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

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ABSTRACT: Syntheses and magnetic and structural characterization of hexa-iron complexes of derivatized salicylaldoximes are discussed. Complexation of Fe(BF₄)₂·6H₂O with each ligand (H₂L₁ and H₄L₂) in a methanolic-pyridine solution resulted in hexa-iron compounds (C₁ and C₂, respectively), which each contain two near-parallel metal triangles of [Fe₃−μ₃-O], linked by six fluoride bridges and stabilized by a hydrogen-bonded proton between the μ₃-O groups. Within each metal triangle of C₂, Fe(III) ions are connected via the amine “straps” of (H₄L₂-2H). 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) Fe(III) centers. For C₁, two quadrupole doublets are observed at room temperature and 5 K, consistent with structural data from which discrete but disordered [Fe₃−μ₃-O] and [Fe₃−μ₃-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 [Fe₃−μ₃-O···H···μ₃-O−Fe₃] species inferred crystallographically from the very short μ₃-O···μ₃-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 oximato 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 oximato oxygen serves to bridge a second metal (Figure 1).

Several examples of this mode have been reported with nuclearities of two, three, and four. The investigation of oxo-bridged multinuclear Fe(III) materials has been a growing field of interest, as these oxo-bridged units are observed in various iron metalloproteins.

which is used in mammalian iron storage, contain an extraordinary polynuclear iron-oxo core.

Structural and magnetic studies of salicylaldoxime-based metal clusters of M₃−μ₃-O units have received increased interest after hexameric species were reported to be single molecule magnets (SMMs). There is now an extensive volume of work surrounding the coordination chemistry of MnIII clusters, which have been synthesized using derivatized salicylaldoxime ligands. 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 began in 2009 with the synthesis and structural characterization of a hexacopper trihelicate complex, [Cu₆(μ₃-OH₄H₂)₂(H₄L-2H)]·(PF₆)₃ (I, H₄L = 3,3′-[N,N′-dimethyl-1,6-hexanediiminobis-(methylene)]bis[2-hydroxy-S-tert-butylbenzaldehyde

Figure 1. General μ₃-η¹:η¹:η¹ coordination mode of the dianionic form of salicylaldoxime; M, metal ion.
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 \([\text{Fe}_6(\mu_2-OH_2)_2(\mu_2-OH)_2(H_2L-2H)_2]^{-}\)\(\cdot\)4H\(_2\)O-9MeOH (2, \(H_2L = 3,3'-[N,N'-dimethyl-1,8-octanediiminobis(methylene)]bis[2-hydroxy-5-tert-butylbenzaldehyde oxime]).\) 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, \([\text{Fe}_6(\mu_2-OH_2)_2(\mu_2-OH)_2(\mu_2-O-Me)_2]^{-}\)\(\cdot\)3. Two analogous hexa-iron complexes using nonderivatized salicylaldoxime (sao), \(\text{Na}_9[\text{Fe}_6(\mu_2-OH_2)_2(sao)_6(\mu_2-OH)_2]^+\) \(\cdot\)H\(_2\)O\(_n\) \(\cdot\)HCl \(\cdot\)H\(_2\)O, were added simultaneously to a stirred solution of \(\text{Et}_3\text{~N} (3.40 \text{~g,} \ 4.68 \text{~mL,} \ 14.8 \text{~mmol})\) in \(\text{CH}_3\text{Cl}_2 \ (80 \text{~mL})\) over 30 min. The resulting yellow solution was stirred for 24 h at RT. The solution was washed with water \((3 \times 100 \text{~mL})\), 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 \((2.99 \text{~g,} \ 86\%\)). IR (KBr pellet): \(1674 \text{ (s),} \ 1151 \text{ (s),} \ 1267 \text{ (m),} \ 1115 \text{ (s),} \ 1233 \text{ (m) cm}^{-1}\). Anal. calc'd for \(\text{C}_{206}\text{H}_{208}\text{N}_2\text{O}_{24}\): C, 74.61; H, 7.37; N, 4.73. 1H NMR (\(\text{CDCl}_3, 500 \text{~MHz})\): \(\delta (ppm) 2.30 \text{ (s,} \ 3\text{H)}, \ 2.57 \text{ (br,} \ 4\text{H)}, \ 3.76 \text{ (s,} \ 2\text{H)}, \ 7.20 \text{ (d,} \ J = 1.72 \text{ Hz,} \ 1\text{H)}, \ 7.41 \text{ (d,} \ J = 1.72 \text{ Hz,} \ 1\text{H)}, \ 10.21 \text{ (s,} \ 1\text{H}). \) 13C NMR (\(\text{CDCl}_3, 126 \text{ MHz})\): \(\delta \text{ (ppm)} 20.2, \ 53.1, \ 59.0, \ 66.7, \ 122.0, \ 123.4, \ 128.5, \ 137.1, \ 158.7, \ 192.7. \) ESI-MS (+ve ion mode, MeOH) \(m/z: 235 [\text{M} + \text{H}]^+\).

**ḦL̈1. 2-Hydroxy-5-methyl-3-(4-morpholinomethyl)benzaldehyde Oxime.** A solution of KOH \((0.662 \text{ ~g,} \ 11.8 \text{ ~mmol})\) in dry EtOH \((100 \text{ ~mL})\) was added to a solution of \(\text{NH}_2\text{OH-HCl (2.78 ~g,} \ 11.8 \text{ ~mmol)}\) in dry EtOH \((100 \text{ ~mL})\). The resulting white precipitate was removed, and the filtrate was added to a solution of \(\text{L̈a (2.78 ~g,} \ 11.8 \text{ ~mmol)}\) in dry EtOH \((200 \text{ ~mL})\) 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 CHCl\(_3\) \((200 \text{ ~mL})\), washed with water \((3 \times 100 \text{ ~mL})\), 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 \((70 \text{ ~mL})\). The resulting white powder was dried in vacuo. Yield \((1.25 \text{ ~g,} \ 42\%\)). mp 194.5–196.5 °C. IR (KBr pellet): \(1618 \text{ (s),} \ 2964 \text{ (m),} \ 1471 \text{ (s),} \ 1267 \text{ (m),} \ 1111 \text{ (s) cm}^{-1}\). Anal. calc'd for \(\text{C}_{37}\text{H}_{42}\text{N}_2\text{O}_4\): C, 74.47; H, 7.53; N, 11.84. Found: C, 74.61; H, 7.43; N, 11.79. 1H NMR (\(\text{CDCl}_3, 500 \text{ ~MHz})\): \(\delta (ppm) 2.30 \text{ (s,} \ 3\text{H)}, \ 2.44 \text{ (br,} \ 4\text{H)}, \ 3.59 \text{ (s,} \ 2\text{H)}, \ 7.22 \text{ (d,} \ J = 1.82 \text{ Hz,} \ 1\text{H)}, \ 8.28 \text{ (s,} \ 1\text{H}). \) 13C NMR (\(\text{CDCl}_3, 126 \text{ MHz})\): \(\delta \text{ (ppm)} 20.5, \ 53.1, \ 66.5, \ 118.4, \ 123.1, \ 126.8, \ 127.9, \ 131.7, \ 147.2, \ 153.5. \) ESI-MS (+ve ion mode, MeOH) \(m/z: 251 [\text{M} + \text{H}]^+\).

**ḦL̈2.** \(3,3'-[N,N'-Didenyl-1,5-pentanediaminobis(methylene)]bis[2-hydroxy-5-methylbenzaldehyde].** Solutions of A \((1.00 \text{ ~g,} \ 8.05 \text{ ~mmol)}\) and B \((0.81 \text{ ~g,} \ 2.77 \text{ ~mmol)}\), each dissolved in dry CH\(_3\)Cl \((20 \text{ ~mL})\), were added simultaneously to a stirred solution of Et\(_3\)N \((1.11 \text{ ~g,} \ 8.05 \text{ ~mmol})\) in dry CH\(_3\)Cl \((30 \text{ ~mL})\) over 30 min. The yellow solution was stirred for 24 h at RT. The solution was washed with water \((3 \times 100 \text{ ~mL})\), and the organic phase was 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 \((2.04 \text{ ~g,} \ 86\%\)). IR (KBr pellet): \(1681 \text{ (s),} \ 2851 \text{ (s),} \ 3028 \text{ (m),} \ 1471 \text{ (cm}^{-1}\). Anal. calc'd for \(\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_2\text{H}_2\text{O}: \text{C,} \ 74.47; \text{H,} \ 7.43; \text{N,} \ 4.69. \) Found: C, 74.61; H, 7.37; N, 4.73. 1H NMR (\(\text{CDCl}_3, 500 \text{ ~MHz})\): \(\delta \text{ (ppm)} 1.22 \text{ (q,} \ J = 7.53 \text{ Hz,} \ 2\text{H)}, \ 1.53 \text{ (q,} \ J = 6.85 \text{ Hz,} \ 4\text{H)}, \ 2.28 \text{ (s,} \ 6\text{H)}, \ 2.45 \text{ (t,} \ J = 7.29 \text{ Hz,} \ 4\text{H)}, \ 3.61 \text{ (s,} \ 4\text{H)}, \ 3.71 \text{ (s,} \ 4\text{H)}, \ 7.15 \text{ (s,} \ 2\text{H)}, \ 7.29 \text{ (d,} \ J = 7.69 \text{ Hz,} \ 4\text{H)}, \ 7.34 \text{ (d,} \ J = 7.28 \text{ Hz,} \ 4\text{H}), \ 3.73 \text{ (d,} \ J = 1.62 \text{ Hz,} \ 2\text{H}). \)
Table 1. Crystal Data and Structural Refinement for Complexes C1 and C2

| data                     | C1                       | C2                       |
|--------------------------|--------------------------|--------------------------|
| empirical formula        | C_{39}H_{51}F_{3}Fe_{3}N_{6}O_{10} | C_{39}H_{51}F_{3}Fe_{3}N_{6}O_{10} |
| formula weight           | 2062.61                  | 2640.86                  |
| crystal system           | triclinic                | monoclinic               |
| space group              | P\(\overline{1}\)         | P2\(1\)/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)             |
| \(α\) (deg)              | 107.161 (8)              | 90                       |
| \(β\) (deg)              | 99.537 (7)               | 113.409 (8)              |
| \(γ\) (deg)              | 100.103 (7)              | 107.161 (8)              |
| volume (Å\(^3\))         | 5651.6 (7)               | 12507.0 (12)             |
| \(Z\) (Z')               | (1.5)                    | 4 (1)                    |
| reflections collected/unique data | 77 177/18 822 [\(R_{	ext{int}} = 0.126\)] | 130 760/21 266 [\(R_{	ext{int}} = 0.197\)] |
| wavelength (Å)           | 1.5418                   | 1.5418                   |
| data collection limits   | 6.60 < \(θ\) < 65.40°    | 6.55 < \(θ\) < 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 (\(I > 2\sigma(I)\)) | \(R_I = 0.1491 (0.1049)\) \(wR_2 = 0.3259 (0.2810)\) | \(R_I = 0.1894 (0.1012)\) \(wR_2 = 0.3043 (0.2518)\) |
| residual density \((e^-/Å\(^3\))\) | 1.62/−0.84               | 0.76/−0.52               |
| CCDC no.                 | 2048582                  | 2048583                  |

Hz, 2H\(\)). 13C NMR (CDCl\(_3\)), 126 MHz: \(δ\) (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]\(^+\). 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\(^{-1}\). 

To the ligand H\(_2\)L\(_2\): 580 \([\text{M + H}]^+\). To the ligand H\(_2\)L\(_2\) (0.304 g, 0.500 mmol) dissolved in MeOH (12.5 mL) was added Fe(BF\(_4\))\(_3\)·6H\(_2\)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. calc for C\(_{116}\)H\(_{131}\)F\(_6\)Fe\(_6\)N\(_{13}\)O\(_{14}\)·3BF\(_4\)·2pyr: 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\(^{-1}\).

X-ray Structural Determination. Single-crystal X-ray data C1 and C2 were collected at −113 and −110 °C, respectively, using Cu \(K\alpha\) (\(λ = 1.54178\) 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 SFCProcess. All structures were solved using direct methods with ShelXS and further refined with ShelXL\(^{15,46}\) as implemented in Olex2.\(^{17}\) All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the ideal positions with a fixed \(U_{iso}\) 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\(_4\)\(^−\) 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 \(\times\) H\(_2\)O solvate species within the solvent mask are seen as just 5 \(\times\) H\(_2\)O in microanalytical data.

Magnetic Measurements. Variable-temperature, direct current (dc) magnetic susceptibility and magnetization measurements on powdered microcrystalline samples of each compound were measured using a quantum design MPMS XL5 SQUID magnetometer in the temperature range of 2–300 K. The temperature dependence of the magnetic susceptibility was measured under an applied field of 1 T. The g factor was calculated from the equation: \(g = \frac{\chi_{mag} \cdot H}{\mu_{B} \cdot B}\), where \(\chi_{mag}\) is the magnetic susceptibility, \(H\) is the applied field, \(\mu_{B}\) is the Bohr magneton, and \(B\) is the magnetic field.
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(NO3)3·6H2O. 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 P1 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 × (OH0.5) (−3), and 6 × (H2L1) ligands, all of which are present in an overall singly deprotonated form as (H2L1-H). Thus, the overall charge of the cation, +3, is balanced by 3 BF4− within the lattice. The complex, C1, contains two [Fe3III] units, each with a central μ3-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 μ1-oxo/μ2-hydroxo moiety with the proton most likely being asymmetrically placed between the two oxygen atoms. Thus, the two triangles are formulated as [Fe3III(μ2-O)]7+ and [Fe3III(μ3-OH)]+ and are disordered by the inversion center. These two triangles are connected via six μ2-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 μ2-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 μ2-F group and the μ3-O/OH group, while the axial positions are coordinated by an oximato O-atom from a neighboring ligand and a μ2-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 P21/c space group. The cation of the complex, C2, is formed from 6 × Fe(III) (+18), 3 × (H2L2-2H2) (−6), 6 × F (−6), and 2 × (OH0.5) (−3). The overall +3 charge is balanced by 3 × BF4− 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 Fe3III triangles that are connected through the twisted amine straps between the two salicylaldoxime “heads” on either end of each ligand molecule and six μ2-F groups.

Each triangle is formed of three Fe(III) ions that are bridged by oximato (−N=O−) and oxo/hydroxo (O2−/OH−) 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 μ3-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 μ3-O-atoms (Figure 4). Important structural parameters, including μ2-O···μ2-O, μ1-O···μ1-O distances between FeO triangles of previously reported analogous hexa-iron complexes, are shown in Table 2. The μ3-O···μ3-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−μ1-O/Fe−μ3-O bond lengths in C1 are similar to those reported in the literature but are noticeably shorter than those of C2. The Fe−μ2-F−Fe angles in C1 and C2 are observed to be larger than those previously reported in the literature for μ2-OH and μ2-OMe bridges. 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 μ3-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).
this is coupled with the noticeably shorter Fe–μ₃-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–μ₃-O/Fe–μ₃-OH moieties, apparent also in the ellipsoids of the central O-atoms, which are elongated along the μ₃-O–μ₃-O axis.

Complexes C1 and C2 differ in having a staggered arrangement of the Fe₃ triangles, compared to 2–5, which have nearly eclipsing to perfectly eclipsing configurations. This leads to each bridging μ₂-F being subject to a marked trans effect with Fe–F bonds trans to Fe–O having substantially greater Fe–F separations (by ∼0.07 Å) than those Fe–F bonds trans to Fe–N bonds. A similar effect is observed for the hexa-μ₂-OH bonds on 2. Interestingly, in complexes 3–5, the Fe–μ₂–O–CH₃ bonds are all trans to Fe–O bonds, whereas the Fe–μ₃–O 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 = S/2, according to the values modeled for chemical isomer shift (δ) and electric quadrupole splitting (ΔE_Q). The room-temperature Mössbauer spectrum of C1 (Figure 5) revealed a pair of quadrupole 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 μ₃–O–Fe₃ moiety and the larger with the μ₃–O–Fe₃ moiety. Nonetheless, both values are unusually high for Fe₃O(H) moieties and may be attributed to the short Fe–μ₃–O bonds. The isosceles-triangled

Table 2. Comparison of Important Structural Parameter Values of the Complexes 2–5 with C1 and C2

| parameter                        | 2           | 3           | 4           | 5           | C1          | C2          |
|----------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Fe–Fe (Å)                        | 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) |
| Fe–O (Å)                         | 2.526(10)   | 2.472(5)    | 2.518(5)    | 2.532(6)    | 2.639(11)–2.681(8) | 2.430(8)    |
| μ₃-O displacement from Fe₃ plane (Å) | 0.317      | 0.331       | 0.330       | 0.263–0.358 | 0.154–0.159  | 0.303       |
| Fe–μ₃-O (Å)                      | 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 rmx (Å)                     | 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 phenolate (Å)               | 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 dist (Å)                    | 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–μ₃–X (Å)                      | 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–μ₃–X–Fe (deg)                 | 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) |

“For complex 4, the stated values are for the hexa-iron cluster only. CCDC deposition numbers: 863633 (2), 755042 (3), 861227 (4), 801228 (5), 2048582 (C1), and 2048583 (C2).

Table 3. Fitting Parameters of ⁵⁷Fe on C1 and C2 at Lower and Higher Temperatures (δ = Isomer Shift, ΔE_Q = Quadrupole Splitting, Γ = Half-Height Line Width, I = Intensity)

| T (K) | δ (mm/s) | ΔE_Q (mm/s) | Γ_L (mm/s) | Γ_H (mm/s) | I (%) |
|-------|---------|-------------|------------|------------|-------|
| 293   | 0.40    | 1.18        | 0.35       | 0.35       | 55    |
|       | 0.40    | 0.57        | 0.40       | 0.40       | 45    |
| 5.0   | 0.57    | 1.22        | 0.28       | 0.28       | 50    |
|       | 0.55    | 0.82        | 0.44       | 0.44       | 50    |
| 293   | 0.43    | 0.77        | 0.27       | 0.31       | 100   |
|       | 5.0     | 0.54        | 0.79       | 0.32       | 100   |

See the text.
Tris(Fe3)Fe3Fe3 value approximately intermediate between those observed for single, albeit slightly asymmetric, quadrupole doublet with a temperature Mo range in an applied coupling scheme shown in Figure 8. The plot on the left is that obtained from a 2 Figure 7. 57Fe Mo Figure 6. 57Fe 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 [Fe3O(TIEO)2(O2CPh)2Cl3] (6) (H-TIEO = 1,1,2-Tris(N-methylimidazol-2-yl)-1-hydroxyethane), where two Fe3−μ3−O bonds are 1.86 Å and the other is 2.07 Å, has very similar quadrupole splittings. In contrast, the room-temperature Mössbauer spectrum for C2 (Figure 6) features a single, albeit slightly asymmetric, quadrupole doublet with a value approximately intermediate between those observed for C1 at room temperature, consistent with the symmetrical Fe3−μ3−O···H···μ3−O−Fe3 species inferred crystallographically. 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 Fe3−μ3−O···H···μ3−O−Fe3 moiety and a compressed and more strongly axial phenolato O−Fe−μ3−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 [Fe3−μ3−O] than with an [Fe3−μ3−O···H···μ3−O−Fe3] 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 = 300−5 K range, in an applied field B = 0.1 T, and are as plotted as the χM versus T product versus T in Figure 7, where χM is the molar magnetic susceptibility. In both cases, the T = 300 K value of χM (C1, 6.53 cm3 K/mol; C2, 8.39 cm3 K/mol) is well below the Curie constant expected for six noninteracting Fe(III) ions (26.25 cm3 K/mol). As the temperature is decreased, the value of χM 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 [Fe3] 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−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 [Fe3] triangle mediated by the oxide and oxime moieties (J1) and a single interaction between the triangles mediated by the fluoride ions (J2); (b) a 3J model assuming an isosceles [Fe3] triangle (J1, J2) and a single interaction (J3) 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:
1: Generalized spin-Hamiltonian used to fit the $\chi_T$ versus $T$ data

\[ \hat{H} = \mu_B B \sum_i g_i S_i^z - 2 \sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j \]  

(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 2$J$ model (Figure 7, left), this afforded the best-fit parameters: $J_1 = -29.77 \pm 0.32$ cm$^{-1}$, $J_2 = -10.10 \pm 0.64$ cm$^{-1}$ (C1); $J_1 = -10.00 \pm 0.001$ cm$^{-1}$, $J_2 = -0.08 \pm 0.26$ cm$^{-1}$ (C2). For the 3$J$ model (Figure 7, right), this afforded the best-fit parameters: $J_1 = -27.67 \pm 0.09$ cm$^{-1}$, $J_2 = -35.22 \pm 0.11$ cm$^{-1}$, $J_3 = -8.47 \pm 0.09$ cm$^{-1}$ (C1); $J_1 = -20.12 \pm 0.05$ cm$^{-1}$, $J_2 = -26.15 \pm 0.07$ cm$^{-1}$, $J_3 = -3.98 \pm 0.05$ cm$^{-1}$ (C2). The 3$J$ 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–μ3-O distances observed for C1.

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

\[ \hat{H} = -2J_1 (\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_4 \cdot \hat{S}_5) - 2J_2 (\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_4 \cdot \hat{S}_6 + \hat{S}_5 \cdot \hat{S}_7) = -2J_3 (\hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_5 + \hat{S}_6 \cdot \hat{S}_7 + \hat{S}_8 \cdot \hat{S}_9 + \hat{S}_1 \cdot \hat{S}_3 + \hat{S}_5 \cdot \hat{S}_8) \]  

(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.59,55 Indeed, both the magnitude and trend of the exchange interactions observed here are very similar to those obtained for the structurally similar complex [Fe(μ3-O)(OH)$_2$(H$_2$L)$_2$]$_3$[BF$_4$]$_3$ ([H$_2$L = 3,3′-[N,N′-dimethyl-1,8-octanediaminobis(methylene)]bis[2-hydroxy-5-tert-butybenzaldehyde oxime]],59 in which the [Fe$_3$] triangles are linked by six hydroxide ions ($J_1 = -21.5$ cm$^{-1}$, $J_2 = -28.0$ cm$^{-1}$, $J_3 = -0.3$ cm$^{-1}$). They are also in agreement with the magnostructural model developed for Fe(III) cages by Canadilla-Vilalta and co-workers.59 There are no reported magnostructural 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.57

**CONCLUSIONS**

Complexes C1 and C2 contain the common metallic core, [Fe$_6$(OH)$_2$]$_2$]$^{15+}$, but in distinctly different configurations at temperatures above ~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 ~150 K, the proton between the two FeO clusters is asymmetrically located, Fe$_1$–μ$_3$-OH···μ$_3$O–Fe$_9$, 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, Fe$_1$–μ$_3$-O···H···μ$_3$O–Fe$_9$. In all other respects, these two complexes are structurally very 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 (~80 K) can be interpreted in terms of a structural phase transition occurring that leads to a more symmetrical Fe$_3$–μ$_3$-OHO–μ$_3$–Fe$_3$ moiety, the magnetic susceptibility data are well fit by the 3$J$ model over the entire temperature range and the Mössbauer data are much better fit by two quadrupole doublets, the larger characteristic of an Fe–μ$_3$-O species and the smaller characteristic of an Fe–μ$_3$-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 μ$_3$-F bridged but also by the ligand backbone, which clearly places additional constraints on conformational flexibility leading to the close μ$_3$-O···(H)···O–μ$_3$ 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–Fe angles are noticeably more acute but the displacements of the μ$_3$-O moieties from the plane of the 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.

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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 or by emailing 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.

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