

# Cooperative spin transition and thermally quenched high-spin state in new polymorph of $[\text{Fe}(\text{qsal})_2]\text{I}_3$

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**Abstract** Novel polymorph of the ferric spin crossover complex,  $\beta$ - $[\text{Fe}(\text{qsal})_2]\text{I}_3$  [qsalH = *N*-(8-quinolyl)salicylaldimine], has been prepared and characterized by magnetic susceptibilities and Mössbauer spectra.  $\beta$  polymorph exhibited a cooperative complete spin transition with a thermal hysteresis of 25 K and a tendency to be quenched in the high-spin (HS) state, which is contrastive to a gradual incomplete spin conversion in  $\alpha$  polymorph.

**Keywords** Spin crossover · Ferric complex · Polymorph · Magnetic properties · Mössbauer spectra

## 1 Introduction

Polymorphism in spin crossover (SCO) compounds affords valuable information on the effects of the coordination geometries and intermolecular interactions upon their magnetic behaviors. Despite a number of examples of polymorphism in the Fe(II) SCO complexes, the polymorphic Fe(III) SCO complexes have been rarely reported [1, 2]. The family of the ferric SCO complexes,  $[\text{Fe}(\text{qsal})_2]\text{X}$  [X = counter anion],

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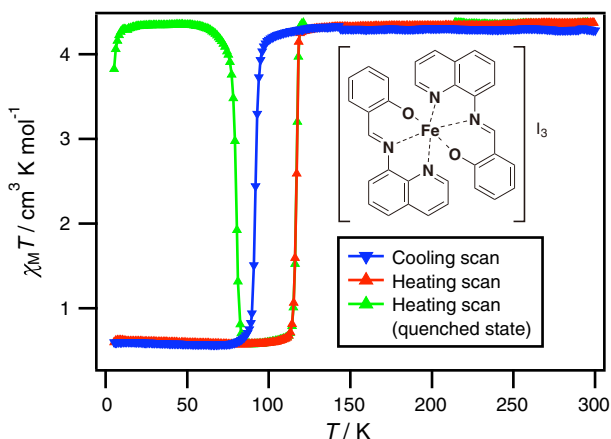
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**Fig. 1** The  $\chi_M T$  versus  $T$  product for  $\beta$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub> at scan speed with 1 K min<sup>-1</sup>



was known as a versatile component for multifunctional SCO compounds [3–7]. Recently we have reported the crystal structures and gradual SCO behaviors under pressures for [Fe(qsal)<sub>2</sub>]<sub>3</sub> (Fig. 1) [8], which is hereafter designated as  $\alpha$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub>. In the course of previous experiments, we have found another polymorph,  $\beta$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub>. In this paper we will report the temperature dependence of magnetic susceptibilities and Mössbauer spectra for  $\beta$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub>, which exhibited a cooperative spin transition with a wide thermal hysteresis of 25 K and a tendency to be quenched in the high-spin (HS) state.

## 2 Experimental

**Preparation of  $\beta$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub>** Tetrabutylammonium triiodide (TBA·I<sub>3</sub>) (80 mg) was dissolved in 160 ml of methanol and filtered off. The solution was poured into the filtered solution of [Fe(qsal)<sub>2</sub>]<sub>3</sub>NO<sub>3</sub> (50 mg) in 100 ml of methanol. The precipitates appeared within a few hours and were filtered off.  $\beta$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub> was obtained as very thin dark brown platelets concomitant with a small amount of tiny black crystalline aggregates of  $\alpha$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub> and large black rectangular parallelepipeds, which was a nonstoichiometric compound designated as [Fe(qsal)<sub>2</sub>]<sub>2.75</sub>. All the measurements were performed on the sample separated under microscope. Anal. Calcd for C<sub>32</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub>I<sub>3</sub>: C, 41.28; H, 2.38; N, 6.02. Found: C, 41.01; H, 2.66; N, 5.80%.

**Magnetic susceptibility measurements** Magnetic susceptibilities were measured on a Quantum Design MPMS SQUID magnetometer under 0.5 T in the temperature range of 2–300 K. Data were corrected for diamagnetic contributions estimated by Pascal constants.

**Mössbauer spectra** The Mössbauer spectra were measured on a constant acceleration spectrometer with a source of <sup>57</sup>Co/Rh in the transmission mode. The measurements at low temperature were performed with a closed-cycle helium refrigerator (Iwatani Co. Ltd.). The obtained Mössbauer spectra were fitted with symmetric Lorentzian doublets by a least squares fitting program.

### 3 Results and discussion

#### 3.1 Preparation and characterization

$\beta$ - $[\text{Fe}(\text{qsal})_2]\text{I}_3$  was prepared by metathesis between  $[\text{Fe}(\text{qsal})_2](\text{NO}_3)$  and TBA- $\text{I}_3$  in methanol. Contamination by  $\alpha$ - $[\text{Fe}(\text{qsal})_2]\text{I}_3$  and  $[\text{Fe}(\text{qsal})_2]\text{I}_{2.75}$  sometimes occurred on more dilute or slower diffusion conditions. The composition for  $\beta$ - $[\text{Fe}(\text{qsal})_2]\text{I}_3$  was confirmed by microanalyses. Powder XRD measurement for  $\beta$ - $[\text{Fe}(\text{qsal})_2]\text{I}_3$  revealed that peak positions were different from the ones simulated from the crystal structure of  $\alpha$ - $[\text{Fe}(\text{qsal})_2]\text{I}_3$ , clearly indicating that  $\beta$ - $[\text{Fe}(\text{qsal})_2]\text{I}_3$  is a new polymorph of  $[\text{Fe}(\text{qsal})_2]\text{I}_3$ .

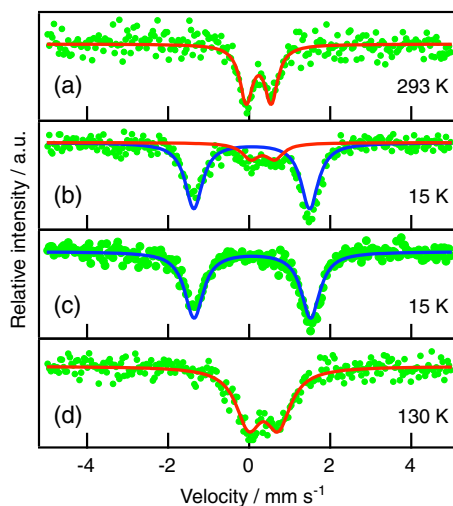
#### 3.2 Magnetic susceptibilities

The variable temperature magnetic susceptibilities were measured on a polycrystalline sample of  $\beta$ - $[\text{Fe}(\text{qsal})_2]\text{I}_3$  at a scan speed of  $1 \text{ K min}^{-1}$ . The  $\chi_{\text{M}}T$  versus  $T$  product is shown in Fig. 1. The  $\chi_{\text{M}}T$  value at 300 K is  $4.30 \text{ cm}^3 \text{ K mol}^{-1}$ , suggesting the  $\text{Fe}(\text{qsal})_2$  cation is almost in the HS state. On lowering the temperature, the  $\chi_{\text{M}}T$  value abruptly decreased at around 95 K ( $T_{1/2} \downarrow = 92 \text{ K}$ ). The  $\chi_{\text{M}}T$  value of  $0.60 \text{ cm}^3 \text{ K mol}^{-1}$  at 5 K indicated the complex is almost in the low-spin (LS) state. On heating the sample, the  $\chi_{\text{M}}T$  value discontinuously increased at around 110 K ( $T_{1/2} \uparrow = 117 \text{ K}$ ). Since the temperature dependences of  $\chi_{\text{M}}T$  on repeating the cooling and heating scans were reproducible,  $\beta$ - $[\text{Fe}(\text{qsal})_2]\text{I}_3$  is a novel SCO compound showing a wide thermal hysteresis loop of 25 K. It should be noted that the  $\chi_{\text{M}}T$  values below the transition temperature depended on the cooling scan speeds. The faster the cooling speeds were, the higher the  $\chi_{\text{M}}T$  values below the transition temperature were. When the room-temperature sample was inserted into an MPMS chamber setting the temperature of 5 K, the sample could be completely quenched in the HS state (Fig. 1, green triangles). On heating the quenched sample at a scan speed of  $1 \text{ K min}^{-1}$ , the quenched HS state was relaxed to the ground LS state at around 80 K. These magnetic behaviors were different from a gradual incomplete spin conversion without a thermal hysteresis in  $\alpha$ - $[\text{Fe}(\text{qsal})_2]\text{I}_3$  ( $T_{1/2} = \text{ca.} 240 \text{ K}$ ).

#### 3.3 Mössbauer spectra

The Mössbauer spectra were measured on a polycrystalline sample of  $\beta$ - $[\text{Fe}(\text{qsal})_2]\text{I}_3$ . The spectrum at 293 K demonstrated one doublet (Fig. 2a), which was ascribed to the HS state (isomer shift (IS) = 0.232, quadrupole splitting (QS) =  $0.616 \text{ mm s}^{-1}$ ). On cooling the sample without temperature control, the spectrum at 15 K consisted of one LS doublet (81.3%, IS = 0.062, QS =  $2.861 \text{ mm s}^{-1}$ ) and one HS doublet (18.7%, IS = 0.331, QS =  $0.595 \text{ mm s}^{-1}$ ) (Fig. 2b). Since the compound was easy to be trapped in the quenched HS state as described above, the spectrum at 15 K cooled after retaining the temperature of 80 K for a few hours was recorded again. Consequently, only one LS doublet spectrum was observed (IS = 0.075, QS =  $2.878 \text{ mm s}^{-1}$ ) (Fig. 2c). This means that the former HS doublet is derived from the quenched HS state. On heating, the LS doublet (IS = 0.349, QS =  $0.734 \text{ mm s}^{-1}$ ) was recovered at 130 K (Fig. 2d).

**Fig. 2** Mössbauer spectra for  $\beta$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub> at **a** 293 K, **b** 15 K after cooling without temperature control, **c** 15 K after annealing at 80 K, and **d** 130 K. *Green circles* indicate the observed spectra. *Blue* and *red lines* show the fitted curves for the high-spin and low-spin states, respectively



### 3.4 External treatments

When the crystals of  $\beta$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub> were poured into pressure transmitting media such as Daphne 7373, Fluorinert, silicone oils, and water-ethanol, they broke into pieces and the spin transition disappeared. On the other hand, the magnetic behavior for  $\alpha$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub> have never changed in the pressure media [8]. Furthermore, grinding the crystals of  $\beta$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub> also resulted in disappearance of the HS to LS conversion on lowering temperature. These observations indicate that the spin crossover behavior in  $\beta$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub> is very sensitive to external treatments.

## 4 Conclusion

The temperature dependence of magnetic susceptibilities and Mössbauer spectra revealed that a new polymorphic ferric complex,  $\beta$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub>, exhibited a complete spin transition between the HS and LS states ( $T_{1/2} \downarrow = 92$  K,  $T_{1/2} \uparrow = 117$  K). This magnetic behavior was quite different from that of  $\alpha$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub> [8]. Furthermore, its magnetic behavior was quite sensitive to external treatments. These observations imply that a large structural change may accompany the spin transition in  $\beta$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub>. Since the comparison between the crystal structures of two polymorphs would provide the insight into a rational design for SCO compounds, the crystal structure analysis for  $\beta$ -[Fe(qsal)<sub>2</sub>]<sub>3</sub> is now in progress.

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