Cooperative spin-crossover transition from three-dimensional purely pi-stacking interactions in a neutral heteroleptic azobisphenolate Fe-III complex with a N3O3 coordination sphere

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A novel neutral heteroleptic Fe\textsuperscript{III} complex from two kinds of \(\pi\)-extended tridentate ligands was designed and prepared. The \(\pi\)-ligands formed a three-dimensional purely \(\pi\)-stacking interaction network. The present complex proved to be the first neutral spin-crossover (SCO) Fe\textsuperscript{III} complex with \(\text{N}_2\text{O}_3\) coordination sphere exhibiting an abrupt SCO transition with a thermal hysteresis of 10 K and the light-induced excited spin-state trapping effect.

Phase transitions are found widely in natural sciences and have aroused considerable attention to elucidation of their fundamental mechanisms as well as their functional applications to intriguing switchable properties such as giant magnetoresistance,\textsuperscript{1} field-induced superconductivity,\textsuperscript{2} electric-field nonlinear conduction,\textsuperscript{3} photo-induced electronic phase transition\textsuperscript{4} in molecular materials. The occurrence of a phase transition in solid-state materials is considered to originate from the competition between the free energies of more than two phases.

Similar situation is found in molecular spin-crossover (SCO) coordination compounds which derive from the competition between the ligand-field splitting energy (LFSE) and spin-pairing energy for a transition metal coordination sphere.\textsuperscript{5} Therefore, the SCO between a high-spin (HS) and low-spin (LS) states represents molecular bistability and can be observed even in the solution, liquid,\textsuperscript{6} or liquid-crystalline\textsuperscript{7} states. On the other hand, the thermal SCO behaviour in the solid state is known to exhibit spin-equilibrium, gradual conversion, and abrupt transition with or without a thermal hysteresis, whose behaviours are considered to reflect the cooperativity of SCO due to the correlation of the spin-states between neighbouring SCO molecules.\textsuperscript{5a,b} Although numerous reports referred to the existence of intermolecular interactions for the cooperative SCO transition, quantitative explanation of the role of intermolecular interactions for the cooperativity of SCO still remains unresolved.

![Molecular structure of [Fe\textsuperscript{III}(azp)(qsal)]·0.5CH\textsubscript{3}OH](Image)

We recently discovered a new family of anionic SCO Fe\textsuperscript{III} complexes from unprecedented ONO-tridentate azp anion derivatives \([\text{H}_2\text{azp} = 2,2’-\text{azobisphenol}]\).\textsuperscript{8} Although the azp derivatives gave the LFSE in the SCO region for the Fe\textsuperscript{III} ions, their anionic SCO complexes showed non-cooperative gradual conversions. Their crystal structures revealed that their crystal packings were typical of ionic crystals and therefore the Coulomb interactions between a counter cation and SCO anion may not contribute to the cooperativity of SCO. Moreover, the coexistence of the Coulomb and \(\pi\)-stacking interactions in the pseudopolymorph may induce the distortion of a coordination octahedron around Fe atom. To elucidate the intrinsic role of \(\pi\)-stacking interactions for the cooperativity of SCO, we focused on a neutral Fe\textsuperscript{III} complex from the azp ligand. To achieve charge neutrality of an Fe\textsuperscript{III} complex, we selected a well-known mono-anionic qsal ligand whose Fe\textsuperscript{III} complexes exhibited various kind of SCO transitions\textsuperscript{9} and furthermore afforded multifunctional compounds\textsuperscript{10} involving \(\pi\)-stacking interactions \([\text{Hqsal} = N-(8-\text{quinoyl})\text{salicylaldimine}]\). We report herein the preparation, physical properties, and crystal structures of the novel neutral heteroleptic Fe\textsuperscript{III} compound, [Fe(azp)(qsal)]·0.5CH\textsubscript{3}OH 1 (Fig. 1), which shows a cooperative abrupt SCO transition with a thermal hysteresis and the light-induced excited spin-state trapping effect.
The heteroleptic complex 1 was synthesized by the ligand exchange reaction between the corresponding homoleptic cationic and anionic complexes in methanol solutions according to a modified procedure in the literature. The composition of obtained black platelet crystals was confirmed by microanalysis and single crystal X-ray structural analysis.

The temperature variations of magnetic susceptibility for 1 were measured by a Quantum Design MPMS-XL magnetometer at 0.5 T in the temperature range of 2–300 K (Figure 2a). The $\chi_m T$ value for 1 was 4.32 cm$^3$ K mol$^{-1}$ at 300 K, suggesting that 1 was in the HS state. On lowering temperatures, the $\chi_m T$ values for 1 were almost constant down to 190 K and then decreased abruptly. The magnetic transition was completed at 175 K ($T_{1/2} = 182$ K) and further cooling the $\chi_m T$ values were almost temperature independent and 0.50 cm$^3$ K mol$^{-1}$ at 10 K, indicating that the complex was in the LS state. On heating the sample, the reverse abrupt transition was observed ($T_{1/2} = 192$ K), resulting in the thermal hysteresis width of 10 K. This abrupt magnetic transition behaviour contrasts with the gradual ones in the anionic SCO Fe$^{III}$ complexes from the azp derivatives.

To confirm the spin states for 1, the temperature dependence of Mössbauer spectrum was recorded at 14.3, 170, and 205 K (Figure 2c). The spectra for 1 at 14.3 and 170 K exhibited only one well-resolved quadrupole doublet. On heating the sample to 205 K, a narrow quadrupole doublet appeared on behalf of the wide well-resolved doublet, indicative of the occurrence of an SCO conversion between 170 and 205 K. Therefore, the wide and narrow doublets are assigned to the LS and HS states, respectively. Assuming each spectrum consisted of one HS and one LS quadrupole doublet, the best fit parameters are listed in Table S1. Consequently, the spin-states at 14.3 and 170 K were ascribed to completely LS, whereas that at 205 K was completely HS, which is consistent with the magnetic susceptibility data. This coincidence provides clear evidence that the magnetic transition in 1 originates from the SCO conversion.

To estimate thermodynamic parameters of the present compound experimentally, the differential scanning calorimetry (DSC) analysis was performed (Fig. S1). On cooling the sample the exothermic peak was observed at 183 K with an enthalpy difference ($\Delta H$) of 5.25 kJ mol$^{-1}$ and entropy difference ($\Delta S$) of 28.7 J K$^{-1}$ mol$^{-1}$. On heating the sample the endothermic peak was at 189 K with $\Delta H = 6.18$ kJ mol$^{-1}$ and $\Delta S = 32.7$ J K$^{-1}$ mol$^{-1}$. To obtain the thermodynamic parameters from the magnetic susceptibility data, the temperature dependence of $\chi_m T$ for 1 was fitted by the regular-solution model	extsuperscript{12} expressed by

$$\ln \left( \frac{1 - \chi_m \gamma_{HS}}{\chi_m \gamma_{HS}} \right) = \frac{\Delta H + \gamma' (1 - 2\gamma_{HS}) - \Delta S}{RT} \frac{\Delta S}{R}$$

where $\chi_m$ denotes the HS fraction, $\gamma'$ denotes the interaction energy involving the cooperativity of SCO, and $R$ is the gas constant. The best fit thermodynamic parameters were $\Delta H = 5.33$ kJ mol$^{-1}$, $\Delta S = 28.7$ J K$^{-1}$ mol$^{-1}$ and $\gamma' = 3.50$ kJ mol$^{-1}$. The thermodynamic parameters $\Delta H$ and $\Delta S$ from the DSC analysis are in good agreement with those from the magnetic susceptibility. Since the expression with $\gamma' > 2RT_{SCD}$ is fulfilled ($T_{SCD} = \Delta H/\Delta S$), the present compound exhibits strong cooperativity of the SCO transition.

To confirm the structural change upon the SCO transition, the temperature variations of single-crystal X-ray analysis for 1 were performed by using a Bruker APEX2 ULTRA system. Most crystals were heavily twinned, but fortunately one of the crystals was successful to determine the crystal structures at 90 and 273 K. The crystallographic data are listed in Table S2. The crystal belongs to triclinic system with P-1. The asymmetric unit contained one [Fe(azp)(qsal)] molecule and a half methanol molecule. Although the azp ligand has potential orientational disorder, the crystal analyses was only successful in assuming an ordered structure of the azp ligand. Either azp divalent anion or qsal monovalent anion was coordinated to an Fe$^{III}$ ion as a tridentate ligand in an almost perpendicular manner, to construct a pseudo-octahedral Fe$_2$NO$_3$ coordination sphere (Fig. S2). The coordination bond lengths and distortion parameters ($\Sigma$ and $\Theta$) along with those of the homoleptic Fe(qsal)$_2$ cation and Fe(azp)$_2$ anion are listed in Table S3. The Fe-O and Fe-N coordination bond lengths for the azp and qsal anions in 1 at 273 K were approximately good agreement with those in the HS states for the corresponding homoleptic complexes, respectively, whereas those at 90 K were similar to those in the LS states. On the other hand, the distortion parameters of $\Sigma$ and $\Theta$ in 1 at 90 and 273 K were those between the Fe(qsal)$_2$ cation and Fe(azp)$_2$ anion in the low and high temperature phases, respectively. These indicate that compound 1 exhibits absolute SCO transition.
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Notes and references


