Novel, Acentric Metal–Organic Coordination Polymers from Hydrothermal Reactions Involving In Situ Ligand Synthesis[**]

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Many solid-state physical properties, such as pyroelectricity, piezoelectricity, ferroelectricity, second harmonic generation (SHG), and triboluminescence, are only found in noncentrosymmetric bulk materials.[1] In spite of the practical importance of these properties in many technological applications, including telecommunications, optical storage, and information processing, the generation of acentric solids from achiral building blocks still depends upon "Edisonian" approaches. The rational construction of structurally ordered noncentrosymmetric and chiral metal–organic solids remains a great challenge. Recently, attempts to generate acentric metal--organic coordination polymers (MOCPs) and organic solids by employing crystal engineering strategies have met with some success.[2] However, crystal engineering has not developed to the stage where a desired structure or crystal symmetry can be ensured.[3]

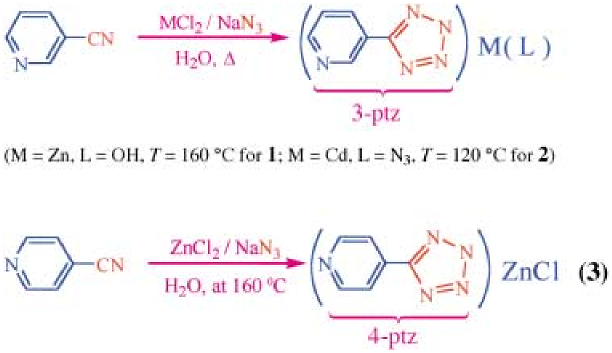
Although it is not always possible to exert synthetic control, a fascinating variety of acentric and novel MOCPs have been obtained from hydrothermal reactions.[4] These reactions are often quite complicated and may involve in situ hydrolysis, oxidation, and ligand synthesis. The products generated under hydrothermal conditions cannot normally be obtained by direct mixing of solutions of metal ions and ligands.[4]

Recently, Sharpless et al. reported a safe, convenient, and environmentally friendly procedure for the synthesis of a variety of 5-substituted 1*H*-tetrazoles in water. The 1*H*-tetrazoles are prepared by addition of azide to nitriles in water with Zn salts as Lewis acid catalysts (Scheme 1).[5] The role of Zn in this reaction is unclear, but it was suggested that the solid intermediate in the reaction of PhCN with $ZnBr_2$ and NaN_3 is $(PhCN_4)_2Zn$. The characterization of such an intermediate may provide important clues to the role of Zn in this reaction, and this in turn may allow synthetic chemists to further optimize this synthetic approach.

(M = Zn^{2+}, Co^{2+}, Mn^{2+}, Cd^{2+}, etc. Lewis acid)

Scheme 1. Synthesis of 1*H*-tetrazoles.

We recently combined metal salts with potentially bridging organic ligands under hydrothermal conditions to produce a range of new materials.[4b–f,6] Our experience with such systems prompted us to conduct structural studies of the products or "intermediates" in the hydrothermal reaction of $ZnCl_2$ (or $CdCl_2$) with 3-cyanopyridine (or 4-cyanopyridine) and NaN_3 in water (Scheme 2). To our surprise, the intermediates trapped or synthesized at high temperature all crystallize in acentric space groups and display SHG responses in the solid state which are unprecedented in tetrazole–metal coordination chemistry, as far as we are aware.[7] Here we report their solid-state structures and preliminary SHG properties.



(M = Zn, L = OH, *T* = 160 °C for **1**; M = Cd, L = N_3, *T* = 120 °C for **2**)

Scheme 2. Synthesis of **1**–**3**.

The reaction of NaN_3, 3-cyanopyridine, and $ZnCl_2$ or $CdCl_2$ in water yields [Zn(OH)(3-ptz)] (**1**) and [CdN_3(3-ptz)] (**2**), respectively, while the corresponding reaction of 4-cyanopyridine with $ZnCl_2$ gives [ZnCl(4-ptz)] (**3**). For each reaction the IR spectrum indicates the absence of the cyano group, which is consistent with a [2+3] cycloaddition between the cyano group and the azide anion. Crystal structure analyses of all products confirm the formation of 5-(3-pyridyl)tetrazolate (3-ptz) and 5-(4-pyridyl)tetrazolate (4-ptz), and show that the new ligand acts as a bridging ligand in each of the products **1**–**3**.

Compound **1** contains hydroxide and the 3-ptz ligand. In this structure parallel -Zn-OH-Zn-OH-Zn- chains extend in the *c* direction, while triply connecting 3-ptz ligands link the chains together (Figure 1 a).[8] The result is a complex two-dimensional (2D) polymer with five-coordinate Zn atoms bound to two OH^- and three 3-ptz ligands. Each ptz ligand coordinates through the 2,3 nitrogen atoms of the tetrazole and the pyridyl nitrogen atom. All donor atoms form reasonably strong bonds with the zinc atom (2.156(4) Å),

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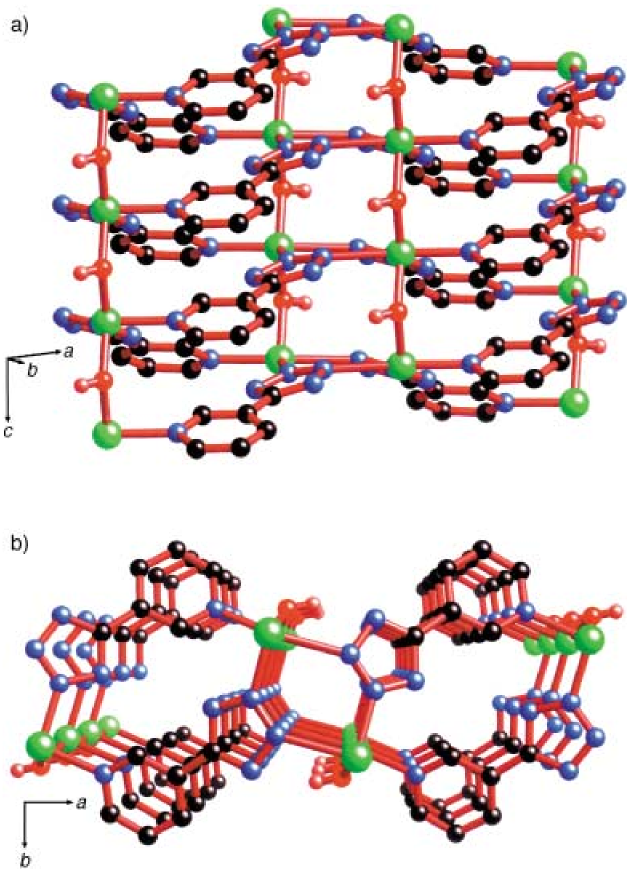

Figure 1. The 2D structure of **1**. a) A view almost normal to the axes of the twofold helices that extend in the *c* direction. b) A perspective view of the sheet structure from a direction parallel to the *c* axis.

except for the tetrazole nitrogen atom *trans* to the pyridyl group, which has a Zn−N distance of 2.464(4) Å. A unique structural feature present in each 2D sheet are helices that extend in the *c* direction. Zinc atoms of neighboring -Zn-OH-Zn-OH-Zn- chains, bridged by the pyridyl and tetrazole units of a single 3-ptz ligand, form part of twofold -Zn-ptz-Zn-ptz-Zn- helices. Two such helices within a sheet are apparent in Figure 1 a. Within a single sheet all helices have the same handedness, while neighboring sheets have helices of opposite handedness. Figure 1 b shows the sheet almost parallel to the axes of the helices.

Compound **2** unexpectedly contains azide.[8] The structure determination indicates a 3D polymer in which azide ligands adopt two distinct bridging modes in the structure. One unique 3-ptz ligand acts as a tetradentate unit. The complex structure is perhaps best understood by first considering zig-zag chains of cadmium atoms extending in the *c* direction (Figure 2 a). The two unique types of azide ions alternate as bridging ligands along the chain. In addition, each ptz ligand is linked to three cadmium atoms within each chain through the 1,2 nitrogen atoms of the tetrazole and the pyridyl nitrogen atom. Figure 2 b shows the chains viewed down the *c* axis. The bridging azide and 3-ptz ligands depicted in Figure 2 a provide five of the six donor atoms attached to the cadmium centers.

Identical parallel zig-zag chains also extend in the *c* direction. In addition to the coordinate bonds shown in Figure 2 a and 2 b each 3-ptz ligand also forms another link from the tetrazole ring (the nitrogen atom in the 4-position) to a cadmium center on a neighboring chain and thus completes the octahedral environment of the metal atom. All Cd−N bond lengths fall in the range 2.320(5)–2.495(12) Å. From each chain, links from the ptz ligands extend to two neighboring chains. Two other neighboring chains provide nitrogen atoms that link to the metal centers. Thus, each chain is linked to four other chains by coordinate bonds that are almost perpendicular to the *c* axis.

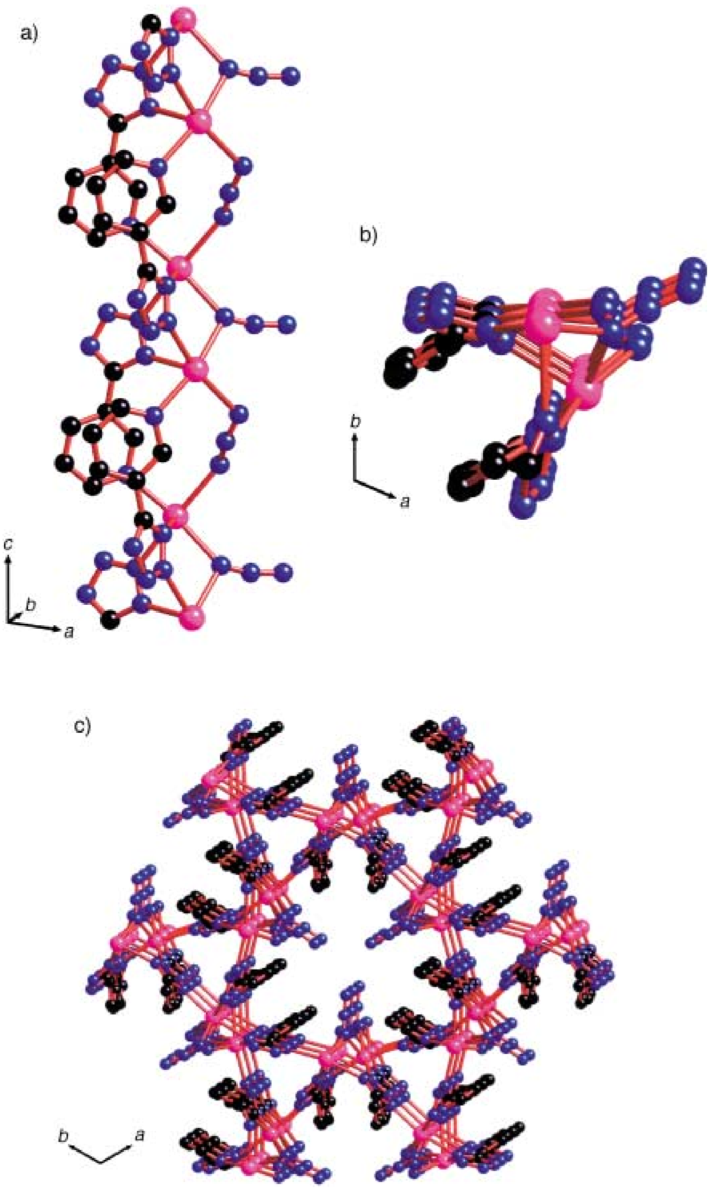

Figure 2. The 3D structure of **2**. a) Part of the zig-zag chain of Cd atoms bridged by azide ions and 3-ptz ligands. b) The zig-zag chains viewed down the *c* axis. c) The 3D structure of **2** viewed down the *c* axis. The interchain connections are almost normal to the *c* axis. Only one orientation for each disordered azide ion is shown.

Trios of connected chains form narrow channels of approximate trigonal cross section (Figure 2 c). Each chain is part of two such trios. Also present are larger channels formed by connection of six chains. Azide ligands extend from three of these chains towards the center of these larger channels and partially fill the network voids. These voids represent 220 Å^3

per unit cell, that is, 14.7% of the cell volume. The distance between cadmium atoms on opposite sides of the channel is equal to the cell dimension *a* of 13.8325(4) Å. The overall structure is chiral, with the crystal adopting the trigonal enantiomeric space group $P3_121$.

Compound **3** has the formula [ZnCl(4-ptz)] and a 3D network structure. Each 4-ptz ligand is bound to three Zn atoms, and each Zn atom is bound to three 4-ptz ligands. The tetrahedral coordination environment of each Zn atom is completed by a terminal chloride ion. All Zn–N distances are in the range between 2.026(4) and 2.037(3) Å. This complex coordination polymer is perhaps best understood in terms of [ZnCl(4-ptz)] strips that extend in the *c* direction. There are two unique four-coordinate Zn atoms and two unique 4-ptz ligands. In the strip shown in Figure 3a, one of the Zn atoms has its tetrahedral coordination environment completed by atoms within a strip. The other zinc atom relies upon coordination of a pyridyl group from a neighboring strip to complete its coordination sphere. Two identical parallel strips lying in a plane beneath the strip represented in Figure 3a provide the pyridyl groups that coordinate to the zinc atoms.

The apparently uncoordinated pyridyl groups represented in Figure 3a are in fact coordinated to Zn atoms of two identical parallel strips that lie above the plane of the strip shown. Thus, each strip is linked to four other strips in this infinite 3D network. Figure 3b shows the interstrip connections viewed parallel to the strips.

Inspection of Figure 3b reveals large channels with an approximately hexagonal cross section. These intraframework voids are occupied by a second identical network. The two networks are represented in Figure 3c.

Thermogravimetric analysis (TGA) of these crystalline complexes showed that **1**–**3** are stable up to about 270, 330, and 390 °C, respectively, while beyond these temperatures, they all decompose and lose their crystallinity.

The adoption of acentric space groups by **1**–**3** prompted an investigation of their optical activity. Preliminary investigations show that **1**–**3** are SHG active, with a relative strength order of **3** > **1** > **2**. The strong powder SHG response of **3** may be attributed to a good donor–acceptor system in which the pyridyl ring acts as acceptor and the tetrazole ring as donor. Such electronic asymmetry is essential for second-order optical nonlinearity.

In conclusion, apart from affording insights into the nature of the solids produced in the reactions by Sharpless et al., the work here provides strong encouragement that a wide variety of coordination polymers can be produced by hydrothermal generation of bridging ligands in the presence of appropriate metal ions. In particular the formation of ligands such as 3-ptz and 4-ptz that tend to place metal atoms in irregular arrangements but still allow the formation of infinite networks offers good prospects for generating acentric crystalline materials that may possess desirable physical properties such as SHG.

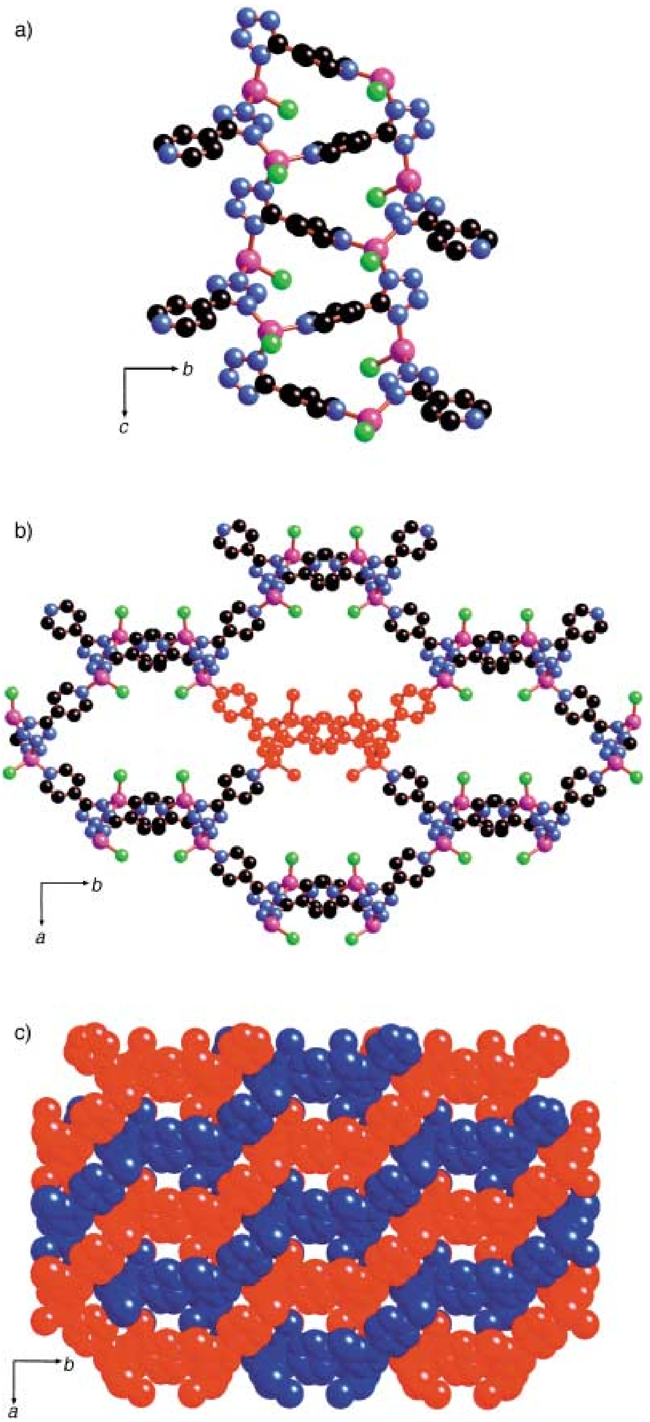

Figure 3. The 3D interpenetrating structure of **3**. a) [ZnCl(4-ptz)] strips extending in the *c* direction. b) A view down the *c* axis of **3** showing the connections between strips. The central strip is highlighted with red spheres. c) A space-filling model showing the interpenetration of the independent networks within the crystal.

Experimental Section

Preparation of $C_6H_5N_5OZn$ (**1**): Hydrothermal treatment of $ZnCl_2$ (2.0 mmol), 3-cyanopyridine (2.0 mmol), NaN_3 (3.0 mmol), and water (3.0 mL) for 1 d at 160 °C yielded crystalline colorless needles. The yield of **1** was about 75% based on 3-cyanopyridine. Elemental analysis (%) calcd for $C_6H_5N_5OZn$ (**1**): C 31.51, H 2.19, N 30.63; found C 31.72, H 2.26, N 30.92. IR (KBr): $\tilde{\nu}$ = 3398(vs), 3077(w), 1614(w), 1473(w), 1424(s), 1198(w), 1168(w), 1148(m), 1129(m), 1099(w), 1045(w), 1018(m), 952(w), 982(w), 818(m), 753(m), 717(m), 696(s), 650(w), 471(m) cm^{-1}.

Preparation of $C_6H_4N_8Cd$ (**2**): The procedure was identical to that of **1**, except that $CdCl_2$ was used instead of $ZnCl_2$ and the temperature was 120 °C. Colorless crystalline needles of **2** were formed in 55% yield. Elemental analysis (%) calcd for $C_6H_4N_8Cd$ (**2**): C 23.95, H 1.33, N 37.26; found: C 23.82, H 1.42, N 37.52. IR (KBr): $\tilde{\nu}$ = 3406(br w), 3089(w), 2075(vs;

ν(N_3^-)), 1612(w), 1585(w), 1457(w), 1428(m), 1363(m), 1291(w), 1202(w), 1165(m), 1128(w), 1022(m), 956(w), 931(w), 816(m), 762(m), 726(w) 696(m), 644(w), 450(w) cm^{-1}.

Preparation of $C_6H_4N_5ClZn$ (**3**): The procedure was identical to that of **1** except that 4-cyanopyridine was used instead of 3-cyanopyridine. Colorless crystalline blocks of **3** were formed with a 55 % yield. Elemental analysis (%) calcd for $C_6H_4N_5ClZn$ (**3**): C 29.16, H 1.62, N 28.34; found: C 29.30, H 1.60, N 28.52. IR (KBr): $\tilde{\nu} = 3538$(s), 3374(m), 3249(w), 3110(w), 3043(w), 2097(s), 1626(s), 1466(w), 1437(s), 1402(w), 1275(w), 1237(w), 1224(w), 1184(w), 1140(w), 1104(w), 1065(m), 1023(m), 847(m), 835(m), 759(w), 721(s), 564(w), 534(w), 472(w) cm^{-1}.

Measurement of SHG response: The second-order nonlinear optical intensity was approximately estimated by measuring a powder sample of 80–150 μm diameter in the form of a pellet (Kurtz powder test[9]) relative to urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate the SHG signal from the sample. The backscattered SHG light was collected by a spherical concave mirror and passed through a filter that transmits only 532 nm radiation. Thus the SHG response of **1–3** are about 0.4, 0.2, and 1.25 times that of urea, respectively.

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[8] Crystal Data for **1**: $C_6H_5N_5OZn$, $M_r = 228.52$, orthorhombic, $Fdd2$, $a = 19.595(4)$, $b = 40.930(8)$, $c = 3.5085(7)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 2813.9(10)$ Å^3, $Z = 16$, $\rho_{calcd} = 2.158$ Mg m^{-3}, $R_1 = 0.0499$, $wR_2 = 0.1142$, $T = 293$ K, $\mu = 3.447$ mm^{-1}, $S = 0.678$; Flack parameter $= 0.52(3)$. **2**: $C_6H_4N_8Cd$, $M_r = 300.57$, hexagonal, $P3_121$, $a = b = 13.8325(4)$, $c = 9.0673(4)$ Å, $\alpha = \beta = 90.00°$, $\gamma = 120.00°$, $V = 1502.48(9)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.993$ Mg m^{-3}, $R_1 = 0.0443$, $wR_2 = 0.1121$, $T = 293$ K, $\mu = 2.160$ mm^{-1}, $S = 0.704$, Flack parameter $= -0.04(5)$. **3**: $C_6H_4N_5ClZn$, $M_r = 246.96$, monoclinic, Pc, $a = 6.7191(5)$, $b = 14.0805(11)$, $c = 9.0468(7)$ Å, $\alpha = \gamma = 90.00$, $\beta = 90.600(2)°$, $V = 855.86(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.917$ Mg m^{-3}, $R_1 = 0.0411$, $wR_2 = 0.0970$, $T = 293$ K, $\mu = 3.135$ mm^{-1}, $S = 0.586$, Flack parameter $= 0.03(1)$. The structures were solved with direct methods by using the program SHELXTL.[10] All non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL by a full-matrix least-squares procedure. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final difference Fourier map was featureless. However, for compound **2**, initial attempts to model the bridging azide ions yielded unreasonable geometries for both types of azide ligand, and hence the azide groups were modeled as disordered units. In the case of ligand N7-N8-N9, which bridges cadmium atoms through a single atom (N7), atoms N8 and N9 are disordered around a twofold axis that passes through the mean positions of the three N atoms. Atoms N8 and N9 were both refined with isotropic displacement parameters. The other azide ligand (N5-N10-N11), which acts as a three-atom bridge between a pair of cadmium atoms, was also treated as a unit disordered over two closely positioned sites related by a twofold axis. In this case the twofold axis is almost perpendicular to the direction of the azide. All atoms of this azide ion were refined with a common isotropic displacement parameter. For both azide ions, interatomic distances were restrained to chemically sensible values. CCDC-184132–184134 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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