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Hydrothermal Preparation of Novel Cd(II) Coordination Polymers Employing 5-(4-Pyridyl)tetrazolate as a Bridging Ligand

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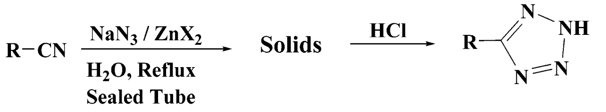
The reaction of 4-cyanopyridine with NaN_3 in the presence of H_2O and a Lewis acid ($CdCl_2$) affords a novel 3D pillared-layered fluorescent and phosphorescent coordination polymer $Cd_3(OH)_2Cl_2(4\text{-PTZ})_2$ (4-PTZ = 5-(4-pyridyl)tetrazolate) (**1**) while the direct reaction of $CdCl_2$ with H-PTZ gives the simpler species $Cd(4\text{-PTZ})_2(H_2O)_2$. The solid-state structure and nature of **1** provide an indication of the type of materials that may be formed as intermediates in the Sharpless–Demko reaction for the generation of 5-substituted 1*H*-tetrazoles.

Sharpless and Demko have recently reported an environmentally friendly, relatively simple synthetic approach for generating 5-substituted 1*H*-tetrazoles. In the general reaction, the tetrazoles are prepared by the addition of azide to nitriles in water with the aid of a Lewis acid such as Zn^{2+} (Scheme 1). The mechanistic role of the zinc is unclear, but it has been suggested that a solid intermediate from the reaction of PhCN with $ZnBr_2$ and NaN_3 is $(PhCN_4)_2Zn$. A structural investigation of such an intermediate would be interesting because it may provide important clues to the role of the Lewis acid in the synthesis. Furthermore, given the potential of tetrazole to coordinate and bridge metal centers, a structural investigation may also reveal a network structure that may be of interest in its own right.

Scheme 1



Due to the potential for producing unusual and possibly useful materials, there has recently been intense interest in the design, synthesis, characterization, and properties of ordered coordination networks formed by using appropriately functionalized organic molecules as bridges between metal centers.[3,4] A major challenge associated with this particular area of synthesis is the generation of high-quality crystalline material suitable for X-ray structural analysis. In our own group we have found that single crystals of coordination polymers can often be generated under hydrothermal conditions.[5] Given our experience in this area we have repeated

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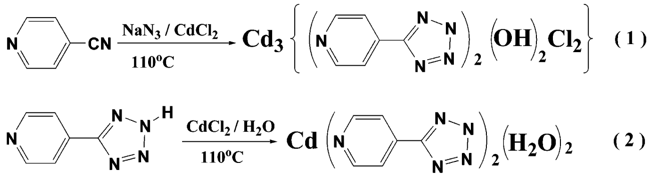
Scheme 2



the Demko−Sharpless reaction under such conditions in an effort to produce crystals that may allow structural elucidation of the solid intermediates in these particular reactions.

Accordingly, we have investigated the hydrothermal reaction of $CdCl_2$ with 4-cyanopyridine and NaN_3 in water (Scheme 2), a reaction which may be expected to generate 5-(4-pyridyl)tetrazole (4-H-PTZ) because Cd^{2+} is also Lewis acid. In addition, it is expected that the composition of a "Cd-intermediate" in this reaction should be different from that of a "Zn-intermediate" since the ion radius of Cd^{2+} is significantly larger than that of Zn^{2+}. It is really identical that tetrazole ligand can also be synthesized by the use of Cd salt instead of Zn salt. For comparison, the direct reaction product of $CdCl_2$ with (4-H-PTZ) under hydrothermal reaction conditions has also been undertaken. To our surprise, the reaction products obtained in the in situ synthesis and the direct synthesis are quite different. Herein we report their solid-state structures and photoluminescent properties.

The reaction of $CdCl_2$ with 4-cyanopyridine in the presence of NaN_3 and water under hydrothermal conditions yields $Cd_3(OH)_2Cl_2(4\text{-PTZ})_2$ (**1**) while $Cd(4\text{-PTZ})_2(H_2O)_2$ (**2**) is obtained by the treatment of 4-H-PTZ, $CdCl_2$, and H_2O under similar conditions.[6] The different composition between **1** and **2** is probably due to different pH in their reaction solutions. In the solution of **1** the beginning pH is ca. 6.5 while the ending pH of the solution ca. 5.8. However, in the solution of **2** the beginning pH is ca. 4.0 while the ending pH of the solution is ca. 3.5. The IR spectrum of **1** shows peaks consistent with the formation of 4-PTZ and the absence of a cyano peak in the 2100 cm^{-1} region. In the IR spectrum of **2** a peak over 3100 cm^{-1} suggests that coordinated water is present.

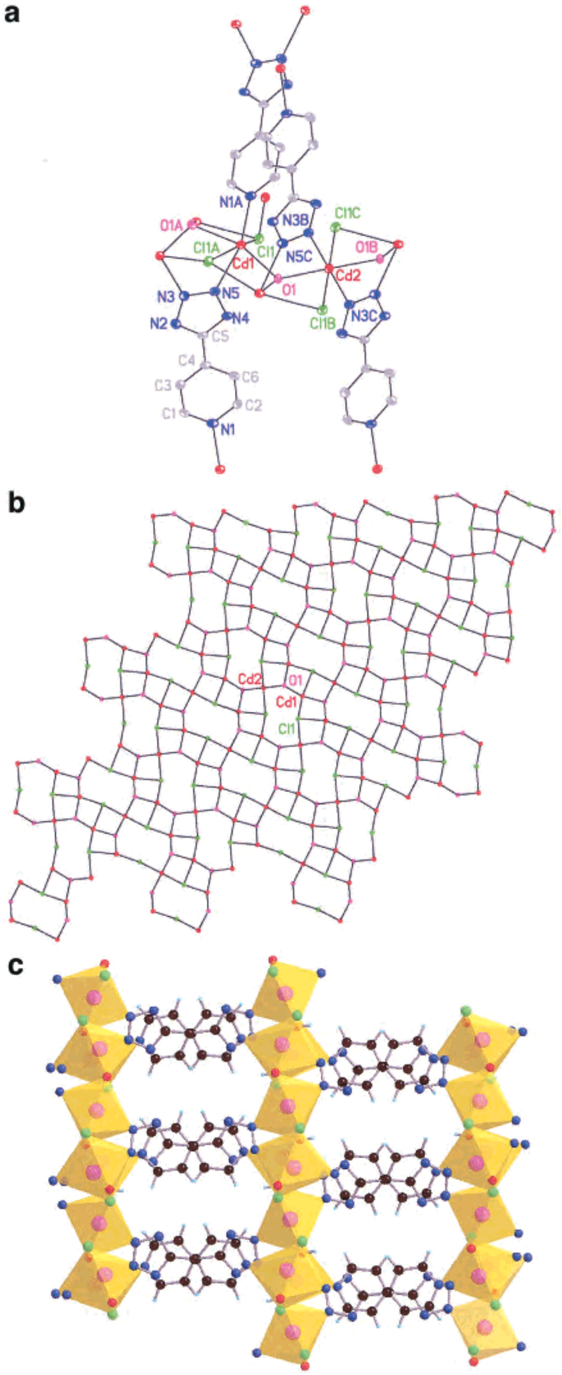


Figure 1. (a) Part of the structure of **1** shows that the local coordination geometry around two Cd centers is slightly octahedral (probability displacement ellipsoids at 30%). (b) The "floor" of the pillared-layered structure of **1** composed of Cl, O, and Cd atoms in **1** (probability displacement ellipsoids at 30%). (c) A polyhedral representation of the pillared-layered structure of **1**. The small spheres that are blue, pale-green, red, and black as well as green represent N, H, O, and C as well as Cl atoms, respectively, while the large pink sphere represents one of the Cd centers.

The chemical composition of **1** is more complicated than the type of Zn intermediate proposed by Sharpless and Demko. The structure incorporates not only the anticipated PTZ which acts as a tridentate bridging ligand but also hydroxide and chloride ions (Figure 1a, an ORTEP representation of **1** showing the local coordination environment of octahedral Cd centers).[7] There are two unique Cd centers, and their coordination geometries may be best described as distorted octahedra. For each Cd, trans chloride and trans hydroxide ions form an approximate square planar arrange-

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(6) Preparation of **1**: Hydrothermal treatment of $CdCl_2$ (3.0 mmol, 0.549 g), 4-CNPY (2.0 mmol, 0.208 g), NaN_3 (3.0 mmol, 0.195 g), and water (3.0 mL) over 1 day at 110−160 °C yielded a colorless block crystalline product with only one pure phase. The yield (ca. 0.478 g) of **1** was about 65% based on 4-CNPY. Anal. Calcd for $C_6H_5N_5OClCd_{1.5}$ [%]: C, 19.61; H, 1.36; N, 19.06. Found [%]: C, 19.76; H, 1.52; N, 19.30. IR (KBr, cm^{-1}): 3567 (m), 3036 (w), 1624 (s), 1558 (w), 1432 (s), 1373 (w), 1221 (m), 1188 (w), 1127 (w), 1057 (m), 1009 (m), 844 (m), 819 (s), 753 (m), 717 (s), 656 (s), 527 (m), 464 (w). Preparation of **2**: Hydrothermal treatment of $CdCl_2$ (1.0 mmol, 0.183 g), 5-(4-pyridyltetrazolate) (2.0 mmol, 0.295 g), and water (2.5 mL) over 2 days at 120−160 °C gave a prismatic crystalline product with only one pure phase. The yield (ca. 0.155 g) of **2** was about 35% based on 5-(4-pyridyltetrazolate). Anal. Calcd for $C_6H_6N_5OCd_{0.5}$ [%]: C, 32.67; H, 2.72; N, 31.77. Found [%]: C, 32.76; H, 2.75; N, 31.87. IR (KBr, cm^{-1}): 3418 (s), 3240 (s), 1620 (s), 1557 (w), 1447 (w), 1432 (m), 1377 (m), 1315 (w), 1226 (w), 1132 (w), 1071 (w), 1034 (w), 1011 (m), 865 (w), 839 (s), 756 (m), 728 (s), 708 (m), 670 (w), 649 (w), 534 (m), 460 (w).

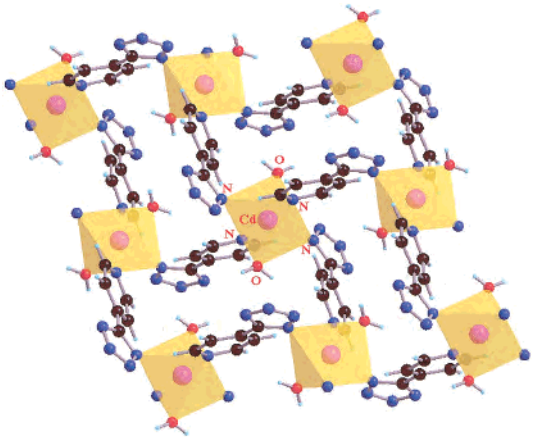

Figure 2. The 2D network structure of **2**. The slightly distorted octahedral environment of the Cd centers is represented by the octahedra. The small spheres that are blue, pale-green, red, and black represent N, H, O, and C atoms respectively; the large pink sphere represents one of the Cd centers.

ment while the remaining trans positions are occupied by N atoms from two 4-PTZ ligands.

Each hydroxide and chloride ion is bound to three Cd centers resulting in the formation of 2D sheets within the network of composition $[Cd_3(OH)_2Cl_2]^{2+}$ (Figure 1b, a simplified "floor" representation of **1** omitting for pillars ligands (4-PTZ)). It is interesting to note that four-membered Cd−OH−Cd−Cl rings apparent within these sheets are also present in the layer structure of Cd(OH)Cl. The 4-PTZ ligands link parallel sheets together giving rise to a 3D network which may be considered as a pillared-layered structure with the $[Cd_3(OH)_2Cl_2]^{2+}$ sheets forming the floors and the 4-PTZ representing the pillars (Figure 1c, 3D network representation of **1** in which "floor" and pillars are shown in octahedral polyhedron Cd layers and 4-PTZ ligands, respectively). The sheets or "floors" of this structure are separated by approximately 10.7 Å.

As indicated earlier the composition **1** is quite different from that found for **2** which is formed from the direct reaction of H-PTZ with $CdCl_2$. The coordination geometry of each Cd center in **2** is a slightly distorted octahedron formed from the coordination of four bridging 4-PTZ ligands and two water molecules.[7] Two trans pyridyl groups and two trans tetrazole groups provide nitrogen atoms that form a square planar arrangement around each Cd center. The remaining trans sites are occupied by water molecules. Each Cd center links to four other Cd centers through the bridging ligands, producing a simple 2D network based on 4-connecting centers (Figure 2). Adjacent layers in the network are linked together by strong H-bonds (between a water molecule and a N atom of a 4-PTZ ligand) and stack in an ABAB sequence.

Of particular interest is the photoluminescent spectrum (a Perkin-Elmer LS50B was used for measurement) of powdered **1**, which shows a strong emission peak at 390 nm ($\tau \approx 1.5$ ns; $\Phi_{em} \approx 0.31$) that can be assigned to an intraligand fluorescent emission since a weak similar emission at 353 nm ($\tau \approx 1.1$ ns; $\Phi_{em} \approx 0.10$) is observed for the ligand (Figure 3). A relatively weak peak at 470 nm ($\tau \approx 2.0$ s; $\Phi_{em} \approx 0.15$) is also observed for **1**. Because of the longer emission lifetime of **1** at 470 nm, this peak may be tentatively assigned to phosphorescence. On the other hand, the Cd−OH−Cl sheet of **1** may be responsible for the phosphorescent emission since **2** only displays a strong emission peak at 380 nm. The exact phosphorescent emission mechanism for **1** is unclear. As far as we are aware, a metal coordination polymer demonstrating both fluorescent and phosphorescent emission is unknown.[8] Thus **1**, with its condensed 3D pillared-layered structure, high thermal stability (stable up to 450 °C), and insolubility in common solvents such as ethanol, chloroform, ethyl acetate, acetone, acetonitrile, benzene, and water, is an attractive candidate for use as a blue fluorescent and phosphorescent material.

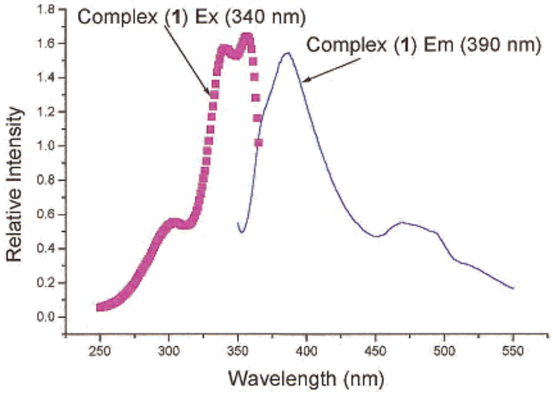

Figure 3. The solid-state fluorescent spectrum of **1** at room temperature in which an emission at 390 nm is fluorescent while the emission at 470 nm may be tentatively assigned to phosphorescence.

Apart from affording insights into the nature of the solids produced in the reaction by Sharpless and Demko, the work described here provides further indication of the usefulness of "one-pot" hydrothermal syntheses for forming coordination polymers involving bridging ligands produced in situ.

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Supporting Information Available: Experimental procedures, IR data, figures depicting a square network representation of **2** and ABAB-type stacking of adjacent layers in **2**, a fluorescent spectrum of the ligand, and an X-ray CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Crystal data for **1**: $C_6H_5N_5OClCd_{1.5}$, $M = 367.20$, orthorhombic, *Pbca*, $a = 7.0056(2)$ Å, $b = 12.6282(6)$ Å, $c = 21.3318(10)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 1887.18(15)$ Å^3, $Z = 8$, $D_c = 2.585$ Mg m^{-3}, R1 = 0.0231, wR2 = 0.0827, $T = 296$ K, $\mu = 3.667$ mm^{-1}, $S = 0.762$. Crystal data for **2**: $C_6H_6N_5OCd_{0.5}$, $M = 220.36$, monoclinic, $P2_1/n$, $a = 8.4360(4)$ Å, $b = 8.0018(4)$ Å, $c = 10.8795(5)$ Å, $\beta = 95.488(1)$, $\alpha = \gamma = 90.00°$, $V = 731.03(6)$ Å^3, $Z = 4$, $D_c = 2.002$ Mg m^{-3}, R1 = 0.0311, wR2 = 0.0833, $T = 296$ K, $\mu = 1.528$ mm^{-1}, $S = 0.609$.

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