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Short communication

A molecular-based phase trasition compound based on ligand 1-ethyl-1, 4-diazonia-bicyclo [2.2.2] octane

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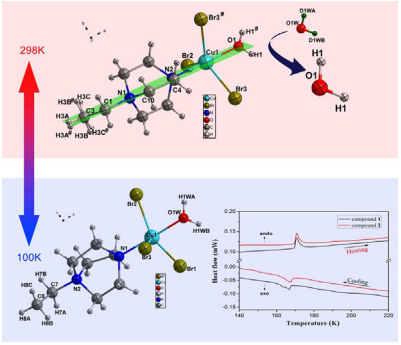
GRAPHICAL ABSTRACT

Differential scanning calorimetry (DSC) showed that the compound [Cu(dabco-CH_2CH_3)(H_2O)Br_3] (**1**) underwent reversible phase transitions. Single crystal X-ray diffraction data detected that it transformed from a room-temperature phase *Pnma* to a low-temperature phase $P2_1/c$. Study of the deuterated compound [Cu(dabco-CH_2CH_3)(D_2O)Br_3] ruled out the effect of isotope effects on the phase transition temperature of the compound [Cu(dabco-CH_2CH_3)(H_2O)Br_3].



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ABSTRACT

The phase trasition compound [Cu(dabco-CH_2CH_3)(H_2O)Br_3] (**1**) was synthesized by solution evaporation method. Dielectric measurements and differential scanning calorimetry (DSC) showed that this compound underwent reversible phase transitions at ca. 170.9 K with the hysteresis widths of 4 K. Single crystal X-ray diffraction data detected that it transformed from a room-temperature phase *Pnma* to a low-temperature phase $P2_1/c$. Crystal structure analysis have indicated that the structural phase transitions of the compound were ascribed to the torsional movement of dabco ring and the disappearance of the mirror plane. Study of the deuterated compound [Cu(dabco-CH_2CH_3)(D_2O)Br_3] ruled out the effect of isotope effects on the phase transition temperature of the compound [Cu(dabco-CH_2CH_3)(H_2O)Br_3].

Phase transition materials are important functional materials with diverse physical characteristics and potential applications [1]. Particularly, ferroelectric phase transition materials can be widely used in large-capacity capacitors, optical switches, and optical information storage devices due to dielectric, electro-optical and photorefractive effects. Besides, phase transition materials with piezoelectric effects can be applied to piezoelectric sensors and transducers [2]. In the past, inorganic compounds (inorganic salts of metals and oxides) have mostly been employed as phase transition materials. In recent years, molecular-based phase transition materials (organic molecules or organic-inorganic hybrids formed by the coordination or recombination of metal ions) have been highlighted [3]. It is crucial to prepare new temperature-triggered molecular-based phase transition materials that help to study the theoretical properties of structures and to explore new

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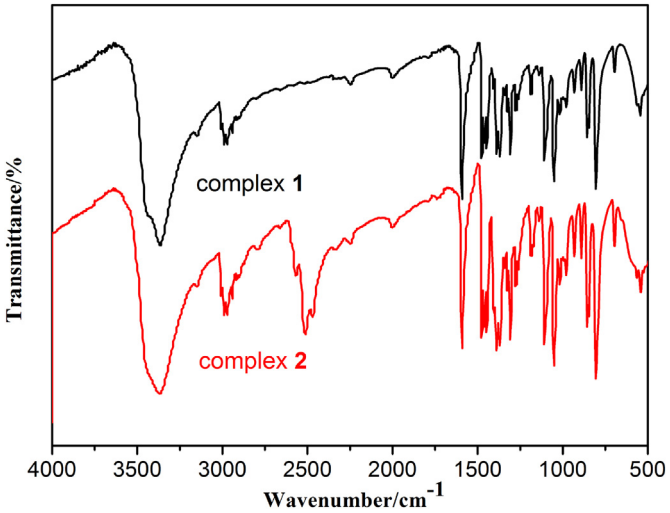


Fig. 1. IR spectra of **1** and **2**.

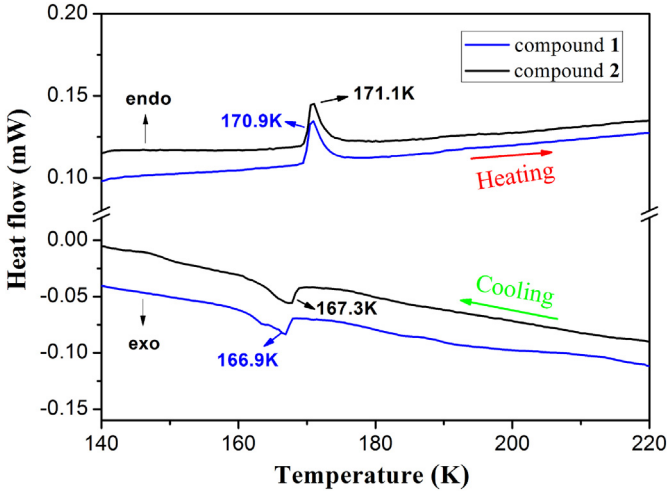


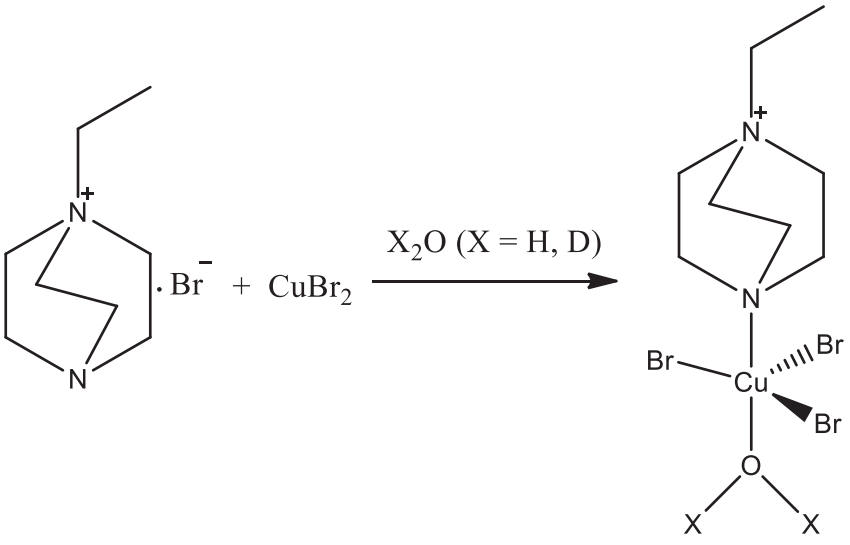
Fig. 2. DSC curves of **1** and **2** obtained in a heating-cooling mode.

physical properties [5]. It is well-known that structural changes at different temperatures mainly contribute to the structural phase transition of crystal, thus requiring the introduction of a part that can be redirected with temperature changes in designing and preparing a molecular-based crystal with phase transition [6]. In particular, 1,4-diazabicyclo [2.2.2] octane (dabco) with higher symmetry can be redirected by molecular rotation like a molecular motor, so dabco series of coordination polymers have attracted wide attention [7]. In 2012, Xiong et al. obtained a ferroelectric phase transition complex [Cu(Hdabco)(H_2O)Cl_3] through self-assembly of $CuCl_2$ and dabco [8], which the $[Hdabco]^+$ cation were utilized in metal-organic hybrid ferroelectrics in which the twisted of the cation ring cause the para-electric-to-ferroelectric phase transitions.

After the above studies, ligands by modifying with different groups were used, as derivatives of 1,4-diazabicyclo [2.2.2] octane, were combined with metal halides, forming a series of hybrid inorganic-organic compounds [9]. For example, by assembling $[dabcoCH_2X]^+$ (X = Cl, Br) cation and $[M^{II}X_2]$ (M = Cu, Mn), into four homologous phase transition metal coordination complexes, [Cu(dabcoCH_2Br)(H_2O)Br_3] (**3**), [Cu(dabcoCH_2Cl)(H_2O) $Br_{2.75}Cl_{0.25}$] (**4**), [Cu(dabcoCH_2Cl)(H_2O)Cl_3] (**5**) and [Mn(dabcoCH_2Cl)(H_2O)Cl_3] (**6**) [10]. Interestingly, all metal ions in these phase transition compounds adopt the penta-coordinated mode in a trigonal-bipyramidal geometry, and the dabco rings act as molecular rotators were redirected with decreasing temperature. Comparing the phase transition behaviors of these compounds, it can be seen that the phase transition temperatures are different. In particular, the comparison of the phase transition temperature of compounds **4**, **5** and **6** has been reported that small changes in the stator may affect the structural phase transition of the molecular rotor [10a]. At the same time, compounds **3** and **4** have similar stator and different molecular rotor, and they were found to exhibit ferroelastic phase transitions at 250 K and 190 K, respectively (Fig. 1). It indicates that the select of the molecular rotor also may affect the structural phase transition of the compounds, however, the specific mechanism needs further exploration. Based on this study, we prepared a novel phase transition material [Cu(dabcoCH_2CH_3)(H_2O)Br_3] (**1**). Herein, we reported the synthesis, phase transition, and dielectric properties of compound **1** (Scheme 1).

Compound **1** was obtained as golden transparent block crystals by treating 1-ethyl-1,4-diazabicyclo[2.2.2] octane and $CuBr_2$ in aqueous solution [11]. Used deuterated water instead of water to obtain the Compound **2** [12]. The structure of **1** and **2** was identified by IR, Thermo gravimetric analyses (TGA) and Powder X-ray diffraction (PXRD) [13].

As we all know, DSC measurements can effectively detect reversible phase transition triggered by temperature changes. A pair of reversible



Scheme 1. Synthesis of **1** (X = H) and **2** (X = D).