

Structures and Dielectric Properties in Thermochromic Nickel(II) Compounds

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Hysteretic dielectric responses of thermochromic compounds, $[\text{Ni}(\text{dieten})_2]\text{X}_2$ (dieten = *N,N*-diethylethylenediamine, $\text{X}^- = \text{BF}_4^-$ and ClO_4^-) have been observed and discussed based on their structures in low- and high-temperature phases.

Bistable compounds having two inherent states with different physical properties are promising materials for application in information storage, switching devices, and sensors.¹⁻⁴ Thermo-chromism is a phenomenon that induces a reversible color change with changes in temperature, which has been practically applied using liquid crystals and leuco dyes. This phenomenon is also well-known in coordination chemistry, and the color change is generally ascribed to temperature-dependent changes in the coordination geometry of the chromophore.⁵ Several compounds exhibit significant discontinuous color changes associated with the first-order structural phase transition between high-temperature phase (HTP) and low-temperature phase (LTP). Such bistable thermo-chromic compounds are expected to show additional switchable properties, e.g., magnetism and dielectricity.

Thermo-chromic copper(II) compounds, $[\text{Cu}(\text{dieten})_2]\text{X}_2$ ($\text{X}^- = \text{BF}_4^-$ and ClO_4^- ; dieten = *N,N*-diethylethylenediamine) have been reported by Paoletti et al.⁶⁻⁸ Their color changes between red at the LTP and purple at the HTP. Grenthe et al. have determined the structures of the LTP (space group: $P\bar{1}$) and the HTP ($I2$) and revealed the phase transition is induced by order-disorder motion of the dieten ligand (Figure 1).^{9,10} Recently, we reported bistable dielectric properties of $[\text{Cu}(\text{dieten})_2]\text{X}_2$ ($\text{X}^- = \text{BF}_4^-$ and ClO_4^-).¹¹ The real part of the dielectric constant was found to be significantly different in the two states, which suggests that the information stored in the bistable compounds can be “retrieved” as electric signal. Such thermo-chromic compounds providing thermally switchable optical and dielectric properties would open interesting prospects for applying information storage and processing devices. From these aspects, we also focused on the thermo-chromic nickel(II) compounds, $[\text{Ni}(\text{dieten})_2]\text{X}_2$ ($\text{X}^- = \text{BF}_4^-$ ($\mathbf{1}\cdot\text{BF}_4$) and ClO_4^- ($\mathbf{1}\cdot\text{ClO}_4$)). The nickel(II) compounds exhibit thermo-chromic behavior between orange in the LTP and red in the HTP;^{5,6} however, only the structure of $\mathbf{1}\cdot\text{ClO}_4$ in the LTP has

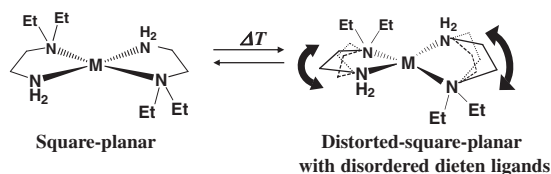


Figure 1. Schematic thermal geometric change of the chromophore in $[\text{M}(\text{dieten})_2]\text{X}_2$.

been reported so far. Here, we report the crystal structure of $\mathbf{1}\cdot\text{ClO}_4$ in the HTP and dielectric properties of $\mathbf{1}\cdot\text{BF}_4$ and $\mathbf{1}\cdot\text{ClO}_4$.

The nickel(II) compounds were prepared according to the literature methods.³ Single crystals of $\mathbf{1}\cdot\text{ClO}_4$ were isolated by slow recrystallization from methanolic solution, whereas $\mathbf{1}\cdot\text{BF}_4$ was not obtained as well-grown single crystals. Powder X-ray diffraction (XRD) of these compounds show an essentially the same pattern in the LTP, whereas their patterns differ from each other in the HTP (Figures S1 and S2).¹² $\mathbf{1}\cdot\text{ClO}_4$ is crystallized in triclinic space group $P\bar{1}$ in the LTP.^{5,6} Single-crystal X-ray analysis for $\mathbf{1}\cdot\text{ClO}_4$ in the HTP was successfully carried out at 385 K and revealed that the space group changed to monoclinic $P2_1/n$ (Figure 2).¹³ In the structure, nickel(II) atom is in a distorted square-planar geometry coordinated by four nitrogen atoms in two dieten ligands. Two chelate rings in $[\text{Ni}(\text{dieten})_2]^{2+}$ are nearly planar with large anisotropic temperature factors perpendicular to the rings owing to mixing δ and λ conformation isomers of dieten ligands and thermal vibration. Thermal factors of ethyl groups of dieten and oxygen atoms of ClO_4^- are also very large because of the structural disorder, which is not observed in the LTP. When the space group Pn was applied to the analysis, an equally possible noncentrosymmetric structure was obtained with flack parameter of 0.00(4). Finally the centrosymmetric structure was adopted according to the diffraction extinction rule here. The large disorder would result in the pseudo-symmetric structure.

In the case of $[\text{Cu}(\text{dieten})_2](\text{ClO}_4)_2$, the space group is changed between $P\bar{1}$ (LTP) and $I2$ (HTP) with similar geometrical change of the chromophore as $\mathbf{1}\cdot\text{ClO}_4$; however, the conformation of ethyl groups in the HTP is different from that of $\mathbf{1}\cdot\text{ClO}_4$.

The temperature dependences of the ac dielectric constants in the frequency range 10^2 – 10^6 Hz for two nickel(II) compounds $\mathbf{1}\cdot\text{BF}_4$ and $\mathbf{1}\cdot\text{ClO}_4$ were measured on a LCR meter in the heating

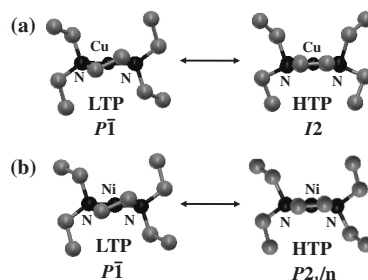


Figure 2. Structures of the LTP and the HTP for (a) $[\text{Cu}(\text{dieten})_2](\text{ClO}_4)_2$ and (b) $[\text{Ni}(\text{dieten})_2](\text{ClO}_4)_2$. Counter anions and hydrogen atoms were omitted for clarity.

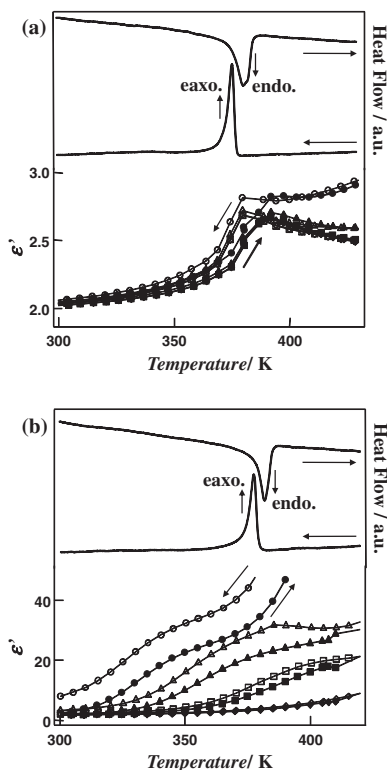


Figure 3. DSC curves and temperature dependences of the dielectric constants for (a) $1\cdot\text{BF}_4$ and (b) $1\cdot\text{ClO}_4$. (●: heating, ○: cooling at 1 kHz), (▲: heating, △: cooling at 10 kHz), (■: heating, □: cooling at 100 kHz), (◆: heating, ◇: cooling at 1 MHz).

and cooling modes. Thermal variations of the dielectric constant at 1, 10, 100 kHz, and 1 MHz in the heating and cooling modes for $1\cdot\text{BF}_4$ and $1\cdot\text{ClO}_4$ are shown in Figure 3. For comparison, DSC curves for $1\cdot\text{BF}_4$ and $1\cdot\text{ClO}_4$ are also shown in Figure 3. The structural transition temperatures, $T_{c\uparrow}$ and $T_{c\downarrow}$, are respectively determined to be 374 and 368 K for $1\cdot\text{BF}_4$ and 382 and 377 K for $1\cdot\text{ClO}_4$ based on the DSC results. In the case of $1\cdot\text{BF}_4$, the value of ϵ' for LTP at 300 K is 2.0 (Figure 3a). On heating, the value of ϵ' increases abruptly around $T_{c\uparrow}$, and reaches to 2.6 at 400 K, which corresponds to HTP. On cooling, the value of ϵ' drops abruptly at $T_{c\downarrow}$. The ϵ' vs. T curves show hysteresis with ΔT of 6 K, which well consistent with the DSC result. This dielectric behavior is explained as change of local electric dipole stemming from the conformation change in the $[\text{Ni}(\text{dieten})_2]^{2+}$ considered as magnetic exciton.¹¹ The dielectric behavior of $1\cdot\text{ClO}_4$ is different from that of $1\cdot\text{BF}_4$. The ϵ' value for $1\cdot\text{ClO}_4$ (LTP) is 3.4 at 300 K, and increases with a rise in temperature (Figure 3b). The ϵ' vs. T curves denote a clear frequency dependence. At 1 MHz, the value of ϵ' slightly changes to the same level as $1\cdot\text{BF}_4$ around T_c . On the other hand, the ϵ' vs. T curves at 1, 10, and 100 kHz show hysteretic behavior with a maximum value of 250 at 1 kHz. The maximum value is a hundred times as high as that of $1\cdot\text{BF}_4$. In addition, the change of dielectric constant is not synchronized with the structural transition, in particular at 1 kHz, which is also a remarkable difference from $1\cdot\text{BF}_4$. Judging from DSC and dielectric results of Cu^{II} and Ni^{II} compounds, the structural phase transition with

the orientational disordering (thermal motion) of the ethyl groups would be one origin of the dielectric response. The out-of-sync behavior of $1\cdot\text{ClO}_4$ with structural transition at the low frequency may be associated with the motion of counter anions, ClO_4^- .

In summary, we have determined the structure of $[\text{Ni}(\text{dieten})_2](\text{ClO}_4)_2$ ($1\cdot\text{ClO}_4$) in the HTP and revealed the structural difference from the copper(II) analog. Remarkably high dielectric constants, ϵ' , were observed for $1\cdot\text{ClO}_4$. Comparative discussions with the bistable thermochromic Cu^{II} and Ni^{II} compounds suggest significant association between the thermochromism and electric dipole moment through the structural transition.

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- Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- X-ray crystallographic data for $1\cdot\text{ClO}_4$ at 385 K ($\text{C}_{12}\text{H}_{32}\text{O}_8\text{N}_4\text{Cl}_2\text{Ni}$): fw 490.03, red block ($0.3 \times 0.2 \times 0.2 \text{ mm}^3$), monoclinic, space group $P2_1/n$, $a = 9.8940(17)$, $b = 8.4677(15)$, $c = 13.425(2) \text{ \AA}$, $\beta = 96.419(3)^\circ$, $V = 1117.7(3) \text{ \AA}^3$, $Z = 2$, $D_{\text{calcd}} = 1.456 \text{ g cm}^{-3}$. The refinements by full matrix least squares gave an R factor of 0.0973 from 1256 reflections with intensity $I > 2\sigma(I)$ for 139 variables. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included but not refined. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-724727. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).