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Isolation and Crystallographic Characterization of a Solid Precipitate/Intermediate in the Preparation of 5-Substituted 1*H*-Tetrazoles from Nitrile in Water

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The reactions of 2-, 3-, and 4-cyanopyridine with NaN_3 in the presence of H_2O and Lewis acid ($ZnCl_2$) afford discrete monomer, $(2\text{-PTZ})_2Zn(H_2O)_2$ (**1**), 3D diamondoid-like network $(3\text{-PTZ})_2Zn$ (**2**), and 2D layered network $(4\text{-PTZ})Zn(OH)(H_2O)$ (**3**), respectively (PTZ = 5-(pyridyl)tetrazolato).Their solid state structures and natures give new insight into the Sharpless reaction of 5-substituted 1*H*-tetrazole. Interestingly, **2** crystallizes in a noncentrosymmetric space group and its powdered sample is second-harmonic generation active.

The tetrazole functional group has found a wide range of applications in coordination chemistry as ligands, in medicinal chemistry as a metabolically stable surrogate for a carboxylic acid group, and in materials science as high-density energy materials.[1] Earlier routes to tetrazoles in the literature usually involve expensive and toxic metal, suffer from severe water sensitivity, or use hydrazoic acid, which is highly toxic, volatile, and explosive.[1−4] Recently, Sharpless et al. explored the preparation of 5-substituted 1*H*-tetrazoles in water (Scheme 1) with zinc salts as catalysts[5] This new synthesis is a breakthrough and offers a safe, convenient, and environmentally friendly synthetic route to tetrazoles.

As pointed out,[5] the exact role of zinc and the mechanistic pathway(s) in this new synthesis of tetrazoles are not clear. A solid precipitate/intermediate, presumably $(PhCN_4)_2Zn$, was observed.[5] Trapping and characterizing the "intermediate" in this new preparation of 5-substituted 1*H*-tetrazole in water may offer organic chemists an opportunity to optimize reaction conditions. We have been interested in the construction of novel supramolecular motifs through in situ hydrothermal reactions.[6] Inspired by Sharpless's pioneering work,[5] we have studied reactions of nitriles 4-cyanopyridine (4-CN-PY), 3-cyanopyridine (3-CN-PY), and 2-cyanopyridine (2-CN-PY) with $ZnCl_2$ and NaN_3 in water under hydrothermal conditions to probe these reactions (Scheme 2). To our surprise, the composition and solid state structures of

Scheme 1

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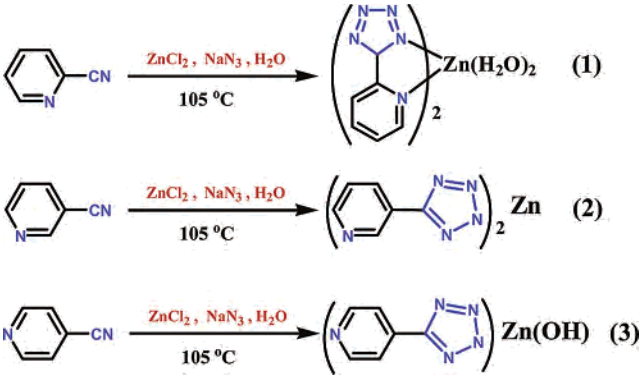
Scheme 2



products isolated are quite different, and depend on complexing ability of the metal ions toward tetrazole and hydroxy groups. Some of novel supramolecular motifs formed in situ under the hydrothermal conditions are not accessible in direct preparation from ZnX_2 and tetrazoles in solution *under ambient conditions*. In addition, these results provide a direct support to Sharpless's proposed mechanism in the formation of 5-substituted 1*H*-tetrazoles from nitriles in water. Herein we report the solid state structures and second harmonic generation (SHG) response of these intermediates which provide the fascinating synthetic method for novel supramolecular motif constructions in situ.

Bis[5-(2-pyridyl)tetrazolato]diaquazinc(II) [$(2\text{-PTZ})_2Zn(H_2O)_2$ (**1**)], bis[5-(3-pyridyl)tetrazolato]zinc(II) [$(3\text{-PTZ})_2Zn$ (**2**)], and {[mono(5-(4-pyridyl)tetrazolato)hydroxyzinc(II)] monoaqua} $(4\text{-PTZ})Zn(OH)(H_2O)$ (**3**) were prepared in the hydrothermal reactions from the corresponding cyanopyridine, NaN_3, and $ZnCl_2$ respectively, under hydrothermal reaction conditions.[5] IR spectra of the products showed that typical peaks (~ 2100 cm^{-1}) of the cyano groups in the corresponding cyanopyridine ligands disappeared and gave peaks (ca. 1500 cm^{-1}) of the tetrazole group.[7]

Figure 1 gives the solid state structure of **1**, in that the local coordination geometry around the Zn center can be best described as a slightly distorted octahedron with four equatorial nitrogen atoms from two 2-PTZ ligands and two apical water molecules, resulting in the formation of a monomeric Zn complex.[8] The result here well supports Sharpless's proposed structures of the intermediate precipitates.[5]

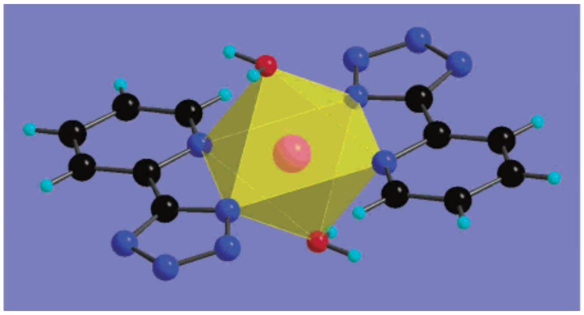


Figure 1. Solid state structure of **1**.

More interestingly, in the solid structure of **2** (Figure 2), the Zn atom only coordinates to four N atoms from the tetrazole of 3-PTZ ligands while the N atom of the pyridyl ring fails to bond to the Zn atom, resulting in the formation of a 3D diamondoid-like framework, as shown in Figure S1 (see Supporting Information).[9,10] It is worth noting that water failed to coordinate to the Zn atom. Similarly, the resulting product of **2** still supports Sharpless's proposed formation mechanism of tetrazole.

Unexpectedly, however, in the solid state structure of **3** (Figure 3) the Zn atom not only coordinates to two atoms from the pyridyl ring and tetrazole of the 4-PTZ ligand, respectively, but also binds to two hydroxy groups, which are presumably formed from water in situ. Thus, **3** shows a two-dimensional layered structural feature with an intercalated water molecule through hydrogen bonding between two

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(7) Preparation of $C_{12}H_{12}N_{10}O_2Zn$ (**1**): Hydrothermal treatment of $ZnCl_2$ (1.0 mmol), 2-cyanopyridine (2.0 mmol), NaN_3 (3.0 mmol), and water (3.0 mL) over 1 day at 105 °C yielded a colorless prismatic crystalline product. The yield of **1** was about 85% based on 2-CN-PY. Anal. Calcd for $C_{12}H_{12}N_{10}O_2Zn$ (**1**): C, 36.58; H, 3.05; N, 35.56. Found: C, 36.47; H, 3.11; N, 35.31. IR spectrum (KBr, cm^{-1}): 3229 (s), 3055 (w), 2331 (w) 1612 (m), 1572 (w), 1470 (w), 1445 (s), 1400 (w), 1295 (w), 1260 (w), 1171 (w), 1139 (w), 1060 (w), 1031 (w), 804 (s), 758 (m), 732 (w), 664 (w), 643 (w). $C_{12}H_8N_{10}Zn$ (**2**): The procedure is identical to that of **1** except that 3-CN-PY was used in place of 2-CN-PY. The yield of **2** was about 75% based on 3-cyanopyridine. Anal. Calcd for $C_{12}H_8N_{10}Zn$ (**2**): C, 40.27; H, 2.24; N, 39.15. Found: C, 40.45; H, 2.43; N, 40.01. IR spectrum (KBr, cm^{-1}): 3424 (w), 3036 (w), 1600(m), 1572 (m), 1517 (w), 1462 (m), 1431 (s), 1385 (m), 1330 (w), 1192 (w), 1100 (m), 1078 (m), 1024 (w), 1009 (w), 934 (w), 829 (m), 761 (m), 711 (m), 618 (w), 546 (m), 444 (w). {[Mono(5-(4-pyridyl)tetrazolato)hydroxyzinc(II)] monoaqua} (**3**): The procedure is identical to that of **1** except that 4-CN-PY was used in place of 2-CN-PY. The yield of colorless block crystalline **3** was about 75% based on 4-CN-PY. Anal. Calcd for $C_6H_7N_5O_2Zn$: C, 29.20; H, 2.84; N, 28.39. Found: C, 29.36; H, 2.92; N, 28.60. IR (KBr, cm^{-1}): 3246 (m), 3043 (w), 1627 (s), 1560 (w), 1452 (w), 1439 (m), 1382 (w), 1231 (m), 1173 (w), 1087 (w), 1049 (w), 1019 (m), 854 (m), 754 (w), 719 (m), 537 (w), 513 (m), 472 (w).

(8) Crystal data for **1**: $C_{12}H_{12}N_{10}O_2Zn$, $M = 393.69$, monoclinic, $P2_1/c$, $a = 8.0738(7)$ Å, $b = 12.8349(11)$ Å, $c = 7.3339(7)$ Å, $\beta = 96.204(2)°$, $\alpha = \gamma = 90.00°$, $V = 755.53(12)$ Å^3, $Z = 2$, $D_c = 1.731$ Mg m^{-3}, R1 = 3.76%, wR2 = 9.57%. $T = 293$ K, $\mu = 1.659$ mm^{-1}, $S = 0.542$. **2**: $C_{12}H_8N_{10}Zn$, $M = 357.63$, tetragonal, $I\bar{4}2d$, $a = 10.1190(7)$ Å, $b = 10.1190(7)$ Å, $c = 13.6166(14)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 1394.3(2)$ Å^3, $Z = 4$, $D_c = 1.704$ Mg m^{-3}, R1 = 0.0305, wR2 = 0.0711, $T = 293$ K, $\mu = 1.788$ mm^{-1}, $S = 0.502$, Flack $\chi = 0.010(19)$. **3**: $C_6H_7N_5O_2Zn$, $M = 246.54$, orthorhombic, *Pbca*, $a = 14.5401(12)$ Å, $b = 6.5807(5)$ Å, $c = 16.5221(13)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 1580.9(2)$ Å^3, $Z = 8$, $D_c = 2.072$ Mg m^{-3}, R1 = 0.0453, wR2 = 0.1302, $T = 296$ K, $\mu = 3.082$ mm^{-1}, $S = 1.027$. The goodness of fit (S) is always based on F^2, and its definition is given below. $S = \{[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

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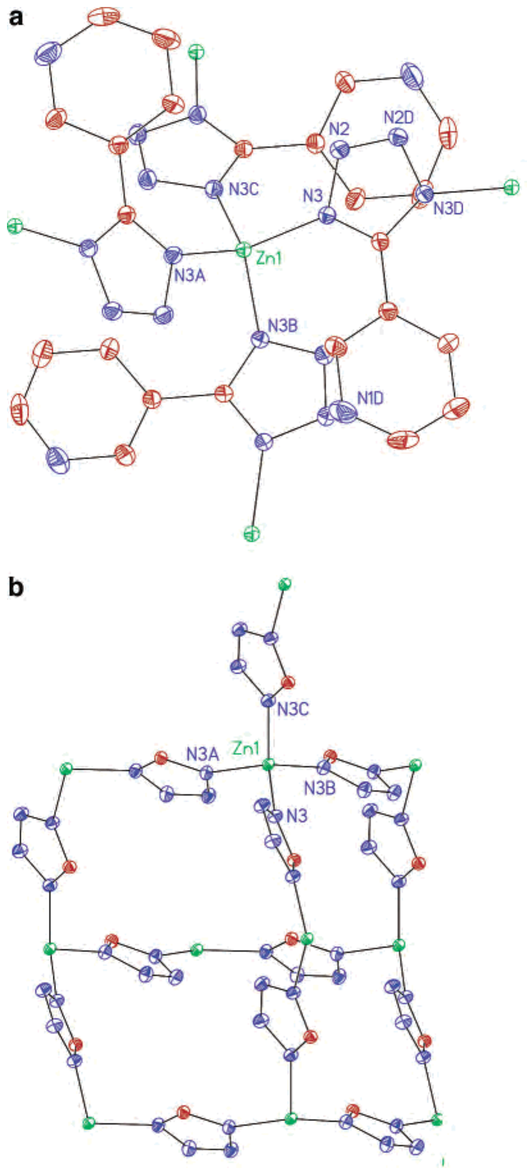

Figure 2. (a) The local coordination geometry around the Zn center in **2**. (b) A diamond-like net of **2** in which the pyridyl ring is omitted for clarity.

layers (see Supporting Information). This result is unexpected, probably suggesting that water is also a reactant.

It is also interesting to note that **2** crystallizes in an acentric space group. Preliminary experimental results show that **2** displays a moderate powder SHG response, ca. 0.4 times that of urea. This feature is similar to that of KDP also with an diamond-like network.[11] Furthermore, thermal stability of **2** up to ca. 300 °C (TGA measurement) and insolubility in common solvents make **2** a good candidate for SHG material.

In conclusion, the composition and solid state structures of "intermediate" in the metal-catalyzed formation of 5-substituted 1*H*-tetrazoles from nitrile in water can be classified into the following three cases: (a) simple monomer such as $(R\text{-}CN_4)_2M(H_2O)_2$ in which two tetrazoles bind to the metal atoms as bidentate ligand; (b) 2D coordination polymer in which hydroxy ligands (from water) as a bridging spacer, 5-substituted coordinating group, and tetrazole all take part in the coordination to the metal atom, resulting in the formation of a 2D framework; (c) 3D coordination polymer in which tetrazole as a bidentate bridging ligand connects two Zn atom centers, resulting in the formation of 3D coordination polymer.

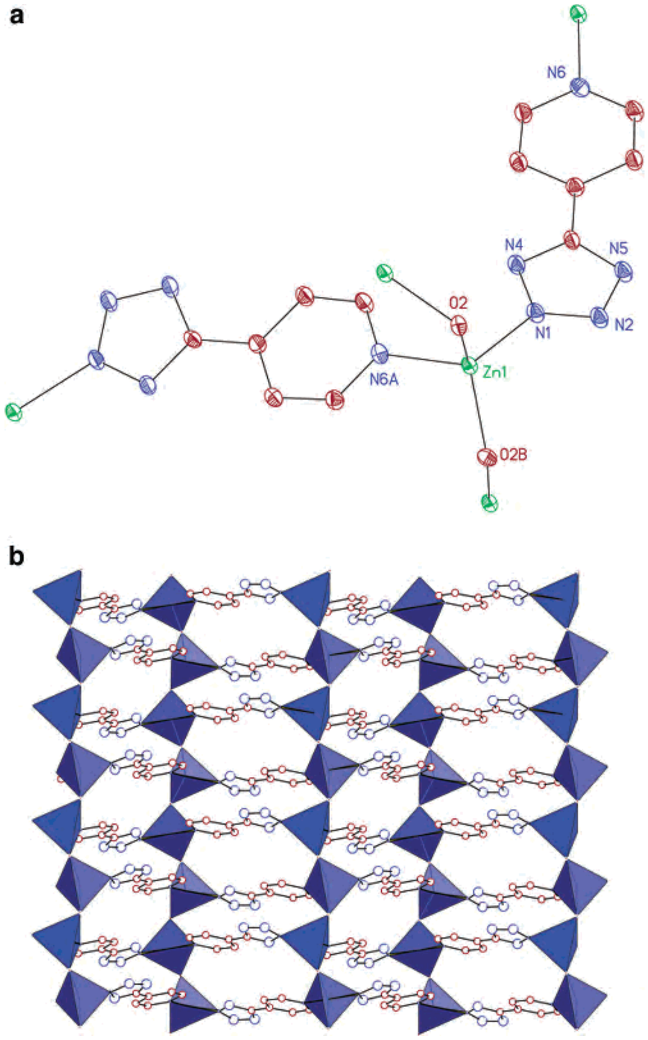

Figure 3. (a) The local coordination geometry around the Zn center in **3**. (b) 2D framework of **3** highlighting the Zn tetrahedron.

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Supporting Information Available: Figures depicting 3D diamond-like network of **2** and 2D layered grid network of **3**. X-ray CIFs. This material is available free of charge via the Internet at http://pubs.acs.org.

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