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Ionic Ferroelectrics Based on Nickel Schiff Base Complexes

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Two novel homochiral enantiomers, trinuclear ionic clusters $[(NiL^1)_2Na]^+NCS^-\cdot MeOH\cdot Et_2O$ (**1**) and $[(NiL^2)_2Na]^+NCS^-\cdot MeOH\cdot Et_2O$ (**2**) [H_2L^1 = *N,N'*-bis(3-methoxysalicylidene)-(1*R*,2*R*)-1,2-diphenylenediamine; H_2L^2 = *N,N'*-bis(3-methoxysalicylidene)-(1*S*,2*S*)-1,2-diphenylenediamine], have been synthesized and structurally characterized. Both complexes have C_2 symmetry and crystallize in space group $P2_1$. Ferroelectric measurements reveal that complexes **1** and **2** represent a new type of ionic ferroelectric based on metal−organic coordination with a polarization value higher than that of KH_2PO_4.

Ferroelectricity is one of the major subjects in the field of materials science because of its wide applications in ferroelectric random-access memories, switchable nonlinear optical devices, electrooptical devices, and light modulators.[1] Ferroelectric materials have fascinated scientists since the discovery of ferroelectricity in Rochelle salt in 1920.[2] To date, the majority of the ferroelectric materials reported are inorganic compounds such as KH_2PO_4 (KDP), $BaTiO_3$, and $LiNbO_3$.[3] Recently, molecule-based ferroelectric materials have received much attention because of their properties distinctive from those of inorganic materials.[4] The synthesis of new ferroelectric materials is still particularly challenging because of the strict requirements that a compound needs to crystallize in noncentrosymmetric space groups belonging to the polar point groups. Some molecular ferroelectric materials based on a neutral metal−organic framework have been reported by our groups[5] and others.[6] However, ionic metal−organic coordination in molecule-based ferroelectrics remains spare. Because of the existence of separated positive and negative charges, ionic metal−organic coordination would be more effective in enlarging the polarity and ferroelectricity than neutral metal−organic coordination. Metal salicylaldimines with alkoxy groups in the 3 and 3′ positions are a fascinating group of ligands that can coordinate with not only p- and d-block metal elements but also alkali-metal ions. These alkali-metal complexes of metal salicylaldimines are important in small-molecule activation,[7] electron storage,[8] and the carrying of polar organometallics.[9] Moreover, they can coordinate with a suitable size metal ion and form a sandwich structure of ion complexes between two sets of Schiff base O atoms.[10] To the best of our knowledge, there are no reports on the ferroelectricity of these complexes with Schiff base ligands. In this paper, two novel homochiral nickel salicylaldimine complexes were synthesized and reacted with NaNCS to form trinuclear ionic clusters, $[(NiL^1)_2Na]^+NCS^-\cdot MeOH\cdot Et_2O$ (**1**) and $[(NiL^2)_2Na]^+NCS^-\cdot MeOH\cdot Et_2O$ (**2**) [H_2L^1 = *N,N'*-bis(3-methoxysalicylidene)-(1*R*,2*R*)-1,2-diphenylenediamine; H_2L^2 = *N,N'*-bis(3-methoxysalicylidene)-(1*S*,2*S*)-1,2-diphenylenediamine].

The reaction of (1*R*,2*R*)-H_2L^1 or (1*S*,2*S*)-H_2L^2 with $Ni(AcO)_2\cdot 4H_2O$ and NaNCS in a methanol solution afforded red block-shaped crystals of **1** and **2**, in which H_2L Schiff base

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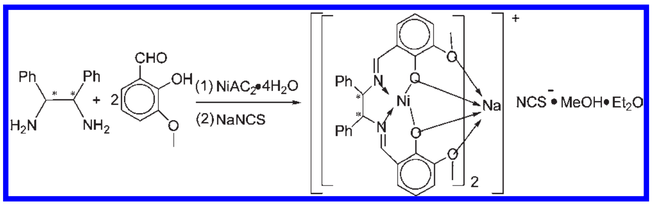
Scheme 1



ligands were obtained by the condensation of 3-methoxysalicylaldehyde with (1*R*,2*R*)-1,2-diphenylenediamine and (1*S*,2*S*)-1,2-diphenylenediamine, respectively (Scheme 1).[11] The IR spectra for both **1** and **2** show C=N stretching absorption at 1609 cm^{-1} and N=C=S stretching absorption at 2064 cm^{-1}.

X-ray analysis reveals that **1** and **2** are enantiomers with a C_2 polar point group ($P2_1$ space group).[12] Their properties are similar, and hence only the results of **1** are discussed in detail here. As shown in Figure 1, complex **1** is a trinuclear cationic Ni_2Na complex with a NCS^- anion as the counterion. A central Na^+ core is linked to two neutral NiL via four phenolate O atoms and four methoxy O atoms from Salen-type Schiff base ligands (H_2L^1). The Na atom is eight-coordinated in trigonal-dodecahedron geometry, which is rarely scarce except for Na^+ coordinated with adequate crown ether ligands. The structure around the Na^+ anion is an unusual 10-membered, metal-containing, crown ether like structure (Figure S2 in the Supporting Information, SI). The two kinds of Na−O distances are between 2.373(4) and 2.646(4) Å, and the distance of Na−O(methoxy) is larger than that of Na−O(phenolate). The dihedral angle between the mean planes of O1−O2−O3−O4 and O5−O6−O7−O8 is 85.1(4)°, suggesting that the two sets of Salen-type Schiff base ligands are almost vertical. The two Ni atoms are all four-coordinated in an approximately square-planar geometry constructed by two imine N atoms and two phenolate O atoms. Adjacent molecules are hold together by a typical hydrogen bond and weak intermolecular C−H···O hydrogen bonding, which link the molecules to form an infinite three-dimensional network (for details on the hydrogen bonds and angles, see Table S1 in the SI).

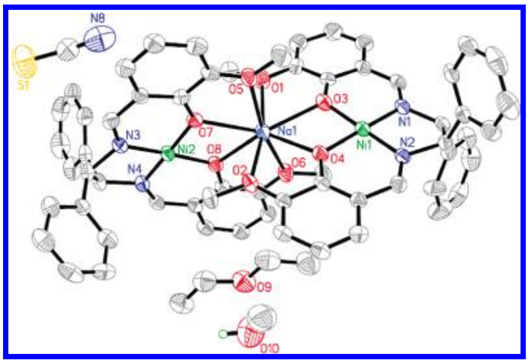


Figure 1. ORTEP view of complex **1** with 30% probability level ellipsoids.

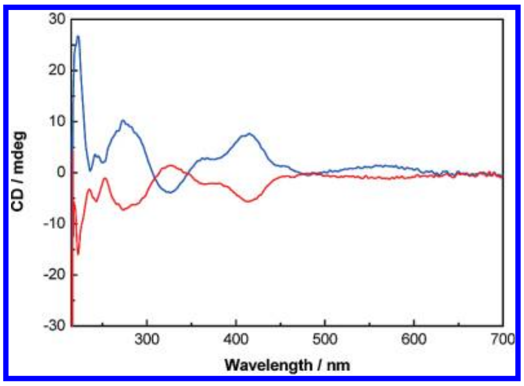


Figure 2. CD spectra of **1** (*R*,*R* isomer; blue line) and **2** (*S*,*S* isomer; red line) in a methanol solution.

To confirm the optical activity and enantiomeric nature of **1** and **2**, the circular dichroism (CD) spectra (Figure 2) were measured in a methanol solution. Compound **1** (an *R*,*R* isomer) exhibits positive Cotton effects at λ_{max} = 222, 243, 273, 362, 414, and 566 nm and a negative dichroic signal centered at λ_{max} = 324 nm. As predicted, the enantiomer complex **2** (an *S*,*S* isomer) displays Cotton effects with opposite signs at corresponding wavelengths and its CD spectrum is a mirror image of that of **1**.

Because the enantiomer complexes **1** and **2** crystallize in a chiral polar space group ($P2_1$) and they also have large dipole moments along the *b* axis according to our semiempirical quantum chemical calculations (PM6; see the SI for details), their second nonlinear optical and ferroelectric properties were studied. The results from powdered samples indicated that they are second-harmonic-generation-active, with approximately 0.8 times that of urea. The ferroelectric property of **1** was first investigated at room temperature with a single-crystal sample and recorded on a Ferroelectric Tester Precision Premier II made by Radiant Technologies, Inc., at room temperature. A single crystal with approximate dimensions of 0.32 × 0.20 × 0.18 mm was carefully selected for the measurement. The ferroelectric measurements along the *b* axis (Figure 3) revealed obvious hysteresis loops that are not like the banana-shaped electric hysteresis loops pointed out by Scott.[13] The ferroelectric effect along the *a* and *c* axes is obviously weaker than that along the *b* axis (Figure S3 and S4 in the SI). The results indicated that complex **1** indeed displays an obvious ferroelectric behavior with a remnant

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(11) Preparation of complexes **1** and **2**: To a solution of 3-methoxysalicylaldehyde (0.304 g, 2 mmol) in 20 mL of methanol was added (1*R*,2*R*)-1,2-diphenylethylenediamine (0.212 g, 1 mmol), and the resulting mixture was heated under reflux for 3 h. A solution of $Ni(AcO)_2 \cdot 4H_2O$ (0.248 g, 1 mmol) and NaNCS (0.243 g, 3 mmol) in 40 mL of methanol was then added, and the mixture was refluxed for another 3 h to give a deep-red solution. Diethyl ether was allowed to diffuse slowly into this solution at room temperature, and red block-shaped crystals of **1** were obtained after 3 days. Yield: 0.798 g, 63.3% [based on $N(iAcO)_2 \cdot 4H_2O$]. Compound **2** was obtained as red block-shaped crystals by a method similar to that of **1**, except that (1*S*,2*S*)-1,2-diphenylethylenediamine (0.212 g, 1 mmol) was used. Yield: 0.750 g, 59.5%. Anal. Calcd for $C_{66}H_{66}N_5NaNi_2O_{10}S$: C, 62.83; H, 5.27; N, 5.55. Found for **1**: C, 62.74; H, 5.15; N, 5.48. Found for **2**: C, 62.84; H, 5.20; N, 5.50. IR (KBr, cm^{-1}): ν(C=N) 1609, ν(N=C=S) 2064.

(12) Crystal data for **1**: $C_{66}H_{66}N_5NaNi_2O_{10}S$, M = 1261.71, T = 293(2) K, monoclinic, $P2_1$, a = 9.7139(14) Å, b = 17.114(3) Å, c = 18.083(3) Å, β = 91.271(2)°, V = 3005.4(8) Å^3, Z = 2, m = 0.730 mm^{-1}, R1 = 0.0580, wR2 = 0.1490, S = 1.01, Flack χ = 0.025(14). Crystal data for **2**: $C_{66}H_{66}N_5NaNi_2O_{10}S$, M = 1261.71, T = 293(2) K, monoclinic, $P2_1$, a = 9.729(5) Å, b = 17.130(8) Å, c = 18.095(9) Å, β = 91.143(7)°, V = 3015(3) Å^3, Z = 2, m = 0.730 mm^{-1}, R1 = 0.072, wR2 = 0.170, S = 0.96, Flack χ = 0.06(2). The crystal structure of **2** is the same as that of **1**, as evidenced by a comparison of the experimental and simulated powder X-ray diffraction patterns (Figure S1 in the SI).

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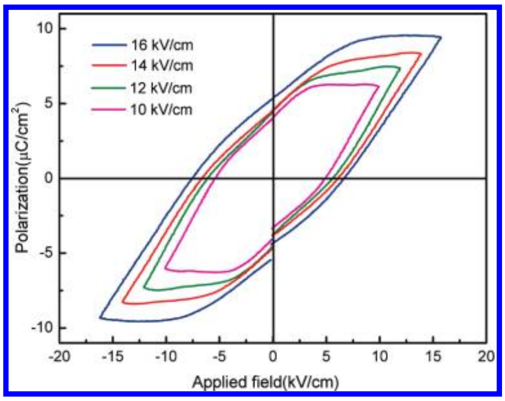

Figure 3. Electric hysteresis loops for a single-crystal sample of complex **1** along the *b* axis at different electric field settings.

polarization (P_r) of ca. 4.18−5.33 μC·cm^{-2} and E_c of ca. 4.92−6.68 kV·cm^{-1}. The saturation spontaneous polarization (P_s) is about 6.15−9.41 μC·cm^{-2}, which is larger than that of the typical ferroelectrics KDP (P_s = 5.0 μC·cm^{-2}), triglycine sulfate (P_s = 3.0 μC·cm^{-2}), and $NaKC_4H_4O_6\cdot 4H_2O$ (Rosal salt; P_s = 0.25 μC·cm^{-2}). Besides polarization of a large organic positive ion, the large P_r and P_s values may also be due to the large polarizability and mobility of the relatively free charge carrier (NCS$^-$). The introduction of organic ligands could reduce the electrostatic attraction between positive and negative charges and increase the polarizability and mobility of charge carriers. In addition, the order−disorder of hydrogen bondings may also contribute to the large remnant and saturation spontaneous polarization.

The ferroelectric properties of powdered samples of complex **1** in pellets were also investigated at room temperature (Figure S5 in the SI). The leakage of single-crystal and powdered samples is not larger than 10^{-7} A·cm^{-2} (Figure S6 in the SI). The applied electric field (E) and frequency (f) dependencies of both the remnant polarization (P_r) and coercive field (E_c) are also given in the SI (Figure S7).

The temperature dependencies of the dielectric constant and dielectric loss of **1** were measured at various frequencies in the range of 10^2−10^6 Hz. A dielectric constant peak at 128 Hz appears at about 330 K (Figure 4a), indicating the presence of a phase transition at ca. T_c = 330 K. The peak slightly moves toward lower temperature, and the height decreases with increasing frequency. As shown in Figure 4b, a relaxation process was also observed, indicating that the dielectric loss changes with temperature at different frequencies, with peak maxima obeying the Arrhenius equation $\tau = \tau_0 \exp(H/\kappa T)$, where T = absolute temperature of relaxation, κ = Boltzmann's constant, H = activation energy, and τ_0 = inverse of the frequency factor. The activation energy is approximately estimated at about 2.94 eV. Additional evidence can be found in the frequency dependence of the dielectric constant and dielectric loss (see Figure S8 in the SI).

In conclusion, two novel homochiral enantiomers, trinuclear ionic clusters, have been successfully synthesized. They are the first examples of ionic metal−organic complexes with Schiff base ligands, which display higher spontaneous polarization than the typical inorganic ferroelectric KDP. Ionic metal−organic compounds are good candidates for exploring novel ferroelectrics.

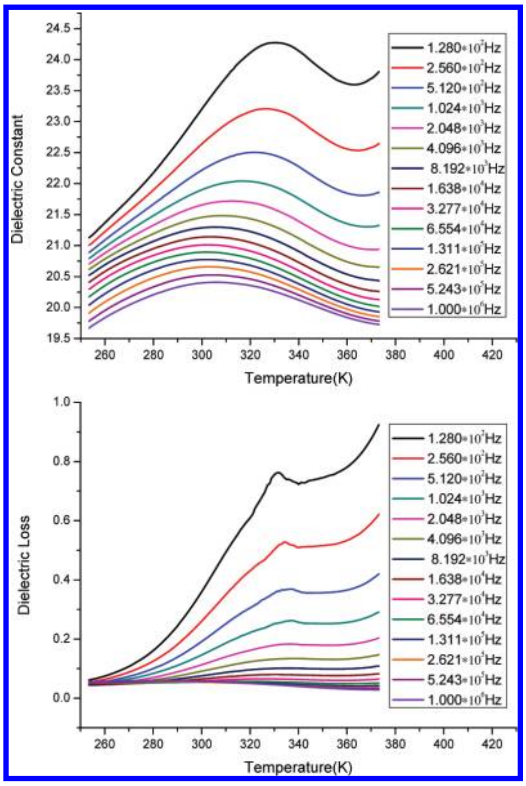

Figure 4. (top) Temperature dependence of the dielectric constant ε' (real part) of complex **1** at various frequencies (10^2−10^6 Hz). (bottom) Temperature dependence of the dielectric loss $\varepsilon''/\varepsilon'$, where ε'' and ε' are the imaginary and real parts of the dielectric constant for complex **1**, at various frequencies (10^2−10^6 Hz).

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Supporting Information Available: X-ray crystallographic CIF files, $E-P$ hysteresis, leakage current, dielectric constant, powder X-ray diffraction, packing diagrams, and details about hydrogen bonds. This material is available free of charge via the Internet at http://pubs.acs.org.