4166 *Chem. Mater.* **2003,** *15,* 4166−4168

Ferroelectric Copper Quinine Complexes

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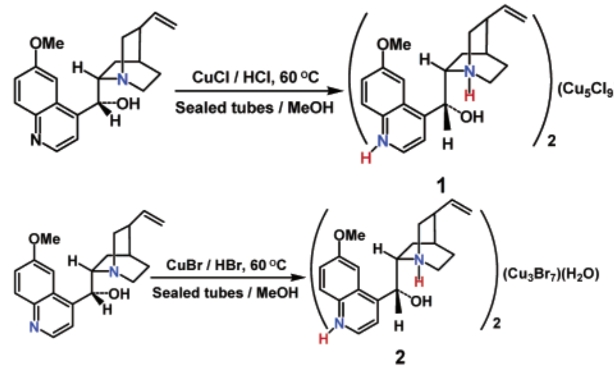
Received April 25, 2003
Revised Manuscript Received August 31, 2003

Materials with a macroscopic polar order display a variety of useful properties, such as second-order nonlinear optical activity, piezoelectricity, ferroelectricity, pyroelectricity, and triboluminescence.[1] Among these properties, ferroelectric behavior is particularly desirable, and materials exhibiting this behavior are the focus of intense studies because it is possible to switch rapidly between different states by an external electric field.[2] Such materials may be useful in a variety of new technologies such as electric-optical devices, information storage, switchable NLO (nonlinear optical) devices, and light modulators.[3]

One well-known ferroelectric compound that is also second-harmonic generation (SHG) active is the *Fdd*2 phase of KDP (KH_2PO_4). There is extensive H-bonding in its structure that gives rise to a diamondoid network.[4] Recent interest in the use of crystal engineering to generate coordination polymers has provided many examples of network structures where H-bonding and coordination bonds are dominant structural influences. It is conceivable that such networks may exhibit the types of properties that make KDP such an important material. We have accordingly become interested in generating coordination polymers that possess useful physical properties such as ferroelectric behavior. We note that ferroelectric behavior requires the adoption of a space group that is associated with one of the polar point groups. For this reason, we have focused on the use of chiral network building blocks to encourage crystallization in an appropriate space group. Quinine, an alkaloid, is an attractive candidate as a component of a network structure with the aforementioned physical properties. The molecule chiral and, in addition, its two nitrogen atoms have the potential to coordinate to a metal center or participate in H-bonding.

Scheme 1



Herein, we report the synthesis, solid-state structures, thermal stabilities, and ferroelectric properties of $Cu_5Cl_9(H_2Quinine)_2$ (**1**) and $Cu_3Br_7(H_2Quinine)_2(H_2O)$ (**2**). **1** was obtained by the reaction of CuCl, quinine, and HCl in methanol under solvothermal conditions at 60−70 °C.[5] **2** was obtained under similar conditions using CuBr and HBr.[5] These reactions are represented in Scheme 1. Thermogravimetric analysis (TGA) of these polycrystalline complexes indicated no weight loss below ca. 200 and 240 °C for **1** and **2**, respectively. EPR spectra of the complexes are all silent, confirming that the oxidation state of Cu ions in these solid complexes is +1.

The crystal structure of **1** reveals an anionic one-dimensional polymer of composition $[Cu_5Cl_9{}^{4-}]_n$ (Figure

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(5) Preparation of compound **1**. Hydrothermal treatment of CuCl (2.5 mmol), quinine (1 mmol), and 2 mL of HCl (4 N) in MeOH (1 mL) for 3 days at 60 °C afford ca. 0.4 mmol (40% yield based on quinine) of pale-yellow plate crystals of **1**. Anal. Calcd for $C_{20}H_{26}Cl_{4.5}N_2O_2Cu_{2.5}$: C, 37.22; H, 4.03; N, 4.34. Found: C, 37.31; H, 4.09; N, 4.42. IR (KBr, cm^{-1}): 3449 (br s), 2951 (m), 1619 (w), 1599 (s), 1541 (w), 1496 (m), 1423 (m), 1384 (m), 1268 (s), 1243 (s), 1146 (w), 1121 (m), 1024 (m), 925 (w), 837 (m), 800 (w), 717 (w), 634 (w). Preparation of compound **2**. The procedure is identical to that of **1** except that CuBr and HBr (4 N) were used in place of CuCl and HCl, respectively. The brown-red block crystals were obtained with 45% yield based on quinine. Anal. Calcd for $C_{20}H_{27}Br_{3.5}N_2O_{2.5}Cu_{1.5}$: C, 33.78; H, 3.80; N, 3.94. Found: C, 33.86; H, 3.89; N, 4.05. IR (KBr, cm^{-1}): 3449 (br s), 2951 (m), 1619 (w), 1599 (s), 1541 (w), 1496 (m), 1423 (m), 1384 (m), 1268 (s), 1243 (s), 1146 (w), 1121 (m), 1024 (m), 925 (w), 837 (m), 800 (w), 717 (w), 634 (w).

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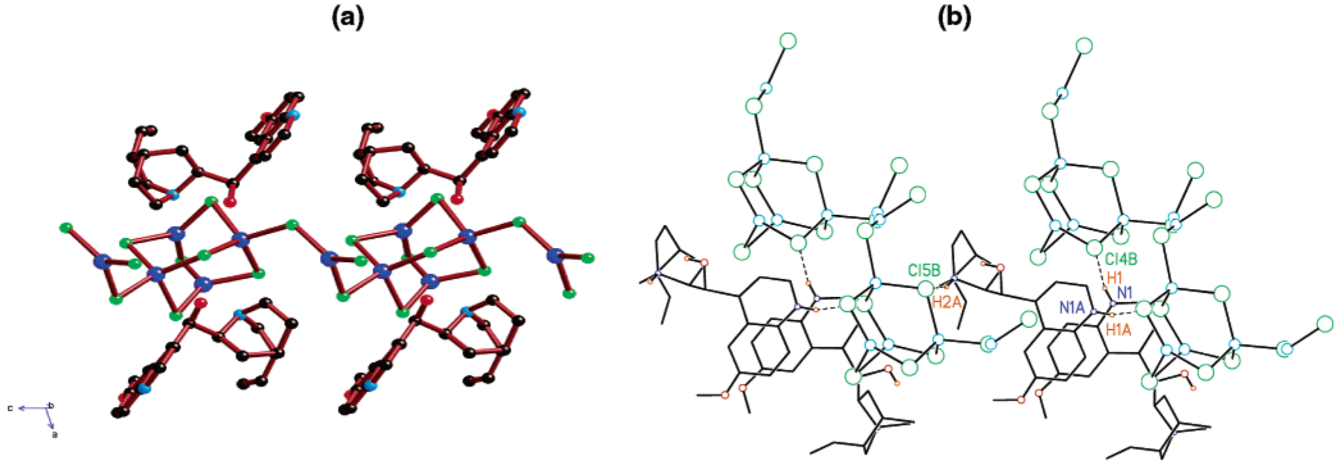

Figure 1. (a) The structure of **1**, showing the [$Cu_5Cl_9{}^{4-}$] anion chain composed of alternating Cu_4Cl_6 and $CuCl_3$ units. The countercations are diprotonated quinines. Each $CuCl_3$ unit is disordered around a 2-fold axis (only one orientation of the $CuCl_3$ unit is shown). Color code: Cu blue, Cl green, O red, N pale blue, C black. H atoms have been omitted for clarity. (b) H-bonds between diamond-like net and diprotonated quinine in a 3D network of **1**.

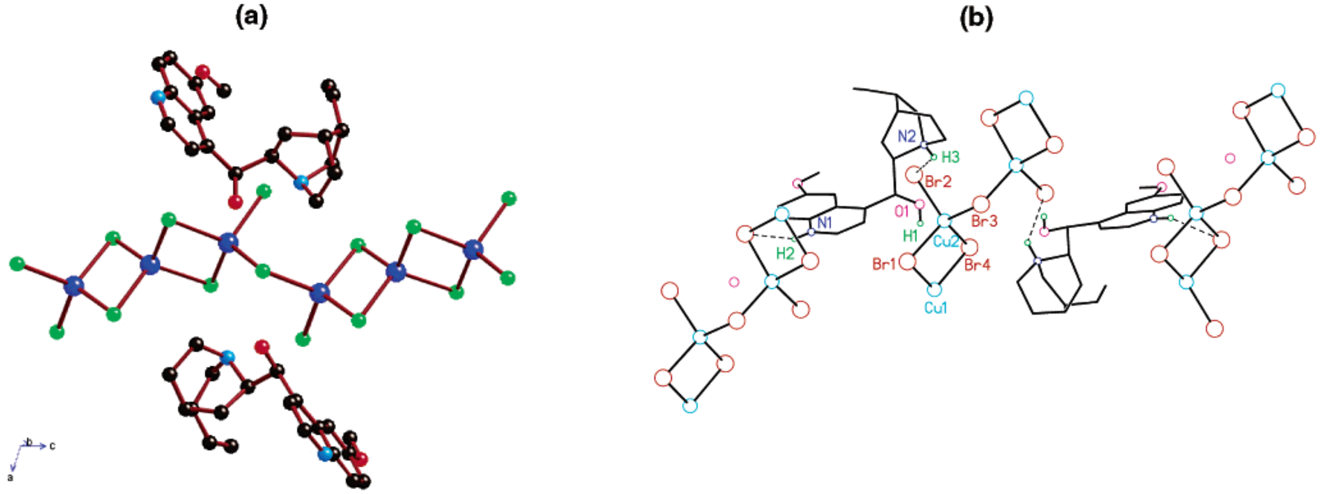

Figure 2. (a) The structure of **2**, showing the [$Cu_3Br_7{}^{4-}$] anion chain. The countercations are diprotonated quinines. Color code: Cu blue, Br green, O red, N pale blue, C black. H atoms have been omitted for clarity. (b) H-bonds between the CuBr cluster and diprotonated quinine in a 3D network of **2**.

1a).[6] This polymer contains $Cu_4Cl_6{}^{2-}$ adamantane-type aggregates that are linked to two identical units by $CuCl_3{}^{2-}$ bridges.[7] The $CuCl_3{}^{2-}$ bridge is disordered around a 2-fold axis. There are three unique Cu atoms, two of which are in trigonal coordination environments while the third is in a tetrahedral environment. The anionic charge of this highly unusual Cu(I)−Cl polymer is balanced by diprotonated quinine cations. The protons that are bound to the nitrogen atoms of the quinoline and quinuclidine ring participate in hydrogen bonding with chlorine atoms belonging to two Cu_4Cl_6 aggregates that are each part of two separate polymeric chains. As a consequence of the extensive coordinate and hydrogen bonding, a homochiral 3D network is produced, as seen in Figure 1b.

In **2**, diprotonated quinines play a similar role, serving as countercations for anionic [$Cu_3Br_7{}^{4-}$]$_n$ chains (Figure 2a).[6] The copper(I) centers in this structure have a distorted tetrahedral environment formed by bridging and terminal bromide ions. As was the case with **1** there are significant interactions between the H atoms bound to the N atoms of the quinoline and quinuclinde rings and Br centers of the $Cu_3Br_7{}^{4-}$ polymer, resulting in the formation of a 3D homochiral network (Figure 2b).

Given that the products **1** and **2** crystallize in a chiral space group (*C*2) which belong to a polar point group (C_2), their optical properties were studied. Preliminary examinations of a powdered sample indicate that both **1** and **2** are SHG-active with approximate responses 4.0 times that of KDP. The space group *C*2 is associated

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(6) Crystal data for **1**, $C_{20}H_{26}Cl_{4.5}N_2O_2Cu_{2.5}$, $M = 644.80$, monoclinic, *C*2, $a = 17.368(9)$ Å, $b = 15.817(8)$ Å, $c = 9.204(4)$ Å, $\alpha = \gamma = 90°$, $\beta = 106.300(9)°$, $V = 2427(2)$ Å^3, $Z = 4$, $D_c = 1.765$ Mg m^{-3}, R1 = 0.0477, wR2 = 0.1164, $\mu = 2.695$ mm^{-1}, $S = 0.532$; **2**, $C_{20}H_{27}Br_{3.5}N_2O_{2.5}Cu_{1.5}$, $M = 710.43$, monoclinic, *C*2, $a = 17.931(3)$ Å, $b = 14.611(2)$ Å, $c = 9.5135(15)$ Å, $\alpha = \gamma = 90$, $\beta = 106.905(3)°$, $V = 2384.6(6)$ Å^3, $Z = 4$, $D_c = 1.979$ Mg m^{-3}, R1 = 0.0434, wR2 = 0.1023, $\mu = 7.236$ mm^{-1}, $S = 0.503$.

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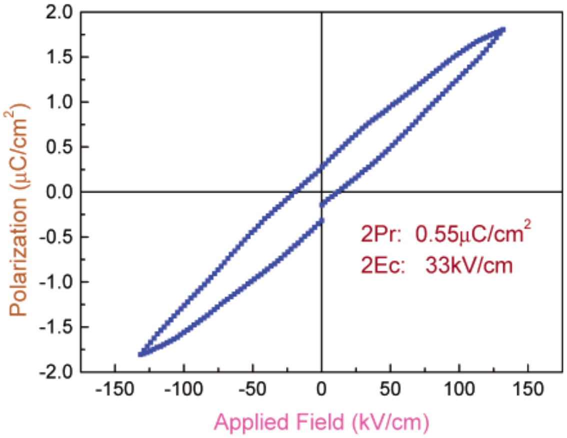

Figure 3. Electric hysteresis loop of a pellet of powdered **1** observed by Virtual Ground Mode using an RT6000 ferroelectric tester at room temperature.

with the point group C_2, one of the 10 polar point groups (C_1, C_2, C_m, C_{2v}, C_4, C_{4v}, C_3, C_{3v}, C_6, C_{6v}) required for ferroelectric behavior. Experimental results indicate that **1** does indeed display good ferroelectric behavior while **2** shows relatively low ferroelectric responses.[8]

Figure 3 clearly shows there is an electric hysteresis loop in **1**, which is a typical ferroelectric feature with a remanent polarization (Pr) of 0.28 μC·cm^{-2} and coercive field (E_c) of 16 kV cm^{-1}.[8] The saturation spontaneous polarization (P_s) of **1** is ca. 2.0 μC cm^{-2} compared to that of ferroelectric KDP, which is 5.0 μC cm^{-2}.[9] The similarity in the values found in **1** and KDP is interesting given that both form 3-D networks that involve H bonding. Furthermore, although **1** does not form a diamond-type net like KDP, it does possess adamantane-type units (in the anionic polymer), which are a characteristic structural feature of diamond nets. To the best of our knowledge, **1** represents the first example of a homochiral metal-organic coordination polymer with a diamondoid-like network that exhibits ferroelectric behavior.

Acknowledgment. This work was supported by The Major State Basic Research Development Program (Grant No. G2000077500), the National Natural Science Foundation of China, EYTP of MOE, P. R. C BK2003204, and the U.S. National Science Foundation.

Supporting Information Available: Experimental procedures, IR data, and additional ORTEP views (PDF) and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) *The measurement of SHG responses*: Approximate estimations of the second-order nonlinear optical intensity were obtained by comparison of the results obtained from a pellet (Kurtz powder test) of powdered sample (80−150 μm diameter),[9] with that obtained for KDP. 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. Thus, the SHG responses of **1** and **2** are about 4 times that of KDP, respectively. *The measurement of an electric hysteresis loop*: The ferroelectric property of the solid-state sample was measured by a pellet of powdered sample using an RT6000 ferroelectric tester at room temperature while the sample was immerged in insulating oil. The electric hysteresis loop was observed by Virtual Ground Mode. The relatively low P_s value is perhaps because the sample pellets are too thick to use a high voltage.

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