

# Synthesis and Characterization of Symmetrically versus Unsymmetrically Proton-Bridged Hexa-Iron Clusters

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Cite This: *ACS Omega* 2021, 6, 16661–16669



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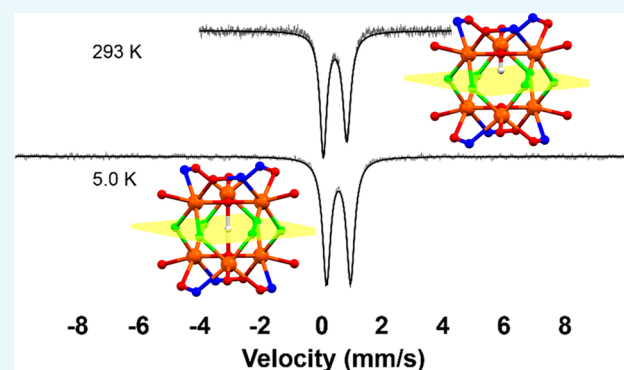


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**ABSTRACT:** Syntheses and magnetic and structural characterization of hexa-iron complexes of derivatized salicylaldoximes are discussed. Complexation of  $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  with each ligand ( $\text{H}_2\text{L1}$  and  $\text{H}_4\text{L2}$ ) in a methanolic-pyridine solution resulted in hexa-iron compounds (**C1** and **C2**, respectively), which each contain two near-parallel metal triangles of  $[\text{Fe}_3-\mu_3-\text{O}]$ , linked by six fluoride bridges and stabilized by a hydrogen-bonded proton between the  $\mu_3-\text{O}$  groups. Within each metal triangle of **C2**,  $\text{Fe}(\text{III})$  ions are connected via the amine “straps” of ( $\text{H}_4\text{L2-2H}$ ). Variable-temperature magnetic susceptibility and Mössbauer data of **C1** and **C2** indicate the presence of dominant antiferromagnetic interactions between the high-spin ( $S = 5/2$ )  $\text{Fe}(\text{III})$  centers. For **C1**, two quadrupole doublets are observed at room temperature and 5 K, consistent with structural data from which discrete but disordered  $[\text{Fe}_3-\mu_3-\text{O}]$  and  $[\text{Fe}_3-\mu_3-\text{OH}]$  species were inferred. For **C2**, a single sharp quadrupole doublet with splitting intermediate between those determined for **C1** was observed, consistent with the symmetric  $[\text{Fe}_3-\mu_3-\text{O} \cdots \text{H} \cdots \mu_3-\text{O}-\text{Fe}_3]$  species inferred crystallographically from the very short  $\mu_3-\text{O} \cdots \mu_3-\text{O}$  separation. The differences in the physical properties of the complexes, as seen in the Mössbauer, X-ray, and magnetic data, are attributed to the conformational flexibility imparted by the nature of the linkages between the closely related ligands.



## INTRODUCTION

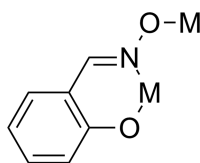
Salicylaldoximes are excellent candidates for the synthesis of multinuclear clusters, as the phenolato and oximate groups are capable of acting as both chelating and bridging units. These salicylaldoximes are monoanionic when the phenol group is deprotonated and dianionic when both the phenol and oxime groups are deprotonated. Thus, the phenolato oxygen can act as a chelating unit for one metal, while the oximate oxygen serves to bridge a second metal (Figure 1).<sup>1,2</sup>

Several examples of this mode have been reported with nuclearities of two,<sup>3–5</sup> three,<sup>6,7</sup> and four.<sup>8,9</sup> The investigation of oxo-bridged multinuclear  $\text{Fe}(\text{III})$  materials has been a growing field of interest, as these oxo-bridged units are observed in various iron metalloproteins.<sup>10–19</sup> Proteins such as ferritin,

which is used in mammalian iron storage, contain an extraordinary polynuclear iron-oxo core.<sup>20,21</sup>

Structural and magnetic studies of salicylaldoxime-based metal clusters of  $\text{M}_3-\mu_3-\text{O}$  units have received increased interest after hexameric species were reported to be single molecule magnets (SMMs).<sup>22–26</sup> There is now an extensive volume of work surrounding the coordination chemistry of  $\text{Mn}^{\text{III}}$  clusters, which have been synthesized using derivatized salicylaldoxime ligands.<sup>25–30</sup> However, the number of analogous iron-based magnetic materials that have been reported to date is comparatively low.

Our interest in the synthesis and characterization of polynuclear derivatized salicylaldoxime clusters<sup>31–37</sup> began in 2009 with the synthesis and structural characterization of a hexacopper trihelicate complex,  $[\text{Cu}_6(\mu_3-\text{OH}_{0.5})_2(\text{H}_4\text{L-2H})_3](\text{PF}_6)_3$  (**1**,  $\text{H}_4\text{L} = 3,3'-[N,N']\text{-dimethyl-1,6-hexanediaminobis(methylene)]\text{bis}[2\text{-hydroxy-5-tert-butylbenzaldehyde}$



**Figure 1.** General  $\mu_2:\eta^1:\eta^1$  coordination mode of the dianionic form of salicylaldoxime; M, metal ion.

Received: April 28, 2021

Accepted: June 1, 2021

Published: June 15, 2021



oxime]).<sup>38</sup> There have been several analogous iron examples reported after the investigation of this copper complex. In 2012, Mason et al. reported an iron complex using a longer analogue of this ligand [ $\text{Fe}_6(\mu_3\text{-OH}_{0.5})_2(\mu_2\text{-OH})_6(\text{H}_4\text{L-2H})_3$ ]- $(\text{BF}_4)_3 \cdot 4\text{H}_2\text{O} \cdot 9\text{MeOH}$  (**2**,  $\text{H}_4\text{L} = 3,3'$ -[ $N,N'$ -dimethyl-1,8-octanediaminobis(methylene)]bis[2-hydroxy-5-*tert*-butylbenzaldehyde oxime]).<sup>39</sup> They found that the increased length of the straps in the ligand led to enhanced flexibility and a subsequent favoring of an octahedral coordination environment at the iron centers. In 2010, a hexa-iron complex utilizing 2-hydroxyacetophenone oxime ligands (Me-sao) was reported to contain a similar metallic core, [ $\text{Fe}_6(\text{Me-sao})(\mu_3\text{-OH}_{0.5})_2(\mu_2\text{-OH})_3(\mu_2\text{-OMe})_3$ ]<sup>3-</sup> (**3**).<sup>40</sup> Two analogous hexa-iron complexes using nonderivatized salicylaldoxime (sao),  $\text{Na}_9[\text{Fe}_6(\mu_3\text{-OH}_{0.5})_2(\text{sao})_6(\mu_2\text{-OMe})_3(\mu_2\text{-OH})_3]_2[\text{Fe}_3(\text{sao})_6]$  (**4**) and  $\text{Na}_3[\text{Fe}_6(\mu_3\text{-OH}_{0.5})_2(\text{sao})_6(\mu_2\text{-OMe})_3(\mu_2\text{-OH})_3]$  (**5**), have since been reported.<sup>41</sup>

Our study focuses on the hexa-iron complexes composed of metal triangles with the  $\text{M}_3\text{-}\mu_3\text{-O}$  moiety. We report the syntheses and analyses of two hexa-iron complexes formed with derivatized “linked” and “nonlinked” salicylaldoxime ligands (Figure 2). We believe these are the first [ $\text{Fe}_3\text{-}\mu_3\text{-O}$ ]

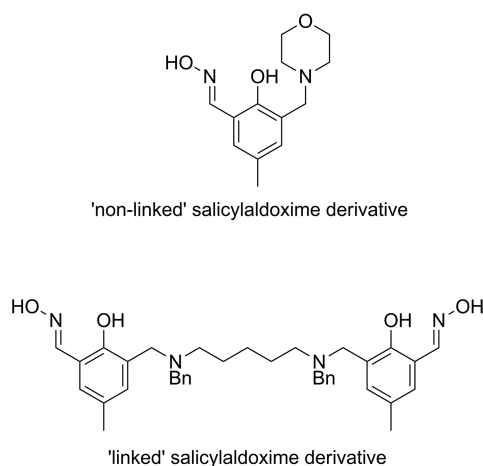


Figure 2. Chemical structures of  $\text{H}_2\text{L1}$  (top) and  $\text{H}_4\text{L2}$  (bottom).

$(\text{OH}_{0.5})_2$  complexes to feature six  $\mu_2\text{-F}$  linkers between the  $\text{Fe}_3$  triangles, in contrast to the more prevalent  $\mu_2\text{-OH}$  linkers or a mixture of  $\mu_2\text{-OH}$  and  $\mu_2\text{-OMe}$  linkers. The structural properties of these complexes will be discussed in relation to the Mössbauer and VT magnetic data.

## EXPERIMENTAL SECTION

**Synthesis.** All reactions were performed under aerobic conditions using chemicals and solvents as received, unless otherwise stated.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer;  $\delta$  values are relative to the corresponding residual solvent. Mass spectra were obtained using a Micromass ZMD 400 electrospray spectrometer. IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer from Thermo Electron Corporation using an ATR sampling accessory. Elemental analyses were determined by the Campbell Microanalytical Laboratory at the University of Otago using crystalline samples, which had been crushed and dried *in vacuo*.

**Synthesis of Ligands and Complexes.** 2-Hydroxy-5-methylbenzaldehyde was synthesized as described in the

literature.<sup>42</sup> The preparation of 3-(bromomethyl)-2-hydroxy-5-methylbenzaldehyde (**A**), and the oxime precursors, was carried out by the procedure of Tasker and Schröder.<sup>43</sup> Synthesis of the secondary amine,  $N,N'$ -dibenzyl-1,5-pentanediamine (**B**), and oximes was carried out according to the procedure of Plieger et al.<sup>44</sup>

**L1a (Precursor for  $\text{H}_2\text{L1}$ ).** 2-Hydroxy-5-methyl-3-(4-morpholinomethyl)benzaldehyde. Solutions of **A** (1.27 g, 5.54 mmol) and morpholine (1.31 g, 1.30 mL, 14.8 mmol), each in  $\text{CH}_2\text{Cl}_2$  (60 mL), were added simultaneously to a stirred solution of  $\text{Et}_3\text{N}$  (3.40 g, 4.68 mL, 14.8 mmol) in  $\text{CH}_2\text{Cl}_2$  (80 mL) over 30 min. The resulting yellow solution was stirred for 24 h at RT. The solution was washed with water ( $3 \times 100$  mL), and the organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Removal of the solvent afforded a yellow oil, which was further dried *in vacuo*. Yield (2.99 g, 86%). IR (KBr pellet): 1674 (s), 1115 (s), 1233 (m)  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{13}\text{H}_{17}\text{NO}_3$ : C, 66.36; H, 7.28; N, 5.95. Found: C, 66.20; H, 7.42; N, 6.12.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 2.30 (s, 3H), 2.57 (br, 4H), 3.67 (s, 2H), 3.76 (t,  $J = 4.76$  Hz, 4H), 7.20 (d,  $J = 1.72$  Hz, 1H), 7.41 (d,  $J = 1.72$  Hz, 1H), 10.21 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz):  $\delta$  (ppm) 20.2, 53.1, 59.0, 66.7, 122.0, 123.4, 128.5, 129.5, 137.1, 158.7, 192.7. ESI-MS (+ve ion mode, MeOH)  $m/z$ : 235 [ $\text{M} + \text{H}$ ]<sup>+</sup>.

**$\text{H}_2\text{L1}$ .** 2-Hydroxy-5-methyl-3-(4-morpholinomethyl)benzaldehyde Oxime. A solution of KOH (0.662 g, 11.8 mmol) in dry EtOH (100 mL) was added to a solution of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (2.78 g, 11.8 mmol) in dry EtOH (100 mL). The resulting white precipitate was removed, and the filtrate was added to a solution of **L1a** (2.78 g, 11.8 mmol) in dry EtOH (200 mL) over 30 min. The resulting pale yellow solution was stirred for 24 h at RT. The solvent was removed, and the yellow solid was dissolved in  $\text{CHCl}_3$  (200 mL), washed with water ( $3 \times 100$  mL), and the organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Removal of the solvent afforded a yellow solid, which was washed with cold EtOH (70 mL). The resulting white powder was dried *in vacuo*. Yield (1.25 g, 42%). mp 194.5–196.5 °C. IR (KBr pellet): 1618 (s), 2964 (m), 1471 (s), 1267 (m), 1111 (s)  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}_3$ : C, 62.38; H, 7.25; N, 11.19. Found: C, 62.34; H, 7.34; N, 10.95.  $^1\text{H}$  NMR ( $d_6\text{-DMSO}$ , 500 MHz):  $\delta$  (ppm) 2.03 (s, 3H), 2.44 (br, 4H), 3.59 (s, 2H), 3.59 (t,  $J = 4.60$  Hz, 4H), 6.98 (d,  $J = 1.82$  Hz, 1H), 7.22 (d,  $J = 1.87$  Hz, 1H), 8.28 (s, 1H).  $^{13}\text{C}$  NMR ( $d_6\text{-DMSO}$ , 126 MHz):  $\delta$  (ppm) 20.5, 53.1, 66.5, 118.4, 123.1, 126.8, 127.9, 131.7, 147.2, 153.5. ESI-MS (+ve ion mode, MeOH)  $m/z$ : 251 [ $\text{M} + \text{H}$ ]<sup>+</sup>.

**L2a (Precursor for  $\text{H}_4\text{L2}$ ).** 3,3'-[ $N,N'$ -Dibenzyl-1,5-pentanediaminobis(methylene)]bis[2-hydroxy-5-methylbenzaldehyde]. Solutions of **A** (1.00 g, 8.05 mmol) and **B** (0.81 g, 2.77 mmol), each dissolved in dry  $\text{CH}_2\text{Cl}_2$  (20 mL), were added simultaneously to a stirred solution of  $\text{Et}_3\text{N}$  (1.11 g, 8.05 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (30 mL) over 30 min. The yellow solution was stirred for 24 h at RT. The solution was washed with water ( $3 \times 100$  mL), and the organic phase dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Removal of the solvent afforded a bright yellow solid, which was further dried *in vacuo*. Yield (2.04 g, 86%). IR (KBr pellet): 1681 (s), 2851 (s), 3028 (m), 1471 (m)  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{37}\text{H}_{42}\text{N}_2\text{O}_4 \cdot \text{H}_2\text{O}$ : C, 74.47; H, 7.43; N, 4.69. Found: C, 74.61; H, 7.37; N, 4.73.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 1.22 (q,  $J = 7.53$  Hz, 2H), 1.53 (q,  $J = 6.85$  Hz, 4H), 2.28 (s, 6H), 2.45 (t,  $J = 7.29$  Hz, 4H), 3.61 (s, 4H), 3.71 (s, 4H), 7.15 (s, 2H), 7.29 (d,  $J = 7.69$  Hz, 4H), 7.34 (d,  $J = 7.28$  Hz, 4H), 7.37 (s, 2H), 7.43 (d,  $J = 1.62$

Table 1. Crystal Data and Structural Refinement for Complexes C1 and C2

data	C1	C2
empirical formula	C <sub>39</sub> H <sub>51</sub> F <sub>3</sub> Fe <sub>3</sub> N <sub>6</sub> O <sub>10</sub> ·C <sub>39</sub> H <sub>50</sub> F <sub>3</sub> Fe <sub>3</sub> N <sub>6</sub> O <sub>10</sub> ·BF <sub>4</sub>	C <sub>116</sub> H <sub>131</sub> F <sub>6</sub> Fe <sub>6</sub> N <sub>13</sub> O <sub>14</sub> ·3BF <sub>4</sub>
formula weight	2062.61	2640.86
crystal system	triclinic	monoclinic
space group	P $\bar{1}$	P2 <sub>1</sub> /c
a (Å)	16.8193(10)	17.9936(4)
b (Å)	17.3271(10)	37.0613(7)
c (Å)	21.1897(15)	20.4370(14)
$\alpha$ (deg)	107.161(8)	90
$\beta$ (deg)	99.537(7)	113.409(8)
$\gamma$ (deg)	100.103(7)	90
volume (Å <sup>3</sup> )	5651.6(7)	12507.0(12)
Z (Z')	1(0.5)	4(1)
reflections collected/unique data	77 177/18 822 [R <sub>int</sub> = 0.126]	130 760/21 266 [R <sub>int</sub> = 0.197]
wavelength (Å)	1.5418	1.5418
data collection limits	6.60 < $\theta$ < 65.40°	6.55 < $\theta$ < 65.08°
completeness	0.977	0.997
temperature (K)	160	163
data/restraints/parameters	18 822/217/1098	21 266/1090/1565
GOOF	1.037	0.970
final R indices (I > 2 $\sigma$ I)	R <sub>1</sub> = 0.1491 (0.1049) wR <sub>2</sub> = 0.3259 (0.2810)	R <sub>1</sub> = 0.1894 (0.1012) wR <sub>2</sub> = 0.3043 (0.2518)
residual density (e <sup>-</sup> /Å <sup>3</sup> )	1.62/−0.84	0.76/−0.52
CCDC no.	2048582	2048583

H<sub>2</sub>, 2H), 10.32 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz):  $\delta$  (ppm) 20.3, 24.7, 26.0, 55.0, 55.5, 58.2, 122.4, 124.4, 127.6, 128.2, 128.3, 128.5, 129.3, 136.3, 137.1, 159.2, 191.8. ESI-MS (+ve ion mode, MeOH) *m/z*: 580 [M + H]<sup>+</sup>.

**H<sub>4</sub>L2.** 3,3'-[N,N'-Dibenzyl-1,5-pentanediaminobis(methylene)]bis[2-hydroxy-5-methylbenzaldehyde Oxime]. A solution of KOH (0.276 g, 4.92 mmol) in dry EtOH (50 mL) was added to a solution of NH<sub>2</sub>OH·HCl (0.342 g, 4.92 mmol) in dry EtOH (50 mL). The resulting white precipitate was removed, and the filtrate was added to a solution of **L2a** (1.00 g, 1.64 mmol) in dry toluene (30 mL) over 30 min. The pale yellow solution was stirred for further 48 h at RT, after which time a white precipitate was obtained. The combined residues were filtered, washed with cold chloroform (3 × 30 mL) followed by cold EtOH (3 × 30 mL). The final yellow waxy product was dried *in vacuo*. Yield (0.892 g, 85%). IR (KBr pellet): 1612 (m), 1280 (s), 1022 (m) cm<sup>-1</sup>. Anal. calcd for C<sub>37</sub>H<sub>44</sub>N<sub>4</sub>O<sub>4</sub>: C, 73.00; H, 7.29; N, 9.20. Found: C, 72.87; H, 6.98; N, 8.92. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  (ppm) 1.18 (q, *J* = 7.22 Hz, 2H), 1.51 (q, *J* = 6.83, 4H), 2.25 (s, 6H), 2.44 (t, *J* = 6.99 Hz, 4H), 3.59 (s, 4H), 3.69 (s, 4H), 6.86 (br, 2H), 7.26 (br, 4H), 7.28 (br, 4H), 7.29 (br, 4H), 7.33 (t, *J* = 7.82 Hz, 4H), 8.48 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz):  $\delta$  (ppm) 20.4, 24.6, 25.7, 52.6, 56.5, 58.1, 118.2, 122.4, 122.7, 126.6, 127.6, 128.1, 128.5, 129.5, 131.4, 136.8, 147.7, 154.2. ESI-MS (+ve ion mode, MeOH) *m/z*: 609 [M + H]<sup>+</sup>.

[Fe<sub>6</sub>(OH<sub>0.5</sub>)<sub>2</sub>F<sub>6</sub>(H<sub>2</sub>L1-H)<sub>6</sub>](BF<sub>4</sub>)<sub>3</sub> (**C1**). To the ligand H<sub>2</sub>L1 (0.125 g, 0.500 mmol) dissolved in MeOH (12.5 mL) was added Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.169 g, 0.500 mmol) in MeOH (12.5 mL). After full dissolution, pyridine (2 mL) was added to the maroon-colored solution. The solution was stirred for 3 h, filtered, and the filtrate was left to evaporate slowly. X-ray quality crystals were produced after 2 weeks. The crystals obtained were washed with diethyl ether and dried *in vacuo*. Yield (0.202 g, 59%). Anal. calcd for C<sub>78</sub>H<sub>102</sub>B<sub>3</sub>F<sub>18</sub>Fe<sub>6</sub>N<sub>12</sub>O<sub>20</sub>·H<sub>2</sub>O·2pyr: C, 43.79; H, 4.76; N, 8.13. Found: C, 43.94; H,

4.92; N, 7.98. IR (KBr pellet): 1617(s), 1465(vs), 1084(m), 520(s), 454(m) cm<sup>-1</sup>.

[Fe<sub>6</sub>(OH<sub>0.5</sub>)<sub>2</sub>F<sub>6</sub>(H<sub>4</sub>L2-2H)<sub>3</sub>](BF<sub>4</sub>)<sub>3</sub> (**C2**). To the ligand H<sub>4</sub>L2 (0.304 g, 0.500 mmol) dissolved in MeOH (12.5 mL) was added Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.348 g, 1.00 mmol) in MeOH (12.5 mL). After full dissolution, pyridine (2 mL) was added to the maroon-colored solution. The solution was stirred for 3 h, filtered, and then the filtrate was left to evaporate slowly. X-ray quality crystals were produced after 2 weeks. The crystals obtained were washed with diethyl ether and dried *in vacuo*. Yield (0.190 g, 14%). Anal. calcd for C<sub>111</sub>H<sub>127</sub>B<sub>3</sub>F<sub>18</sub>Fe<sub>6</sub>N<sub>12</sub>O<sub>14</sub>·5H<sub>2</sub>O·pyr: C, 51.00; H, 5.24; N, 6.67. Found: C, 50.80; H, 5.02; N, 6.84. IR (KBr pellet): 1617(s), 1460(vs), 1293 (s), 1084(m), 759 (m), 522(m) cm<sup>-1</sup>.

**X-ray Structural Determination.** Single-crystal X-ray data **C1** and **C2** were collected at −113 and −110 °C, respectively, using Cu K $\alpha$  ( $\lambda$  = 1.54178 Å) radiation on a Rigaku-Spider diffractometer equipped with a curved image-plate detector. Data collection was carried out with the CrystalClear software package, and data reduction and cell refinement were carried out with PROCESS-AUTO and FSPProcess. All structures were solved using direct methods with ShelXS and further refined with ShelXL,<sup>45,46</sup> as implemented in Olex2.<sup>47</sup> All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the ideal positions with a fixed *U*<sub>iso</sub> value, riding on their respective non-hydrogen atoms.

For complex **C1**, the cation occupied only 75% of the unit cell and in the void volume lurks, *inter alia*, two BF<sub>4</sub><sup>-</sup> ions, a water molecule, and two pyridine molecules, which are also required to fit the microanalytical data. On the other hand, complex **C2** is tightly packed in its unit cell, although the 6 × H<sub>2</sub>O solvate species within the solvent mask are seen as just 5 × H<sub>2</sub>O in microanalytical data.

**Magnetic Measurements.** Variable-temperature, direct current (dc) magnetic susceptibility and magnetization measurements on powdered microcrystalline samples of each

complex were performed using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants.<sup>48</sup>

**Mössbauer Measurements.** <sup>57</sup>Fe Mössbauer spectra were recorded with a <sup>57</sup>Co source in a Rh matrix on an SEE Co. (Science Engineering & Education Co., MN) spectrometer equipped with a closed-cycle refrigerator system. Data were collected in a constant acceleration mode in transmission geometry. Isomer shifts are given relative to metallic iron foil at room temperature. Analysis of the spectra was conducted using the WMOSS program (SEE Co., formerly WEB Research Co. Edina, MN).

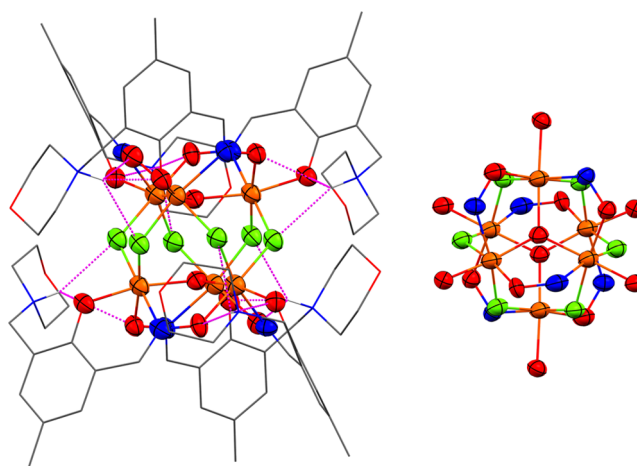
## RESULTS AND DISCUSSION

**C1** and **C2** were isolated as dark maroon orthorhombic-shaped single crystals by slow evaporation of the complexation filtrate at room temperature. The coordination of iron to the ligand, accompanied by oxidation to Fe(III), was immediately evidenced by a color change of the ligand suspension from pale yellow to dark maroon upon addition of Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O. The data measurement and other refinement parameters for crystal structures of **C1** and **C2** are given in Table 1.

Complex **C1** crystallizes in the triclinic space group  $P\bar{1}$  with two structurally similar half-clusters in the asymmetric unit. Crystallographic inversion symmetry generates the full cluster. Each independent unit of **C1** comprises 6 × Fe(III) (+18), 6 × F (−6), 2 × (OH<sub>0.5</sub>) (−3), and 6 × (H<sub>2</sub>L1) ligands, all of which are present in an overall singly deprotonated form as (H<sub>2</sub>L1-H). Thus, the overall charge of the cation, +3, is balanced by 3 × BF<sub>4</sub><sup>−</sup> within the lattice. The complex, **C1**, contains two [Fe<sub>3</sub><sup>III</sup>] units, each with a central μ<sub>3</sub>-O-atom. The central oxygen atoms are displaced from the metal planes toward the central cavity of the complex by 0.154 and 0.159 Å. The short distances (2.639(11) and 2.681(8) Å) between the pairs of oxygen atoms suggest that each cluster contains a disordered μ<sub>3</sub>-oxo/μ<sub>3</sub>-hydroxo moiety with the proton most likely being asymmetrically placed between the two oxygen atoms.<sup>49</sup> Thus, the two triangles are formulated as [Fe<sub>3</sub><sup>III</sup>(μ<sub>3</sub>-O)]<sup>7+</sup> and [Fe<sub>3</sub><sup>III</sup>(μ<sub>3</sub>-OH)]<sup>8+</sup> and are disordered by the inversion center. These two triangles are connected *via* six μ<sub>2</sub>-fluoride groups (Figure 3), such that each Fe(III) within the upper triangle is connected to two Fe(III) ions within the lower triangle by two μ<sub>2</sub>-F groups. The triangles of iron atoms are rotated by exactly 60° to each other as a result of the inversion center and are parallel. Selected structural parameters of **C1** are shown in Table 2.

Each Fe(III) atom sits in an octahedral geometry where equatorial positions are taken by an oximato N-atom and a phenolato O-atom from one ligand, a μ<sub>2</sub>-F group and the μ<sub>3</sub>-O/OH group, while the axial positions are coordinated by an oximato O-atom from a neighboring ligand and a μ<sub>2</sub>-F group. The distances between amine N-atoms and phenolato O-atoms within a given ligand all fall in the range of 2.570(11)–2.847(12) Å and are consistent with hydrogen-bond interactions.

Complex **C2** crystallizes in the monoclinic  $P2_1/c$  space group. The cation of the complex, **C2**, is formed from 6 × Fe(III) (+18), 3 × (H<sub>4</sub>L2-2H) (−6), 6 × F (−6), and 2 × (OH<sub>0.5</sub>) (−3). The overall +3 charge is balanced by 3 × BF<sub>4</sub><sup>−</sup> within the lattice, although only one of these was crystallographically observed. The complex **C2**, like **C1**, is also composed of two, in this case, near-parallel Fe<sub>3</sub><sup>III</sup> triangles



**Figure 3.** Left: the cation, [(Fe<sub>6</sub>(OH<sub>0.5</sub>)<sub>2</sub>F<sub>6</sub>(H<sub>2</sub>L1-H)<sub>6</sub>)]<sup>3+</sup>, of **C1** (noninteracting H atoms are omitted for clarity; C, gray; N, blue; O, red; F, green; Fe, orange; H, white; hydrogen bonds, pink; ellipsoids are drawn at the 30% probability level). Right: off-axis view of the core along the μ<sub>3</sub>-O···μ<sub>3</sub>-O axis.

that are connected through the twisted amine straps between the two salicylaldoxime “heads” on either end of each ligand molecule and six μ<sub>2</sub>-F groups.

Each triangle is formed of three Fe(III) ions that are bridged by oximato (−N−O−) and oxo/hydroxo (O<sup>2−</sup>/OH<sup>−</sup>) groups. Each Fe(III) sits in an octahedral geometry, and the equatorial and axial positions around each Fe(III) are occupied by the same groups as in **C1**. Thus, the approximately parallel metal triangles of **C2** are twisted by almost exactly 60°. As observed in **C1**, the oximato bridging sequence on both metal triangles of **C2** is also Fe−N−O−Fe. The μ<sub>3</sub>-O-atoms within the triangles of **C2** are shifted by 0.303 Å from the metal planes toward the internal cavity of the complex, leading to a short O···O separation of 2.430(8) Å, suggesting the presence of a proton symmetrically placed between the μ<sub>3</sub>-O-atoms (Figure 4).<sup>49</sup> Important structural parameters, including μ<sub>3</sub>-O···μ<sub>3</sub>-O distances between Fe<sub>3</sub>O triangles of previously reported analogous hexa-iron complexes, are shown in Table 2. The μ<sub>3</sub>-O···μ<sub>3</sub>-O distances for the complexes **2**, **4**, and **5** are very similar to each other at 2.472(5)–2.561(16) Å, despite complex **2** containing flexible derivatized salicylaldoxime ligands and complexes **4** and **5** containing salicylaldoxime itself. In comparison to these numbers, the corresponding distances for **C1** (2.639(11) and 2.681(8) Å) and **C2** (2.430(8) Å) are significantly different from those reported for related hexa-iron(III) species and from each other. In **C2**, the H atoms bound to the amine N-atoms on either end of each ligand appear to form moderately strong hydrogen bonds with the phenolato O-atoms of the same ligand, falling in the range of 2.679(12)–2.828(10) Å. The Fe−μ<sub>3</sub>-O/Fe−μ<sub>3</sub>-OH bond lengths in **C1** are similar to those reported in the literature but are noticeably shorter than those of **C2**. The Fe−μ<sub>2</sub>-F−Fe angles in **C1** and **C2** are observed to be larger than those previously reported in the literature for μ<sub>2</sub>-OH and μ<sub>2</sub>-OMe bridges.<sup>39,41</sup> The amine straps in **C2** are more flexible than the longer amine straps in **2**, as they bring the triangles closer to each other. The simplest salicylaldoxime ligands in **4** and **5** bring the triangles closer to each other than in complex **C1**. Moreover, the displacements of the μ<sub>3</sub>-O-atom from the metal triads in both units of the complex **C1** are observed to be smaller than those reported for **2**–**5**, as well as **C2** (Table 2);

Table 2. Comparison of Important Structural Parameter Values of the Complexes 2–5 with C1 and C2<sup>b</sup>

parameter	2	3	4	5	C1	C2
Fe...Fe (Å) <sup>a</sup>	3.392(2)–3.447(2)	3.441(1)	3.439(1)	3.379(2)–3.522(2)	3.262(2)–3.281(2)	3.407(2)–3.446(2)
O...O (Å) <sup>a</sup>	2.526(10)	2.472(5)	2.518(5)	2.532(6)	2.639(11)–2.681(8)	2.430(8)
$\mu_3$ -O displacement from Fe <sub>3</sub> plane (Å) <sup>a</sup>	0.317	0.331	0.330	0.263–0.358	0.154–0.159	0.303
Fe– $\mu_3$ -O (Å) <sup>a</sup>	1.978(5)–2.019(7)	2.014(1)	2.011(1)–2.013(1)	1.970(5)–2.081(5)	1.867(4)–1.927(5)	1.971(5)–2.020(5)
Fe–N <sub>oximate</sub> (Å) <sup>a</sup>	2.104(8)–2.138(6)	2.118(2)	2.108(3)	2.093(6)–2.147(5)	2.107(6)–2.139(6)	2.075(9)–2.147(7)
Fe–O <sub>phenolato</sub> (Å) <sup>a</sup>	1.892(6)–1.920(1)	1.935(2)	1.915(2)	1.919(4)–1.942(5)	1.894(4)–1.979(6)	1.902(6)–1.941(5)
Fe–O <sub>oximate</sub> (Å) <sup>a</sup>	1.951(8)–2.002(5)	1.980(2)	2.004(2)	1.961(5)–2.019(4)	1.967(5)–2.008(6)	1.941(6)–1.984(7)
Fe– $\mu_2$ -X (Å) <sup>a</sup>	1.943(5)–2.112(6)	2.019(1)–2.071(2)	2.000(2)–2.115(2)	1.981(5)–2.114(5)	1.955(5)–2.068(4)	1.947(4)–2.060(4)
Fe– $\mu_2$ -X–Fe (deg) <sup>a</sup>	102.4(2)–104.0(3)	98.4(1)–101.9(1)	97.7(1)–103.3(1)	97.4(2)–104.5(2)	121.1(2)–123.7(2)	126.0(2)–131.8(2)

<sup>a</sup>For complex 4, the stated values are for the hexa-iron cluster only. <sup>b</sup>CCDC deposition numbers: 863633 (2),<sup>39</sup> 755042 (3),<sup>40</sup> 861227 (4),<sup>41</sup> 861228 (5),<sup>41</sup> 2048582 (C1), and 2048583 (C2).

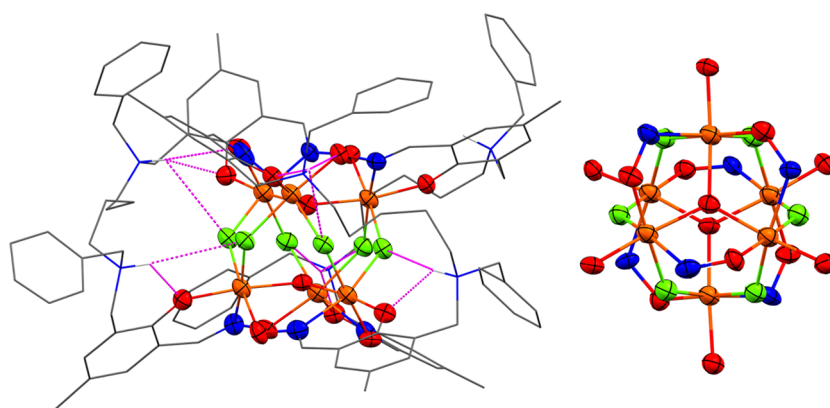


Figure 4. Left: the cation,  $[(\text{Fe}_6(\text{OH}_{0.5})_2\text{F}_6(\text{H}_2\text{L}2\text{-}2\text{H})_6)]^{3+}$ , of C2 (noninteracting H atoms are omitted for clarity; C, gray; N, blue; O, red; F, green; Fe, orange; H, white; hydrogen bonds, pink; ellipsoids are drawn at the 30% probability level). Right: off-axis view of the core along the  $\mu_3$ -O– $\mu_3$ -O axis.

this is coupled with the noticeably shorter Fe– $\mu_3$ -O(H) separations, compared to other species in Table 2 except 5 and C2. The differences in C1 compared to those in the other species are attributed to the crystallographic disorder imposed on the Fe– $\mu_3$ -O/Fe– $\mu_3$ -OH moieties, apparent also in the ellipsoids of the central O-atoms, which are elongated along the  $\mu_3$ -O... $\mu_3$ -O axis.

Complexes C1 and C2 differ in having a staggered arrangement of the Fe<sub>3</sub> triangles, compared to 2–5, which have nearly eclipsing to perfectly eclipsing configurations. This leads to each bridging  $\mu_2$ -F being subjected to a marked trans effect with Fe–F bonds trans to Fe–O having substantially greater Fe–F separations (by  $\sim 0.07$  Å) than those Fe–F bonds trans to Fe–N bonds. A similar effect is observed for the hexa- $\mu_2$ -OH bonds on 2. Interestingly, in complexes 3–5, the Fe– $\mu_2$ -O–CH<sub>3</sub> bonds are all trans to Fe–O bonds, whereas the Fe– $\mu_2$ -OH bonds are all trans to Fe–N bonds.

**Mössbauer Measurements and Discussion.** The Mössbauer measurements were performed on C1 and C2 at 293 and 5 K. Parameters derived from fitting the spectra are summarized in Table 3.

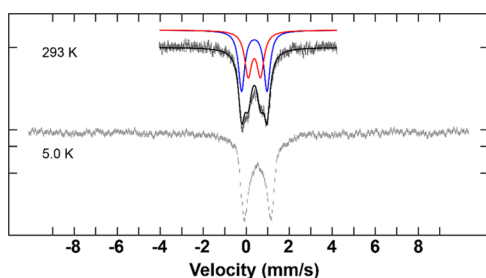
The hexa-iron complexes C1 and C2 were observed to contain only high-spin iron,  $S = 5/2$ , according to the values modeled for chemical isomer shift ( $\delta$ ) and electric quadrupole splitting ( $\Delta E_Q$ ).<sup>2,50,51</sup> The room-temperature Mössbauer spectrum of C1 (Figure 5) revealed a pair of quadrupole

Table 3. Fitting Parameters of <sup>57</sup>Fe on C1 and C2 at Lower and Higher Temperatures ( $\delta$  = Isomer Shift,  $\Delta E_Q$  = Quadrupole Splitting,  $\Gamma$  = Half-Height Line Width,  $I$  = Intensity)

T (K)	$\delta$ (mm/s)	$\Delta E_Q$ (mm/s)	$\Gamma_L$ (mm/s)	$\Gamma_R$ (mm/s)	$I$ (%)
C1					
293	0.40	1.18	0.35	0.35	55
	0.40	0.57	0.40	0.40	45
5.0 <sup>a</sup>	0.57	1.22	0.28	0.28	50
	0.55	0.82	0.44	0.44	50
C2					
293	0.43	0.77	0.27	0.31	100
5.0	0.54	0.79	0.32	0.32	100

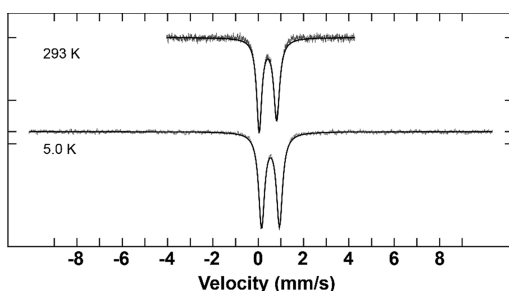
<sup>a</sup>See the text.

doublets, of approximately equal area, both with an isomer shift of 0.40 mm/s but with quadrupole splittings of 1.18 and 0.57 mm/s. This is attributed to the asymmetry that occurs within this complex at room temperature (and at the crystallographic data collection temperature) and is masked by the crystallographic disorder discussed above. The smaller quadrupole doublet is associated with the  $\mu_3$ -OH–Fe<sub>3</sub> moiety and the larger with the  $\mu_3$ -O–Fe<sub>3</sub> moiety. Nonetheless, both values are unusually high for Fe<sub>3</sub>O(H) moieties and may be attributed to the short Fe– $\mu_3$ -O bonds. The isosceles-triangled



**Figure 5.**  $^{57}\text{Fe}$  Mössbauer spectra of complex **C1** at high and low temperatures, overlaid with corresponding fits using the parameters given in Table 3 at high temperature.

species  $[\text{Fe}_3\text{O}(\text{TIEO})_2(\text{O}_2\text{CPh})_2\text{Cl}_3]$  (**6**) (H-TIEO = 1,1,2-Tris(*N*-methylimidazol-2-yl)-1-hydroxyethane), where two  $\text{Fe}_3-\mu_3\text{-O}$  bonds are 1.86 Å and the other is 2.07 Å, has very similar quadrupole splittings.<sup>52</sup> In contrast, the room-temperature Mössbauer spectrum for **C2** (Figure 6) features a



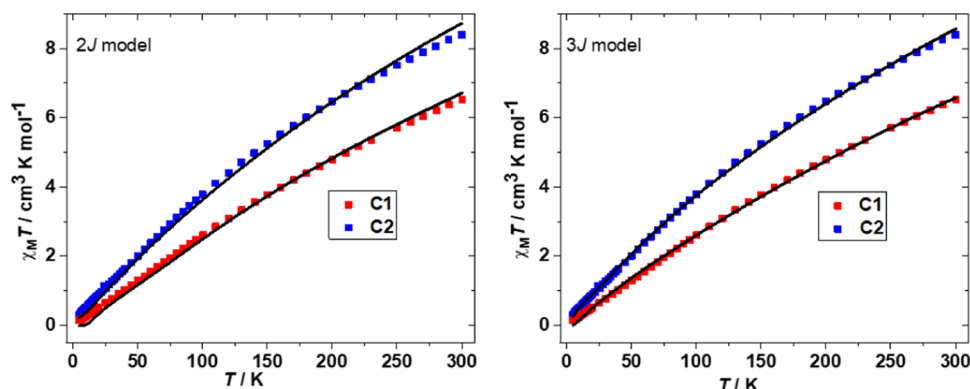
**Figure 6.**  $^{57}\text{Fe}$  Mössbauer spectra of complex **C2** at high and low temperatures, overlaid with corresponding fits using the parameters given in Table 3 at high temperature.

single, albeit slightly asymmetric, quadrupole doublet with a value approximately intermediate between those observed for **C1** at room temperature, consistent with the symmetrical  $\text{Fe}_3-\mu_3\text{-O}\cdots\text{H}\cdots\mu_3\text{-O}-\text{Fe}_3$  species inferred crystallographically.<sup>53</sup> At low temperature, the Mössbauer spectrum for **C2** is a single symmetrical doublet with a slightly larger isomer shift but essentially unchanged quadrupole splitting. However, for **C1**, the pair of quadrupole doublets appears to have collapsed into a single symmetrical quadrupole doublet, with a quadrupole splitting of 1.2 mm/s and a slightly larger isomer

shift of 0.51 mm/s. Tentatively, this might be ascribed to a phase transition (occurring below the structure-determination temperature) that leads to a symmetric  $\text{Fe}_3-\mu_3\text{-O}\cdots\text{H}\cdots\mu_3\text{-O}-\text{Fe}_3$  moiety and a compressed and more strongly axial phenolato  $\text{O}-\text{Fe}-\mu_3\text{-O}$  group. However, the fit is poor, given the pronounced asymmetry of each peak in the doublet; moreover, the isomer shift with temperature is less than expected and the quadrupole splitting is more consistent with an  $[\text{Fe}_3-\mu_3\text{-O}]$  than with an  $[\text{Fe}_3-\mu_3\text{-O}\cdots\text{H}\cdots\mu_3\text{-O}-\text{Fe}_3]$  species (see above for **C1**). A much better fit is obtained with a pair of equal area quadrupole doublets, respectively, with the isomer shifts of 0.57 and 0.55 mm/s, quadrupole splittings of 1.22 and 0.82 mm/s, and peak widths of 0.28 and 0.44 mm/s.

**Magnetic Measurements and Discussion.** Magnetic susceptibility data for **C1** and **C2** were collected in the  $T = 300\text{--}5$  K range, in an applied field  $B = 0.1$  T, and are as plotted as the  $\chi_M T$  product versus  $T$  in Figure 7, where  $\chi_M$  is the molar magnetic susceptibility. In both cases, the  $T = 300$  K value of  $\chi_M T$  (**C1**,  $6.53$  cm<sup>3</sup> K/mol; **C2**,  $8.39$  cm<sup>3</sup> K/mol) is well below the Curie constant expected for six noninteracting Fe(III) ions ( $26.25$  cm<sup>3</sup> K/mol). As the temperature is decreased, the value of  $\chi_M T$  decreases monotonically, reaching values close to zero in each case. This behavior is clearly indicative of strong antiferromagnetic exchange interactions between the Fe(III) ions, resulting in diamagnetic ground states for both **C1** and **C2** (Figure 8).

Inspection of the molecular structures of **C1** and **C2** reveals that in each case the upper and lower  $[\text{Fe}_3]$  triangles are scalene in nature, with three different Fe–O–Fe and Fe–O–N–Fe angles. In addition, **C1/C2** display three/six different Fe–F–Fe angles between triangles, potentially resulting in a total of 6/12 different exchange interactions. Clearly, this would lead to overparameterization, and so for simplicity, we used two models to fit the magnetic susceptibility data: (a) a  $2J$  model assuming a single interaction within an equilateral  $[\text{Fe}_3]$  triangle mediated by the oxide and oxime moieties ( $J_1$ ) and a single interaction between the triangles mediated by the fluoride ions ( $J_3$ ); (b) a  $3J$  model assuming an isosceles  $[\text{Fe}_3]$  triangle ( $J_1, J_2$ ) and a single interaction ( $J_3$ ) between the triangles. The latter model is a better representation of the structure when considering the Fe–O–N–Fe torsion angles in **C1** and **C2**, which are grouped into two distinct regions (**C1**:



**Figure 7.** Plot of the magnetic susceptibility, as the product  $\chi_M T$  versus  $T$  for **C1** (red squares) and **C2** (blue squares) measured in the  $300\text{--}5$  K temperature range in an applied field,  $B = 0.1$  T. The solid black lines are fits of the experimental data to spin-Hamiltonian eq 1 using the exchange coupling scheme shown in Figure 8. The plot on the left is that obtained from a  $2J$  model ( $J_1 = J_2$ ), and the plot on the right is that obtained using a  $3J$  model.

4.7–5.1 and  $\sim 12.9$  Å; C2: 9.3–14.8 and 24.0–26.2 Å). To fit the susceptibility data, we employed spin-Hamiltonian eq 1

**1: Generalized spin-Hamiltonian used to fit the  $\chi_M T$  versus  $T$  data**

$$\hat{H} = \mu_B B \sum_i g_i \hat{S}_i - 2 \sum_{i,j < i} J_{ij} \hat{S}_i \hat{S}_j \quad (1)$$

where the indices  $i$  and  $j$  refer to the Fe(III) ions,  $\mu_B$  is the Bohr magneton,  $B$  is the applied magnetic field,  $g$  is the  $g$ -factor of the Fe(III) ions (fixed at  $g = 2.00$ ),  $\hat{S}$  is a spin operator, and  $J$  is the isotropic exchange interaction.

For the 2J model (Figure 7, left), this afforded the best-fit parameters:  $J_1 = -29.77 (\pm 0.32) \text{ cm}^{-1}$ ,  $J_3 = -10.10 (\pm 0.64) \text{ cm}^{-1}$  (C1);  $J_1 = -10.00 (\pm 0.001) \text{ cm}^{-1}$ ,  $J_3 = -0.08 (\pm 0.26) \text{ cm}^{-1}$  (C2). For the 3J model (Figure 7, right), this afforded the best-fit parameters:  $J_1 = -27.67 (\pm 0.09) \text{ cm}^{-1}$ ,  $J_2 = -35.22 (\pm 0.11) \text{ cm}^{-1}$ ,  $J_3 = -8.47 (\pm 0.09) \text{ cm}^{-1}$  (C1);  $J_1 = -20.12 (\pm 0.05) \text{ cm}^{-1}$ ,  $J_2 = -26.15 (\pm 0.07) \text{ cm}^{-1}$ ,  $J_3 = -3.98 (\pm 0.05) \text{ cm}^{-1}$  (C2). The 3J model provides a superior fit, with better agreement between the two complexes. The stronger antiferromagnetic coupling for C1 compared to that for C2 apparent in Figure 7 and in the derived  $J_1$  and  $J_2$  values can be tied to the short Fe– $\mu_3$ -O distances observed for C1.

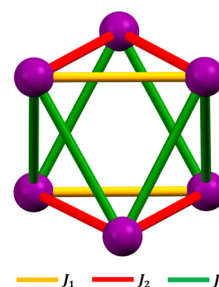
**2: Isotropic spin-Hamiltonian used to fit the  $\chi_M T$  versus  $T$  data**

$$\begin{aligned} \hat{H} = & -2J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_4 \cdot \hat{S}_5) \\ & -2J_2(\hat{S}_2 \cdot \hat{S}_3 + \hat{S}_1 \cdot \hat{S}_3 + \hat{S}_4 \cdot \hat{S}_6 + \hat{S}_5 \cdot \hat{S}_6) \\ & -2J_3(\hat{S}_1 \cdot \hat{S}_4 + \hat{S}_1 \cdot \hat{S}_6 + \hat{S}_2 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_5 + \hat{S}_3 \cdot \hat{S}_5 + \hat{S}_3 \cdot \hat{S}_6) \end{aligned} \quad (2)$$

The values obtained are similar to those observed for structurally similar Fe(III) cages bridged by a combination of oxo, hydroxo, and oxime ligands.<sup>39,54,55</sup> Indeed, both the magnitude and trend of the exchange interactions observed here are very similar to those obtained for the structurally similar complex  $[\text{Fe}_6^{\text{III}}\text{O}(\text{OH})_7(\text{H}_4\text{L}-2\text{H})_3](\text{BF}_4)_3$  ( $\text{H}_4\text{L} = 3,3'$ -[ $N,N'$ -dimethyl-1,8-octanediaminobis(methylene)]bis[2-hydroxy-5-*tert*-butylbenzaldehyde oxime]),<sup>39</sup> in which the  $[\text{Fe}_3]$  triangles are linked by six hydroxide ions ( $J_1 = -21.5 \text{ cm}^{-1}$ ,  $J_2 = -28.0 \text{ cm}^{-1}$ ,  $J_3 = -0.3 \text{ cm}^{-1}$ ). They are also in agreement with the magnetostructural model developed for Fe(III) cages by Cañada-Vilalta and co-workers.<sup>56</sup> There are no reported magnetostructural correlations for the Fe(III)–F–Fe(III) moiety, and of the few examples that exist in the literature, all are characterized by very small exchange interactions, as seen here.<sup>57</sup>

## CONCLUSIONS

Complexes C1 and C2 contain the common metallic core,  $[\text{Fe}_6(\text{OH}_{0.5})_2]^{15+}$ , but in distinctly different configurations at temperatures above  $\sim 150$  K, as evidenced by Mössbauer spectroscopy. C1 consists of two crystallographically independent half-units from which the full clusters are generated by inversion symmetry. At temperatures above  $\sim 150$  K, the proton between the two  $\text{Fe}_3\text{O}$  clusters is asymmetrically located,  $\text{Fe}_3-\mu_3\text{-OH}\cdots\mu_3\text{-O}-\text{Fe}_3$ , giving rise to strong antiferromagnetic coupling and large quadrupole splitting in the Mössbauer spectrum. On the other hand, for C2, where the asymmetric unit comprises the full hexa-iron cluster, the proton is symmetrically located,  $\text{Fe}_3-\mu_3\text{-O}\cdots\text{H}\cdots\mu_3\text{-O}-\text{Fe}_3$ . In all other respects, these two complexes are structurally very



**Figure 8.** Exchange interaction scheme used to fit the susceptibility data for C1 and C2. The model depicted assumes two different coupling constants within each  $[\text{Fe}_3]$  triangle ( $J_1$  and  $J_2$ ) and a single coupling constant between triangles ( $J_3$ ). For the 2J model discussed in the text,  $J_1 = J_2$ .

similar. The magnetic susceptibility analyses for these complexes indicate the presence of strong antiferromagnetic exchange interactions between the metal centers.

Although the Mössbauer data of C1 at low temperatures ( $\sim 80$  K) can be interpreted in terms of a structural phase transition occurring that leads to a more symmetrical  $\text{Fe}_3-\mu_3\text{-OHO}-\mu_3\text{-Fe}_3$  moiety, the magnetic susceptibility data are well fit by the 3J model over the entire temperature range and the Mössbauer data are much better fit by two quadrupole doublets, the larger characteristic of an  $\text{Fe}-\mu_3\text{-O}$  species and the smaller characteristic of an  $\text{Fe}-\mu_3\text{-OH}$  species. On the other hand, C2 remains symmetrical at all temperatures. While not conclusive, an explanation for such behavior may lie in the ligands that stabilize each hexa-iron cluster. In C2, the iron triads are linked not only by the  $\mu_2\text{-F}$  bridged but also by the ligand backbone, which clearly places additional constraints on conformational flexibility leading to the close  $\mu_3\text{-O}\cdots(\text{H})\cdots\text{O}-\mu_3$  interaction, aided by the staggered arrangement of the tri-iron planes. Greater conformational flexibility is, however, present in C1, where the iron triads are noticeably closer than for C2 (and also for complexes 2–5 in Table 2) and the Fe–F–Fe angles are noticeably more acute but the displacements of the  $\mu_3\text{-O}$  moieties from the plane of the  $\text{Fe}_3$  triangles are substantially less.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c02255>.

CCDC 2048582 (C1) (CIF)

CCDC 2048583 (C2) (CIF)

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## Notes

The authors declare no competing financial interest. The data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data center, 12 Union Road, Cambridge CB2 1EZ, U.K.; Fax: +44 1223 336033.

## ACKNOWLEDGMENTS

T.N.D. and P.G.P. thank Massey University for the award of a Massey University Doctoral Scholarship for Maori to T.N.D.

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