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A Neutral Fe(III) Compound Exhibiting A Two-Step Spin Transition and Dielectric Anomalies

中性鉄(III)錯体の二段階スピン転移と誘電特性

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Introduction

Spin-crossover (SCO) compounds have been the subjects of intense research efforts for many decades, activity that is motivated by their potential applications in molecular-level sensors, switches and memory devices.¹ Large numbers of polymeric and polynuclear compounds with two-step spin transitions have been reported, behaviour that is associated with relatively strong covalent bonds from the ligands that bridge the metal centres. In the case of mononuclear SCO compounds, the cooperative interactions can be derived from hydrogen bonds, which are often mediated through anions or solvent molecules. The first two-step Fe(II) spin-crossover compound, $[\text{Fe}^{\text{II}}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ (pic = picolylamine), in which hydrogen bonds play an important role in the spin transition was discovered by Gülich and co-workers in 1985.² In terms of relevance to the present work, we note that Morgan and co-workers reported an example of a concerted two-step SCO and symmetry breaking in a d^5 ion for the Fe(III) salt $[\text{Fe}^{\text{III}}(\text{L})]\text{ClO}_4$ but that neutral mononuclear ferric compounds with wide hysteresis, two-step spin transitions have not been intensively studied.³

The aim of the present study was to design a mononuclear ferric compound that exhibits dielectric, spin-crossover and photochemical properties. Multifunctional SCO materials that simultaneously respond to electric and magnetic stimuli have attracted increasing attention in recent years. Herein we report the photo-responsive compound, $[\text{Fe}^{\text{III}}(\text{H-5-Cl-thsa-Me})(\text{5-Cl-thsa-Me})] \cdot \text{H}_2\text{O}$ (H₂-5-Cl-thsa-Me = 5-chlorosalicylaldehyde methylthiosemicarbazone) (**1**), that exhibits a two-step spin transition and dielectric anomalies. For the H₂-5-Cl-thsa-Me ligand, we note that an anionic SCO compound based on the H₂-5-Br-thsa ligand has been reported by Boillot and coworkers and characterized using powder X-ray diffraction.

Experiments

The Schiff base ligand 5-Cl-thsa-Me (2 mmol, 0.548 g) and DMA (4 mmol, 0.45 g in MeOH) were reacted in 50 mL of methanol and 5 mL of water at 80°C and 1 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was slowly added to the refluxing mixture. After 8 h, the reaction was cooled to room temperature and left to stand overnight. The resulting black precipitate was collected and washed with acetone/water and then dried under vacuum for 4 h. Single crystals suitable for X-ray diffraction had deposited in the bottom of flask. Yield is ~ 92%. Elemental analysis (%) for compound **1**: Calc. (found) for $\text{C}_{18}\text{H}_{19}\text{O}_3\text{N}_6\text{S}_2\text{Cl}_2\text{Fe}$: C 38.73% (38.45%), H 3.43% (3.33%), N 15.05% (15.00%).

Results and Discussion

As depicted in Fig. 1a, the asymmetric unit of **1** consists of one Fe(III) centre, mono-deprotonated H-5-Cl-thsa-Me and di-deprotonated 5-Cl-thsa-Me ligands, and an uncoordinated water molecule. The Fe(III) metal centre is six-coordinate and at 110 K the Fe–N and Fe–S bond distances are 1.933(5)/1.948(5) Å and 2.2389(15)/2.2566(16) Å, respectively, indicating a low spin state for Fe(III). At room temperature the Fe–N and Fe–S bond distances are elongated, namely they are 2.111(10)/2.124(9) Å and 2.391(4)/2.453(4) Å,

respectively, which is indicative of a high spin state for Fe(III). The structure of this intermediate state was further probed at 260 K using both synchrotron and Mo(K α) X-ray radiation; for Mo(K α) diffraction the Fe–N and Fe–S bond distances are 1.999(8)/2.016(9) Å and 2.308(4)/2.338(4) Å, respectively whereas for the synchrotron diffraction data, the distances are 2.034(4)/2.030(4) Å and 2.3051(16)/2.3465(16) Å, respectively. These results are clear evidence of the structural transformation between high-spin (HS) and low-spin (LS) states but the structure is averaged so that the independent ½HS/½LS coexistence could not be observed.

Magnetic susceptibility data for compound **1** acquired on a sample obtained from a bulk reaction revealed that χT (3.89 cm³ K mol⁻¹) is slightly lower than that expected for one high spin Fe(III) metal centre (4.375 cm³ K mol⁻¹) at 300 K if one assumes that $g = 2$. With decreasing temperature, χT is nearly constant down to 275 K and then undergoes a two-step transition as shown in Fig. 1b. The transition temperatures of the two steps were calculated as $\delta(\chi T)/\delta T$; $T_c(\downarrow)$ to be 270 K and 245 K in the cooling mode and $T_c(\uparrow) = 249$ K and 278 K in the heating mode.

The hysteresis widths are 4 and 8 K for the two-step spin transition. It is important to note that the purity and crystallinity of the bulk samples were confirmed using powder X-ray diffraction analysis.

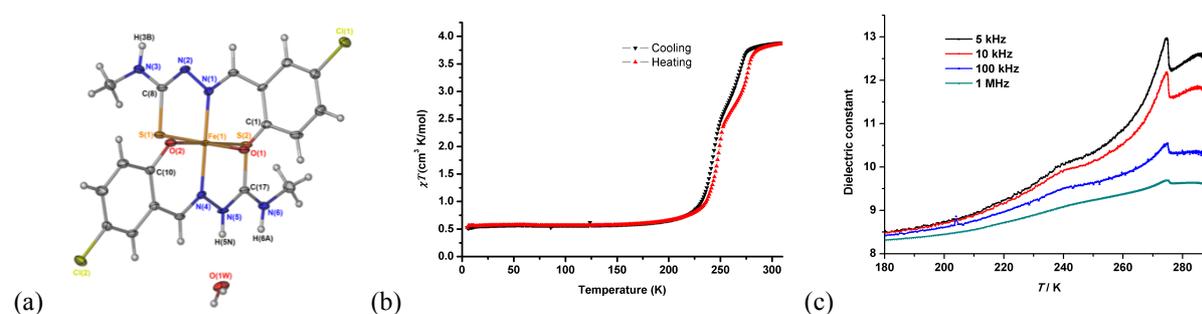


Fig. 1 (a) Unit cell structure of compound **1** at 110 K. (b) Magnetic susceptibility of compound **1** from 5 to 300 K. (c) Dielectric constant vs T plot of compound **1** under different frequencies.

Temperature-dependent dielectric constant measurements of compound **1** revealed dielectric anomalies at approximately 270 and 240 K upon cooling at high frequencies, which is consistent with that of the DSC anomalies and the spin transition temperatures. As shown in Fig. 1c, an increase of dielectric constant with increasing temperature was observed. The first anomaly temperature shifts to higher temperature with an increase in frequency. From the dielectric losses plot, two-step anomalies are observed at 1 MHz. The dielectric hysteresis was not obtained for compound **1** because of the relatively weak cooperativity showing a small magnetic hysteresis loop.

References

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