

Electronic Supplementary Information (ESI)

## **Conglomerate Crystallization, Chiral Recognition, and Spin-Crossover in a Host-Guest Complex Consisting of Fe<sup>III</sup> Complexes (Host) and [Cr(ox)<sub>3</sub>]<sup>3-</sup> (Guest)**

Yukinari Sunatsuki,<sup>\*a</sup> Sho Miyahara,<sup>a</sup> Yuu Sasaki,<sup>a</sup> Takayoshi Suzuki,<sup>a</sup> Masaaki Kojima<sup>a</sup> and Naohide Matsumoto<sup>b</sup>

<sup>a</sup> *Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan*

<sup>b</sup> *Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan*

\*E-mail: [sunatsuki@cc.okayama-u.ac.jp](mailto:sunatsuki@cc.okayama-u.ac.jp)

Experimental Section	2
Comment for checkcif alerts	3
Table S1	3
Table S2	3
Fig. S1. Solid state CD spectra of <b>1</b>	4
Fig. S2. X-ray structure of the [Cr(ox) <sub>3</sub> ] <sup>3-</sup> ion of <b>1</b>	5
Fig. S3. Views of space-filling representation of the guest L-[Cr <sup>III</sup> (ox) <sub>3</sub> ] <sup>3-</sup> anion	6
Fig. S4. X-ray structure of the [Cr(ox) <sub>3</sub> ] <sup>3-</sup> ion of <b>1</b>	7
References	8

## Experimental Section

**Materials.** All reagents and solvents used in the syntheses were of reagent grade and they were used without further purification.

**Synthesis of  $[\text{Fe}^{\text{III}}(\text{H}_3\text{L})][\text{Fe}^{\text{III}}(\text{L})][\text{Cr}^{\text{III}}(\text{ox})_3]\cdot 3\text{H}_2\text{O}$  (**1**).** An aqueous solution (40 mL) of  $[\text{Fe}^{\text{III}}(\text{H}_3\text{L})](\text{ClO}_4)_3\cdot(4\text{-formylimidazole})\cdot\text{H}_2\text{O}^1$  (0.425 g, 0.5 mmol) was converted into the chloride by use of a Dowex 1X8 in the  $\text{Cl}^-$  form. The resulting  $[\text{Fe}^{\text{III}}(\text{H}_3\text{L})]\text{Cl}_3$  (0.5 mmol) in water (40 mL) was mixed with 1.0 M NaOH (0.75 mmol, 0.75 mL) to form the formally hemideprotonated species,  $[\text{Fe}^{\text{III}}(\text{H}_{1.5}\text{L})]\text{Cl}_{1.5}$  ( $= [\text{Fe}^{\text{III}}(\text{H}_3\text{L})][\text{Fe}^{\text{III}}(\text{L})]\text{Cl}_3$ ). The solution was warmed to dissolve the precipitate and an aqueous solution (10 mL) of *rac*- $\text{K}_3[\text{Cr}^{\text{III}}(\text{ox})_3]\cdot 3\text{H}_2\text{O}^2$  (0.25 mmol, 122 mg) was diffused slowly into the resulting solution. The mixture was left undisturbed to yield dark red crystals of **1**. They were collected by filtration. Yield: 51 mg (16%). Anal. Found: C, 40.44; H, 3.77; N, 22.34. Calcd for  $[\text{Fe}^{\text{III}}(\text{H}_3\text{L})][\text{Fe}^{\text{III}}(\text{L})][\text{Cr}^{\text{III}}(\text{ox})_3]\cdot 3\text{H}_2\text{O} = \text{C}_{42}\text{H}_{51}\text{CrFe}_2\text{N}_{20}\text{O}_{13}$ : C, 40.69; H, 4.15; N, 22.60. IR (KBr disk):  $\nu_{\text{C}=\text{N}}$  (imine) 1593, 1603  $\text{cm}^{-1}$ .

**Physical measurements.** The infrared spectra were measured using a JASCO FT/IR-550 spectrophotometer. The CD spectra were recorded using a JASCO J-720 spectropolarimeter. Magnetic susceptibilities were measured using a Quantum Design MPMS2 XL5 SQUID susceptometer at Okayama University of Science in the 5–350 K temperature range under an applied magnetic field of 0.5 T. Diamagnetic corrections were applied using Pascal's constants. Since the crystal water molecules are lost around 350 K, the change in molecular weight was taken into consideration.

**X-ray crystal structure analysis.** The X-ray data were collected using a Rigaku R-AXIS RAPID II imaging plate area detector employing graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved using direct methods, and refined using full-matrix least-squares procedures using the CrystalStructure crystallographic software package.<sup>3</sup> The absolute configuration was determined based on the Flack parameters.<sup>4</sup> CCDC-859999 (93 K) and CCDC-860000 (273 K) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### Comment for checkcif alerts

Since the oxalate moiety of  $[\text{Cr}(\text{ox})_3]^{3-}$  is highly disordered, we could not completely determine the positions of some atoms of oxalate. Thus, ADP max/min ratio of them remain large. In addition, water molecule is also disordered around three-fold axis. Some short interatomic contacts were observed between oxalate and water oxygen atoms. However, **both the oxalate and the water** are disordered.

**Table S1.** Selected bond distances and angles of  $[\text{Fe}^{\text{III}}(\text{H}_3\text{L})][\text{Fe}^{\text{III}}(\text{L})][\text{Cr}^{\text{III}}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$  (**1**) at 93 and 293 K

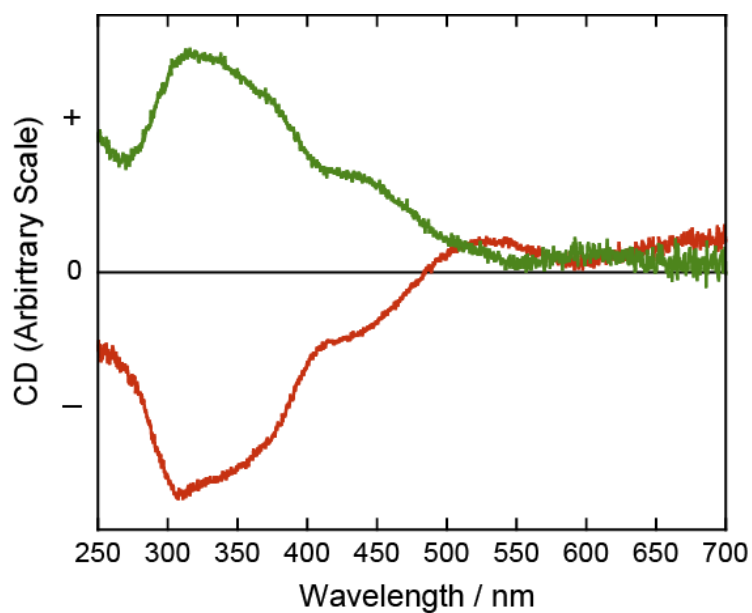
	93 K	293 K
Distance/Å		
Fe(1)–N(2)	1.970(4)	1.985(4)
Fe(1)–N(3)	1.947(5)	1.957(5)
Cr(1)–O(1)	1.935(9)	1.96(4)
Cr(1)–O(2)	1.943(11)	1.922(16)
Angles/°		
N(2)–Fe(1)–N(3)	80.44(19)	79.97(19)

**Table S2.** Selected inter-atomic distances (Å) of the actual  $\Delta$ - $[\text{Fe}(\text{H}_{1.5}\text{L})]_2$ - $\Lambda$ - $[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$  (**1**) and the imaginary  $\Delta$ - $[\text{Fe}(\text{H}_{1.5}\text{L})]_2$ - $\Delta$ - $[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}^*$  (293 K)

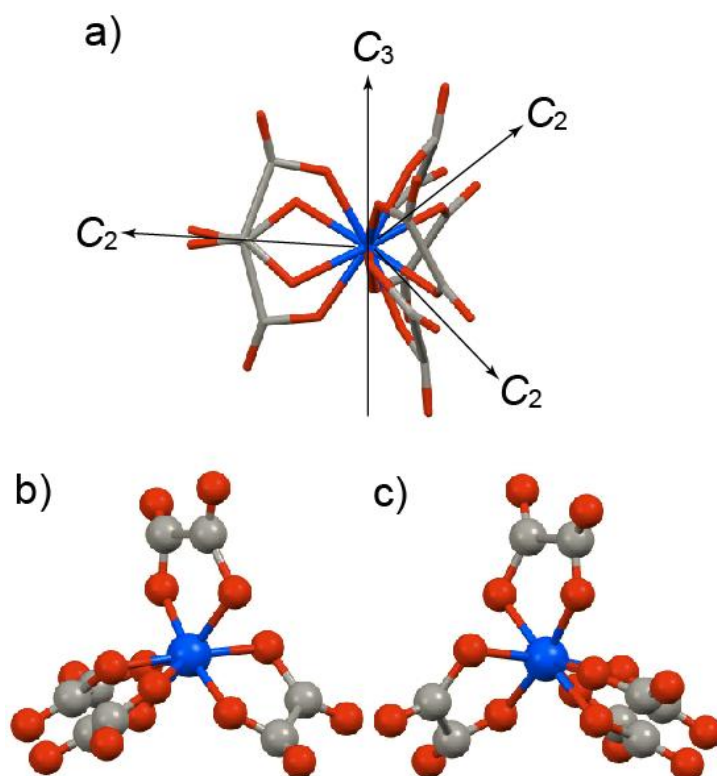
$\Delta$ - $[\text{Fe}(\text{H}_{1.5}\text{L})]_2$ - $\Lambda$ - $[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ ( <b>1</b> )		$\Delta$ - $[\text{Fe}(\text{H}_{1.5}\text{L})]_2$ - $\Delta$ - $[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$	
C(3)–O(4) <sup>1</sup>	3.23(3)	C(3)–O(4) <sup>1</sup>	2.60(3)
C(4)–O(4) <sup>1</sup>	3.57(3)	C(4)–O(4) <sup>1</sup>	2.79(3)
C(6)–O(1) <sup>2</sup>	3.35(2)	C(6)–O(1)	2.893(19)
C(6)–O(4) <sup>1</sup>	3.65(2)	C(6)–O(4) <sup>1</sup>	2.85(2)
C(6)–C(8) <sup>1</sup>	3.55(3)	C(6)–C(8) <sup>1</sup>	3.00(3)

Symmetry Operators: (1)  $-X, -X + Y, -Z + 1$  (2)  $-X + Y, -X, Z$

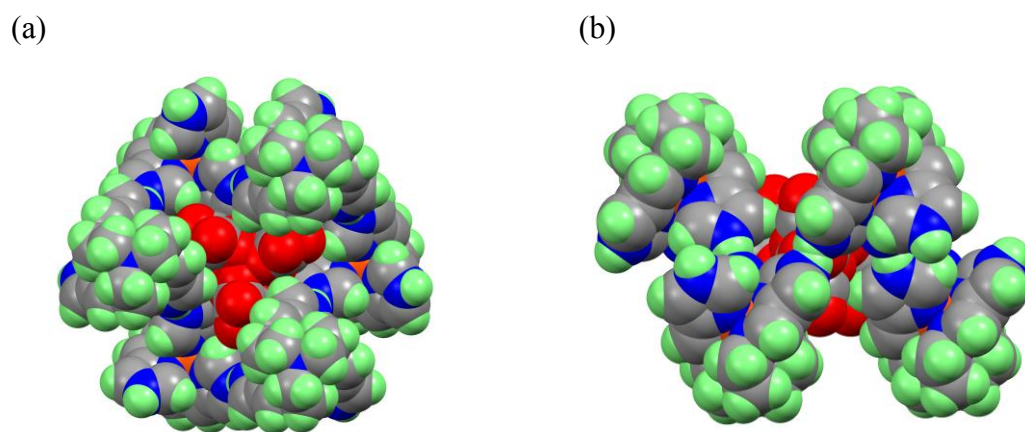
\* The imaginary  $\Delta$ - $[\text{Fe}(\text{H}_{1.5}\text{L})]_2$ - $\Delta$ - $[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$  was constructed by the combination of the atom coordinates of the original  $\Delta$ - $[\text{Fe}(\text{H}_{1.5}\text{L})]^{1.5+}$  cation and the imaginary  $\Delta$ - $[\text{Cr}(\text{ox})_3]^{3-}$  anion. The atom coordinates of imaginary molecule were determined by the operations of the inversion, the rotation by  $60^\circ$  along with  $c$  axis, then the parallel translation of those of the original  $\Lambda$ - $[\text{Cr}(\text{ox})_3]^{3-}$  anion (see also Fig. S4).



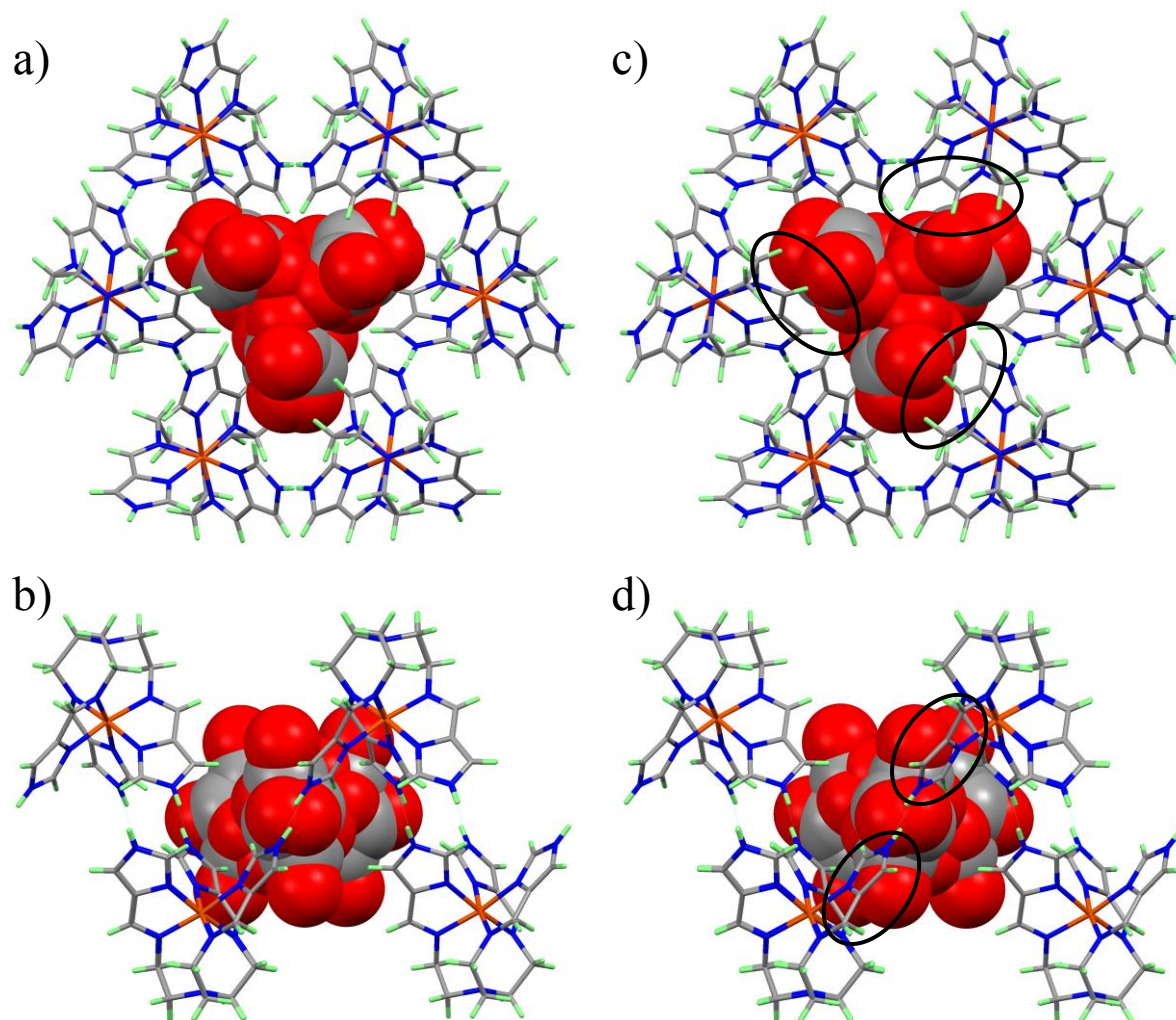
**Fig. S1.** Enantiomeric CD spectra of selected crystallites of **1**,  $\Delta$ -[Fe<sup>III</sup>(H<sub>3</sub>L)][Fe<sup>III</sup>(L)]- $\Lambda$ -[Cr<sup>III</sup>(ox)<sub>3</sub>] (red) and  $\Lambda$ -[Fe<sup>III</sup>(H<sub>3</sub>L)][Fe<sup>III</sup>(L)]- $\Delta$ -[Cr<sup>III</sup>(ox)<sub>3</sub>] (green), in KBr pellets confirming spontaneous resolution. The absolute configurations were assigned on the basis of the CD spectra of  $\Lambda$ -[Cr<sup>III</sup>(ox)<sub>3</sub>]<sup>3-</sup> and  $\Delta$ -[Cr<sup>III</sup>(ox)<sub>3</sub>]<sup>3-</sup> shown in Fig. 4.



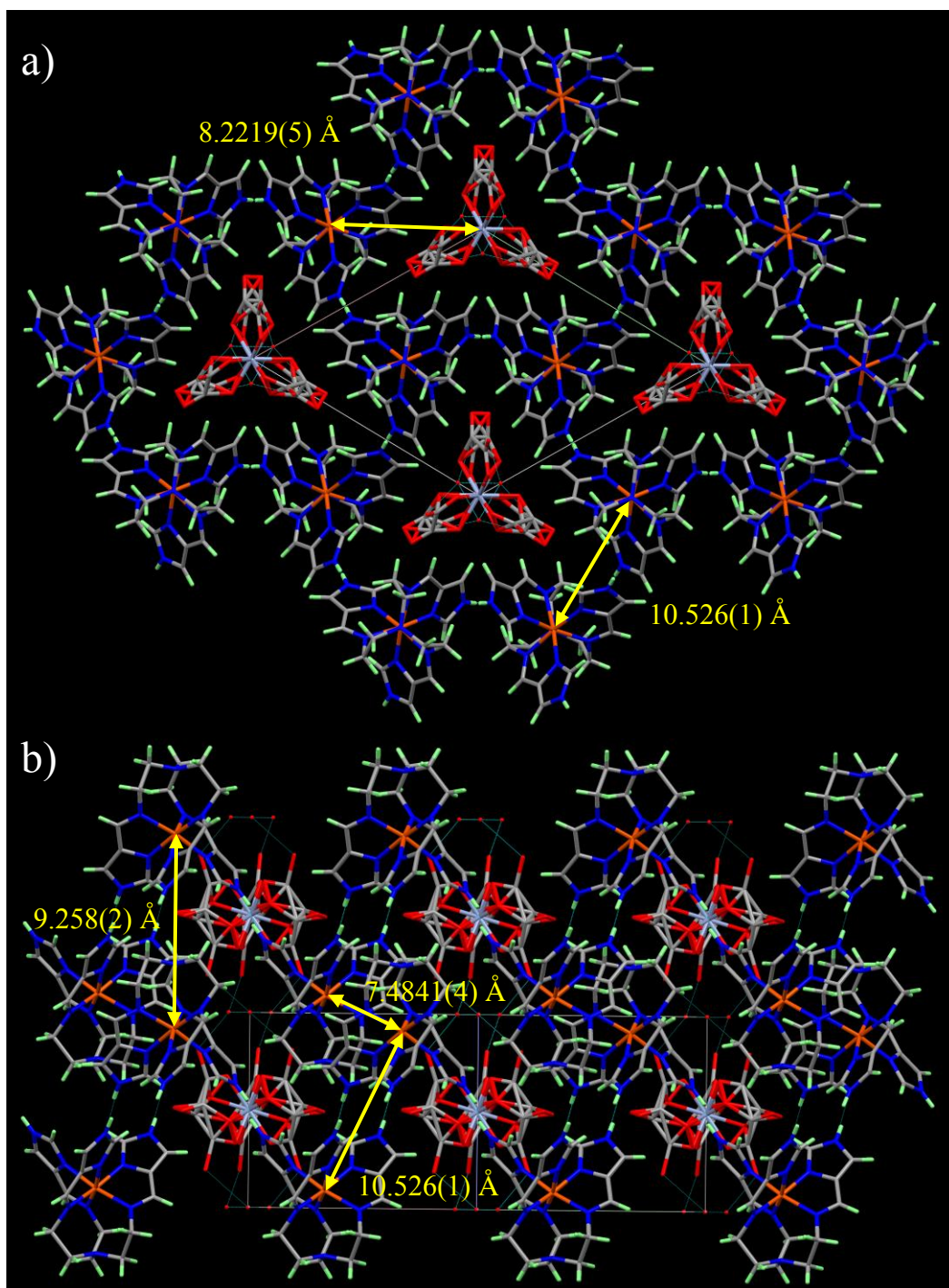
**Fig. S2.** (a) The X-ray structure of the  $[\text{Cr}(\text{ox})_3]^{3-}$  ion of  $[\text{Fe}^{\text{III}}(\text{H}_3\text{L})][\text{Fe}^{\text{III}}(\text{L})][\text{Cr}^{\text{III}}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$  (**1**), the oxalate ions being disordered. Both disintegrated  $\text{Cr}^{\text{III}}$  complexes, (b) and (c), have the  $\Lambda$  configuration.



**Fig. S3.** (a) Top and (b) side views of space-filling representation of the guest  $\Lambda$ -[Cr<sup>III</sup>(ox)<sub>3</sub>]<sup>3-</sup> anion in a hexanuclear host comprised of  $\Delta$ -[Fe<sup>III</sup>(H<sub>3</sub>L)]<sup>3+</sup> and  $\Delta$ -[Fe<sup>III</sup>(L)].



**Fig. S4.** Comparison of  $\Delta$ -[Fe<sup>III</sup>(H<sub>1.5</sub>L)]<sub>2</sub>- $\Delta$ -[Cr<sup>III</sup>(ox)<sub>3</sub>] $\cdot$ 3H<sub>2</sub>O (**1**, a: top view and b: side view) with  $\Delta$ -[Fe<sup>III</sup>(H<sub>1.5</sub>L)]<sub>2</sub>- $\Delta$ -[Cr<sup>III</sup>(ox)<sub>3</sub>] $\cdot$ 3H<sub>2</sub>O (simulated (see also Table S2), c: top view and d: side view). The steric hindrances (surrounded by black oval lines) were observed in the simulated complex.



**Fig. S5.** (a) Top view and (b) side view of the three dimensional structure of  $\Delta$ -[Fe<sup>III</sup>(H<sub>1.5</sub>L)]<sub>2</sub>- $\Lambda$ -[Cr<sup>III</sup>(ox)<sub>3</sub>] $\cdot$ 3H<sub>2</sub>O (**1**) with selected inter-atomic distances: the intra-layer Fe $\cdots$ Fe(hydrogen bonded), 10.526(1) Å; the intra-layer Fe $\cdots$ Cr, 8.2219(5) Å; the inter-layer Fe $\cdots$ Fe(along with the *c* axis), 9.258(2) Å; the inter-layer Fe $\cdots$ Fe(closest), 7.4841(4) Å.



## References

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