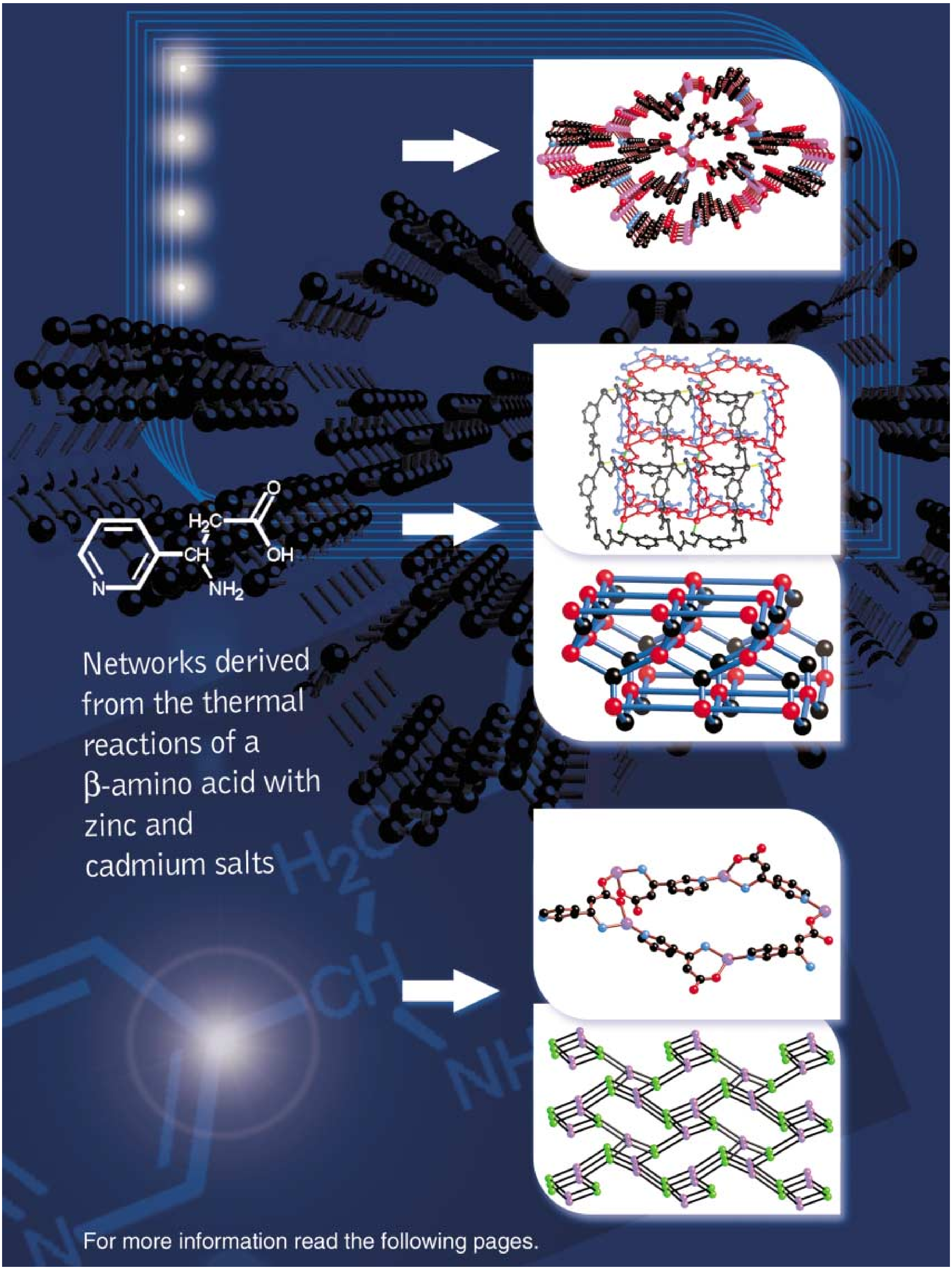

Networks derived from the thermal reactions of a β-amino acid with zinc and cadmium salts

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Synthesis of Novel Chiral and Acentric Coordination Polymers by the Reaction of Zinc or Cadmium Salts with Racemic 3-Pyridyl-3-aminopropionic Acid

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Abstract: Under hydrothermal (solvothermal) reaction conditions chiral compounds **1**, **2**, and **3** and one acentric compound **4** were obtained by the reaction of Zn^{2+} or Cd^{2+} with racemic 3-(3-pyridyl)-3-aminopropionic acid (*rac*-HPAPA). Compounds **1** and **2** crystallized in chiral space group $P2_12_12_1$. At 105 °C, racemic 3-pyridyl-3-aminopropionic acid (*rac*-HPAPA) reacted with $Zn(ClO_4)_2 \cdot 6H_2O$ and dehydrogenated in situ to form the first chiral coordination polymer [Zn{(*E*)-3-C_5H_4N–C(NH_2)=CH–COO}]ClO_4 (**1**) with a β-dehydroamino acid. Beyond 120 °C, the reaction of *rac*-HPAPA with $Zn(ClO_4)_2 \cdot 6H_2O$ deaminates in situ to form chiral coordination polymer [Zn{(*E*)-3-C_5H_4N–CH=CH–COO}(OH)] (**2**). At relatively low temperatures (70 °C), the solvothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$ with *rac*-HPAPA in methanol does not lead to any change in the ligand and results in the formation of a chiral ($P2_12_12_1$) coordination polymer [Zn(papa)(NO_3)] (**3**). The same reaction of $Cd(ClO_4)_2 \cdot 6H_2O$ with HPAPA also does not lead to any change in ligand and results in the formation of noncentric (*Cc*) coordination polymer [Cd(papa)(Hpapa)]$ClO_4 \cdot H_2O$ (**4**). The network topology of both **1** and **3** is 10,3a, while **2** has a diamondoid-like (KDP-like, KDP = potassium dideuterophosphate) network. Particularly interesting from a topological perspective is that **4** has an unprecedented three-dimensional network. Compounds **1**, **2**, **3**, and **4** are all second harmonic generation (SHG) active with **1** exhibiting the strongest response, while only **4** also displays good ferroelectric properties.

Keywords: cadmium · ferroelectric materials · nonlinear optics · polymers · zinc

Introduction

Triboluminescence, second harmonic generation (SHG), piezoelectricity, pyroelectricity, and ferroelectricity are only found in noncentrosymmetric bulk materials.[1] Due to the practical importance of these properties in many technological applications, such as telecommunications, optical storage, and information processing, there has been very strong interest in employing crystal-engineering strategies to generate desirable materials. Such approaches have succeeded in producing chiral or acentric coordination polymers and organic compounds.[2–3]

Ferroelectric materials in particular are of great interest, because they can be rapidly switched between different states by applying an external electric field. Furthermore, they display good memory capacity in the absence of an external field due to their hysteresis-loop behavior. It is this property that is of value in the aforementioned applications. In ferroelectric compounds such as KDP (KD_2PO_4) and TGS (triglycine sulfate, $(NH_2CH_2COOH)_3 \cdot H_2SO_4$) the hydrogen-bonding interactions are responsible for the arrange-

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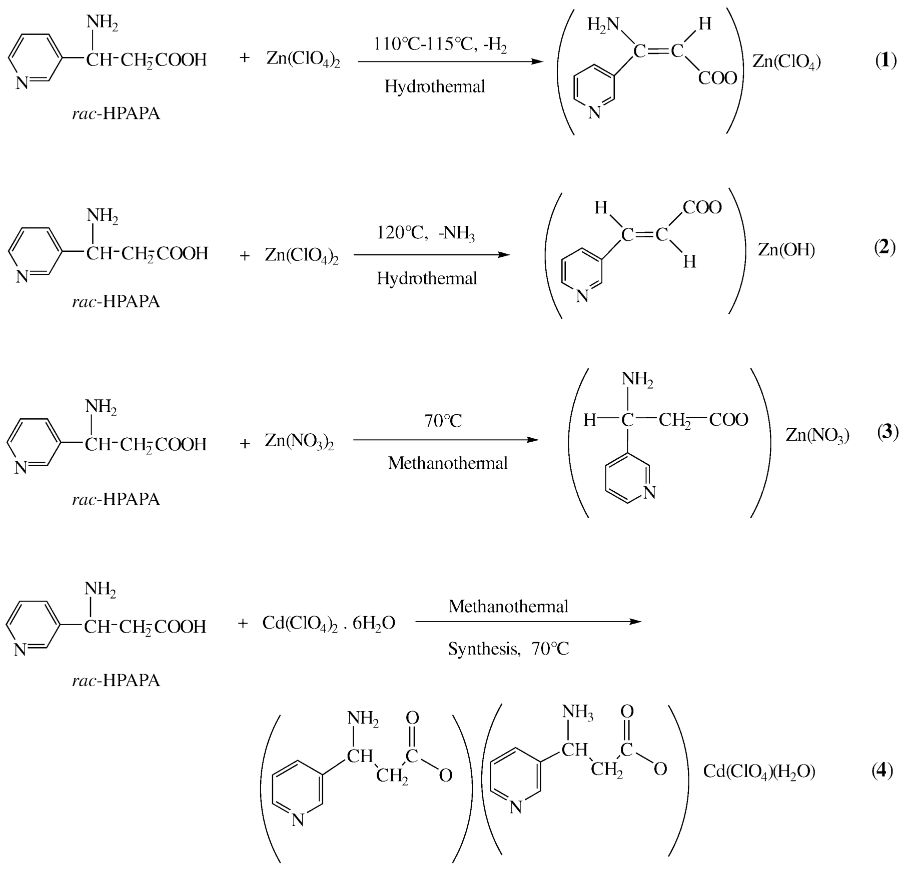
ments of the ions that lead to the adoption of the polar-space groups, *Fdd*2 and $P2_1$, respectively. It is not unreasonable to expect that the use of low-symmetry-bridging ligands in coordination polymers may lead to structures that also exhibit desirable physical properties such as ferroelectric behavior. In this regard, crystal engineering offers great scope in the quest for new materials that exhibit useful properties.

Of special interest to us is the generation of polar metal-coordination polymers using hydrothermal techniques. Under such conditions, in situ hydrolysis[4a] and oxidation[4b] can lead to the conversion of cyano, ester, and aldehyde groups to carboxylate. Recently it has been demonstrated that hydrothermal conditions may be used to form SHG-active coordination polymers incorporating tetrazole-based ligands, formed in situ by the 1,3-polar addition reaction between cyano and azide in the presence of metal ions.[4c] It is worth noting that these products could not be obtained using conventional solution synthesis techniques.



Scheme 1.

Although there has been recent interest in the employment of α-amino acids in the construction of novel supramolecular structures,[5] the use of β-amino acids as bridging ligands in coordination polymers has remained largely unexplored. The chiral anion 3-pyridyl-3-aminopropionate (PAPA, an anion of a β-amino acid) is an attractive ligand for use in the generation of polar coordination polymers, especially when one considers that the ferroelectric compound TGS possesses amino acid functionality. Not only does PAPA have the capability to act as an asymmetric bridge between metal centers, but its potential to behave as a chelating anion is likely to enhance the stability of coordination polymers in which it is incorporated. Accordingly, the solvothermal reactions of zinc and cadmium salts ($Zn(ClO_4)_2$ or $Zn(NO_3)_2$ and $Cd(ClO_4)_2$) with racemic 3-pyridyl-3-aminopropionic acid (*rac*-HPAPA) were undertaken at a range of temperatures (Scheme 1).

Results and Discussion

The hydrothermal reaction of $Zn(ClO_4)_2$ and *rac*-HPAPA in the temperature range 105–115 °C yields a coordination polymer with formula $[Zn\{(E)\text{-}3\text{-}C_5H_4N\text{–}C(NH_2)\text{=}CH\text{–}COO\}]ClO_4$ (**1**). In this compound, dehydrogenation of the PAPA anion has occurred to yield the anion of a β-dehydroamino acid. A strong peak at approximately 1120 cm^{-1} in the IR spectrum of **1** indicates the presence of perchlorate, while two peaks at 1549 and 1442 cm^{-1} are consistent with the coordination of carboxylate to a Zn ion. A medium broad peak at 3400–3247 cm^{-1} may be attributed to the amino group in **1**.

The IR spectrum of **1** is consistent with the structure determination, which shows one unique ligand and one unique zinc center. The double bond arising from the dehydrogenation is indicated by a C–C separation of 1.368(17) Å. Steric constraints prevent the pyridyl group from lying in the same plane as the rest of the ligand. An oxygen of the carboxylate and the amino nitrogen are the donor atoms of a six-membered chelate ring, while the other oxygen atom of the carboxylate and the pyridyl nitrogen atom bind to two other equivalent zinc centers. Thus each ligand is bound to three zinc centers and each zinc atom is bound to three ligands (see Figure 1). The donor atoms form a distorted tetrahedral environment around the metal center. Two oxygen atoms belonging to perchlorate anions are very weakly coordinated with Zn–O separations of ~2.6 Å. To the best of our knowledge, **1** represents the first example of a coordination polymer containing a β-dehydroamino acid anion as a bridging ligand.

The ability of the pyridyl amino acid to act as a bridging ligand results in the formation of a three-dimensional coordination network. In this cationic network each ligand serves as a three-connecting center, as does each metal

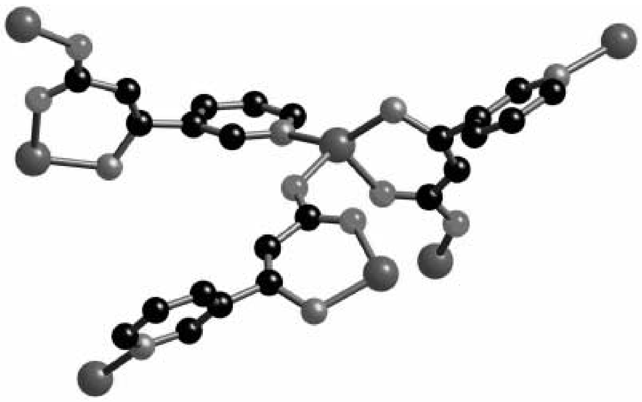


Figure 1. Part of the structure of the cationic framework of **1** (L = 3-amino-3-pyridylacrylate) showing the four-coordinate zinc atoms and the ligand linking to three other zinc centers. H atoms and perchlorate have been omitted for clarity. Typical bond lengths (Å): Zn–N 2.024(7)–2.029(8); Zn–O 1.967(7)–2.005(7).

center. The network has the topology of the 10,3a net—a net that possesses a particularly high symmetry in its most regular geometric form. The ideal net, which is represented at the top of Figure 2, is characterized by fourfold helices that run in three perpendicular directions and have all the same handedness, resulting in a chiral net. The shortest circuit including a pair of connections from a single node is a ten-membered circuit. At the bottom of Figure 2, two types of three-connecting nodes are represented: one corresponding to the position of the zinc center, the other indicating the three-connecting ligand (the position of this point is arbitrary). Although there is a severe geometric distortion of the ideal 10,3a net, as shown in Figure 2 (bottom), it is clear that the connectivity of the net is the same.[6] In Figure 3, one of the ten-membered circuits of the real structure (five ligands and five zinc centers) is represented. The intra-network voids are occupied by perchlorate anions. An attempt to exchange perchlorate with nitrate within the crystals was unsuccessful.

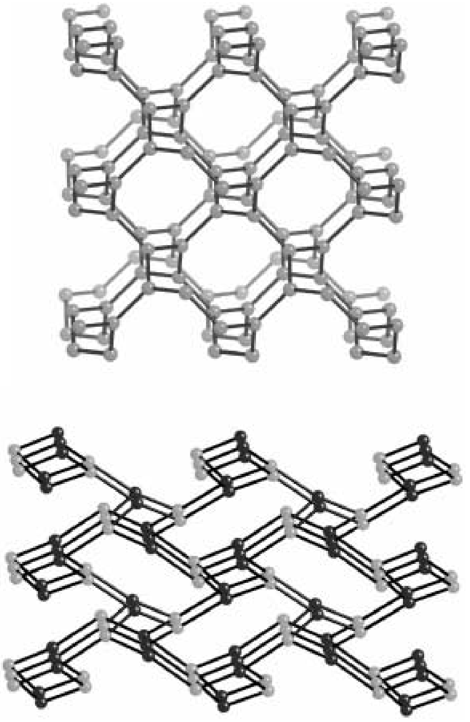


Figure 2. Top: The ideal cubic 10,3a network; bottom: The geometrically distorted 10,3a network representing the connectivity of **1**. Black spheres represent the zinc centers, gray spheres represent the ligand, placed in an arbitrary position.

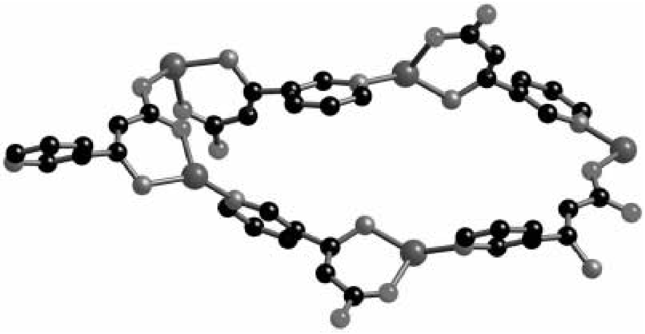


Figure 3. A "ten-membered circuit" in the structure of **1** constructed from five ligands and five zinc centers. H atoms have been omitted for clarity.

When the hydrothermal reaction of $Zn(ClO_4)_2$ and *rac*-HPAPA is repeated at 120 °C, deamination occurs, resulting in the formation of a coordination polymer with formula $[Zn\{(E)\text{-}3\text{-}C_5H_4N\text{–}CH{=}CH\text{–}COO\}(OH)]$ (**2**) (see Scheme 1). Two strong peaks at 1650–1596 and 1356 cm^{-1} in the IR spectrum of **2** support the presence of a carboxylate group, while the absence of a peak in the 3300 cm^{-1} region is consistent with the loss of the amino group. The ligand, which is essentially planar, is bound to only two zinc centers, through a carboxylate oxygen atom and the pyridyl nitrogen atom. Each zinc atom is coordinated by two such ligands and two bridging hydroxide ions, giving rise to a distorted tetrahedral environment (see top diagram of Figure 4). The structure is supported by hydrogen-bonding interactions extending from the hydroxide ions to the coordinated oxygen atom on neighboring zinc centers.

From a topological perspective each zinc center may be considered as a four-connecting node, which links to equivalent four-connecting centers through bridging ligands (two hydroxides and two pyridyl propenoates). Since each of these ligands is only two-connecting they are only considered as connections and not nodes in the resulting net. The net has the same topology as that found in diamond, although there is a considerable geometric distortion of the ideal net (see bottom of Figure 4). The adamantane-type unit, which is composed of ten nodes and four six-membered circuits, is a feature of all diamond nets and is represented in Figure 5 (left) in its most symmetrical form.[7] In Figure 5 (right) the connections between the zinc centers in an adamantane-type unit in **2** are represented by linear connections. A comparison of the two diagrams in Figure 5 highlights the distortion of the net.

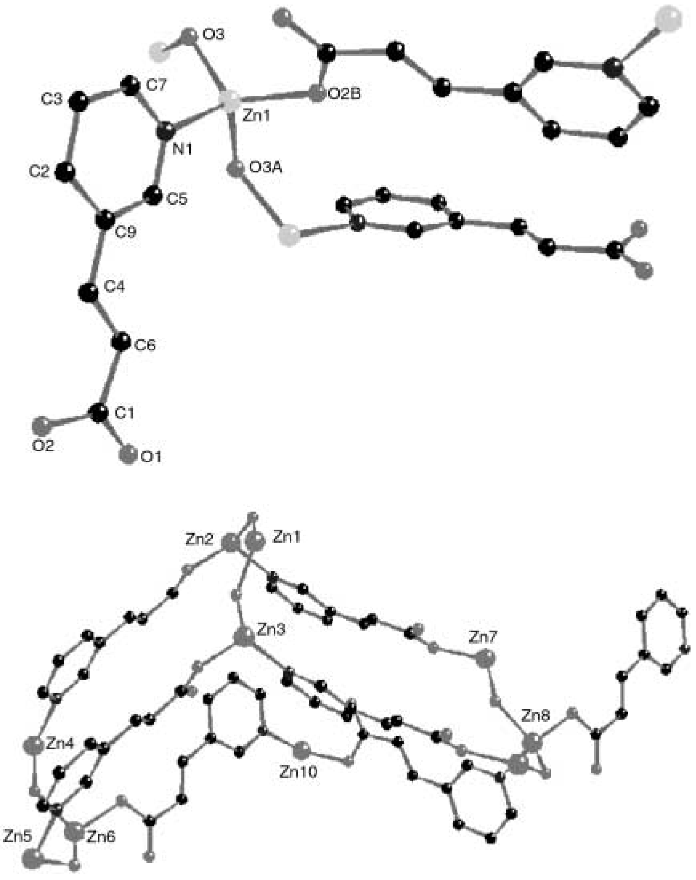


Figure 4. Top: Asymmetric unit representation of **2**. Typical bond lengths (Å): Zn–N 2.055(2); Zn–O 1.911(2), 1.944(2)–1.951(2); bottom: A diamond-like net representation in **2** showing that ten Zn atoms could be composed of net.

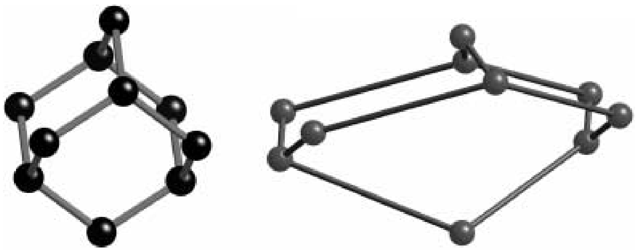


Figure 5. Left: A typical diamond-like net representation; right: Distorted diamond-like net representation of **2**.

The solvothermal reaction of $Zn(NO_3)_2$ with *rac*-HPAPA in methanol at 70 °C does not lead to any change in the ligand and results in the formation of a coordination polymer with the formula $[Zn(papa)(NO_3)]$ (**3**). The IR spectrum shows a strong peak at $1200\,cm^{-1}$ indicating the presence of nitrate, while a broad peak at approximately $3300\,cm^{-1}$ is consistent with the presence of an amino group.

The coordination mode of the ligand is similar to that found in **1**. Each Zn center is bound to three PAPA ligands and a monodentate nitrate anion resulting in a five-coordinate environment (see Figure 6). As far as the network connectivity is concerned, both the ligand and the zinc center serve as three-connecting centers as in **1**, and indeed the resulting network has the 10,3a topology.

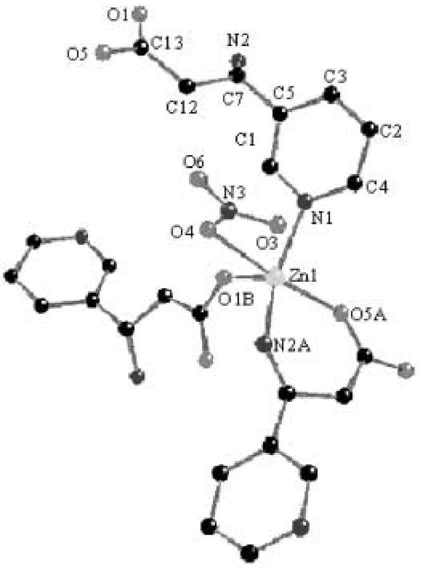


Figure 6. Asymmetric unit representation of **3** showing Zn center has a five-coordinate mode in which its structural topology is similar to that found in **1**. Typical bond lengths (Å): Zn–O 1.988(3), 2.046(4)–2.054 (4); Zn–N 2.054(5)–2.086(4).

Crystals of $[Cd(papa)(Hpapa)]ClO_4{\cdot}H_2O$ (**4**) were also obtained by a methanothermal reaction at 70 °C. In this reaction, $Cd(ClO_4)_2{\cdot}6\,H_2O$ and *rac*-HPAPA were heated over a period of a week. A strong peak at about $1114–1036\,cm^{-1}$ suggests the presence of perchlorate anion, while a broad peak at approximately $3300\,cm^{-1}$ is consistent with the presence of an amino group.

The coordination polymer is a three-dimensional anionic network containing a unique cadmium atom and two unique bridging ligands. The connectivity of the network is perhaps most easily understood in terms of square-grid sheets that extend in the *ab* plane (see Figure 7 (top)). The ligands that extend down the page (vertical ligands) in Figure 7 (top) are identical, but are different to the ligands that bridge Cd atoms across the page (horizontal ligands). For the vertical ligands, the primary amino groups are protonated, forming primary ammonium groups. This nitrogen atom and the non-coordinated carboxylate oxygen atom are involved in an intra-ligand hydrogen bond.

The amino groups of the horizontal ligands coordinate to Cd atoms of a symmetry-related sheet lying above the plane of the sheet shown in Figure 7 (top). The Cd atoms are also coordinated by nitrogen atoms from amino groups belonging to a symmetry-related sheet lying below the plane. The links between these three planes are indicated in Figure 7 (bottom) with the black spheres representing the atoms depicted in the upper part of Figure 7. Coordination bonds, which extend from the amino groups of the black sheet to the Cd atoms of the red sheet, are indicated by green bonds. Yellow bonds from the amino groups of the blue sheet to the Cd atoms of the black sheet also represent coordination bonds. This stacking and linking of sheets extends in the *c* direction with the blue and the red sheet, related by a unit-

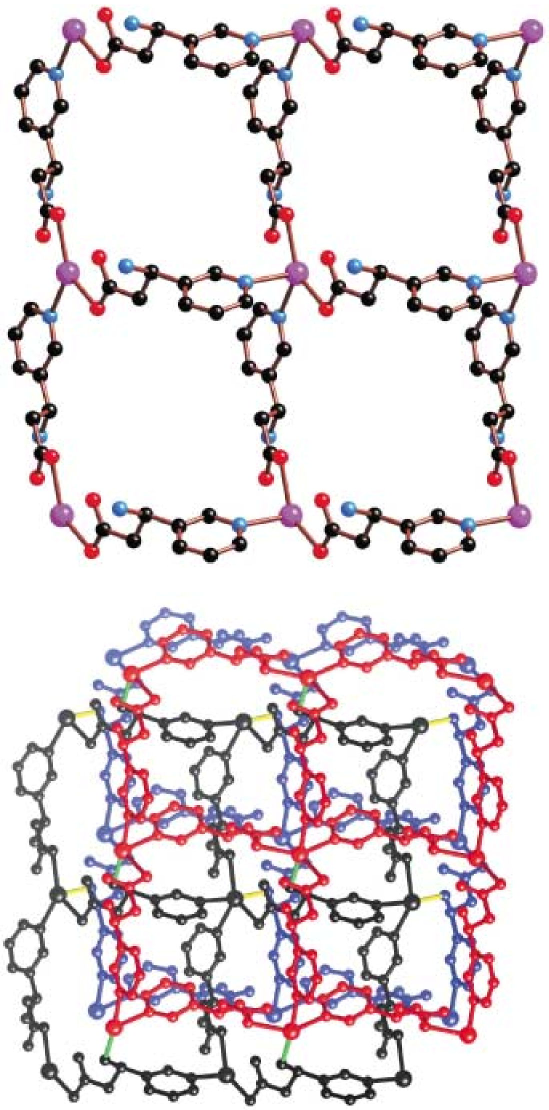


Figure 7. Top: Part of the structure of **4** showing a 2D sheet that extends in the *ab* plane; bottom: The 3D structure of **4** showing the links between neighboring sheets (yellow and green bonds). Typical bond lengths(Å): Cd–N 2.334(4), 2.345(3)–2.372(4); Cd–O 2.322(6), 2.351(3)–2.552(4).

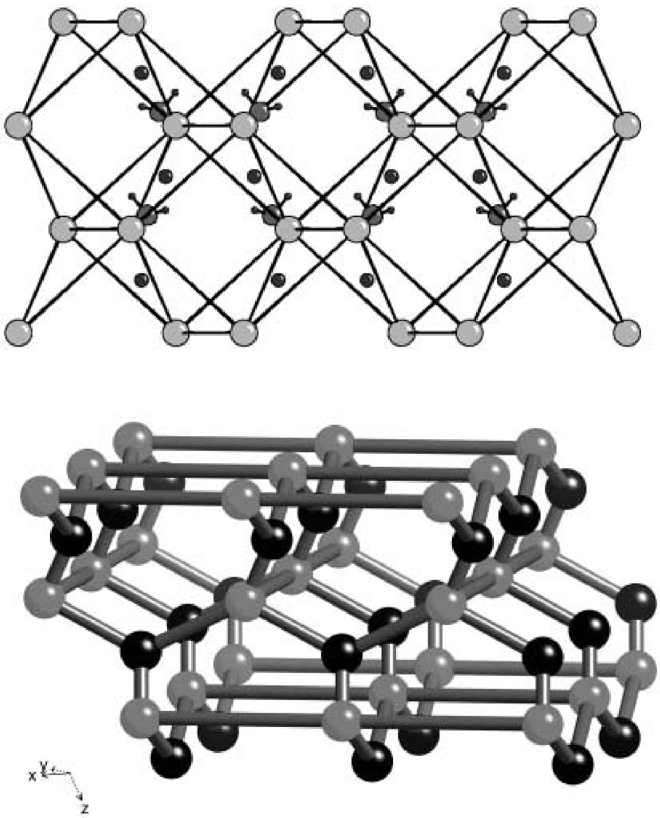


Figure 8. Top: A simplified network representation of **4** showing there are many hydrogen bonds between perchlorate, water, and protonated amino groups (not shown) along the *c* axis. Black, dark gray, and pale gray balls represent O, Cl, and Cd atoms respectively; bottom: a topological representation of **4**. The gray spheres indicate Cd centers; the black spheres represent the three-connecting ligands and the Cd–Cd connections represent the two-connecting ligands.

cell translation in the *c* direction. Interestingly, there is extensive hydrogen bonding between protonated amino groups, perchlorate anions, and water, as is the case in TGS (Figure 8 top diagram).

From a topological perspective the underlying network is particularly interesting. Although the two unique ligands are chemically similar, the roles they play in the net connectivity are quite different. One of the ligands connects to three cadmium centers and is therefore considered as a three-connecting node in the network structure. These nodes are represented by the black spheres in Figure 8 (bottom) and have been placed in an arbitrary position. The other type of ligand is only two-connecting and for this reason it is not treated as a node in the network. It is represented in the net by direct connections between Cd centers (gray spheres). Thus the net (Figure 8 bottom) contains equal numbers of three- and five-connecting nodes that form the infinite three-dimensional network. As far as we are aware this net has not previously been observed; however, there is a close relationship with the 10,3b net. If the direct connections between the gray spheres are ignored then all nodes are three-connecting and the net has the same topology as 10,3b.[8]

Given that products **1**, **2**, and **3** all crystallize in a chiral space group ($P2_12_12_1$), while **4** adopts a polar space group, an investigation of their optical properties was undertaken. Preliminary examinations of powdered samples indicate that **1**, **2**, **3**, and **4** are all SHG active, with **1** exhibiting the strongest response. The presence of the amino group, which can be considered as a very good donor, may be expected to enhance the electronic asymmetry (pull–push effect) that is essential for nonlinear optical behavior, such as in the case of **1**. The space group $P2_12_12_1$ is associated with the point group $D2$ and accordingly **1**, **2**, and **3** fail to display ferroelectric properties. These cases are similar to that found for SHG-active KDP (the hydrogen-bonded network is diamond-like and it crystallizes in $P2_12_12_1$). Interestingly, **4** crystallizes in the space group *Cc*, which corresponds to the polar point group C_s, one of the point groups required for ferroelectric behavior. Experimental results indicate that **4** does indeed display ferroelectric behavior. Figure 9 clearly shows there is an electric hysteresis loop that is a typical ferroelectric feature with a remnant polarization (*Pr*) of 0.18–

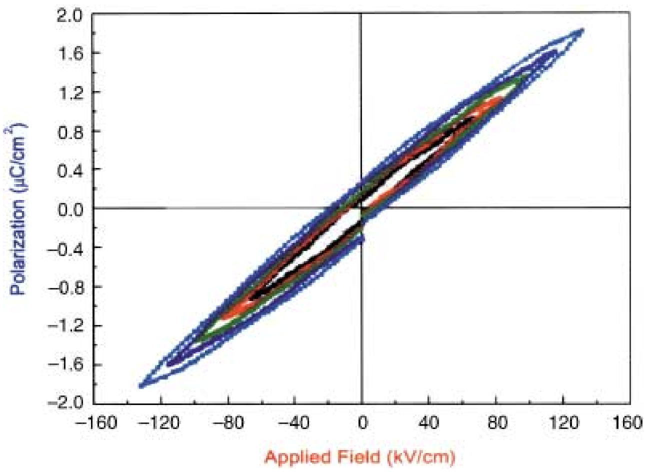


Figure 9. The electric hysteresis loop of **4** was observed by Virtual Ground Mode for a powdered sample in the form of a pellet using an RT6000 ferroelectric tester at room temperature.

0.28 μC cm^{-2} and coercive field (*Ec*) of 12 kV cm^{-1}. The saturation spontaneous polarization (*Ps*) of **4** is about 1.2–1.8 μC cm^{-2}, while that of ferroelectric KDP and TGS are 5.0 and 3.0 μC cm^{-2}, respectively.[9] It is interesting to note that comparable values are found for **4** and TGS, given that both contain protonated amino groups which participate in extensive hydrogen bonding. To the best of our knowledge, **4** represents the first example of a polar coordination polymer that exhibits ferroelectric behavior.

In conclusion, the successful synthesis of chiral or acentric coordination polymers with SHG and ferroelectric properties from the reaction of racemic, low-symmetry, multifunctional ligands with metal salts under solvothermal conditions has been achieved. Although it is difficult to predict the nature of the ligand rearrangements and connectivity of the resulting network, the results presented indicate that the generation of interesting and perhaps technologically useful asymmetric networks can be readily achieved using racemic reactants and a relatively straightforward synthetic approach.

Experimental Section

General: In all cases only one-component pure crystals grew on the wall of the Pyrex tube used and their powder X-ray diffraction pattern was identical to that of single-crystal X-ray diffraction determination.

Preparation and analysis of $C_8H_7ClN_2O_6Zn$ (1): Hydrothermal treatment of $Zn(ClO_4)_2\cdot 6H_2O$ (1.0 mmol) and HPAPA (1 mmol) over one day at 115 °C yielded colorless crystalline needles. Yield: ca. 35 %, based on HPAPA. IR (KBr): $\tilde{\nu}=3448$ (w), 3327 (w), 3246 (w), 1619 (w), 1576 (w), 1549 (s), 1492 (w), 1443 (s), 1396 (w), 1121 (vs), 1088 (s), 995 (w), 955 (w), 857 (w), 823 (w), 706 (m), 666 (w), 626 cm^{-1} (m); elemental analysis calcd (%) for $C_8H_7ClN_2O_6Zn$: C 29.28, H 2.13, N 8.54; found C 29.36, H 2.06, N 8.72.

Preparation and analysis of $C_8H_7NO_3Zn$ (2): The procedure was identical to that used for **1** except that the temperature was increased to above 120 °C. Colorless crystalline needles of **2** were formed with a 55 % yield. IR (KBr): $\tilde{\nu}=3537$ (vw), 3061 (vw), 1650 (s), 1596 (s), 1479 (m), 1437 (m), 1356 (s), 1298 (w), 1208 (w), 1127 (m), 1058 (m), 986 (s), 903 (w), 882 (w), 815 (m), 744 (m), 686 (m), 654 (w), 611 (w),547 (w), 509 (w), 421 cm^{-1} (w); elemental analysis calcd (%) for $C_8H_7NO_3Zn$: C 41.65, H 3.04, N 6.07; found: C 41.80, H 3.12, N 6.32.

Preparation and analysis of $C_8H_9N_3O_5Zn$ (3): The procedure was identical to that used for **1** except that the temperature was decreased to 70 °C and methanol was used instead of water. Colorless crystalline blocks of **3** were formed with a 25 % yield. IR (KBr): $\tilde{\nu}=3298$ (w), 3243 (w), 3161 (w), 3077 (w), 2966 (w), 1604 (vs), 1568 (s), 1442 (vs), 1385 (s), 1323 (s), 1196 (w), 1118 (w), 1062 (w), 1042 (w), 1001 (w), 955 (w), 886 (w), 821 (w), 713 (m), 680 (w), 655 (w), 622 (w), 538 (w), 447 cm^{-1} (w); elemental analysis calcd (%) for $C_8H_9N_3O_5Zn$: C 32.81, H 3.08, N 14.36; found: C 32.65, H 3.16, N 14.52.

Preparation and analysis of $C_{16}H_{21}N_4O_9ClCd$ (4): The procedure was identical to that used for **3** except that $Cd(ClO_4)_2$ was used instead of $Zn(NO_3)_2$ and the mixture was heated for one week. Colorless crystalline blocks of **4** were formed with a 25 % yield. IR (KBr): $\tilde{\nu}=3448$ (w), 3325 (w), 3254 (w), 3085 (w), 3022 (w), 2963 (w), 2923 (w), 1550 (vs), 1483 (m), 1429 (s), 1127 (m), 1114 (vs), 1036 (vs), 995 (w), 945 (w), 923 (w), 890 (w), 880 (w), 856 (w), 843 (w), 823 (m), 810 (m), 712 (m), 651 (m), 634 (m), 538 (w), 548 (w), 496 cm^{-1} (w); elemental analysis calcd (%) for $C_{16}H_{21}N_4O_9ClCd$: C 34.21, H 3.74, N 9.98; found: C 34.35, H 3.66, N 10.12.

X-ray crystallography

Crystal data for 1: $M_r=327.88$; orthorhombic; $P2_12_12_1$; $a=7.1497(8)$, $b=9.5284(10)$, $c=16.0211(17)$ Å; $V=1091.4(2)$ Å^3; $Z=4$; $\rho_{calcd}=1.996$ Mg m^{-3}; $R_1=0.0727$; $wR_2=0.1712$; $T=293$ K; $\mu=2.517$ mm^{-1}; $S=1.090$; Flack value: $\chi=-0.04(5)$.

Crystal data for 2: $M_r=230.52$; orthorhombic; $P2_12_12_1$; $a=5.3597(5)$, $b=9.9042(10)$, $c=15.6760(16)$ Å; $V=832.14(14)$ Å^3; $Z=4$; $\rho_{calcd}=1.840$ Mg m^{-3}; $R_1=0.0206$; $wR_2=0.0637$; $T=293$ K; $\mu=2.919$ mm^{-1}; $S=0.578$; Flack value: $\chi=0.015(14)$.

Crystal data for 3: $M_r=292.55$; orthorhombic; $P2_12_12_1$; $a=7.2039(9)$, $b=8.7309(11)$, $c=16.234(2)$ Å; $V=1021.1(2)$ Å^3; $Z=4$; $\rho_{calcd}=1.903$ Mg m^{-3}; $R_1=0.0561$; $wR_2=0.1496$; $T=293$ K; $\mu=2.421$ mm^{-1}; $S=0.946$; Flack value: $\chi=0.08(3)$.

Crystal data for 4: $M_r=561.22$; monoclinic; Cc; $a=14.0169(12)$, $b=13.5045(12)$, $c=12.5050(11)$ Å; $\beta=116.318(2)°$; $V=2121.7(3)$ Å^3; $Z=4$; $\rho_{calcd}=1.757$ Mg m^{-3}; $R_1=0.0291$; $wR_2=0.0867$; $T=293$ K; $\mu=1.211$ mm^{-1}; $S=0.797$; Flack value: $\chi=0.05(3)$.[10]

The crystal structures were solved with direct methods using the program SHELXTL.[11] All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using 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 found to be featureless.

CCDC-202451–202454 contain the supplementary crystallographic data (excluding structure factors) for this paper. This 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 CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

The measurement of SHG responses: Approximate estimations of the second-order-nonlinear optical intensity were obtained by comparison of the results obtained from a powdered sample (80–150 μm diameter) in the form of a pellet (Kurtz powder test[12]), with that obtained for urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate the SHG signal. The backward-scattered SHG light was collected using a spherical concave mirror and passed through a filter that transmits only 532 nm radiation. The SHG responses of **1–4** are about 1.30, 0.40, 0.30, and 0.50 times than that of urea, respectively.

Measurement of the electric hysteresis loop: The ferroelectric property of a solid-state sample was measured using a powdered sample in the form of a pellet. An RT6000 ferroelectric tester was used at room temperature with the sample immersed in insulating oil. The electric hysteresis loop was observed by Virtual Ground Mode. The relatively low *Ps* values may be due to the sample being too thick to enable the use of high voltages.

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