# Hysteresis Loops in Dielectric Properties of the Thermochromic Copper(II) Compounds

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The dielectric changes of thermochromic compounds, $[Cu(dieten)_2]X_2$ ($X = BF_4$ and $ClO_4$, dieten = *N*,*N*-diethylethylenediamine), have been induced by the transformation between square-planar and distorted-square-planar.

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Thermochromic compound is one which changes its color as the temperature is varied. The thermochromism is also a well-known phenomenon in coordination chemistry and is usually ascribed to temperature dependent changes in the coordination geometry of chromophore.[1] More interesting class of the compounds involves a discontinuous color change associated with the onset of a first-order structural phase transition between high-temperature phase (HTP) and low-temperature phase (LTP). The conversion between the HTP and LTP leads to a molecular compound presenting a hysteresis loop when the two states of the molecules are equally obtained under a given external perturbation. The switching between HTP and LTP states is governed by short and long range cooperative interactions in the compound, which result in the occurrence of the hysteresis loop.

Thermochromic behavior for the copper(II) compounds, $[Cu(dieten)_2](BF_4)_2$ (**1•BF$_4$**) and $[Cu(dieten)_2](ClO_4)_2$ (**1•ClO$_4$**) has been reported by Paoletti and co-workers[2–4] It was revealed that the compounds **1•BF$_4$** and **1•ClO$_4$** exhibit thermochromic behavior between red color at LTP and purple color at HTP (phase-transition temperature $T_c = 298$ and 321 K for **1•BF$_4$** and **1•ClO$_4$**). Lever and Kennedy have suggested a temperature dependent tetragonal distortion of the copper(II) coordination with an accompanying change in the d-orbital energies as a probable mechanism for thermochromism (Figure 1).[5] Grenthe et al. have described the structures of the red (LTP) and purple (HTP) forms of the thermochromic copper(II) compound **1•ClO$_4$**.[6] Furthermore, Sato et al. have investigated the illumination effects for a thermochromic copper(II) compound.[7] When the compound, **1•BF$_4$**, was illuminated with UV-light, a structural change involving a color change was induced.

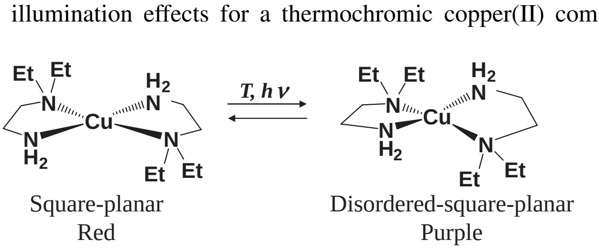

**Figure 1.** Chromophore geometry change accompanying with thermochromism for the compounds **1•BF$_4$** and **1•ClO$_4$**.

The copper atom has a square-planar coordination geometry in both of LTP and HTP for **1•ClO$_4$**. The thermochromic behavior in **1•ClO$_4$** is caused by an effect of a change in the in-plane field strength.[6] Nishimori et al. reported that the value of the enthalpy change of the transition, $\Delta H$, for **1•BF$_4$** was estimated to be 16.62 kJ mol$^{-1}$, and the value of the entropy change, $\Delta S$, was also estimated to be 55.35 J K$^{-1}$ mol$^{-1}$.[8] The origins of the very large entropy may arise from the onset of the motion in the cation involving the puckering of the copper-ligand ring and orientational disordering of the ethyl groups. In order to understand the phase transition, they applied the Chesnut exciton model, and suggested that the conformation change in the cation can be treated as a "magnetic exciton."[8] Therefore, the local electrical dipoles in the thermochromic compounds must be different in the HTP and LTP states, leading to a change in dielectric properties of the compounds upon thermochromism.

In this paper, we report for the first time the change of dielectric constants upon thermochromic compounds in the copper(II) complexes $[Cu(dieten)_2]X_2$ ($X = BF_4$ and $ClO_4$, dieten = *N*,*N*-diethylethylenediamine). The copper(II) compounds, $[Cu(dieten)_2](BF_4)_2$ (**1•BF$_4$**) and $[Cu(dieten)_2](ClO_4)_2$ (**1•ClO$_4$**) was prepared by the method reported earlier[3] and a sample annealed to 60 °C was used for all of the measurements.[8]

The temperature dependences of the ac dielectric constants in the frequency range $10^2$–$10^6$ Hz for two copper(II) compounds **1•BF$_4$** and **1•ClO$_4$** were measured on a LCR meter in the heating and cooling modes. The frequency sweeps were carried out isothermally. Thermal variations of the dielectric constant obtained by this method at 1, 10, 100, and 1 MHz frequency in the heating and cooling modes for **1•BF$_4$** and **1•ClO$_4$** are shown in Figures 2a and 2b. For comparison, DSC curves for **1•BF$_4$** and **1•ClO$_4$** are also shown in Figures 2a and 2b.

The dielectric property shows that the value of $\varepsilon'$ for **1•BF$_4$** at 270 K is equal to 4.3, which corresponds to LTP. On heating mode, the value of $\varepsilon'$ increases abruptly around $T_c\uparrow = 299$ K. The $\varepsilon'$ value at 320 K is equal to 6.8, which corresponds to HTP. On cooling, the value of $\varepsilon'$ drops abruptly at $T_c\downarrow = 293$ K. The abrupt change of the dielectric constants shows a hysteresis loop ($\Delta T = 6$ K). The thermochromic behavior of **1•BF$_4$** between HTP to LTP is well observed in the temperature dependences of the dielectric constants. The copper(II) com-

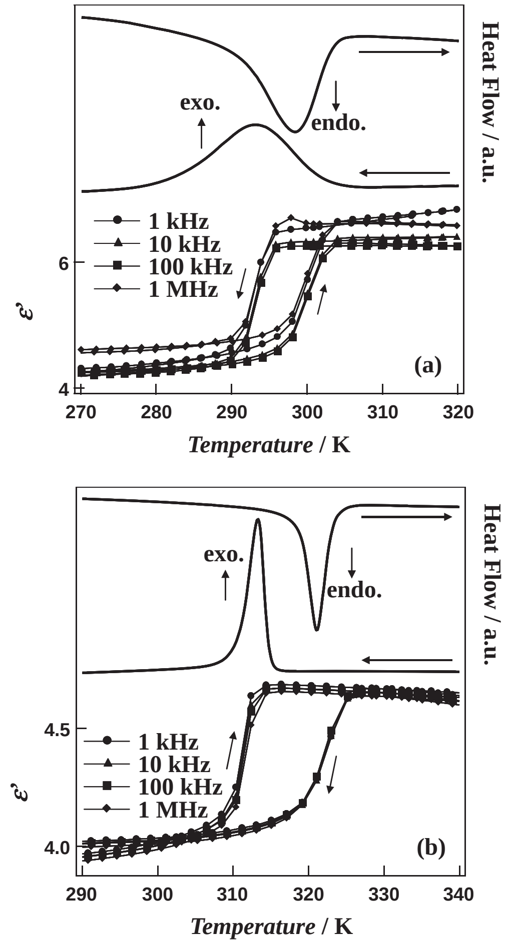

**Figure 2.** DSC curves and temperature dependences of the dielectric constants for the compounds (a) **1•BF$_4$** and (b) **1•ClO$_4$**.

pound **1•BF$_4$** exhibits a dielectric hysteresis loop, in agreement with the DSC measurements (Figure 2a). The thermal hysteresis loop was recorded in about 12 h. Additional thermal cycles did not modify the thermal hysteresis loop. The dielectric property of the compound **1•ClO$_4$** is also represented in Figure 2b in the form of the $\varepsilon'$ versus $T$ curve. The dielectric property for **1•ClO$_4$** is similar to that for **1•BF$_4$**. The $\varepsilon'$ value for **1•ClO$_4$** is equal to 4.0 at 290 K, which corresponds to LTP. As the temperature is increased over 320 K, the value of $\varepsilon'$ increase abruptly at $T_c\uparrow = 322$ K. The $\varepsilon'$ value at 340 K is equal to 4.6, which corresponds to HTP. On cooling, the value of $\varepsilon'$ drops abruptly at $T_c\downarrow = 311$ K. The change of the dielectric constants show the hysteresis loop ($\Delta T = 11$ K).

Recently, Bousseksou and co-workers reported about the first observation of the hysteretic bistability in the dielectric properties and the photoswitching of the dielectric constants for the spin-crossover compounds.[9,10] In the spin-crossover compounds, the hysteresis results from cooperative interactions between the spin-crossover metal centers, and is sometimes associated with a structural phase transition. The variation originates from two different populations of electronic orbitals characterized by different spin states: high-spin ($S = 2$) and low-spin ($S = 0$) for iron(II) compounds.

In thermochromic compounds, as a first explanation, upon LTP $\rightleftharpoons$ HTP thermochromism, the change in dielectric constants of these compounds results from the structural phase transition. The local symmetry distortion modifies significantly the local field, inducing a large change in the dipole moment detected through dielectric spectroscopy. This produces a significant variation in the dielectric constants, $\varepsilon'$, with a thermal hysteresis loop characteristic of a first-order phase transition.

Calculations of dipole moments ($\mu$) for $[\mathrm{Cu(dieten)_2}]^{2+}$ cation based on the single crystal structures for the LTP and HTP was performed in order to gain a deeper insight into the quantitative aspects of the variation of the dielectric constant upon thermochromism.[11] The value of the dipole moment in LTP was $\mu_{\mathrm{LTP}} = 0.00$ ($\mu_x = 0.00$, $\mu_y = 0.00$, $\mu_z = 0.00$). On the other hand, the value of the moment in HTP was $\mu_{\mathrm{HTP}} = 1.88$ ($\mu_x = 0.0029$, $\mu_y = -0.0793$, $\mu_z = 1.8751$). Therefore, the copper(II) compounds **1•BF$_4$** and **1•ClO$_4$** exhibit a switching of the dipole moment ($\mu_{\mathrm{LTP}} = 0 \rightleftharpoons \mu_{\mathrm{HTP}} = 1.88$) accompanying with thermochromism.

In summary, the changes of the dielectric constants with the hysteresis loop have been observed experimentally for the thermochromic compound $[\mathrm{Cu(dieten)_2}]\mathrm{X_2}$ (X = BF$_4$ (**1•BF$_4$**) and ClO$_4$ (**1•ClO$_4$**)). It has been revealed that the thermochromic behavior for copper(II) compounds is the first-order phase transition with thermal hysteresis loop. Furthermore, it has been thought from DFT calculations that the origin of the variation of the dielectric constants upon the thermochromism correlated with the changes in dipole moments through the structural phase transition.

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11 The ab initio calculations were performed with the Gaussian 03 program package. The Møller-Plesset MP2 method was used with 6-311+G**.

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