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New Ferroelectrics Based on Divalent Metal Ion Alum

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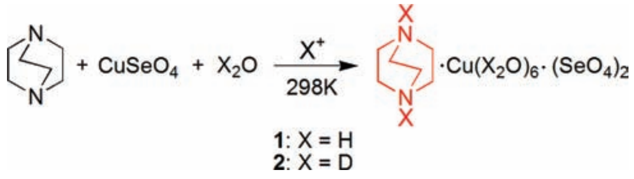
Because of their excellent ferroelectric, piezoelectric, pyroelectric, and optical properties, ferroelectric compounds have found a variety of technical applications, such as ferroelectric random access memories (FeRAM), ferroelectric field-effect transistors, infrared detectors, piezoelectric sensors, nonlinear optical devices, and fast displays in electronic equipment, since the first ferroelectric, Rochelle salt (potassium sodium tartrate tetrahydrate, $NaKC_4H_4O_6 \cdot 4H_2O$), was discovered by Valasek in 1920.[1,2] There are still intensive research activities in the ferroelectric field, including exploration of multiferroic compounds and the search for new ferroelectrics.[3] Most new ferroelectric metal−organic coordination compounds reported in the literature have been found to meet only the necessary requirements for ferroelectric properties, i.e., crystallizing in one of ten polar point groups (C_1, C_2, C_s, C_{2v}, C_4, C_{4v}, C_3, C_{3v}, C_6, C_{6v}). However, sufficient conditions (or requirements) required in this system, such as a phase transition (transformation), a good electric hysteresis loop and electric domain, and a dielectric anomaly, are often missed. In current molecule-based ferroelectric research groups, representatives include Katrusiak and Szafranski, Horiuchi and Tokura, and Nakamura and Akutagawa, whose excellent work has paid attention to both the necessary and sufficient conditions for ferroelectric behavior.[4−6]

More than 50 years has passed since alums based on trivalent metal ions (Al, Ga, In, and Cr) were found to be good ferroelectrics.[7] No new ferroelectric metal complex alum analogues with SeO_4^{2-} anion have been found to be ferroelectrics. During our systematic search for new ferroelectrics,[8] we discovered that diprotonated 1,4-diazoniabicyclo[2.2.2]octane hexaaquacopper(II) bis(selenate) [$(H_2dbco)Cu(H_2O)_6(SeO_4)_2$, (**1**)] (Scheme 1) undergoes a phase transition from a paraelectric phase (nonpolar point group C_{2h}) at room temperature to a ferroelectric phase (polar point group C_2) at low temperature (ca. −140 °C) and thus meets the necessary and sufficient requirements for ferroelectrics. Of great importance is the fact that **1** displays a dielectric anomaly and a good electric hysteresis loop. Herein, we report the synthesis, crystal structure, and ferroelectric properties of **1** and its deuterated analogue $(D_2dbco)Cu(D_2O)_6(SeO_4)_2$ (**2**) [see the Supporting Information (SI)].

Differential scanning calorimetry (DSC) of **1** revealed a heat anomaly at ca. −140 °C, indicating that there may be a reversible phase transition occurring in this system. Additionally, no heat hysteresis phenomenon was observed during heating and cooling processes (see the SI). Temperature-dependent dielectric constant measurements on powdered **1** also showed a small reversible anomaly at ca. −140 °C (Figure 1a), suggesting that there is a structural phase transition, in agreement with the DSC results. A fit of the plot of reciprocal dielectric constant (real part) versus temperature to the Curie−Weiss law [$\varepsilon = \varepsilon_0 + C/(T - T_0)$] gave Curie−Weiss constants $C_{ferro} = 1.0 \times 10^3$ K and $C_{para} = 1.667 \times 10^3$ K for the ferroelectric and paraelectric phases, respectively (Figure 1b). The C_{para}/C_{ferro} ratio of 1.667 is smaller than 4.0, suggesting a second-order-like phase transition (see the SI).

Scheme 1



The crystal-structure determination of **1** at 293 K revealed that **1** crystallizes in a centrosymmetric space group ($P2_1/c$) belonging to a nonpolar point group (C_{2h}).[9] The H_2dbco cation is seriously disordered (Figure 2), which may result in the formation of higher symmetry, while the $Cu(H_2O)_6$ cation is a perfect octahedron. Below −140 °C, a new phase appeared. The crystal structural determination at 103 K disclosed that the mirror plane disappears, resulting in a decrease in the number of symmetric elements from four (E, I, C_2, and δ_h) to two (E and C_2) (space group $P2_1$). The new point group (C_2) is still a subgroup of the paraelectric phase (point group C_{2h}), obeying the Landau theory and also suggesting that this phase transition may be successive.[10] At the same time, this phase transition obeys the Aizu rule, written as $2/mF2$.[11] Consequently, this is a continuous second-order phase transformation. A similar case occurred in triglycine sulfate (TGS), where the mirror disappears in going from a paraelectric phase (space group $P2_1/m$, point group C_{2h}) above T_C (>49 °C) to a ferroelectric phase (space

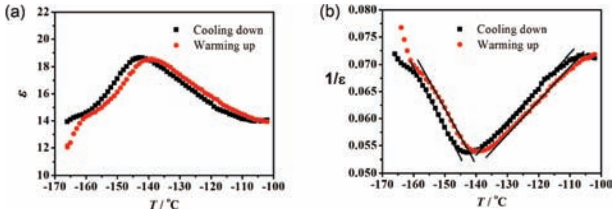


Figure 1. Plots of (a) dielectric constant (real part) and (b) reciprocal dielectric constant (real part) vs temperature for **1**.

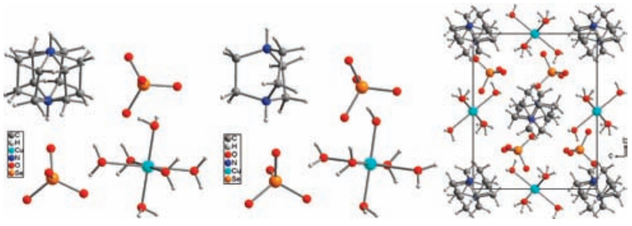


Figure 2. (left) Asymmetric unit and (right) packing diagram for **1** at 293 K, in which the $[H_2dbco]^{2+}$ cation displays seriously disorder. (middle) Asymmetric unit of **1** at 103 K, where the $[H_2dbco]^{2+}$ cation becomes more ordered (the packing view of **1** at 103 K is given in the SI).

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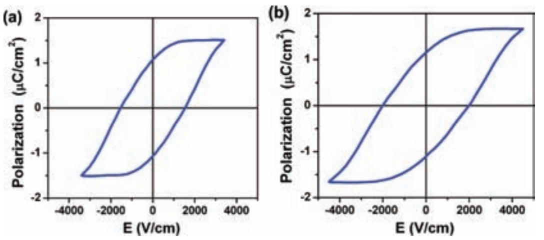

Figure 3. Plots of polarization vs electric field for (a) **1** and (b) **2** measured ∼1−8 °C below T_c and approximately along the *b* axis.

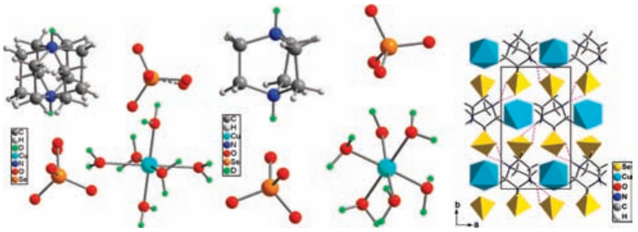

Figure 4. (left) Asymmetric unit and (right) packing diagram for **2** at 298 K, in which the $[D_2dbco]^{2+}$ cation and selenate anion display serious and partial disorder, respectively. (middle) Asymmetric unit of **2** at 93 K, where $[D_2dbco]^{2+}$ and SeO_4^{2-} become more ordered (the packing view of **2** at 93 K is given in the SI).

group $P2_1$, point group C_2) upon a temperature decrease, halving the number of symmetric elements from four (E, I, C_2, and δ_h) to two (E and C_2) in accord with Landau second-order phase transition theory and an Aizu presentation of $2/mF2$.[7a,11,12]

Furthermore, according to Landau theory, the Gibbs potential can be written as an infinite power series in the order parameter, η: $G(\eta) = G_0 + {}^1/_2A\eta^2 + {}^1/_4B\eta^4 + {}^1/_6C\eta^6 + \cdots$. Near the phase transition temperature (T_c), η can be determined by minimizing the truncated Gibbs potential, i.e., by solving $\partial G/\partial\eta = A\eta + B\eta^3 = 0$. Thus, the solution $\eta = 0$ can be assigned to the paraelectric phase above T_c ($T > -140$ °C; disordered state and higher symmetry at high temperature), while $\eta = \pm(-A/B)^{1/2}$ (in which $A < 0$ and $B > 0$) can be assigned to the ferroelectric phase ($T < -140$ °C; ordered state and lower symmetry at low temperature).

Figure 3 clearly shows a good electric hysteresis loop with remanent polarization $P_r = 1.02$ μC/cm² and spontaneous polarization $P_s = 1.51$ μC/cm² recorded approximately along the (010) face or *b* axis. The value of the coercive electric field is $E_c \approx 1.5$ kV/cm. Compared with that of trivalent metal alums ($P_s = 0.35-0.47$ μC/cm²), the present P_s is slightly larger. Interestingly, the P_s of the deuterated compounds [formulated as $RM(SeO_4)\cdot 6D_2O$, M = trivalent metal ion] remained the same value as for the nondeuterated compounds. No evident isotopic effect was observed in the system. This indicated that the H bond may not be responsible for the ferroelectricity in the alum analogue system but that the ferroelectricity instead may originate from the order−disorder changes of the cation (H_2dbco) and anion (selenate). To confirm this hypothesis, the analogue compound **2** was synthesized. Its DSC results revealed that T_c remained almost unchanged (contrarily, it was a little bit smaller than that of **1**). The real part of the complex dielectric constant also showed an anomaly at ca. −138 °C (see the SI). The room- and low-temperature single-crystal structures (Figure 4) show that **2** is isostructural to **1** and has an evident structural phase transition like that in **1**. Thus, there no isotopic effect was observed in the present case, suggesting that the order−disorder feature may be responsible for the ferroelectric property of **1**.

Quantum-chemical calculations were performed using the Gaussian 03 program package. The optimized geometry of **1** (Figure S5 in the SI) shows that dabco is singly protonated. The same phenomenon is present in **2**. Compound **1** can be treated as two fragments, A (dabcoH) and B $[HSeO_4\cdot Cu(H_2O)_6\cdot SeO_4]$. The phase transition is mainly based on the disorder of $dabcoH^+$. If the transition from order to disorder of $dabcoH^+$ is performed, $dabcoH^+$ must overcome the interaction between fragments A and B. The interaction can be calculated using the expression

$$\Delta E_{\text{int}} = E_{\text{total}} - \sum_i E_i \qquad (1)$$

where E_{total} is the total energy of the system and E_i is the energy of subsystem *i*. The total energy of the system was found to be very similar to that of the deuterated (D) system, i.e., $E_{\text{total}} = -6406.2047136$ au for the H system and -6406.2047122 au for the D system (see the SI). Thus, the interaction is a little stronger in the D system than in the H-system, indicating that the transition is a little more difficult for the D system than for the H-system, in good agreement with the experimental results.

In conclusion, the present work has opened an avenue for exploration of new ferroelectrics based on divalent metal ion alum analogues through the combination of crystal engineering and Landau phase transition theory.

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Supporting Information Available: Theoretical calculations, TGA data, powder XRD patterns, IR and DSC spectra, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Crystal data for **1** (103 K): $C_6H_{26}CuN_2O_{14}Se_2$, $M_r = 571.76$, monoclinic, $P2_1$, $a = 7.1471(5)$ Å, $b = 12.6152(8)$ Å, $c = 9.9519(7)$ Å, $\beta = 91.730(3)°$, $V = 896.88(11)$ Å³, $Z = 2$, $D_{\text{calcd}} = 2.117$ Mg m^{-3}, $R_1(I > 2\sigma) = 0.0281$, wR_2 (all data) = 0.0648, $\mu = 5.347$ mm^{-1}, $S = 1.063$, Flack value = 0.514(13). **1** (293 K): $C_6H_{26}CuN_2O_{14}Se_2$, $M_r = 571.76$, monoclinic, $P2_1/c$, $a = 7.1294(14)$ Å, $b = 12.629(3)$ Å, $c = 12.142(4)$ Å, $\beta = 124.84(2)°$, $V = 897.3(4)$ Å³, $Z = 2$, $D_{\text{calcd}} = 2.116$ Mg m^{-3}, $R_1(I > 2\sigma) = 0.0345$, wR_2 (all data) = 0.0786, $\mu = 5.345$ mm^{-1}, $S = 1.106$. **2** (93 K): $C_6H_{12}CuD_{14}N_2O_{14}Se_2$, $M_r = 585.83$, monoclinic, $P2_1$, $a = 7.1403(5)$ Å, $b = 12.6022(9)$ Å, $c = 9.9441(6)$ Å, $\beta = 91.936(2)°$, $V = 894.29(10)$ Å³, $Z = 2$, $D_{\text{calcd}} = 2.176$ Mg m^{-3}, $R_1(I > 2\sigma) = 0.0266$, wR_2 (all data) = 0.0703, $\mu = 5.363$ mm^{-1}, $S = 1.047$, Flack value = 0.492(10). **2** (298 K): $C_6H_{12}CuD_{14}N_2O_{14}Se_2$, $M_r = 585.83$, monoclinic, $P2_1/c$, $a = 7.124(6)$ Å, $b = 12.634(9)$ Å, $c = 12.164(7)$ Å, $\beta = 125.16(4)°$, $V = 895.1(11)$ Å³, $Z = 2$, $D_{\text{calcd}} = 2.174$ Mg m^{-3}, $R_1(I > 2\sigma) = 0.0934$, wR_2 (all data) = 0.2199, $\mu = 5.358$ mm^{-1}, $S = 1.185$.
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