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Nonlinear Optically Active Polymeric Coordination Networks Based on Metal *m*-Pyridylphosphonates

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A family of polymeric coordination networks based on *meta*-pyridylphosphonate bridging ligands has been synthesized and characterized by single-crystal X-ray crystallography. Compounds $[\mathrm{M}_2(\mathbf{L}\text{-Et})_4(\mu\text{-H}_2\mathrm{O})]$ (M = Mn, **1**; Co, **2**; Ni, **3**; **L**-Et = ethyl-4-[2-(3-pyridyl)ethenyl]phenylphosphonate) were obtained by hydro(solvo)thermal reactions between diethyl-4-[2-(3-pyridyl)ethenyl]phenylphosphonate ($\mathbf{L}\text{-Et}_2$) and corresponding metal salts, while $[\mathrm{Cd}(\mathbf{L}\text{-H})_2]$, **4** (**L**-H is monoprotonated 4-[2-(3-pyridyl)ethenyl]phenylphosphonate), was obtained by a hydro(solvo)thermal reaction between $(\mathbf{L}\text{-H}_2)\cdot\mathrm{HBr}$ and $\mathrm{Cd(CF_3SO_3)_2\cdot 6H_2O}$. Compounds **1**–**3** are isostructural and crystallize in noncentrosymmetric space group *Fdd*2, and they adopt a complicated 3D framework structure composed of $[\mathrm{M}_2(\mathbf{L}\text{-Et})_4(\mu\text{-H}_2\mathrm{O})]$ building units, while compound **4** adopts a centrosymmetric 3D network structure resulted from linking 1D sinusoidal cadmium phosphate chains with **L**-H bridging ligands. Consistent with their polar structures, compounds **1**–**3** exhibit powder second harmonic generation signals larger than that of potassium dihydrogen phosphate.

Metal–organophosphonate hybrid frameworks have received significant attention in recent years owing to their potential applications in catalysis,[1] molecular recognition,[2] ion exchange,[3] and nonlinear optics (NLO).[4] Compared to more labile metal–bipyridine and metal–dicarboxylate linkages[5] that have been extensively used to construct single-crystalline metal–organic coordination networks, metal phosphonates tend to produce microcrystalline materials and are thus more difficult to characterize. Recent work by Clearfield et al.,[6] Bujoli et al.,[7] and Zubieta et al.[8] has established many novel pathways to single-crystalline metal–organophosphonates of X-ray diffraction quality. Motivated by our recent success in the rational synthesis of NLO-active polar solids based on bifunctional pyridinecarboxylate ligands,[9,10] we have recently explored the synthesis of metal–organic frameworks based on pyridylphosphonate bridging ligands. We report here the synthesis, X-ray structures, and preliminary second-order NLO properties of a family of polar 3D metal *meta*-pyridylphosphonates $[\mathrm{M}_2(\mathbf{L}\text{-Et})_4(\mu\text{-H}_2\mathrm{O})]$ (M = Mn, **1**; Co, **2**; Ni, **3**; **L**-Et = ethyl-4-[2-(3-pyridyl)ethenyl]phenylphosphonate). For comparison, the structure of centrosymmetric solid $[\mathrm{Cd}(\mathbf{L}\text{-H})_2]$, **4**, is also described.

As illustrated in Scheme 1, new compound *E*-diethyl-4-[2-(3-pyridyl)ethenyl]phenylphosphonate, $\mathbf{L}\text{-Et}_2$, was synthesized in good yields by a palladium-catalyzed phosphonation reaction of 3-(4-bromostyryl)pyridine, which was

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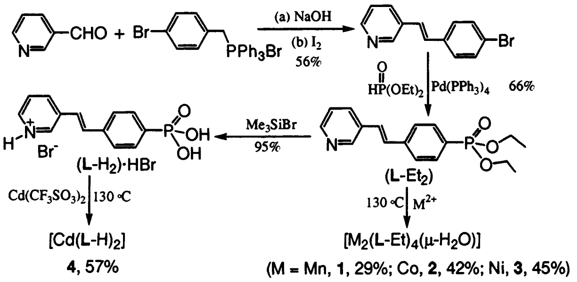
Scheme 1



prepared by a Wittig reaction between 3-pyridylaldehyde and (4-bromobenzyl)triphenyl phosphonium bromide followed by an iodine-catalyzed isomerization reaction.[11] New compound 4-[2-(3-pyridyl)ethenyl]phenylphosphonic acid hydrobromide, (**L**-H_2)·HBr, was obtained by treating **L**-Et_2 with trimethylsilylbromide. Both **L**-Et_2 and (**L**-H_2)·HBr have been characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Compounds **1**−**3** were prepared by reacting **L**-Et_2 with corresponding metal salts at 130 °C, while compound **4** was obtained by treating $Cd(CF_3SO_3)_2 \cdot 6H_2O$ with (**L**-H_2)·HBr at 130 °C.[12] The formulations of **1**−**4** have been supported by microanalysis and thermogravimetric results.[13,14] The IR spectra of **1**−**4** exhibited several bands between 1250 and 950 cm^{-1} that correspond to the characteristic stretching modes of the PO_3 groups.

Single-crystal X-ray diffraction studies reveal that compounds **1**−**3** are isostructural and crystallize in noncentrosymmetric space group *Fdd*2.[15] Their asymmetric unit consists of one metal center, two ethyl-4-[2-(3-pyridyl)-ethenyl]phenylphosphonate (**L**-Et) groups, and a bridging water molecule lying on a 2-fold axis (Figure 1). The **L**-Et ligand has two different bonding modes: an *exo*-tridentate linkage with a coordinating pyridyl nitrogen atom and a μ_2,η_2-phosphonate group, and an *exo*-bidentate linkage with a coordinating pyridyl nitrogen and a monodentate phosphonate group. Each metal atom is coordinated to three different phosphonate oxygen atoms, two pyridyl nitrogen atoms, and a bridging water oxygen atom to afford a slightly distorted octahedral geometry. A C2 operation around the *c* axis (passing through the bridging water molecule) generates a bimetallic moiety $[M_2(\mathbf{L}\text{-Et})_4(\mu\text{-}H_2O)]$ which serves as the building block for a complicated 3D solid.

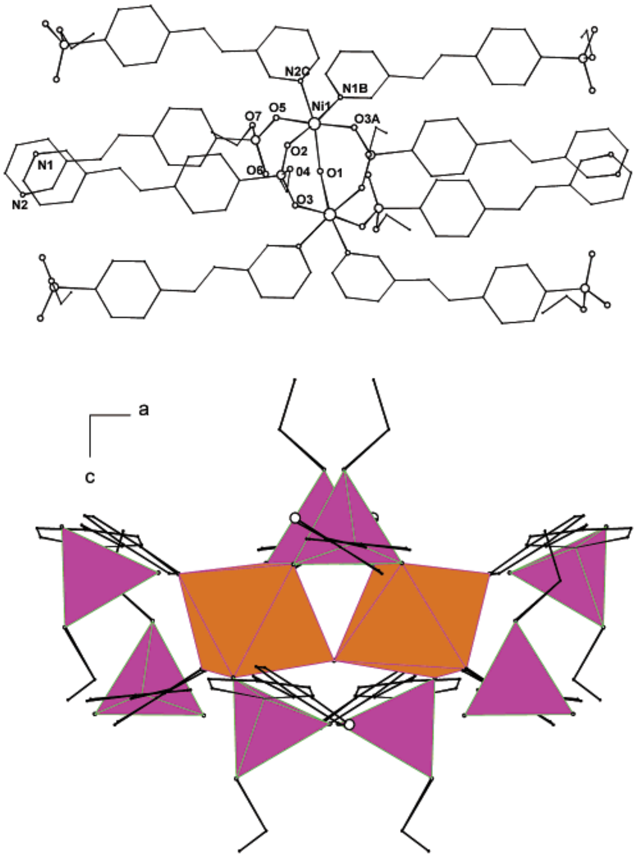


Figure 1. Top: view of the $[Ni_2(\mathbf{L}\text{-Et})_4(\mu\text{-}H_2O)]$ building unit of **3**. The circles with increasing sizes represent C, N, O, P, and Ni, respectively. Key bond distances (Å): Ni1−O1, 2.188(6); Ni1−O2, 2.039(7); Ni1−O3A, 2.064(6); Ni1−O5, 2.094(7); Ni1−N1B, 2.124(8); Ni1−N2C, 2.091(7). The cis angles around the Ni center range from 85.4(3)° to 99.5(3)°. Bottom: polyhedral presentation of the $[Ni_2(\mathbf{L}\text{-Et})_4(\mu\text{-}H_2O)]$ building unit showing the polar axis along the *c* axis.

Within an $[M_2(\mathbf{L}\text{-Et})_4(\mu\text{-}H_2O)]$ building unit, each metal center is connected to the other metal center through two μ_2,η_2-phosphonate groups and one bridging water molecule. Each $[M_2(\mathbf{L}\text{-Et})_4(\mu\text{-}H_2O)]$ unit is then linked to four adjacent $[M_2(\mathbf{L}\text{-Et})_4(\mu\text{-}H_2O)]$ units via double **L**-Et bridges to form a complicated 3D solid (Figure 2). Flexible ethoxy groups on the **L**-Et ligands effectively fill all the void spaces generated within the 3D framework, and compounds **1**−**3** do not have any included solvent molecules. Although compounds **1**−**3** crystallize in polar space group *Fdd*2, all the **L**-Et ligands adopt a centrosymmetric arrangement with all their dipoles canceling each other. The polar axes of **1**−**3** lie along the *c* axes; their polarity results from parallel arrangement of all the bridging water molecules as well as all the phosphonate groups.

Preliminary Kurtz powder second harmonic generation (SHG) measurements on compounds **1**−**3** confirm their acentricity.[16] Compounds **1**−**3** exhibit powder second har-

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(12) Detailed experimental procedures can be found in Supporting Information.

(13) Anal. Calcd (Found) for $C_{60}H_{62}N_4O_{13}P_4Mn_2$, **1**: C, 56.3 (55.8); H, 4.88 (4.34); N, 4.37 (4.68). Anal. Calcd (Found) for $C_{60}H_{62}N_4O_{13}P_4Co_2$, **2**: C, 55.9 (55.5); H, 4.85 (4.54); N, 4.35 (4.18). Anal. Calcd (Found) for $C_{60}H_{62}N_4O_{13}P_4Ni_2$, **3**: C, 55.9 (56.2); H, 4.85 (4.54); N, 4.35 (4.24). Anal. Calcd (Found) for $C_{26}H_{22}N_2O_6P_2Cd$, **4**: C, 49.4 (48.6); H, 3.50 (3.41); N, 4.43 (3.92).

(14) TGA results for **1**−**4** show no weight loss at temperatures below 210 °C, consistent with the absence of any included solvent molecules.

(15) Crystal data for **1**: space group *Fdd*2, $a = 16.3695(4)$ Å, $b = 55.4983(9)$ Å, $c = 13.8680(3)$ Å, $V = 12598.8(5)$ Å^3, $Z = 8$. Least-squares refinement based on 4166 reflections with $I > 2\sigma(I)$ and 365 parameters led to convergence, with a final R1 = 0.058, wR2 = 0.138, GOF = 1.04, and Flack parameter = 0.02(3). Crystal data for **2**: space group *Fdd*2, $a = 16.224(1)$ Å, $b = 54.869(1)$ Å, c = 13.801(1) Å, $V = 12286(1)$ Å^3, $Z = 8$. Least-squares refinement based on 4218 reflections with $I > 2\sigma(I)$ and 376 parameters led to convergence, with a final R1 = 0.058, wR2 = 0.111, GOF = 1.04, and Flack parameter = 0.00(1). Crystal data for **3**: space group *Fdd*2, $a = 16.111(2)$ Å, $b = 54.694(6)$ Å, $c = 13.820(2)$ Å, $V = 12178(2)$ Å^3, $Z = 8$. Least-squares refinement based on 1890 reflections with $I > 2\sigma(I)$ and 365 parameters led to convergence, with a final R1 = 0.048, wR2 = 0.105, GOF = 1.12, and Flack parameter = 0.00(3).

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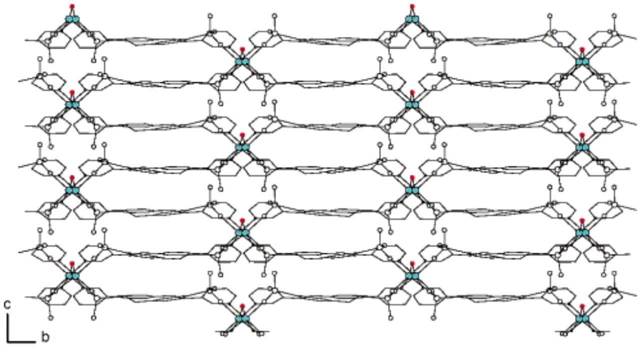

Figure 2. View of 3D network of **3** down the *a* axis. The parallel arrangement of bridging water molecules is shown in color. The ethyl groups have been omitted for clarity.

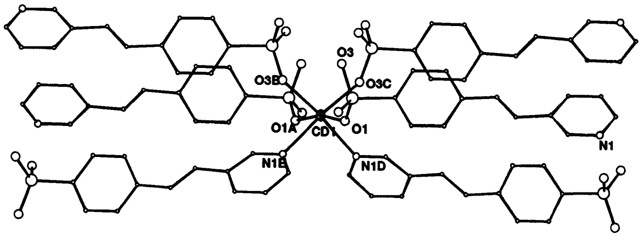

Figure 3. View of coordination environment of **4**. Key bond distances (Å): Cd1−O1, 2.244(2); Cd1−O3B, 2.307(2); Cd1−N1D, 2.375(2). The cis angles around the Ni center range from 82.9(1)° to 103.1(1)°.

monic intensities of 80, 10, and 70 versus α-quartz, respectively. These powder second harmonic intensities compare favorably with potassium dihydrogen phosphate (KDP has an $I^{2\omega}$ of 10 vs α-quartz).[16] The second harmonic responses of **1**−**3** evidently resulted from the polar arrangement of all the bridging water molecules and the phosphonate groups.

In contrast to compounds **1**−**3**, compound **4** crystallizes in centrosymmetric space group *Pbcn*.[17] The asymmetric unit contains one 4-[2-(3-pyridyl)ethenyl]phenylphosphonate (**L**-H) ligand and one Cd center lying on a crystallographic 2-fold axis (Figure 3). The **L**-H ligand adopts an *exo*-tridentate linkage with a coordinating pyridyl nitrogen atom and a μ_2,η_2-phosphonate bridge; the third phosphonate oxygen atom is present as a hydroxyl group with a P−O distance of 1.568(2) Å. The cadmium center is thus coordinated to four oxygen atoms of four different **L**-H groups and two different pyridyl nitrogen atoms to afford a distorted octahedral geometry.

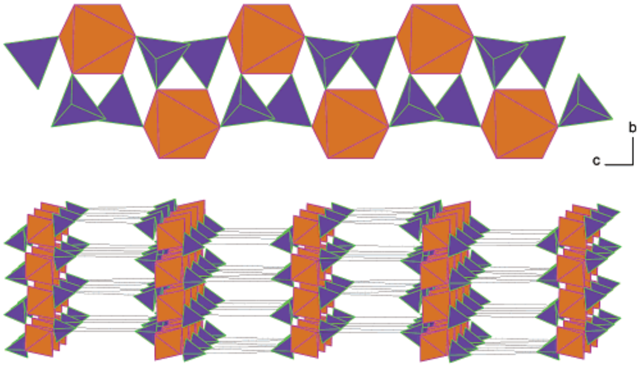

Figure 4. Top: polyhedral representation of the 1D sinusoidal cadmium phosphonate chain of **4** as viewed down the *a* axis. Bottom: view of the 3D network of **4** slightly off the *b* axis. The stilbazoles are represented with straight lines.

Each Cd center in **4** is doubly bridged by two phosphonate groups to two adjacent Cd centers to form a 1D sinusoidal cadmium phosphonate chain along the *c* axis (Figure 4). These 1D polymeric chains are further linked by **L**-H ligands to form a complicated 3D solid. There is no void space within the 3D framework to accommodate any solvent molecules. In contrast to compounds **1**−**3** which are built from [M_2(**L**-Et)$_4$(μ-H_2O)] building units, both the 1D sinusoidal cadmium phosphonates and **L**-H ligands in compound **4** are arranged in a centrosymmetric fashion. Compound **4** thus crystallizes as a centrosymmetric solid.

In summary, we have synthesized and characterized a series of 3D polymeric coordination networks based on metal *m*-pyridylphosphonates. These polar metal−organophosphonate hybrid frameworks exhibit powder second harmonic generation signals larger than that of KDP. This work thus illustrates the potential of combining high stability of metal−phosphonates and the tunability of the bifunctional pyridylphosphonate ligands in designing novel materials with interesting properties.

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Supporting Information Available: Experimental procedures, two tables of structural data, three figures of structures and TGA curves, and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Crystal data for **4**: space group *Pbcn*, $a = 27.904(8)$ Å, $b = 11.640(3)$ Å, $c = 7.546(2)$ Å, $V = 2451(2)$ Å^3, $Z = 4$. Least-squares refinement based on 2344 reflections with $I > 2\sigma(I)$ and 168 parameters led to convergence, with a final R1 = 0.024, wR2 = 0.060, and GOF = 1.06.