle.

In summary, we show here that pyridine-2,4,6-tricarboxylic acid can be broken almost instantaneously at room temperature, by Zn(II) ion in the presence of pyridine. The anion present has no role in this reaction, and the reaction is driven forward due to high stability of the product.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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