Molecular spin frustration in mixed-chelate Fe$_5$ and Fe$_6$ oxo clusters with high ground state spin values

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The synthesis, structures, and magnetic properties are reported of three new polynuclear Fe$^{III}$ complexes containing the anions of picolinic acid (picH) and triethanolamine (teaH$_3$) as chelates. The complexes [Fe$_4$O$_2$(OH)$_2$(O$_2$CR)$_6$(pic)$_4$(teaH)$_2$] (R = Me, Ph, Bu$_3$) (1) and [Fe$_5$O$_2$(O$_2$CR)$_4$(pic)$_3$(teaH)$_2$] (2) were obtained from the reaction of [Fe$_3$O(O$_2$CR)$_6$(H$_2$O)$_3$](NO$_3$) (R = Me, Ph, Bu$_3$) with picH and teaH$_3$ in a 1:2:1 ratio in MeCN. The core of 1 and 2 consists of an [Fe$_{12}$O$_6$] planar-butternfly unit to which is attached an Fe atom on either side by bridging O atoms. The core of 3 consists of an [Fe$_{18}$O$_2$]$_{11+}$ unit comprising two near-perpendicular vertex-sharing [Fe$_4$(µ$_3$-O)]$^{11+}$ triangular units. Variable-temperature (T) and -field (H) solid-state dc and ac magnetization (M) studies in the 5.0–300 K temperature range revealed that 1 and 2 have an S = 5 ground state spin whereas 3 has an S = 7/2 ground state. $J_{ij}$ exchange couplings were calculated by DFT and a magnetostructural correlation (MSC) for polynuclear Fe$^{III}$/O complexes. This allowed rationalization of the observed ground states from the analysis of the spin frustration effects operative, and provided good input values for fits of the experimental $\chi_m$ vs $T$ data to obtain the $J_{ij}$ values.

1. Introduction

The chemistry of iron(III)-oxo complexes continues to attract considerable research interest owing to its significance and relevance to a wide range of areas including bioinorganic chemistry, molecular magnetism, and materials science. A large number of Fe$^{III}$/O complexes of various nuclearities have consequently been synthesized over the years – from dinuclear ones to model the Fe$_2$ sites of biomolecules such as methane monooxygenase [1–6], hemerythrin [7–9], ribonucleotide reductase [1,2,10], and others [11–13], through to higher nuclearity clusters useful for studies of interesting magnetic properties and spin frustration effects [14–17], and even to model intermediate stages in the growth of the giant Fe/O core of the iron storage protein ferritin [18–22], which comprises a highly symmetrical near-spherical shell of 24 polypeptide subunits and encapsulates up to 4500 Fe atoms [23–26].

In Fe$^{III}$ chemistry, high nuclearity Fe/O$^{2-}$ clusters are facilitated by the high charge-to-size ratio of Fe$^{III}$, which favors deprotonation of H$_2$O to form O$^{2-}$ bridges [14,27,28]. This also leads to strong Fe$^{III}$ exchange coupling and, although this is essentially always antiferromagnetic (AF), certain Fe$^{III}$ topologies can lead to spin frustration effects from competing exchange interactions, which can yield high spin ground states and even single-molecule magnets if sufficient magnetic anisotropy from a significant and negative zero-field splitting is present [14,29–35].

For the above reasons, there is continuing interest in developing new synthetic routes to Fe$^{III}$/O clusters. In the past, the use of various chelating and/or bridging ligands has led to many Fe$^{III}$/O core topologies and nuclearities up to Fe$_22$ [14,32,36–39]. Most procedures employ two ligand types, such as carboxylates and a chelate, but the use of three or more ligand types is poorly explored. Therefore, we have been investigating combining carboxylates with two different types of chelates in a search for new Fe$^{III}$/O clusters, and describe in this report some recent results using picolinic acid (picH) and triethanolamine (teaH$_3$). Both picH and teaH$_3$ have separately yielded a variety of Fe/O clusters [40–48], but to our knowledge they have not been used together in Fe chemistry. We herein describe the syntheses, structures, and magnetochemical characterization of three new Fe$^{III}$/O clusters containing pic$^-$ and teaH$^{2-}$. 

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2. Experimental

2.1. Syntheses

All preparations were performed under aerobic conditions using reagents and solvents as received, unless otherwise stated. [Fe₆O₂(O2CMe)₆(H₂O)₃][NO₃] ³, [Fe₆O₂(O2CPh)₆(H₂O)₃][NO₃] ³ and [Fe₆O₂(C₆H₅)₆(H₂O)₃][NO₃] ³ were prepared as reported previously [49].

2.1.1. [Fe₆O₂(OH)₃(O2CMe)₆(pic)₆](teaH₃) ³ (1)

To a stirred red solution of [Fe₆O₂(O2CMe)₆(H₂O)₃][NO₃] ³ (0.32 g, 0.50 mmol) in MeCN (15 mL) was added picH ³ (0.12 g, 1.0 mmol) followed by teaH₃ ³ (0.07 g, 0.50 mmol). The mixture was stirred for one hour at room temperature and filtered to remove any undissolved solids. The red filtrate was allowed to concentrate at ambient temperature by slow evaporation over three days, during which time red crystals of 1·4MeCN grew. These were collected by filtration, washed with Et₂O, and dried under vacuum; the yield was 34% with respect to Fe. Anal. Calc. (Found) for 1·MeCN (C₆₆H₇₇Fe₆N₆O₂₂): C, 44.06 (44.32), 5.48 (5.88), 5.93 (5.64) %. Selected IR data (KBr, cm⁻¹): 3450(br), 2962(m), 1676(s), 1655(m), 1409(s), 1290(m), 1069(w), 1044(w), 719(m), 645(m), 459(m).

2.1.2. [Fe₆O₂(OH)₃(O2CPh)₆(pic)₆](teaH₂) ³ (2)

Complex 2 was prepared following the same procedure as for 1 but with [Fe₆O₂(O2CPh)₆(H₂O)₃][NO₃] ³ (0.50 g, 0.50 mmol). The yield was 42% with respect to Fe. Anal. Calc. (Found) for 2·MeCN (C₄₆H₅₉Fe₆N₆O₂₆·½teaH₃): C, 36.13 (36.22); H, 3.99 (4.09); N, 5.71 (5.41) %. Selected IR data (KBr, cm⁻¹): 3450(br), 1672(m), 1655(m), 1591(m), 1539(s), 1474(w), 1405(s), 1290(m), 1069(w), 1044(w), 719(m), 645(m), 459(m).

2.1.3. [Fe₆O₂(OH)₃(C₆H₅)₆(pic)₆](teaH₂) ³ (3)

To a stirred orange-red solution of [Fe₆O₂(C₆H₅)₆(H₂O)₃][NO₃] ³ (0.45 g, 0.50 mmol) in MeCN (15 mL) was added picH ³ (0.12 g, 1.0 mmol) followed by teaH₂ ³ (0.07 g, 0.50 mmol). The dark brown mixture was stirred for one hour at room temperature and filtered to remove any undissolved solids. The filtrate was allowed to concentrate at ambient temperature by slow evaporation over 3 days, during which time black crystals of 3·½teaH₂·2MeCN grew. These were collected by filtration, washed with Et₂O, and dried under vacuum; the yield was 37% with respect to Fe. Anal. Calc. (Found) for 3·MeCN (C₄₆H₅₉Fe₆N₆O₂₂·½teaH₂·2MeCN): C, 36.13 (36.22), 5.48 (5.88), 5.93 (5.64) %. Selected IR data (KBr, cm⁻¹): 3408(br), 2962(m), 1676(s), 1655(m), 1591(m), 1539(s), 1474(w), 1409(s), 1290(m), 1069(w), 1044(w), 719(m), 645(m), 459(m).

2.2. X-ray crystallography

X-ray data were collected at 100 K on a Bruker DUO diffractometer using Mo Kα radiation (λ = 0.71073 Å) and an APEXI CCD area detector. Raw data frames were read by program SAIN'T and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections, and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects, and numerical absorption corrections were applied based on indexed and measured faces. The structures were solved and refined in SHELXL2014 using full-matrix least-squares cycles [50]. The non-H atoms were refined with anisotropic thermal parameters, and all the H atoms were placed in calculated, idealized positions and refined as riding on their parent atoms. The refinement was carried out by minimizing the wR₂ function using P² rather than F values. R₁ is calculated to provide a reference to the conventional R-value, but its function is not minimized. Unit cell data and structure refinement details are listed in Table 1.

For 1·4MeCN, the asymmetric unit consists of a half Fe₆ cluster and four partial MeCN solvent molecules. For one MeCN, with N₈H, this is caused by disorder in the uncoordinated alcohol arm of a teaH²⁻ ligand, which was refined in two parts and with the H atom of its –OH placed in a calculated position. The other MeCN molecules had their site occupancies fixed at 50%, 50%, and 25%. In the final cycle of refinement, 8179 reflections (of which 7400 are observed with I > 2σ(I)) were used to refine 415 parameters, and the resulting R₁, wR₂ and S (goodness of fit) were 5.89%, 16.17% and 1.101, respectively.

For 3·½teaH₂·2MeCN, the asymmetric unit consists of a Fe₆ cluster, a half teaH₂ molecule, and two MeCN solvent molecules. The H atoms of the –OH groups of the lattice teaH₂ and ligated teaH²⁻ groups were placed in idealized positions. In the final cycle of refinement, 16285 reflections (of which 13700 are observed with I > 2σ(I)) were used to refine 826 parameters and the resulting R₁, wR₂ and S (goodness of fit) were 4.09%, 10.67% and 1.043, respectively.

2.3. Physical measurements

Infrared spectra were recorded in the solid-state (KBr pellets) on a Thermo Scientific Nicolet iS FTIR spectrometer in the 400–4000 cm⁻¹ range. Elemental analyses (C, H, N) were performed by Atlantic microlab in Norcross, Georgia, USA. Variable-temperature dc and ac magnetic susceptibility data were collected at the University of Florida using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet and operating in the 1.8–300 K range. Samples were embedded in solid eicosane to prevent torquing. Pascal’s constants were used to estimate the diamagnetic corrections [51], which were subtracted from the experimental susceptibility to give the molar paramagnetic susceptibility (χM).

2.4. DFT calculations

DFT calculations were performed using the hybrid version of the Perdew–Burke–Ernzerhof (PBEh) functional, which includes 25% of exact (Hartree–Fock type) exchange. This functional is known to perform well for magnetic exchange couplings [52–55].

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Crystallographic and structure refinement data for complexes 1 and 3.</th>
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<td>Formula³</td>
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<tr>
<td>1·4MeCN</td>
<td>C₆₆H₇₇Fe₆N₆O₂₂</td>
</tr>
<tr>
<td></td>
<td>FW (g mol⁻¹)</td>
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<tr>
<td>Space group</td>
<td>P2₁/n</td>
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<tr>
<td>Unit cell dimensions</td>
<td>a (Å)</td>
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<td>b (Å)</td>
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<td>V (Å³)</td>
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<td>µ (µm⁻¹)</td>
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<td>R₁,²,³</td>
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<td>wR₂,²,³</td>
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³ Including solvent molecules.
² I > 2σ(I).
³ R₁ = Σ||Fo| – |Fc||/Σ||Fo||.
⁴ wR₂ = Σ[w(Fo² – Fc²)²]/Σ[w(Fo²)]²]¹/².
and for the particular case of oxo-bridged Fe–Fe couplings is expected to yield an RMS error of ~10% [56], Pople’s 6-311+G** basis was used for Fe atoms and 6-31G** for lighter elements [57]. All calculations included all the electrons and neglected scalar and spin-orbit relativistic effects. The structures of 1 and 3 for the DFT calculation were obtained from the cif’s by cleaning extraneous atoms (lattice solvent and minor ligand disorder positions) and are provided as supporting material. To determine the exchange couplings, DFT calculations were carried out on the high-spin (all spins parallel) and all possible broken symmetry spin configurations: (i) 6 configurations with a single spin inversion, 15 with two inversions, and 10 with three inversions at the six Fe centers of 1 (32 configurations in total); and (ii) 10 single inversions and 10 double inversions for the five Fe centers of 3 (21 configurations in total). The resulting energies for the different magnetic configurations were used to perform an overdetermined linear fit of the Ising-type energy expression in Eq. (1), where $\langle ij \rangle$

$$E(\{S\}) = -2 \sum_{\langle ij \rangle} J_{ij} S_i S_j + E_0$$

stands for all $ij$ pairs, giving 15 and 10 distinct couplings for 1 (Fe6) and 3 (Fe5), respectively. This strategy has been successfully used by others to extract exchange couplings in multicenter transition metal complexes [58]. As a way of testing the consistency of the fitting procedure, second-neighbor couplings were fixed at zero, and the fitted first-neighbor couplings were verified as being minimally affected. We have also verified that the atomic spin populations obtained are consistent with the expected broken spin symmetry configuration. All calculations were performed using an in-house version of the Gaussian 16 program that allows for simple spin version of the Gaussian 16 program. No symmetry was assumed at any point in the model or the DFT calculations. A threshold of $10^{-6}$ Ha = 0.2 cm$^{-1}$ in the energy was used in all calculations.

Axial magnetic anisotropy (zero-field splitting) parameters, $D$, were calculated using the method of Pederson and Khanna [60] employing the PBE functional and the same basis set used for $J_{ij}$ couplings, and taking the lowest energy broken-symmetry solution as the reference state. This approach has been shown to provide reasonable $D$ parameters for a variety of large multinuclear transition metal complexes [61].

3. Results and discussion

3.1. Syntheses

A standard synthetic procedure to high-nuclearity FeIII clusters that we and others have employed on numerous occasions in the past is the reaction of $[\text{Fe}_6\text{O}_2\text{O}_2\text{CR}_6\text{H}_2\text{O}_3\text{H}_{2}\text{O}]^{16+}$ (L = H$_2$O or similar) salts with potentially chelating ligands. The $[\text{Fe}_6\text{O}]^{18+}$ core serves as a useful building block to higher nuclearity species, and the chelates have the dual function of facilitating non-polymeric products and fostering high nuclearity products, especially for chelates containing alkoxide groups since these are excellent bridging groups. We thus chose to explore the reactions of $[\text{Fe}_6\text{O}_2\text{O}_2\text{CR}_6\text{H}_2\text{O}_3\text{H}_{2}\text{O}]^{16+}$ salts with picH and teaH$_2$. Since it is also frequently seen that the product nuclearity and/or structure can vary with the carboxylate employed, such as in the reaction of $[\text{Fe}_6\text{O}_2\text{O}_2\text{CR}_6\text{H}_2\text{O}_3\text{H}_{2}\text{O}]^{16+}$ with dimemH (Me$_2$NCH$_2$CH$_2$N(Me)$_2$CH$_2$CH$_2$OH) [62], we also explored the effect in the present work of varying the carboxylate.

A number of reaction reagent ratios were explored before the present syntheses were developed. The reaction of $[\text{Fe}_6\text{O}_2\text{O}_2\text{CR}_6\text{H}_2\text{O}_3\text{H}_{2}\text{O}]^{16+}$ (R = Me or Ph) with picH and teaH$_2$ in a 1:2:1 ratio in MeCN gave red solutions from which were subsequently isolated $[\text{Fe}_6\text{O}_2\text{O}_2\text{CR}_6\text{H}_2\text{O}_3\text{H}_{2}\text{O}]^{16+}$ (R = Me (1) or Ph (2)). The reaction is summarized in Eq. (2).

$$[\text{Fe}_6\text{O}_2\text{O}_2\text{CR}_6\text{H}_2\text{O}_3\text{H}_{2}\text{O}]^{16+} + 9\text{picH} + 6\text{teaH}_2 \rightarrow [\text{Fe}_6\text{O}_2\text{O}_2\text{CR}_6\text{H}_2\text{O}_3\text{H}_{2}\text{O}]^{16+} + 8\text{RCO}_2\text{H} + 4\text{H}_2\text{O} + 2\text{H}^+$$

(2)

Other reactions using small variations in the FeIII/picH/teaH$_2$ ratios also gave compounds 1, 2, and 3 but in lower yields.

3.2. Description of structures

A stereoview of the centrosymmetric structure of 1 and its labeled core are shown in Fig. 1, and selected bond distances are shown in Table S1. The core consists of a $[\text{Fe}_4\mu_3\text{O}^{2-}\text{O}_2\text{CR}_6\text{H}_2\text{O}_3\text{H}_{2}\text{O}]^{24+}$ 'planar-butterfly' unit on either side of which is attached an $[\text{Fe}_2\mu_3\text{O}^{2-}\text{O}_2\text{CR}_6\text{H}_2\text{O}_3\text{H}_{2}\text{O}]^{24+}$ unit (Fe3/Fe3'), respectively. This strategy has been successfully used by others to extract exchange couplings in multicenter transition metal complexes [58]. As a way of testing the consistency of the fitting procedure, second-neighbor couplings were fixed at zero, and the fitted first-neighbor couplings were verified as being minimally affected. We have also verified that the atomic spin populations obtained are consistent with the expected broken spin symmetry configuration. All calculations were performed using an in-house version of the Gaussian 16 program that allows for simple spin version of the Gaussian 16 program. No symmetry was assumed at any point in the model or the DFT calculations. A threshold of $10^{-6}$ Ha = 0.2 cm$^{-1}$ in the energy was used in all calculations.

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Fig. 1. A stereopair of the complete structure of complex 1, and its labeled core; H atoms have been omitted for clarity except those on the $\mu$-OH' ion. Color code: Fe, green; O, red; N, blue; C, gray. (Color online.)
are alkoxy arms of \( \text{teaH}^2 \) groups. All metals atoms are \( \text{Fe}^{III} \) with near-octahedral geometry [63]. The protonated \( \mu-\text{OH}^- \) nature of O4 was confirmed by an O bond valence sum (BVS) calculation, which gave a value of 1.10 (Table S2). Peripheral ligation is provided by two N,O,O-chelating \( \text{teaH}^2 \) groups also bridging to the butterfly unit as described (and with the protonated alcohol arm unbound), four acetate groups in their common \( \text{syn, syn} \ \mu- \text{bridging mode}, \) and four N,O-chelating \( \text{pic}^- \) groups, one each on Fe2, Fe3, and their symmetry partners; the complete molecule has crystallographic \( C_1 \) symmetry. It is interesting to note that the [\( \text{Fe}_2\text{O}_3\text{O}_2\text{CR}_7\text{pic}_2^- \)] anion with a butterfly structure has been previously reported [42], so 1 can be considered as resulting from the replacement of some of its acetate groups on either side by the two [\( \text{Fe}^{III}(\mu-\text{OH})(\mu-\text{OR})_2 \)] units.

Each molecule of 1 is hydrogen-bonded to four neighboring molecules to give planar 2-D sheets, each contact involving an unbound \( \text{teaH}^+ \) alcohol arm (O13) and an unbound O12 atom of the pic group (O13 ... O12 = 2.655(4) Å). Between the sheets lie the MeCN solvent molecules.

There are a large number of \( \text{Fe}_6 \) complexes in the literature, with a variety of topologies such as chair, twisted boat, parallel tri-angles, planar, octahedral, ladder-like, cyclic, etc. Previous compounds with some similarity to 1 nevertheless differ in the means of connection of additional Fe atoms to the Fe4 butterfly unit and in the identity of the peripheral ligands [39,62,64–66].

A stereoview of the centrosymmetric structure of 3 and its labeled core are shown in Fig. 2, and selected bond distances are shown in Table S3. The core consists of an \( [\text{Fe}_3(\mu_3-O)_2]^{11+} \) unit comprising two near-perpendicular (84.6°) vertex-sharing \( [\text{Fe}_3(\mu_3-O)]^{17+} \) triangular units connected at Fe4. In addition, four Fe2 edges are each bridged by an O atom (O73, O77, O83, O84) from the alkoxy arms of two \( \text{teaH}^2 \) groups that are N,O,O-chelating on Fe2 and Fe4. The non-protonated (i.e., \( O^2^- \)) nature of O3 and O4 were confirmed by BVS calculations (Table S4). The peripheral ligation is completed by three chelating pic- and four \( \text{syn, syn} \ \mu- \text{pivalate groups}. \) As for 1, there are intermolecular hydrogen-bonding contacts between adjacent molecules involving an unbound \( \text{teaH}^2^- \) alcohol arm (O87) and an unbound O11 of a pic-chelate (O11 ... O87 = 2.741(5) Å), but unlike 1 these just form hydrogen-bonded dimers.

The core topology of 3 is unprecedented in FeO cluster chemistry. In fact, there are only a handful of clusters known with an \( [\text{Fe}_5(\mu_3-O)_2]^{11+} \) core: \( [\text{Fe}_2\text{O}_2(\text{OMe})(\text{bta})\text{(btaH)}\text{(MeOH)}\text{Cl}_2] \) (bta = benzotriazole) (4) [67], \( [\text{Fe}_2\text{O}_2(\text{OH})_2\text{L}_2\text{(py)}\text{(H}_2\text{O})] \) (H$_4$L = pyrazole-expanded EDTA) (5) [68], \( [\text{Fe}_2\text{O}_2(\text{L}_2\text{O}_2\text{CPh})_2] \) \( \text{(HL)} = 3\text{-amino-1-propanol or 2-} \text{(hydroxymethyl)piperidine} \) (6) [69], \( [\text{Fe}_2\text{O}_2(\text{OH})_2\text{CMe}_2\text{hmbp}]_2 \) \( \text{(hmbp)} = \text{6-hydroxyethyl-2,2'-bipyridine} \) (7) [64], and \( [\text{Fe}_2\text{O}_2\text{CPh}_2]_2\text{(edte)}\text{[(H}_2\text{O})]_2} \) (H$_4$edte = N,N,N,N-tetakis[2-hydroxyethyl]ethylenediamine) (8) [70]. The Fe3 topology of 4 and 5 is an Fe-centered elongated-tetrahedron, whereas that of 7 and 8 is a butterfly unit with an additional Fe atom attached to the top. Like 3, the core of 6 consists of two vertex-sharing \( [\text{Fe}_3(\mu_3-O)]^{17+} \) triangles, but with an overall different structure with the two Fe3 triangles nearly coplanar (dihedral angle = 23.5°).

### 3.3. Magnetochemistry

Solid-state, variable-temperature dc magnetic susceptibility data in the 5.0–300 K range were collected in a 1 kG (0.1 T) dc field on crushed microcrystalline samples of vacuum-dried 1 MeCN, 2 MeCN, and 3 MeCN restrained in eicosane to prevent torquing. The obtained data are plotted as $\chi_M T$ versus $T$ in Fig. 3.

The $\chi_M T$ versus $T$ plots for 1 MeCN and 2 MeCN are nearly superimposable, supporting the conclusion above that they are near-isostuctural except for the acetate versus benzoate difference. For this reason, we will only discuss the properties of 1 below, for which the crystal structure was obtained. For 1, $\chi_M T$ decreases from 9.75 cm$^3$ K mol$^{-1}$ at 300 K to a minimum of 9.57 cm$^3$ K mol$^{-1}$ at 230 K, and then increases to a maximum of 14.60 cm$^3$ K mol$^{-1}$ at 11 K before a slight drop to 14.14 cm$^3$ K mol$^{-1}$ at 5.0 K. The 300 K value is much less than the spin-only value ($g = 2$) for 26.25 cm$^3$ K mol$^{-1}$ expected for six non-interacting \( \text{Fe}^{III} \) ions, indicating antiferromagnetic (AF) interactions, as expected for oxo-bridged high-spin \( \text{Fe}^{III} \) ions. The 11 K peak value suggests a spin $S = 5$ ground state spin (15.00 cm$^3$ K mol$^{-1}$ for $g = 2$) for 1 MeCN (2 MeCN). The small decrease below 11 K is likely due to ZFS splitting, Zeeman effects, and weak intermolecular interactions.
For 3 MeCN, $\chi_{M}T$ steadily decreases from 6.50 cm$^3$ K mol$^{-1}$ at 300 K to 4.19 cm$^3$ K mol$^{-1}$ at 65 K, and then stays essentially constant, decreasing slightly below 8.0 K to 4.10 cm$^3$ K mol$^{-1}$ at 5.0 K. The 300 K value is again much less than that for five non-interacting Fe$^{3+}$ ions (21.87 cm$^3$ K mol$^{-1}$) indicating strong AF interactions, and the 4.19 cm$^3$ K mol$^{-1}$ plateau value at low $T$ indicates an $S = 5/2$ ground state.

To confirm the above ground state spin estimates for 1 MeCN and 3 MeCN, variable-field ($H$) and −temperature magnetization ($M$) data were collected in the 0.1−7 T and 1.8−10 K ranges, and the data are plotted in Fig. 4 as reduced magnetization ($M/N_{\text{Bohr}}$) versus $H/T$, where $N$ is Avogadro’s number and $\mu_B$ is the Bohr magneton. The saturation values at the highest fields and lowest temperatures are 9.76 and 4.85, respectively, supporting $S = 5$ and $S = 5/2$ ground state, with $g$ slightly less than 2. The data were fit, using the program MAGNET [71], by diagonalization of the spin Hamiltonian matrix assuming only the ground state is populated, incorporating axial anisotropy ($D S_z^2$) and Zeeman terms, and employing a full powder-average. The corresponding spin Hamiltonian is given by Eq. (4), where $S_z$ is the z-axis spin operator, $g$ is the electronic $g$

$$\mathcal{H} = D S_z^2 + g \mu_B H \cdot \hat{S}$$  \hspace{1cm} (4)

![Fig. 4. Plots of reduced magnetization ($M/N_{\text{Bohr}}$) vs $H/T$ data for (a) 1 MeCN (top) and (b) 3 MeCN at applied dc fields of 0.1−7.0 T in the 1.8−10 K temperature range. The solid lines are the fit of the data; see the text for the fit parameters.]

3.4. Rationalization of ground state spins

It is important to understand why and how a polynuclear cluster has a particular ground state spin value. For 1 and 3, all the exchange couplings are likely to be AF, and so the non-zero ground states are clearly due to spin frustration effects within the multiple Fe$_2$ triangular subunits. Spin frustration is here defined in the way most useful to molecular chemists, i.e., competing exchange interactions of comparable magnitude that prevent (frustrate) the preferred spin alignments. To rationalize the ground states, we thus need to determine the various exchange couplings in order to identify the relative spin alignments at the metal ions and any spin-frustrated pathways. The obvious way is to fit the experimental $\chi_{M}T$ versus $T$ data but, as we have shown elsewhere, with a significant number of symmetry-inequivalent $J_{ij}$ couplings it is possible to obtain excellent fits that are nevertheless unrelated to ‘reality’ [72]. The best solution to this problem is to use input values for the fit that are already good estimates for the actual $J_{ij}$ couplings, and in the present work we have obtained these in two ways, from the use of a magnetostructural correlation (MSC) and from DFT calculations.

The MSC was formulated specifically for Fe$^{3+}$/O clusters and allows a predicted $J_{ij}$ to be obtained for each Fe$_2$ pair using its factor, and $\mu_0$ is the vacuum permeability; the last term is the Zeeman energy associated with an applied magnetic field. The obtained fits are shown as the solid lines in Fig. 4 and were obtained with $S = 5$, $D = -0.18(2)$ cm$^{-1}$, and $g = 1.96(1)$ for 1 MeCN, and $S = 5/2$, $D = -0.51(2)$ cm$^{-1}$, and $g = 1.96(1)$ for 3 MeCN. Comparable quality fits were also obtained with positive $D$ values: $S = 5$, $D = +0.27(1)$ cm$^{-1}$, and $g = 1.97(1)$ for 1 MeCN, and $S = 5/2$, $D = +0.63(1)$ cm$^{-1}$, and $g = 1.97(1)$ for 3 MeCN. The fits are visible in the $g$ versus $D$ error surfaces in Figs. S3 and S4. An independent determination of the sign and magnitude of the $D$ values was obtained from DFT calculations; these revealed that $D$ for both 1 MeCN and 3 MeCN are negative, with values of $D = -0.22$ cm$^{-1}$ and $D = -0.52$ cm$^{-1}$, respectively, in satisfying agreement with the results of the reduced magnetization fits.

<table>
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<th>$J_{ij}$</th>
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<th>$J_{\text{far}}$</th>
<th>$J_{\text{far}}$</th>
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</table>

* cm$^{-1}$.

* Fit of experimental $\chi_{M}T$ vs $T$ data.
bridging Fe–O bond lengths and Fe–O–Fe angles [72]. For 1, the resulting $J_{MSC}$ are summarized in Table 2, together with the $J_{DFT}$ obtained from a broken-symmetry DFT calculation using the hybrid version of the Perdew–Burke–Ernzerhof (PBEh) functional. The MSC predicts all $J_{MSC}$ to be AF confirming that spin frustration effects should be operative within each Fe$_3$ triangular subunit. With one exception, the MSC and DFT values are satisfyingly similar, the exception being for the Fe1···Fe1' interaction, where they predict weakly AF and weakly F interactions, respectively. The reason for this difference is not clear but since this interaction is completely frustrated by the stronger interactions around it (vide infra), we cannot deduce from the available data in the present work whether it is really AF or F, since both possibilities would yield the same magnetic results discussed below. Certainly weak F coupling between Fe25 centers is very rare but not unknown, having been seen in a few bis-oxo–[73] and bis-1,1-azido-bridged [74] complexes. For 3, the obtained $J_{MSC}$ and $J_{DFT}$ values using the PBEh functional (Table 3) are now all AF and again in satisfying agreement.

The diagrammatic structure of 1 is shown in Fig. 5a with the MSC-predicted $J_{MSC}$ values indicated for each Fe$_2$ pair. The two edge-fused Fe$_3$ triangles in the central butterfly unit each possess two strong (−34.4, −36.8 cm$^{-1}$) and one weak (−8.4 cm$^{-1}$) competing AF couplings. Thus, the weak $J_{11}$ is completely frustrated and the spin alignments are determined by the strong couplings, giving a classical “spin-up, spin-down” pattern corresponding to $m_z = \pm \frac{1}{2}$ $z$-components of spin. As a result, the spin vectors at Fe1 and Fe1' are forced to be parallel, and this same situation would prevail for a weakly F $J_{11}$, as predicted by the DFT calculation. For Fe3 and Fe3', they each interact with three Fe atoms with comparable AF $J_{ii}$ values but the two interactions with the two parallel Fe1/Fe1' spins should overcome the one interaction with Fe3, so that the Fe2Fe3 interaction is frustrated and the spins of Fe3 and Fe3' are locked parallel to each other. The predicted ground state of 1 is then $S = 10 - 5 = 5$, in agreement with the experimental value. Using the $J_{DFT}$ values instead would lead to the same predicted spin alignments and ground state. An $S = 5$ ground state was also found for another complex with a similar Fe$_3$ topology as 1 but different ligation [64].

The diagrammatic structure of 3 with $J_{MSC}$ values (Fig. 5b) reveals that all Fe$_3$ triangular subunits possess two strong (−28.2 to −35.8 cm$^{-1}$) and one weak (−5.4 to −9.7 cm$^{-1}$) interactions except for the Fe2Fe3Fe5 triangle, which has two similarly weak $J_{35}$ (−9.7 cm$^{-1}$) and $J_{25}$ (−11.3 cm$^{-1}$) interactions consistent with their similar alkoxide bridging ligands. Nevertheless, the spin alignments are dominated by the strong interactions, frustrating the interactions in red and giving the spin alignments shown. The topology of the Fe$_3$ unit means that $J_{35}$ is competing with the strong $J_{34}$ for alignment of the Fe2 spin and is consequently frustrated, whereas $J_{25}$ is not competing with the strong interactions and is satisfied by the antiparallel alignment of the Fe2 and Fe5 spins forced by the latter. The ground state is thus predicted as $S = \frac{1}{2} S = \frac{3}{2}$, rationalizing the experimental data. Again, using the $J_{DFT}$ values would lead to the same predicted ground state spin alignments and thus would equally rationalize the experimental data.

3.5. Fit of experimental data

As stated above, an important use of $J_{MSC}$ and/or $J_{DFT}$ data is to provide input values for fits of high nuclearity Fe$_n$ complexes to minimize problems from over-parameterization, especially for complexes with no virtual symmetry to decrease the number of independent $J_{ij}$ parameters. Thus, for centrosymmetric 1-MeCN the dc $Z_mT$ versus $T$ data in the 11.0–300 K range (to avoid the lower-$T$ drop due to intermolecular interactions and/or ZFS) were fit using the program PHI [75] with the six $J_{MSC}$ as input values, $g$ fixed at 1.96, and a TIP term of $100 \times 10^{-6}$ cm$^3$ mol$^{-1}$ per Fe. An excellent fit was obtained (solid line in Fig. 6) with $J_{DFT}$ values only slightly different from the $J_{MSC}$ inputs (Table 2). For 3-MeCN, there is no crystallographic or even virtual symmetry to help, and thus eight unique $J_{ii}$ values. Nevertheless, using the $J_{MSC}$ as inputs, $g$ fixed at 1.96, and TIP as for 1-MeCN, an excellent fit for the 11.0–300 K data was obtained (solid line in Fig. 6) with the $J_{DFT}$ values in Table 3. The fit parameters for 1-MeCN reveal the first and second excited states are both $S = 4$ at energies of 46.2 and 92.5 cm$^{-1}$, respectively, above the $S = 5$ ground state. For 3-MeCN, the first and second excited states are $S = \frac{1}{2} S = \frac{3}{2}$ at energies of 101.8 and 151.4 cm$^{-1}$, respectively, above the $S = \frac{5}{2}$ ground state.

4. Conclusions

The use of a mixed-chelate reaction system with [Fe$_5$(O$_2$CR)$_6$](H$_2$O)$_3$ has yielded three new clusters 1, 2, and 3 of two structural types, Fe$_6$ and Fe$_5$, whose cores consist of fused Fe$_3$ triangular

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* cm$^{-1}$.

b Fit of experimental $J_{DFT}$ vs $T$ data.
subunits and thus experience spin frustration effects from competing AF interactions yielding $S = 5$ ground states for 1/2 and $S = 5/2$ for 3. The cohesive analysis of the magnetic properties using a combination of DFT calculations, use of a MSC, and fit of experimental data emphasizes the power of such a multi-component approach to rationalize ground states and extract credible J$_{AB}$ values.

Acknowledgments

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Appendix A . Supplementary data

CCDC 1950286 and 1950285 contains the supplementary crystallographic data for 1-4MeCN and 3i/teaH3·MeCN, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/contents/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2019.114182.

References