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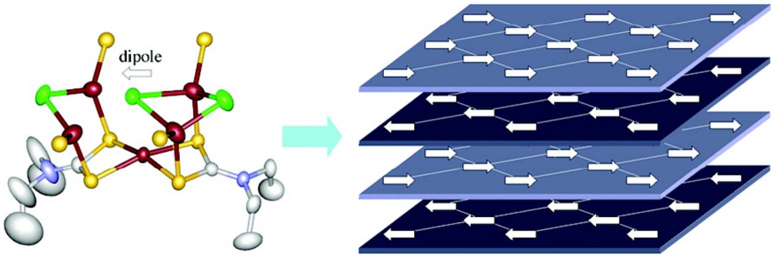

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A Mixed-Valence Coordination Polymer Featuring Two-Dimensional Ferroelectric Order: $\{[Cu^{I}_4Cu^{II}(Et_2dtc)_2Cl_3][Cu^{II}(Et_2dtc)_2]_2(FeCl_4)\}_n$ (Et_2dtc^- = diethyldithiocarbamate)

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Extensive research has been devoted to the synthesis of coordination polymers with characteristic physical and/or chemical properties, including magnetism, conductivity, nonlinear optical responses, catalysis, gas storage, and ion exchange.[1−3] Studies of mixed-valence coordination polymers are less developed than those of conventional homo-valent coordination polymers because of synthetic challenges, despite the potential for new functional materials based on the occurrence of inter-valence charge transfer (IVCT), the diversity of the spin states, and the availability of versatile frameworks, like Prussian blue derivatives,[4] 1-D halogen-bridged complexes,[5] and a dithiooxalate-bridged iron polymer.[6] Ferroelectricity would be one of the most important properties to target for a mixed-valence coordination polymer, both for fundamental scientific reasons and for application as ferroelectric random access memories (FeRAMs). Additionally, they should behave as second-order nonlinear optical (NLO) materials since they would fulfill the requirements for the NLO materials in the IVCT and the polar structures. To the best of our knowledge, however, there are no examples of mixed-valence coordination polymers showing ferroelectric properties, and just three ferroelectric homo-valent coordination polymers have been reported recently.[7] In this paper, we describe the synthesis, crystal structure, and physical properties of a new mixed-valence coordination polymer, $\{[Cu^{I}_4Cu^{II}(Et_2dtc)_2]$-$[Cu(Et_2dtc)_2]_2(FeCl_4)\}_n$ (Et_2dtc^- = diethyldithiocarbamate) (**1**), displaying two-dimensional (2-D) ferroelectric structural order.

Complex **1** was synthesized by a reaction of a $CHCl_3$ solution of $Fe(Et_2dtc)_3$ and an acetone solution of $CuCl_2{\cdot}2H_2O$. Black single crystals suitable for X-ray diffraction were obtained from the mixture by recrystallization with hexane in a glass tube over a period of more than 1 week.

A single-crystal X-ray analysis reveals[8] that the asymmetric unit of **1** consists of a pentanuclear copper fragment of $Cu_5(Et_2dtc)_2Cl_3$, two bridging mononuclear copper units of $Cu(Et_2dtc)_2$, and a counteranion of $FeCl_4^-$. The pentanuclear copper fragment, $Cu_5(Et_2dtc)_2Cl_3$, is shown in Figure 1, together with the four sulfur atoms of the bridging mononuclear copper units, $Cu(Et_2dtc)_2$, binding to the Cu(2), Cu(2*), Cu(4), and Cu(4*) ions. The Cu(3) in the $Cu_5(Et_2dtc)_2Cl_3$ fragment exhibits a distorted square-planar geometry with four sulfur atoms of the two Et_2dtc ligands, while the Cu(2) and Cu(4) have distorted trigonal and tetrahedral geometries, respectively. Each Cu ion is bound by two sulfur atoms in the bridging unit of $Cu(1)(Et_2dtc)_2$, the $Cu(3)(Et_2dtc)_2$ fragment in the pentanuclear fragment, and bridging Cl(1) or Cl(3) ions, and additionally, a Cl(2) ion for the Cu(4). Here, the Cl(2) ion bridging the Cu(4) and Cu(4*) ions is also located a short distance from the Cu(2) and Cu(2*) ions (2.794(2) Å)—only slightly longer than the Cu(4)−Cl(2) distance (2.565(2) Å), as if the Cl(2) ion is bridging the four copper ions. Assuming that the square-planar Cu(1) and Cu(3) are Cu(II) ions and the trigonal Cu(2) and tetrahedral Cu(4) are Cu(I) ions, the total charge would be zero, consistent with the results of magnetic measurements reported below.

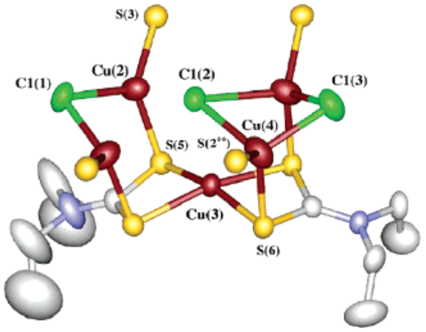

Figure 1. Thermal ellipsoid plot showing a mixed-valence copper pentanuclear fragment, $[Cu^{I}_4Cu^{II}(Et_2dtc)_2Cl_3]^+$; here S(3) and S(2**) bonding to Cu(I) ions, Cu(2) and Cu(4), are parts of bridging mononuclear units, $[Cu^{II}(Et_2dtc)_2]$. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Cu(2)···Cl(1) 2.279(2), Cu(2)···Cl(2) 2.794(2), Cu(4)···Cl(2) 2.565(2), Cu(4)···Cl(3) 2.309(3), Cu(2)···S(3) 2.237(2), Cu(2)···S(5) 2.309(2), Cu(4)···S(2**) 2.272(2), Cu(4)···S(6) 2.361(2), Cu(3)···S(5) 2.327(2), Cu(3)···S(6) 2.324(2).

In the coordination network, each pentanuclear copper fragment, $Cu_5(Et_2dtc)_2Cl_3$, is connected by the two mononuclear copper units, $Cu(Et_2dtc)_2$, to afford a 2-D square lattice infinite structure, as shown in Figure 2a. The counteranions, $FeCl_4^-$, are located between the layers (Figure 2b). Note that all of the bonds of Cu(4)−Cl(2)−Cu(4*) face the same direction in the *bc* plane (upper direction in Figure 2a) to form a 2-D ferroelectric order in the layer. While the adjacent layers have the opposite ordering, resulting in a nonpolar space group, *Pnma* (No. 62), at room temperature.

The XPS spectrum of the bulk sample shows a peak of $2P_{3/2}$ at 932.3 eV, which is lower than that of a Cu(II) complex, $Cu(Et_2dtc)_2$ (933.6 eV) (Figure S1). It could be because of the presence of Cu(I) ions in this system. The weak satellite peak around 943 eV indicates that **1** also contains Cu(II) ions. The magnetic measurement of **1** by SQUID at 10 kOe suggests weak interactions ($\theta = -1.03$ K) between the unpaired electrons of the Cu(II) ions (Figure S2), where the nearest Cu(II)−Cu(II) distance is 5.1505 Å. The effective magnetic moment at 300 K is 6.88 μ_B, in accord with the expected value (6.63 μ_B) for the one copper(II) ion ($S = 1/2$) in the pentanuclear unit, $[Cu^{I}_4Cu^{II}(Et_2dtc)_2Cl_3]^+$, two copper(II) ions ($S = 1/2$) in the two bridging mononuclear copper(II) units, $[Cu^{II}(Et_2dtc)_2]$, and the one iron(III) ion ($S = 5/2$) in the counteranion, $FeCl_4^-$, as characterized by the X-ray study. The thermal degradation behavior of **1** shows that the structural skeleton of **1**

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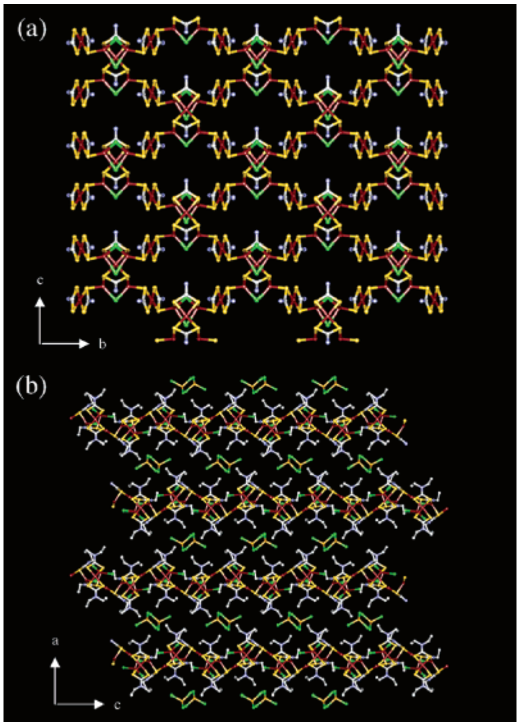

Figure 2. (a) Two-dimensional layer structure of **1** along *a* axis: C, red-brown; Cl, green; S, yellow; C, white. Hydrogen atoms, carbon atoms of alkyl groups in Et_2dtc^-, and counteranions of $FeCl_4^-$ are omitted for clarity. Mixed-valence pentanuclear fragments, $[Cu^I_4Cu^{II}(Et_2dtc)_2Cl_3]^+$, are bridged by mononuclear units, $[Cu^{II}(Et_2dtc)_2]$, to construct an infinite 2-D square lattice structure. In this picture, all the halogen ions of Cl(2), which are in the middle of three bridging chloride ions shown as green points, coordinate to the upper sides of Cu^I ions, Cu(4), to form ferroelectric structural ordering in this layer. (b) Stacking 2-D layer structure of **1** along *b* axis. Hydrogen atoms are omitted for clarity. Counteranions, $FeCl_4^-$, are incorporated between the layers consisting of the pentanuclear units and the bridging mononuclear unites. The interlayer distance is 14.4344(10) Å.

remains stable until ca. 370 K (Figure S3). The thermogravimetric curve shows gentle weight losses of 3.8% from 370 to 420 K, 11.1% from 420 to 450 K, and 33.1% from 450 to 500 K.

The temperature dependence of the ac dielectric permittivity of **1** was measured on a LCR meter. The dielectric constants gradually increase with increasing temperature (Figure 3a). The measurement of the dc conductivity with the pellet sample at room temperature indicates the high insulating of **1** (1.7×10^{-11} S/cm), suggesting that the unusual dielectric behavior could not be due to the electronic and ion conductivities based on the mixed-valence layer and the counteranions, $FeCl_4^-$. In addition, experimental results with a ferroelectric tester also indicate that **1** exhibits ferroelectric behavior (Figure 3b). The data below 200 K do not have spontaneous polarization, and the slopes never change. The dielectric constants ($\epsilon_r = 6.1$) estimated from the slopes are close to the values observed by the LCR meter at low temperatures and high frequencies. The slopes increase with increasing temperature above 200 K and the hysteresis loops derived from the ferroelectricity are clearly observed.

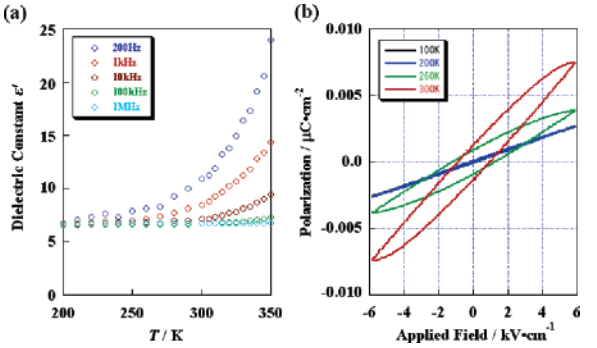

Figure 3. (a) Temperature dependence of the dielectric constants of **1**. (b) Hysteresis loops of electric polarization at various temperatures for **1**, observed for a powdered sample in the form of a pellet using a ferroelectric tester.

In summary, we have succeeded in synthesizing a mixed-valence coordination polymer with 2-D ferroelectric order and confirmed the ferroelectricity. This kind of ferroelectric mixed-valence coordination polymer may open up new opportunities for developing ferroelectric and/or NLO materials based on metal complexes.

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Supporting Information Available: Complete ref 5a, synthesis, XPS, magnetic susceptibility, TGA, additional dielectric properties, and crystallographic data. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Crystal data of compound **1**: $C_{30}H_{60}N_6S_{12}Cl_7Cu_7Fe$, $M = 1638.40$, orthorhombic, space group *Pnma* (No. 62), $a = 28.8687(10)$ Å, $b = 17.4304(4)$ Å, $c = 12.8504(4)$ Å, $V = 6466.2(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.683$ g/cm^3, $\lambda = 0.71069$ Å, $\mu = 31.778$ cm^{-1}, $F(000) = 3288$, GOF = 1.657; a total of 8062 reflections were collected, and 1076 were unique ($R_{int} = 0.049$). *R*1 and *wR* are 0.0743 and 0.1829, respectively, for 332 parameters and 5277 reflections [$I > 3\sigma(I)$].

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