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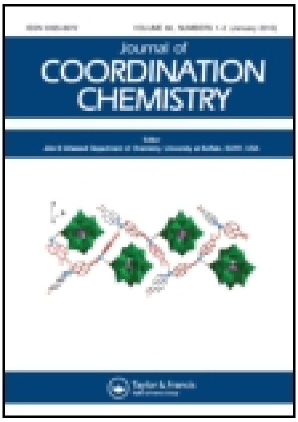

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Syntheses, structures, dielectric and ferroelectric properties of a chiral coordination compound with m-nitro-benzoic acid

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Syntheses, structures, dielectric and ferroelectric properties of a chiral coordination compound with m-nitro-benzoic acid

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One polar noncentrosymmetric complex, [Zn(phen)(H_2O)$_2$L]L (HL = m-nitro-benzoic acid, phen = 1,10-phenanthroline) has been prepared and characterized. The title complex is crystallized in a noncentrosymmetric space group $P2_1$. The compound is a typical ferroelectric and its electric hysteresis loop shows a remnant polarization (P_r) of ca. $0.04\,\mu C\,cm^{-2}$ and coercive field (E_c) of 1.26 V/cm. It may be a potential ferroelectric with a relatively large spontaneous polarization (P_s) of $0.11\,\mu C\,cm^{-2}$. Moreover, permittivity property measurements reveal a dielectric constant (ε_r) of 5.63 and dielectric loss (tan δ) of 2.5%.

Keywords: Zinc; m-nitro-benzoic acid; Ferroelectric; Dielectric; Complex

1. Introduction

Ferroelectrics are an interesting class of materials discovered by Valasek, in 1920, during the study of Rochelle salt ($NaKC_4H_4O_6 \cdot 4H_2O$, potassium sodium tartrate tetrahydrate) [1]. Ferroelectric coordination complexes have numerous potential applications in a variety of new technologies, such as electric devices, information storage, and nonlinear optical devices [2–4]. For a complex to exhibit ferroelectricity, the complex must crystallize in one of the 10 polar noncentrosymmetric crystal classes, namely, 1, m, 2, 2 m, 3, 3 m, 4, 4 m, 6, 6 m crystal classes [5, 6]. Although a great deal of progress has been made in the syntheses of ferroelectric complexes, challenges still remain in engineering of crystalline complexes that exhibit polar order [7]. Because of the close relationship that exists between chirality and ferroelectricity in the 1, 2, 3, 4, and 6 crystal classes, one efficient synthetic strategy to prepare ferroelectric complexes is to use chiral organic ligands that form a homochiral structure, a geometric arrangement in a crystal in which all the chiral ligands show the same dextrorotary or levorotary chirality. Another more challenging synthetic strategy is to use achiral organic ligand. An achiral ligand may induce 1, m, 2, 2 m, 3, 3 m, 4, 4 m, 6, 6 m chirality in the complex because of its flexibility or simply lead to a complex crystallizing in a noncentrosymmetric crystal class. Coordination complexes constructed from mixed-ligands including N-heterocycles and carboxylate ligands are particularly good candidates to produce unique structural motifs with beautiful esthetics

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*Corresponding author. Email: yqzhengmc@163.com and useful functional properties owing to their flexibility and conformational freedom [8–10]. Furthermore, special attention has been focused on mixed-ligand complexes [11–14]. Herein, we report the syntheses, structures, dielectric, and ferroelectric properties of a polar noncentrosymmetric mononuclear mixed-ligand coordination complex, [Zn(phen)(H_2O)$_2$L]L (HL = m-nitro-benzoic acid, phen = 1,10-phenanthroline), that represents the first example of polar noncentrosymmetric complexes based on an achiral organic ligand (m-nitro-benzoic acid).

2. Experimental

2.1. *Materials and physical methods*

All chemicals of reagent grade were commercially available and used without purification. Powder X-ray diffraction measurements were carried out with a Bruker D8 Focus X-ray diffractometer to check phase purity. C, H, and N microanalyses were performed with a Perkin Elmer 2400II CHN/S elemental analyzer. FTIR spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Shimadzu FTIR–8900 spectrometer. Thermogravimetric measurements were carried out from R.T. to 600 °C on preweighed samples in a nitrogen stream using a Seiko Exstar 6000 TG/DTA 6300 apparatus with a heating rate of 10 °C/min. The dielectric and ferroelectric properties of solid-state samples were measured by a pellet of powdered sample at room temperature, while the sample was immersed in insulating oil. The pellet sample was made through a pressure of 60 kN. The dielectric constant (ε_r) and dielectric loss (tan δ) of the samples were obtained by using a computer-controlled impedance analyzer (Agilent 4294A). The remnant polarization (P_r) and coercive field (E_c) were determined from polarization versus electric field (P–E) hysteresis loops measured by Radiant technologies RT Premier II (USA). Single crystal X-ray diffraction data were collected by a Rigaku *R*-Axis Rapid X-ray diffractometer.

2.2. *Synthesis of [Zn(phen)(H_2O)$_2$L]L*

Dropwise addition of 1.0 mL (1 M) of NaOH to a stirred aqueous solution of Zn (CH_3COO)$_2$·2H_2O (0.108 g, 0.5 mM) in 5.0 mL of H_2O gave a fine white precipitate, which was separated by centrifugation and washed with doubly distilled water for five times. The collected white precipitate was added to a solution of m-nitro-benzoic acid (0.167 g, 1.00 mM) in EtOH/water (40 mL, 1 : 1, v/v) and stirred for 3 min. To the mixture 1,10-phenanthroline monohydrate (0.100 g, 0.5 mM) was added to form a colorless solution (pH = 5.25). Slow evaporation at room temperature during one day afforded colorless crystals (yield = 80.5% based on the initial Zn(CH_3COO)$_2$·2H_2O). Anal. Calcd for $C_{26}H_{20}N_4O_{10}Zn$ (%): C, 50.82; H, 3.26; N, 9.12. Found: C, 51.03; H, 3.40; N, 9.30. IR spectrum (KBr, cm^{-1}, supplementary material): 3294(w), 2983(w), 1814(w), 1591(m), 1548(w), 1525(s), 1429(m), 1373(w), 1346(vs), 1066(w), 854(w), 819(vw), 788(w), 717(s), 667(w).

2.3. *X-ray crystallography*

Suitable single crystal is selected under a polarizing microscope and fixed with epoxy cement on fine glass fiber, which are then mounted on a Rigaku *R*-Axis Rapid IP X-ray diffractometer with graphite-monochromated Mo *Kα* radiation ($\lambda = 0.71073$ Å) for cell determination and subsequent data collection. The data are corrected for L_p and absorption effects. The SHELXS-97 and SHELXL-97 programs are used for structure solution and refinement [15, 16]. The respective structures are solved by using direct methods and all non-hydrogen atoms located are in the subsequent difference Fourier syntheses. After several cycles of refinement, all hydrogens associated with carbons are geometrically generated and the rest of the hydrogens are located from successive difference Fourier syntheses. Finally, all non-hydrogen atoms are refined with anisotropic displacement parameters by full-matrix least-squares and hydrogens with isotropic displacement parameters set to 1.2 times the values for the associated heavier atoms. Detailed information about the crystal data and structure determination is summarized in table 1. Selected interatomic distances and bond angles are tabulated in table 2.

3. Results and discussion

3.1. *Syntheses*

At first $[Zn(phen)(H_2O)_2L]L$ was synthesized by reactions of freshly prepared $Zn(OH)_2 \cdot xH_2O$ precipitate with 1,10-phenanthroline and m-nitro-benzoic acid in $EtOH/H_2O$ at the ratio of 1 : 2 : 2 (pH = 5.4, yield = 20.4% based on the initial $Zn(CH_3COO)_2 \cdot 2H_2O$). In order to raise

Table 1. Crystal data and structure refinement parameters for $[Zn(phen)(H_2O)_2L]L$ ($T = 293(2)$ K).

Compound	$[Zn(phen)(H_2O)_2L]L$
Temperature (K)	293(2)
Empirical formula	$C_{26}H_{20}N_4O_{10}Zn$
Formula weight	613.83
Description	Colorless, block
Crystal size (mm)	0.10 × 0.10 × 0.10
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	6.112(1)
b (Å)	21.804(4)
c (Å)	9.609(2)
α (°)	90
β (°)	97.75(3)
γ (°)	90
Volume (Å^3)	1268.8(4)
Z	2
D_{calc} (g cm^{-3})	1.607
$F(0\ 0\ 0)$	628
μ (mm^{-1})	1.036
θ Range (°)	3.36–27.41
Reflections collected	12,497
Unique reflections (R_{int})	5738 ($R_{int} = 0.059$)
Data, restraints, parameters	3938, 0, 369
Goodness of fit on F^2	1.230
R_1, wR_2 [$I \geqslant 2\sigma(I)$][a]	0.0419, 0.0769
R_1, wR_2 (all data)[a]	0.0887, 0.1284
Extinction coefficients	0.00000
A, B values in w[b]	0, 1.5649
$\delta\rho_{max}$, $\delta\rho_{min}$ (e Å^{-3})	0.917, −0.991
Flack parameter[c]	0.017(17)

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

[b] $w = [(2(F_o^2)+(AP)2 + BP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$.

[c] Absolute structure parameter [17–20].

Table 2. Selected interatomic distances (Å) and bond angles (deg) for [Zn(phen)(H_2O)$_2$L]L (T = 293(2) K).

Zn–O1	2.030(5)	Zn–O9	2.008(5)	Zn–O10	2.044(3)
Zn–N1	2.167(4)	Zn–N2	2.103(5)		
O1–Zn–O9	107.8(2)	O1–Zn–O10	91.8(2)	O1–Zn–N1	153.4(2)
O1–Zn–N2	88.2(2)	O9–Zn–O100	99.9(2)	O9–Zn–N1	98.4(2)
O9–Zn–N2	110.9(2)	O10–Zn–N1	88.2(2)	O10–Zn–N2	147.6(2)
N1–Zn–N2	77.9(2)				
Hydrogen bonding contacts					
D–H	d(D–H)	d(H···A)	∠DHA	d(D···A)	A
O9–H9C	0.71	1.958	156	2.619(6)	O5$^{\#4}$
O9–H9B	0.92	1.829	158	2.702(6)	O6$^{\#5}$
O10–H10C	0.98	1.632	168	2.599(7)	O2
O10–H10C	0.98	2.271	123	2.927(6)	O1
O10–H10B	0.83	1.879	159	2.665(7)	O6$^{\#4}$
C8–H8A	0.93	2.52	154	3.380(7)	O2$^{\#3}$

Symmetry transformations used to generate equivalent atoms: #1 = x, y, z; #2 = $-x$, $-y$, $-z$; #3 = $x+1$, y, $z+1$; #4 = $-x+2$, $y+1/2$, $-z+2$; #5 = $-x+1$, $y+1/2$, $-z+2$.

the yields of the title complex, when the molar ratio of $Zn(OH)_2{\cdot}xH_2O$ precipitates (or replaced by $Zn(CH_3COO)_2{\cdot}2H_2O$), phen and m-nitro-benzoic acid is 1 : 1 : 2; one obtains crystals of the title complex with 80% yield, indicating that the proportion of molecules is irrelevant to the production of the title complex. The title compound was stable in air and insoluble in common solvent such as water, ethanol, acetone, etc. The above synthetic reactions could be schematized as follows:

$$Zn(CH_3COO)_2 \cdot 2H_2O + 2HL + 2phen \rightarrow [Zn(phen)(H_2O)_2L]L + 2CH_3COOH + phen$$

$$Zn(CH_3COO)_2 \cdot 2H_2O + 2HL + phen \rightarrow [Zn(phen)(H_2O)_2L]L + 2CH_3COOH$$

3.2. *Description of the crystal structures*

Single crystal X-ray diffraction reveals that the structural unit comprises of a mononuclear [Zn(phen)(H_2O)$_2$L]$^+$ and L$^-$. The local coordination environment around zinc(II) is shown in figure 1. Each Zn(II) coordinates with two nitrogens from phen, one carboxylic oxygen from HL and two oxygens of H_2O generate a tetragonal pyramidal coordination geometry. The equatorial plane has two N of phen, one carboxylato O of L, and one water (O10), while the apical position is occupied by water (O9). The Zn–O and Zn–N bond distances fall in the ranges 2.008–2.044 and 2.103–2.167 Å, respectively (table 2), comparable with those reported for [$Zn(C_7H_4ClO_3)_2(C_{12}H_8N_2)(H_2O)$] [21]. The angles are 98.4(2)–153.4(2), which are normal.

As depicted in figure 2, the projection of the unit-cell packing onto the *bc* plane illustrated polar packing along the *b* axis [22–28]. The intermolecular hydrogen bonds from water (O9) to non-chelating oxygen (O5$^{\#4}$) of the m-nitro-benzoic acid ligand, as well as those from water (O10) to non-chelating oxygen (O6$^{\#4}$) of the m-nitro-benzoic acid, interlink [Zn(phen)(H_2O)$_2$L]$^+$ and L$^-$ into [Zn(phen)(H_2O)$_2$L]L units. The interplanar distance of 3.43 Å between neighboring aromatic rings of different m-nitro-benzoic acid ligands indicates significant face-to-face π–π stacking interactions making a contribution to formation of a

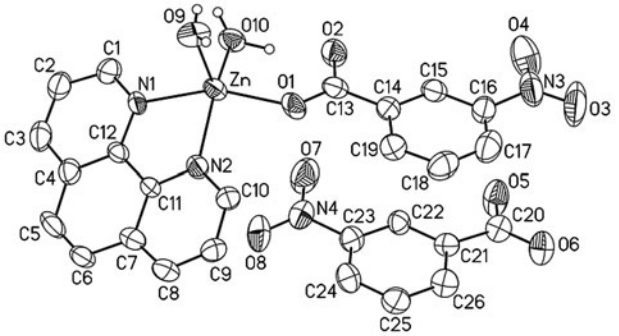

Figure 1. ORTEP view of [Zn(phen)(H_2O)$_2$L]L with ellipsoids at 45% probability; hydrogens were omitted for clarity.

one-dimensional chain [29]. C8 of phen donates one hydrogen to carboxylate oxygen ($O2^{\#3}$) to form interchain hydrogen bonds with $d(\text{C–H}\cdots\text{O}) = 3.380$ Å and $\angle(\text{C–H}\cdots\text{O}) = 154°$, leading to a 2D supramolecular layer parallel to the *bc* plane. Along the crystallographic *a* axis, the 2D layers are stacked and interlayer hydrogen bonds are from O9 to $O6^{\#5}$ of the uncoordinating carboxylate of m-nitro-benzoic acid anion with $d(\text{O–H}\cdots\text{O}) = 2.702$ Å is responsible for stabilization of a 3D framework.

3.3. *Comparison of the relevant m-nitro-benzoic complexes*

A Cambridge Structural Database survey indicated more entries about m-nitro-benzoic-containing metal complexes. According to the literature, 45 complexes for m-nitro-benzoic could be grouped into five classes. For instance, the complexes in the centrosymmetric triclinic space group *P*–1(24), centrosymmetric monoclinic space group *C*2/*c*(10), $P2_1/c$(2), $P2_1/n$(4), *P*2/*c*(1) and four compounds with orthorhombic space group *Pbca* [30–34]. From the space group viewpoints, title complex with Zn, m-nitro-benzoic, and phen crystallizes in the polar chiral monoclinic space group $P2_1$, representing the first example of polar noncentrosymmetric complexes based on the achiral m-nitro-benzoic acid.

3.4. *Infrared spectra*

The IR spectrum shows a broad band centered at 3394 cm^{-1}, indicating the presence of water in the complex. The strong and sharp bands at 1591 and 1373 cm^{-1} can be ascribed to carboxylic stretches (ν_{as}, ν_s) [35–37]. The $\Delta\nu$ ($\Delta\nu = \nu_{as}–\nu_a = 218$ cm^{-1}) between the two bands of coordinated carboxyl is more than 200 cm^{-1}, which indicates strong coordination of carboxylate oxygen to manganese [37]. The strong peaks at 1525 and 1346 cm^{-1} could be assigned to ν_{as} and ν_s of $–NO_2$ [38], while sharp peaks at 1548 and 1429 cm^{-1} can be attributed to phen [39].

3.5. *PXRD and thermal analysis*

To check the phase purity of the complex, powder X-ray diffraction (PXRD) patterns were recorded at room temperature. As shown in supplementary material, peak positions of

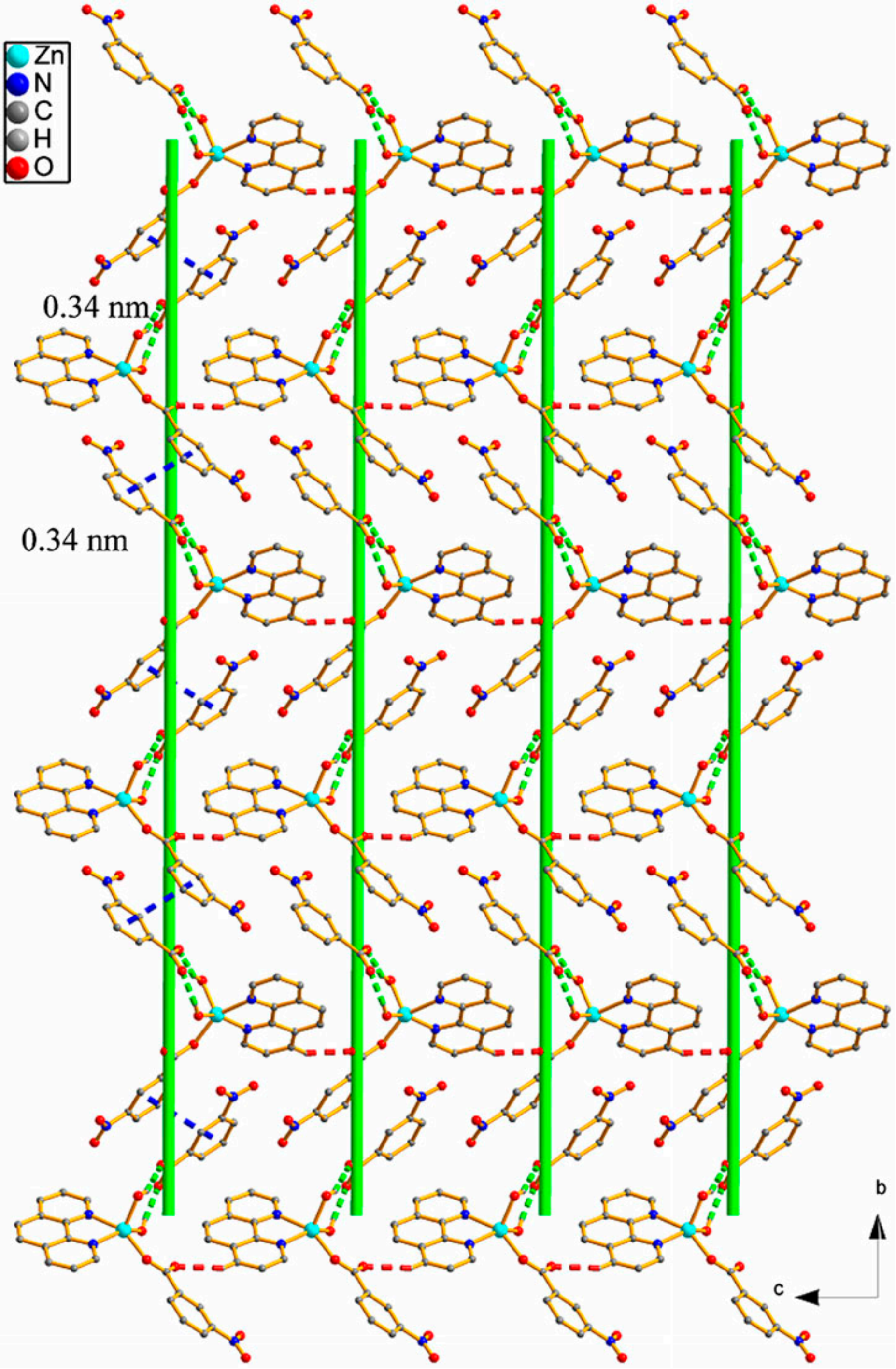

Figure 2. Projection of the unit-cell packing onto the *bc* plane to illustrate the polar packing along the *b* axis. For clarity, the majority of hydrogens were omitted.

simulated and experimental PXRD patterns are in agreement, confirming its phase purity. The difference in intensity of some diffraction peaks may be attributed to the preferred orientation of the crystalline powder samples.

In order to characterize the complex more fully in terms of thermal stability, its thermal behavior was studied by TG/DTA in dry nitrogen from 30 to 600 °C (supplementary material). The DTA curve reveals two endothermal peaks and an exothermic peak during decomposition and the TG curve corresponds to three weight loss steps. Weight loss of the first step is 6.4% from 30–87 °C, attributed to loss of lattice water (calcd 5.9%) with an endothermal peak at 84 °C. Upon further heating, weight loss of 4.1% is observed between 87 and 255 °C accompanying a weak exothermic process at 286 °C, consistent with the decarboxylation of the carboxyl ligands. The third weight loss of 42.1% from 255 to 430 °C results from release of the organic ligands. When further heated, the resulting intermediate loses weight very slowly and the black residue is assumed to be a mixture of Zn and C.

3.6. *Ferroelectric and dielectric properties*

As shown in figure 3, $[Zn(phen)(H_2O)_2L]L$ exhibits ferroelectric behavior presented here as electric hysteresis loops with remnant polarizations. The complex crystallized in a noncentrosymmetric space group $P2_1$ which is associated with the point group 2, that is, one of the 10 polar point groups required for ferroelectric behavior. The ferroelectric data of the powder pellet sample of $[Zn(phen)(H_2O)_2L]L$ were measured at room temperature at different voltages. Polarization (P) versus applied electric field (E) plots at room temperature with applying field up to $\pm 50\,\mathrm{kV\,cm^{-1}}$ showed (figure 3) a clear electric hysteresis loop. The remnant electric polarization (P_r) and coercive field (E_c) were calculated to be $0.04\,\mu\mathrm{C\,cm^{-2}}$ and of $1.26\,\mathrm{kV\,cm^{-1}}$, respectively [40]. The saturation spontaneous polarization (P_s) of $[Zn(phen)(H_2O)_2L]L$ is $0.11\,\mu\mathrm{C\,cm^{-2}}$. Besides polarization of a large organic positive ion, the large P_s value may also be due to large polarizability and mobility of the relatively free charge carrier (L^-). The introduction of organic ligands could reduce

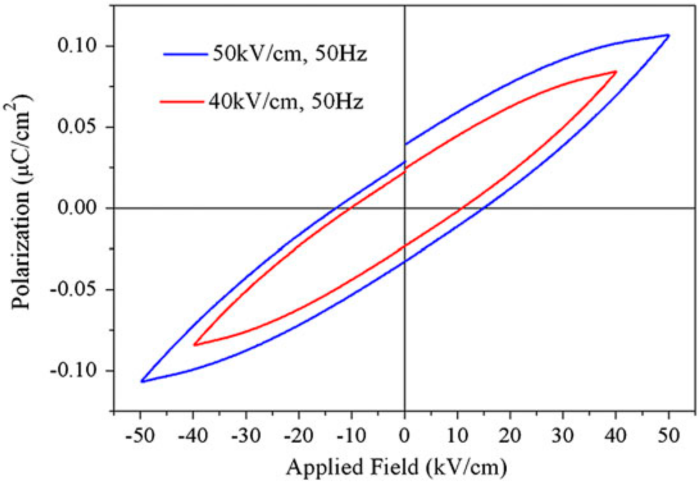

Figure 3. P–E hysteresis loops at room temperature.

electrostatic attraction between positive and negative charges and increase the polarizability and mobility of charge carriers. The order-disorder of hydrogen bonds may also contribute to the large remnant and saturation spontaneous polarization [41]. The dielectric constant (ε_r) and dielectric loss (tan δ) for [Zn(phen)(H_2O)$_2$L]L are 5.63 and 2.5%, respectively.

4. Conclusion

One chiral complex possessing ferroelectric and dielectric properties in a simple molecule has been synthesized. Though several ferroelectric coordination polymers or ferromagnetic coordination polymers are known, the title complex is the first example based on achiral m-nitro-benzoic acid. This complex also showed low dielectric loss and low dielectric constant. Further investigations on chiral m-nitro-benzoic acid compounds with both ferroelectric and magnetic properties are underway in our laboratory. Our target is to prepare chiral metal complexes with other metals.

Supplementary material

Crystallographic data for **1** deposited with the Cambridge Crystallographic Data Center, CCDC-903398 [CCDC, 12 Union Road, Cambridge CB2 1EZ, United Kingdom; Fax: (44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk; website: http://www.ccdc.cam.ac.uk].

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