

Analysis of spin frustration in an Fe^{III}_7 cluster using a combination of computational, experimental, and magnetostructural correlation methods

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ABSTRACT

The synthesis, structure, and magnetic properties are reported for $[\text{Fe}_7\text{O}_3(\text{O}_2\text{C}^t\text{Bu})_9(\text{mda})_3(\text{H}_2\text{O})_3]$ (**1**), where mdaH_2 is *N*-methyldiethanolamine. **1** was prepared from the reaction of $[\text{Fe}_3\text{O}(\text{O}_2\text{C}^t\text{Bu})_6(\text{H}_2\text{O})_3](\text{NO}_3)$ with mdaH_2 in a 1:~3 ratio in MeCN. The core of **1** consists of a central octahedral Fe^{III} ion held within a non-planar Fe_6 loop by three $\mu_3\text{-O}^{2-}$ and three $\mu_2\text{-RO}^-$ arms from the three mda^{2-} chelates. Variable-temperature dc and ac magnetic susceptibility studies revealed dominant antiferromagnetic coupling, leading to a ground state spin of $S = 5/2$. The ground state was confirmed by a fit of magnetization data collected in the 0.1–7.0 T and 1.8–10.0 K ranges. The four Fe_2 pairwise exchange parameters (J_1 – J_4) were estimated by independent methods: theoretical calculations using either broken symmetry energy differences (–46.3, –16.2, –3.9, and –28.1 cm^{-1} , respectively) or Green's function approximation methods (–41.4, –14.8, –13.2, and –24.7 cm^{-1}), and a magnetostructural correlation (MSC) previously developed for high nuclearity $\text{Fe}^{\text{III}}/\text{O}$ complexes (–39.5, –13.8, –6.7, and –23.5 cm^{-1}). Additionally, the J_1 – J_4 obtained from the MSC and theoretical methods were used with the program PHI to both simulate $\chi_M T$ vs T as well as to serve as reasonable input values to fit the experimental data (–41.0, –11.4, –5.0, and –27.3 cm^{-1}). Analysis of the J_{ij} led to identification of the spin frustration effects operative and the resultant spin vector alignments at each Fe^{III} ion, thus allowing for the rationalization of the experimental ground state.

1. Introduction

$\text{Fe}^{\text{III}}/\text{oxo}$ chemistry lies at the intersection of diverse areas such as bioinorganic chemistry and molecular magnetism, giving rise to a rich library of $\text{Fe}^{\text{III}}/\text{oxo}$ complexes ranging from synthetic mimics of diiron biomolecules, such as ribonucleotide reductase [1,2], hemerythrin [3], the soluble methane monooxygenase [2,4], and others [5], to high nuclearity complexes that could provide insight into the formation of potential nanoscale $\text{Fe}^{\text{III}}/\text{O}/\text{OH}$ intermediates during the loading of the ferritin protein [6]. The formation of polynuclear $\text{Fe}^{\text{III}}/\text{oxo}$ clusters results from the controlled hydrolysis of Fe^{III} , as the high charge-to-size ratio and Lewis acidity of Fe^{III} favour the formation of O^{2-} bridges via deprotonation of H_2O in situ. As oxo-bridged high-spin Fe^{III} ($S = 5/2$) pairs almost always exhibit antiferromagnetic (AF) exchange couplings,

high nuclearity $\text{Fe}^{\text{III}}/\text{oxo}$ complexes provide many opportunities to analyze molecular spin frustration, i.e., competing exchange interactions, J_{ij} , of comparable magnitude that hinder or frustrate the preferred spin alignments [7]. Large ground state spins, S , often result from such spin frustration, providing the opportunity for the discovery of new Fe^{III} SMMs despite the lack of substantial magnetic anisotropy typically present in Fe^{III} clusters [8].

As the magnetic properties of $\text{Fe}^{\text{III}}/\text{oxo}$ clusters are important for various applications, it is crucial to quantitatively understand the nature of the pairwise Fe_2 magnetic exchange interactions, J_{ij} , to enable rationalization and/or prediction of ground state spin values. Such a quantitative assessment of J_{ij} can also lead to identification of structural features that favor spin frustration and yield large ground state spins, S . Although multiple magnetostructural correlations (MSCs) for dinuclear

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Table 1
Crystallographic information and structure refinement data for **1**.

Formula	C ₆₀ H ₁₁₄ Fe ₇ N ₃ O ₃₀
FW (g/mol)	1748.49
Space group	R3
<i>a</i> (Å)	26.5134(8)
<i>b</i> (Å)	26.5134(8)
<i>c</i> (Å)	10.5013(6)
β (°)	90
γ (°)	120
<i>V</i> (Å ³)	6393.0(5)
<i>Z</i>	3
<i>T</i> (K)	173(2)
λ (Å)	0.71073
ρ_{calc} (g/cm ³)	1.362
<i>R</i> ₁ ^{a,b}	0.0388
w <i>R</i> ₂ ^{a,c}	0.0792

$$w = 1/[\sigma^2(F_o^2) + (m \cdot p)^2 + n \cdot p], \quad p = [\max(F_o^2, 0) + 2 \cdot F_c^2]/3, \quad m \text{ and } n \text{ are constants.}$$

$$^a I > 2\sigma(I).$$

$$^b R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|.$$

$$^c wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}.$$

Fe^{III}/oxo compounds have been developed over the years, we have found them poorly applicable to higher nuclearity Fe^{III}/oxo complexes [7,9]. The various J_{ij} in high nuclearity Fe^{III}/oxo complexes are also particularly difficult to determine from experimental or computational methods, owing to: (1) the many inequivalent J_{ij} typically present as nuclearity increases; (2) the lack of a reliable MSC for high nuclearity Fe^{III}/oxo clusters; (3) the increasing computational demands of theoretical methods as nuclearity increases; and (4) overparameterization and resulting false fits when fitting data with available fitting software. To address these issues, we developed the Mitchell-Christou (M–C) semiempirical MSC for polynuclear Fe^{III}/oxo complexes [9] based on the angular overlap model, finally providing a convenient route to reliable J_{ij} from the Fe–O bond lengths and Fe–O–Fe angles within each Fe₂ pair of a polynuclear cluster. This has allowed, among other things, rationalization of experimental ground state *S* values and reliable inputs for simulating and fitting the experimental data [9]. The development of the M–C polynuclear Fe^{III}/oxo MSC combined with the continually improving power of computational methods makes polynuclear Fe^{III}/oxo complexes enticing opportunities to analyze magnetic exchange couplings in greater detail than the status quo of the past.

In search of new polynuclear Fe^{III}/oxo complexes, a prolific synthetic strategy from our group and others is preparation of complexes containing both carboxylate and polyalkoxide chelating/bridging ligands, which has afforded an array of molecular architectures. For example, we previously reported an EPR spectral study of a new heptanuclear Fe^{III}/oxo complex, [Fe₇O₃(O₂C^tBu)₉(mda)₃(H₂O)₃] (**1**) [10], discovered from such a reaction using *N*-methyl-diethanolamine (mdaH₂) as the polyalcohol reagent. However, we never published the full synthetic, structural, and magnetic details as we could not obtain a suitably-refined publishable X-ray crystal structure at that time.

In the present work, we have optimized the synthesis of **1**, determined its crystal structure to a publishable level, and carried out a SQUID magnetometry study. Since **1** is an attractive candidate to test independent approaches to evaluating magnetic exchange couplings (J_{ij}), we have carried out a three-pronged experimental, computational, and magnetostructural correlation study, comprising (i) a detailed analysis of the exchange-coupling (J_{ij}) parameters from use of the M–C polynuclear MSC and theoretical calculations, (b) a comparison of two different theoretical methods for evaluating J_{ij} , standard broken symmetry energy differences and the Green's function approximation, (c) fitting using program PHI [11] of experimental $\chi_M T$ vs *T* data to obtain J_{ij} , and (d) rationalization of both the spin frustration effects operative and the resulting experimentally determined ground state spin.

2. Experimental

2.1. Synthesis

All manipulations were performed under aerobic conditions using chemicals as received from Fisher Scientific. [Fe₃O(O₂C^tBu)₆(H₂O)₃](NO₃) was prepared as described elsewhere [12].

2.1.1. [Fe₇O₃(O₂C^tBu)₉(mda)₃(H₂O)₃] (**1**)

To a stirred orange solution of [Fe₃O(O₂C^tBu)₆(H₂O)₃](NO₃) (0.50 g, 0.55 mmol) in MeCN (25 mL) was added mdaH₂ (0.21 g, 1.8 mmol), causing a color change to brown. The solution was stirred for a further 4 h, filtered, and the filtrate carefully layered with an equal volume of Et₂O. Brown plate crystals of **1** slowly grew over a few days and were either maintained in the mother liquor for single-crystal X-ray crystallography, or collected by filtration, washed with MeCN, and dried in vacuo for other studies. The yield was 0.11 g (28 % based on Fe). Vacuum-dried material analyzed as solvent free. Anal. Calc (Found) for C₆₀H₁₂₀Fe₇N₃O₃₀: C 41.08 (41.27); H 6.90 (7.11); N, 2.40 (2.27). Selected IR data (KBr disk, cm^{−1}): 3522 (b,m), 2972 (m,sh), 2901 (m,sh), 2867 (m,sh), 2809 (w,sh), 2361 (w,sh), 2336 (w,sh), 1606 (s,sh), 1575 (s,sh), 1521 (w,sh), 1483 (s,sh), 1457 (w,sh), 1424 (s), 1363 (m,sh), 1262 (w,sh), 1228 (m,sh), 1098 (m,sh), 1058 (m), 1029 (m,sh), 1000 (m,sh), 904 (w,sh), 880 (w,sh), 789 (w,sh), 761 (w,sh), 679 (m,sh), 602 (m,sh), 581 (m,sh), 528 (m,sh), 484 (w), 438 (w,sh), 419 (w).

2.2. X-ray crystallography

Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoK α radiation (λ = 0.71073 Å). Cell parameters were refined using 8192 reflections. A full sphere of data (1850 frames) was collected using the ω -scan method (0.3° framewidth). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on *I* was <1 %). Absorption corrections by integration were applied based on measured indexed crystal faces. The structure was solved by direct methods and refined in SHELXL [13] using full-matrix least squares refinement on *F*². The non-H atoms were refined with anisotropic displacement parameters, and all H atoms were placed in calculated idealized positions and refined as riding on their parent atoms. *R*₁ is calculated to provide a reference to the conventional *R* value but its function is not minimized.

The asymmetric unit consists of 1/3 of the Fe₇ cluster located on a 3-fold rotation axis. The H atoms (H8) on the coordinated H₂O molecule could not be found in a difference Fourier map and were thus calculated in idealized positions from the O8–H8...O9 hydrogen-bonding involving the H₂O ligand (O8) and an adjacent pivalate O atom, O9, resulting in twofold disorder of the second H (H8X/H8Y) of the H₂O ligands. Initial attempts to solve the structure in space group R3 did not refine well, as the w*R*₂ and *R*₁ remained at values over 50 % and 23 %, respectively. However, the structure refined very well and to low *R* values once the data were treated as a merohedral twin by switching the *a* and *b* axes and changing the sign of the *c* axis. In the final cycle of refinement, 6396 reflections (of which 5629 are observed with *I* > 2 σ (*I*)) were used to refine 302 parameters, and the resulting *R*₁, w*R*₂ and *S* (goodness of fit) were 3.88 %, 7.92 %, and 0.978, respectively. Crystal data and structure refinement parameters are listed in Table 1.

2.3. Physical measurements

Infrared spectra were recorded on crushed polycrystalline samples as KBr pellets on a Nicolet Nexus 670 FTIR spectrometer in the 400–4000 cm^{−1} range. Elemental analyses (C, H and N) were performed by Atlantic Microlab in Norcross, Georgia, USA. Variable-temperature dc and ac magnetic susceptibility data were collected using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 Tesla magnet and

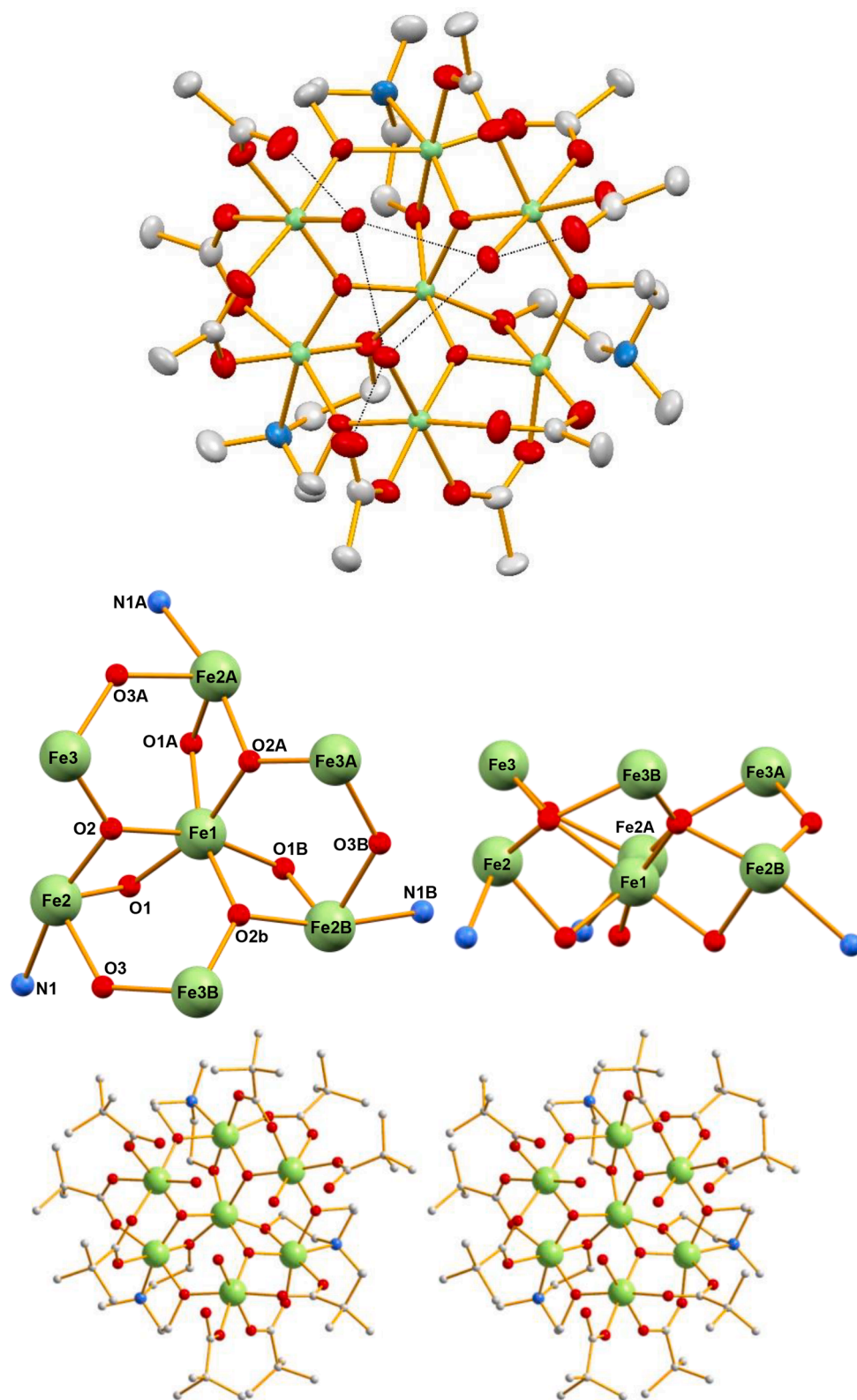


Fig. 1. (top) Complete structure of **1** with ^tBu groups omitted for clarity; (middle) Top-view (left) and side-view (right) of the labelled Fe^{III}/O/N core; and (bottom) stereopair of the complete structure with H atoms are omitted for clarity. Color code: Fe^{III} lime green, O red, N powder blue, C grey. ((Colour online.))

operating in the 1.8–300 K range. Samples were embedded in solid eicosane to prevent torquing. Magnetization vs field and temperature data were fit using the program MAGNET [14], and *D* vs *g* fit error surfaces were generated using the program GRID [15]. Pascal's constants were used to estimate the diamagnetic correction [16], and contributions from

the eicosane and gel capsule were measured as a blank. All these were subtracted from the experimental susceptibility to give the molar paramagnetic susceptibility (χ_M). Ac magnetic susceptibility measurements were carried out on a microcrystalline vacuum-dried sample in the 1.8 – 15.0 K range using a 3.5 G ac field and a 1000 Hz oscillation frequency.

Table 2Selected interatomic distances (Å) and angles (°) for **1**.

Fe1-O1A	1.990(5)	Fe2-N1	2.232(7)
Fe1-O2A	2.024(5)	Fe3-O2	1.863(5)
Fe2-O2	1.883(5)	Fe3-O3B	1.989(6)
Fe2-O1	1.977(5)	Fe3-O7	2.032(5)
Fe2-O3	2.007(5)	Fe3-O10	2.034(6)
Fe2-O5	2.027(6)	Fe3-O8	2.072(5)
Fe2-O4	2.048(6)	Fe3-O6	2.073(6)
Fe2-O1-Fe1	96.9(2)	Fe3-O2-Fe2	119.8(3)
Fe3-O2-Fe1	134.6(3)	Fe2-O2-Fe1	98.9(2)
Fe3A-O3-Fe2	127.9(3)		

Table 3Bond valence sums (BVS) and assignments ^a for the Fe and O atoms in **1**.

Atom	Fe ^{II}	Fe ^{III}
Fe1	2.64	3.15
Fe2	2.61	3.10
Fe3	2.63	3.14
Atom	BVS	Assignment
O2	2.00	O ²⁻
O8	0.42	H ₂ O
O4	1.87	^t BuCO ₂
O5	1.80	^t BuCO ₂
O6	2.01	^t BuCO ₂
O7	1.87	^t BuCO ₂
O9	1.55	^t BuCO ₂
O10	1.78	^t BuCO ₂
O1	2.01	mda ²⁻
O3	1.96	mda ²⁻

^a The Fe oxidation state is the nearest integer to the bold value, which is the closest to the charge for which it was calculated. For O, values in the ~ 1.8–2.0, ~ 1.0–1.2, and ~ 0.2–0.4 ranges indicate non-, single- and double-protonation, respectively, but can be affected by hydrogen-bonding.

2.4. Theoretical calculations

All magnetic exchange DFT calculations for the Fe₇ complex were performed using the X-ray structural data obtained in this work. These

couplings were determined from DFT calculations by mapping broken-symmetry solutions to Ising-type spin configurations {*S*} using the high-spin, all single-spin inversions, and all first-neighbor two-spin inversions. The energies of these configurations are expressed in terms of a sum over single-center interactions, Eq. (1), where ⟨*ij*⟩ means all *ij* pairs, *S_k* = ±⁵/₂ for Fe^{III}, and *E*₀ is a constant introduced to match the spin model with the DFT energies.

$$E(\{S\}) = -2 \sum_{\langle ij \rangle} J_{ij} S_i \cdot S_j + E_0 \quad (1)$$

It should be noted that this approach reduces to the broken-symmetry formulation of Noodleman [17] for the case of two centers, Eq. (2),

$$J_{\Delta E} = \frac{E_{BS} - E_{HS}}{4S_A S_B} \quad (2)$$

where *E*_{BS} and *E*_{HS} are the energies of the broken symmetry (BS) and high spin (HS) solutions, and *S_A* and *S_B* are the ideal spin quantum numbers for each center. To determine the exchange couplings *J_{ij}*, the energies of all spin configurations {*S*} from broken spin-symmetry DFT calculations were employed to perform a linear regression fit of the Ising-type energy formula in Eq. (1). This approach has been successfully used in the past to determine magnetic exchange couplings in multi-center transition metal complexes [18]. The linear regression *R*² parameter differs from 1 by less than 10^{−6}, which shows that the magnetization is localized at the magnetic centers, and thus the broken-symmetry DFT solutions are reliably represented by the Ising-type model configurations. We have also verified that the atomic spin populations from the DFT calculations are consistent with the expected broken symmetry spin configuration.

The Green's function (GF) approach is another method to extract the exchange couplings from DFT calculations, initially developed by Liechtenstein [19] for the solid state. The GF approach has been formulated for its use in molecular complexes [20,21] by Steenbock et al. and adopted in this work. The GF approach, in brief, relies on an approximate expression that relates magnetic exchange couplings with differential local spin rotations [22]. The equation resulting from that

Table 4Fe₇ clusters^a containing a central Fe within an Fe₆ loop, and their cores and ground state spin.

Formula ^a	Core	Central Fe	<i>S</i>	Ref.
[Fe ₇ O ₃ (O ₂ C ^t Bu) ₉ (mda) ₃ (H ₂ O) ₃] ^b	[Fe ^{III} ₆ O ₃] ¹⁵⁺	oct Fe ^{III}	⁵ / ₂	t.w.
[Fe ₇ O ₃ (O ₂ CPh) ₉ (mda) ₃ (H ₂ O)] ^b	[Fe ^{III} ₆ O ₃] ¹⁵⁺	oct Fe ^{III}	⁵ / ₂	27
[Fe ₇ O ₃ (O ₂ C ^t Bu) ₉ (bda) ₃ (H ₂ O) ₃] ^b	[Fe ^{III} ₆ O ₃] ¹⁵⁺	oct Fe ^{III}	⁵ / ₂	28
[Fe ₇ O ₃ (O ₂ C ^t Bu) ₉ (phda) ₃ (H ₂ O) ₃] ^b	[Fe ^{III} ₆ O ₃] ¹⁵⁺	oct Fe ^{III}	⁵ / ₂	28
[Fe ₇ O ₃ (O ₂ C ^t Bu) ₉ (teaH) ₃ (H ₂ O) ₃] ^b	[Fe ^{III} ₆ O ₃] ¹⁵⁺	oct Fe ^{III}	⁵ / ₂	28,29
[Fe ₇ O ₃ (O ₂ C ^t Bu) ₉ (bheapH) ₃ (H ₂ O) ₃] ^b	[Fe ^{III} ₆ O ₃] ¹⁵⁺	oct Fe ^{III}	⁵ / ₂	29
[Fe ₇ O ₃ (OH) ₃ (hmpip) ₆ (O ₂ CPh) ₇] ^c	[Fe ^{III} ₆ O ₃ (OH) ₃] ¹²⁺	tet Fe ^{III}	²¹ / ₂	30
[Fe ₇ O ₃ (OMe) ₃ (heen) ₃ Cl _{4.5} (solv) ₂] ^{1.5+ c}	[Fe ^{III} ₆ O ₃] ¹⁵⁺	tet Fe ^{III}	¹⁵ / ₂	31
[Fe ₇ O ₃ (OH) ₃ Cl(paeo) ₆] ^{5+ c}	[Fe ^{III} ₆ O ₃ (OH) ₃] ¹²⁺	tet Fe ^{III}	²¹ / ₂	31
[Fe ₇ O ₃ (OMe) ₆ (O ₂ CR) ₆ (MeOH) ₆ Cl] ^{2+ c}	[Fe ^{III} ₆ O ₃] ¹⁵⁺	tet Fe ^{III}	⁷ / ₂ *	32
[Fe ₇ O ₃ (OH) ₃ (quin) ₆] ^d	[Fe ^{III} ₆ O ₃ (OH) ₃] ¹²⁺	oct Fe ^{III}	³ / ₂	33
[Fe ₇ (OH) ₆ (quin) ₆] ^{1+ d}	[Fe ^{III} ₆ (OH) ₆] ¹⁵⁺	oct Fe ^{III}	³ / ₂	33
[Fe ₇ (bmsae) ₆ (OMe) ₆] ^{2+ d}	[Fe ^{II} Fe ^{III} ₆] ²⁰⁺	oct Fe ^{II}	n.r.	34
[Fe ₇ (tea) ₆] ^{2+ d}	[Fe ^{II} Fe ^{III} ₆] ²⁰⁺	oct Fe ^{II}	⁵ / ₂ *	35
[Fe ₇ (L ¹) ₆ Cl ₆] ^e	[Fe ^{II} Fe ^{III} ₄] ¹⁸⁺	oct Fe ^{III}	n.r.	36
[Fe ₇ (Hbmsae) ₆ (OMe) ₆] ^{2+ e}	[Fe ^{II}] ¹⁴⁺	oct Fe ^{II}	10*	34
[Fe ₇ (OMe) ₆ (HL ²) ₆] ^{3+ e}	[Fe ^{II} Fe ^{III} ₆] ¹⁵⁺	oct Fe ^{III}	²⁹ / ₂	37
[Fe ₇ L ₆] ^{2+ e}	[Fe ^{II}] ¹⁴⁺	oct Fe ^{II}	n.r.	38

t.w. = this work, n.r. = not reported, oct = octahedral, tet = tetrahedral, * = some uncertainty.

^a mdaH₂ = *N*-methyl-diethanolamine; bdaH₂ = *N*-butyl-diethanolamine; phdaH₂ = phenyl-diethanolamine; teaH₃ = triethanolamine; bheapH₃ = 1-[*N,N*-bis(2-hydroxyethyl)-amino]-2-propanol; hmpip = 2-hydroxymethylpiperidine; heenH₂ = *N,N'*-bis(2-hydroxyethyl)ethylenediamine; paeoH = 2-(2-pyridylmethyl)amino-ethanol; quinH₅ = D-(−)-quinic acid; H₂bmsae = 5-bromo-3-methoxysalicylideneaminoethanol; H₂L¹ = 2-amino-2-methyl-1,3-propanediol; H₂L² = 3-methoxy-2-salicylideneamino-1-ethanol; H₂L³ = 2-(2-hydroxy-3-methoxybenzylideneamino)phenol; solv = MeOH or H₂O.

^b central Fe surrounded by a non-planar Fe₆ loop.

^c non-planar dome or central Fe above a planar Fe₆ loop.

^d central Fe surrounded by a coplanar Fe₆ loop.

^e central Fe surrounded by a nearly planar Fe₆ loop.

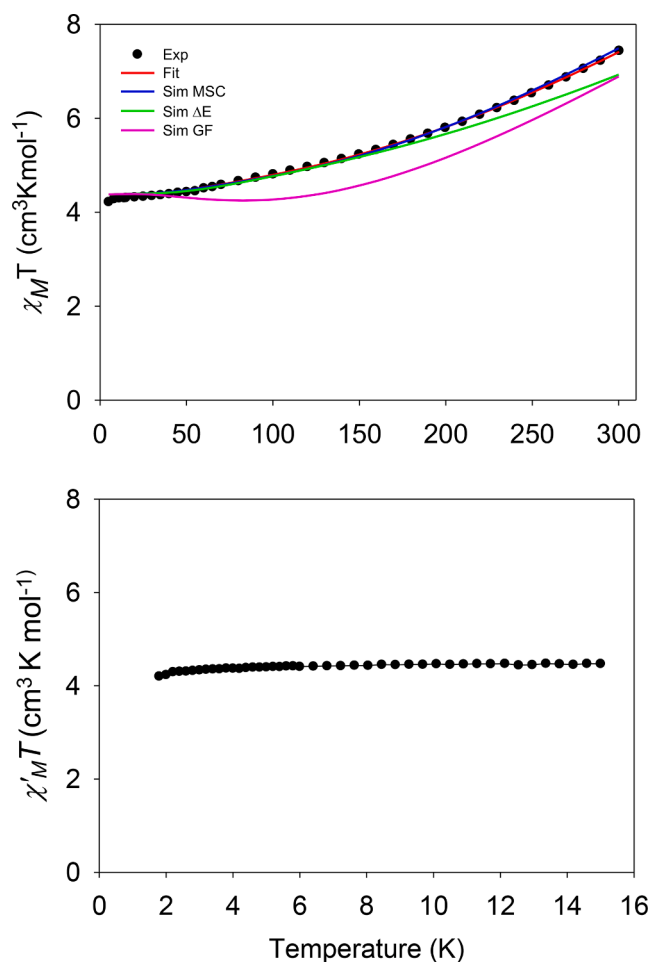


Fig. 2. (top) $\chi_M T$ vs T in a 0.1 T dc field, its simulations using the J_{MSC} (—), the $J_{\Delta E}$ (—), and the J_{GF} (—) values, and the J_{PHI} fit (—); (bottom) ac in-phase $\chi'_M T$ vs T plot with a 1000 Hz oscillation frequency (Colour online).

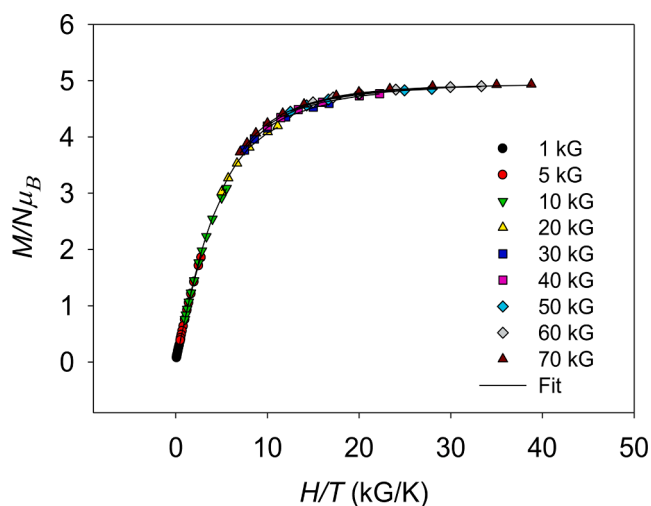


Fig. 3. Plot of reduced magnetization ($M/N\mu_B$) vs H/T data for **1** in the 1.8–10.0 K range at the indicated applied dc fields. The solid lines are the fit of the data; see the text for the fit parameters (Colour online).

produce a convenient initial guess for self-consistent calculations. No symmetry was assumed in the broken-symmetry, GF, or DFT calculations. A self-consistency convergence threshold of 10^{-6} Ha = 0.2 cm^{-1} in the energy and 10^{-8} in the RMS changes in the density matrix was used in all calculations. The GF approach results were calculated using an in-house post-processing code.

3. Results and discussion

3.1. Synthesis

After investigating many reagent ratios, the reaction of $[\text{Fe}_3\text{O}(\text{O}_2\text{C}^t\text{Bu})_6(\text{H}_2\text{O})_3](\text{NO}_3)$ with mdaH_2 in a 1:~3 ratio in MeCN was found to lead to subsequent isolation of brown X-ray quality crystals of $[\text{Fe}_7\text{O}_3(\text{O}_2\text{C}^t\text{Bu})_9(\text{mda})_3(\text{H}_2\text{O})_3]$ (**1**) in analytical purity from an MeCN/ Et_2O layering; the preparation is summarized in Eq. (4).



approximation is given by Eq. (3),

$$J_{GF} = \frac{1}{4S_A S_B} \left[\sum_{i,a} \sum_{\mu,\nu \in A} \sum_{\mu',\nu' \in B} \frac{f_i^\alpha - f_a^\beta}{\epsilon_i^\beta - \epsilon_a^\alpha} C_{\mu i}^\alpha (F_{\mu\nu}^\alpha - F_{\mu\nu}^\beta) C_{\nu a}^\beta C_{\mu' i}^\alpha (F_{\mu' \nu'}^\alpha - F_{\mu' \nu'}^\beta) C_{\nu' a}^\beta \right] \quad (3)$$

where F is the local Kohn-Sham (KS) Fock matrix and C is the KS molecular orbital coefficients in a Löwdin orthonormalized basis. The sum runs over the spin center indices μ and ν of site A , μ' and ν' of site B , and i and a are over occupied and virtual orbitals, respectively. For full details of the formulation, we refer the reader to the work of Steenbeck [21].

Electronic structure calculations were performed using the Gaussian 16 computation software suite [23]. The Pople all-electron 6-311 + G** basis set is used for Fe and the 6-31G** is used for the ligand atoms. DFT calculations in this work employ the hybrid PBE approximation (PBEh) [24,25] without including relativistic effects. All broken-symmetry DFT energies were obtained using an in-house version of the Gaussian 16 program that allows for a local spin inversion at any magnetic center to

1 can also be obtained by slow evaporation of the filtrate, but with a lower crystal quality.

3.2. Description of structure

Complex **1** crystallizes in the rhombohedral space group $R\bar{3}$ with the Fe_7 cluster lying on a C_3 symmetry axis. The complete structure, labeled core, and a stereopair are shown in Fig. 1, and selected bond distances and angles are listed in Table 2. The core consists of a central Fe^{III} ion ($\text{Fe}1$) held within a non-planar Fe_6 loop ($\text{Fe}2$, $\text{Fe}3$, and their symmetry-equivalent partners) by three $\mu_3\text{-O}^{2-}$ ($\text{O}2$) ions and three $\mu_2\text{-EtO}^-$ ($\text{O}1$) arms from the three mda^{2-} groups. All Fe^{III} have near-octahedral geometry, and both the Fe oxidation states and O protonation levels were confirmed by bond valence sum (BVS) calculations [26] (Table 3). Each mda^{2-} group is O,N,O- tridentate chelating on the $\text{Fe}2$ ions, with one alkoxide $\text{O}1$ bridging to the central $\text{Fe}1$, as stated, and the other, $\text{O}3$, bridging to $\text{Fe}3$. As a result, monoatomic bridging of $\text{Fe}2$ pairs around

Table 5Exchange interactions $J_1 - J_4$ for **1** from MSC calculations, DFT computations, and fits of the experimental dc data.

J^a	Fe-O bonds ^b	Fe-O-Fe angles ^b	Calculated J_{ij}			J_{ij} from fits			J_0^e	J_{-10}^e	J_{-20}^e
			J_{MSC}	$J_{\Delta E}^c$	J_{GF}^c	$J_{PHI}^{MSC^d}$	$J_{PHI}^{\Delta E^d}$	$J_{PHI}^{GF^d}$			
J_1	1.872	119.8	-39.5	-46.3	-41.4	-39.6	-41.0	-34.1	-49.8	-86.4	-37.0
J_2	1.998	127.9	-13.8	-16.2	-14.8	-15.1	-11.4	-16.1	+54.4	-42.9	-14.7
J_3	1.982	97.0	-6.7	-3.9	-13.2	-6.3	-5.0	-9.0	-115.0	+3.4	-7.1
J_4	1.942	134.8	-23.5	-28.1	-24.7	-24.3	-27.3	-36.0	+72.9	+63.0	-29.7

^acm⁻¹; $\hat{H} = -2J_{ij}\hat{S}_i\cdot\hat{S}_j$ convention. See labeling in Fig. 4.^bAverage in Å and deg.^cThe DFT calculations gave all J_{ij} values independently, so only one is shown for symmetrically equivalent sets. For J_1 and J_3 , all three were identical. For J_2 and J_4 , one value differed by 0.1 cm⁻¹.^dFits of experimental data using the indicated J_{ij} as inputs; a constant TIP = 700×10^{-6} cm³/mol was also included.^eThe $J_{\#}$ are the fit values obtained using the given # as $J_1 - J_4$ input values.

the outer Fe₆ loop alternates between an mda²⁻-μ₂-EtO⁻ (O3) and a μ₃-O²⁻ (O2). Each of the latter Fe₂Fe₃ pairs is also bridged by two syn,syn η¹:η¹-μ⁻BuCO₂ ligands, and peripheral ligation is completed by a monodentate tBuCO₂ group and a terminal water molecule (O8) on each Fe₃, and these form intramolecular hydrogen-bonds between them involving the unbound carboxylate O9 atom (O8...O9 = 2.574(8) Å). There are also hydrogen-bonds between the terminal O8 water ligands (O8...O8 = 2.986(8) Å) [Fig. S1]. Complex **1** joins a family of eighteen Fe₇ complexes with the general description of a central Fe surrounded by an Fe₆ array (Table 4) [27–38]. Only five of these, however, have the same structural topology as **1**, i.e., a [Fe^{III}O₃]¹⁵⁺ core with a central octahedral Fe^{III} ion surrounded by a non-planar Fe₆ loop [27–29].

3.3. SQUID magnetometry

3.3.1. Magnetic susceptibility studies

Solid-state, variable-temperature dc magnetic susceptibility (χ_M) data for **1** in the 5.0–300 K range were collected on crushed vacuum-dried microcrystalline samples restrained in eicosane to prevent torquing. $\chi_M T$ decreases steadily from 7.4 cm³ K mol⁻¹ at 300 K to 4.2 cm³ K mol⁻¹ at 5.0 K [Fig. 2]. The 300 K value is much lower than the 30.6 cm³ K mol⁻¹ calculated for seven non-interacting high-spin Fe^{III} ions ($S = 5/2$) with $g = 2.00$, indicating dominant antiferromagnetic (AF) interactions. The near-constant value at 5.0 K suggests an $S = 5/2$ ground state and was supported by ac magnetic susceptibility measurements performed in the 1.8 to 15 K range in a 3.5 G ac field at a 1000 Hz oscillation frequency. The ac in-phase $\chi'_M T$ vs T and out-of-phase χ''_M vs T plots are shown in Fig. 2 and Fig. S2, respectively. $\chi'_M T$ is near-constant at ~4.3 cm³ K mol⁻¹ in the 1.8–15 K range, confirming a well-isolated $S = 5/2$ ground state. There was no χ''_M signal.

Further confirmation for a $S = 5/2$ ground state was obtained from magnetization (M) vs field (H) and T data collected in the 0.1–7.0 T and 1.8–10.0 K ranges and plotted as $M/N\mu_B$ vs H/T in Fig. 3, where N is Avogadro's number and μ_B is the Bohr magneton. The data were fit by diagonalization of the spin Hamiltonian matrix using program MAGNET [14], which assumes that only the ground state is occupied, includes axial zero-field splitting (zfs), $D\hat{S}_z^2$, and the Zeeman interaction, and incorporates a full powder average. The corresponding spin Hamiltonian is given by Eq. (5), where μ_B is the Bohr magneton, D is the axial zfs parameter, and μ_0 is the vacuum permeability. An excellent fit

$$H = D\hat{S}_z^2 + g\mu_B\mu_0\hat{S}\cdot H \quad (5)$$

(solid lines in Fig. 3) was obtained with $S = 5/2$, $D = -0.42$ cm⁻¹ and $g = 1.98$. A second fit with a positive D also gave an excellent fit to the data, as expected, with $S = 5/2$, $D = +0.51$ cm⁻¹, and $g = 1.99$. The D vs g error surface generated using the program GRID [15] (Fig. S3) revealed both fits to be of essentially equal quality, with a slightly greater softness in the positive D . The fit values obtained in the present work are reasonably comparable with those obtained by our previous EPR study of **1**, in which simulations of the EPR spectra indicated an $S = 5/2$ ground state

with $g = 2.00(1)$ and $D = +0.36$ cm⁻¹ [10].

3.3.2. Ground state spin rationalization using MSC and DFT methods

An important objective in molecular magnetism is to achieve insight into how the spin vectors at the various paramagnetic metal ions in a polynuclear cluster are aligned in the ground state and thus lead to the experimentally observed ground state spin. Such a rationalization of an experimental conclusion requires determination of the pairwise exchange couplings (J_{ij}) between the metal ions, which would then allow the strongest couplings to be identified, as well the presence of any spin frustration effects. To achieve this for **1**, we implemented a three-pronged analysis consisting of (i) a semiempirical MSC for polynuclear Fe^{III}/O clusters [9] to obtain J_{MSC} , (ii) DFT computations using both standard broken symmetry energy differences to obtain $J_{\Delta E}$ and the Green's function approximation method to get J_{GF} , and (iii) fits of experimental $\chi_M T$ vs T data using the program PHI [11] to obtain J_{PHI} . We first carried out approaches (i) and (ii) to compare the obtained J_{MSC} , $J_{\Delta E}$, and J_{GF} , followed by then using them as credible input values in fits of the experimental data; we have found in previous work that this approach minimizes problems with overparameterization and thus resulting 'false' fits not related to the real J_{ij} of the cluster. The calculated J_{MSC} , $J_{\Delta E}$, J_{GF} , and J_{PHI} for **1** are listed in Table 5.

In accord with the protocol set forth for the Mitchell-Christou polynuclear Fe^{III}/O MSC [9], the Fe-O bond lengths (r) and Fe-O-Fe angles (φ) for each Fe₂ pair were used with Eq. (6) to generate the J_{MSC} for **1**. In instances of multiple monoatomic oxo bridges between two Fe^{III} ions, the longer average Fe^{III}-O bond was used, as per the protocol [9].

$$J_{ij} = (1.23 \times 10^9)(-0.12 + 1.57 \cos \varphi + \cos^2 \varphi)e^{-8.99r} \quad (6)$$

The crystallographic C_3 symmetry of **1** gives rise to four independent J_{ij} parameters: J_1 and J_2 in the outer Fe₆ loop, and J_3 and J_4 to the central Fe1 (Fig. 4). The $J_1 - J_4$ determined from the M-C MSC and the two types of theoretical calculations are in agreement in both sign and magnitude (Table 5), with the biggest discrepancy being in the magnitude of J_3 between the J_{MSC} (-6.7 cm⁻¹) and $J_{\Delta E}$ (-3.9 cm⁻¹) values and the J_{GF} (-13.2 cm⁻¹) value. Note that the DFT calculations are on the complete heptanuclear complex, and are thus affected by the total metal nuclearity, whereas the MSC calculations are performed on one Fe₂ pair at a time and are not affected by the metal nuclearity. The resulting agreement between the different approaches is thus very satisfying and reflects the power of modern computational methods.

All $J_1 - J_4$ interactions are AF, which is almost always the case for high spin Fe^{III} systems, with the weakest interaction being J_3 in the Fe₂ pairs with two monoatomic oxo bridges giving small Fe-O-Fe angles (97.0° and 99.0°); the stronger J_1 , J_2 , and J_4 all involve single monoatomic oxo bridges and consequently larger Fe-O-Fe angles (119.8–134.8°). Since all interactions are AF and the Fe₇ topology comprises six edge-fused Fe₃ triangles, the complex is expected to experience spin frustration, here defined in the way most appropriate for molecular systems as competing exchange interactions that prevent

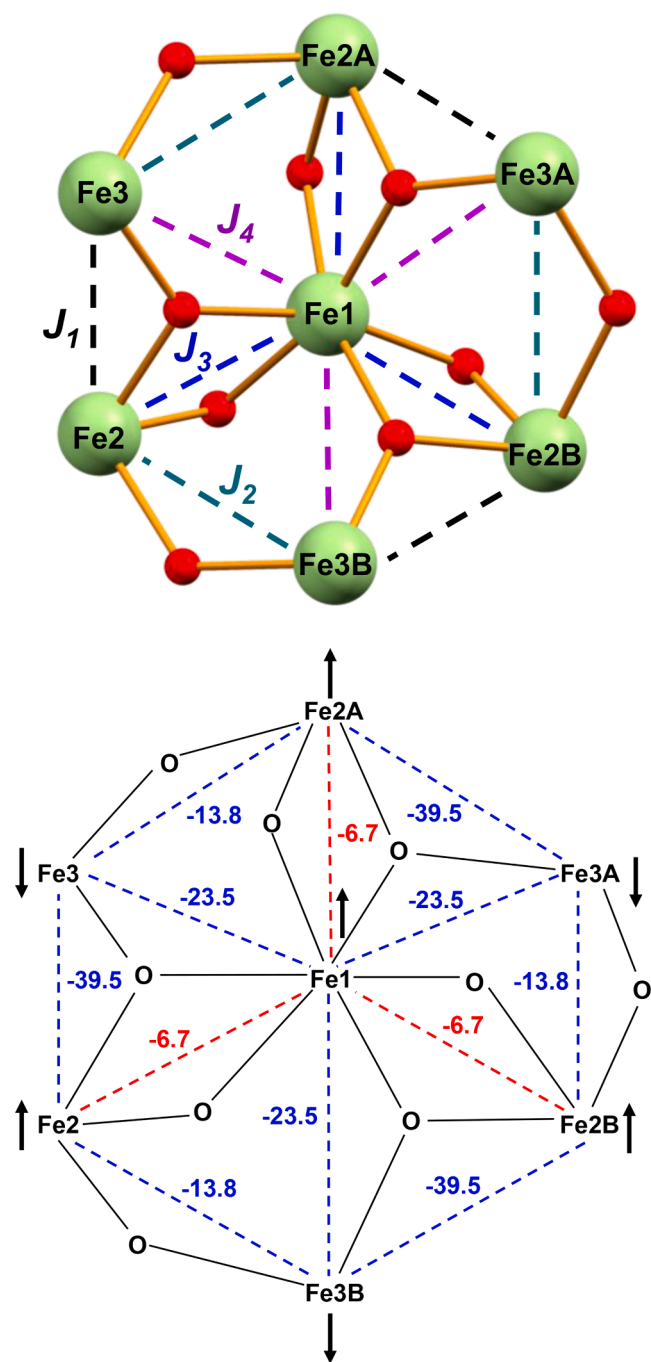


Fig. 4. (top) Fe^{III}/O/OR core of **1** showing the $J_1 - J_4$ exchange-coupling scheme for the J_{MSC} , J_{AE} , and J_{GF} calculations. Color code: Fe^{III} lime green, O red. (bottom) Diagrammatic representation of the Fe atoms in **1** showing the J_{MSC} exchange-couplings (cm⁻¹), the spin frustrated pathways, and the relative spin alignments determined from them. The latter are the same when the J_{AE} or J_{GF} values are employed. Color code: satisfied pathways are blue, frustrated pathways are red. The $m_s = \pm 5/2$ z-components of spin are shown as up and down black arrows. ((Colour online.))

(frustrate) the preferred spin vector alignments. J_1 and J_4 are both strong relative to J_2 and J_3 , which are intermediate and weak, respectively, so the former two dominate leading to antiparallel alignments both between Fe1 and the Fe3/Fe3A/Fe3B set, and between the latter and the Fe2/Fe2A/Fe2B set. This gives an alternating ‘spin-up, spin-down’ alignment pattern around the outer Fe₆ loop corresponding to $m_s = \pm 5/2$ z-components of spin, and ‘spin-up’ on the central Fe1 (Fig. 4). This situation also satisfies the J_2 interactions, but the resulting parallel

alignments between Fe1 and the Fe2/Fe2A/Fe2B set frustrate J_3 (red dashed lines in Fig. 4, bottom), which is AF but much too weak to compete with J_1 and J_4 . This is the reason that an Ising-like ‘spin-up’/‘spin-down’ alignment corresponding to $m_s = \pm 5/2$ z-components of spin results, rather than any intermediate spin vector alignments. Thus, the total spin of **1** is $S = 20/2 - 15/2 = 5/2$, rationalizing the experimentally observed ground state. Note that the same spin vector alignments and overall $S = 5/2$ are obtained when either the J_{MSC} , J_{AE} , or J_{GF} values for $J_1 - J_4$ are used in this analysis (Fig. S4).

The J_{MSC} and J_{AE} both give good simulations using program PHI [11] of the experimental χ_{MT} vs T data (blue and green lines, respectively, in Fig. 2), but the simulation with J_{GF} was poorer. We then used all the calculated values in turn as inputs for fits of the experimental data and all gave excellent fits with the fit parameters in Table 5; the fit using J_{MSC} is shown in as the solid red line in Fig. 2). The three sets of fit parameters are all satisfyingly comparable, with those from the J_{MSC} and J_{AE} inputs being particularly similar to each other and to the input values they came from. Those from J_{GF} inputs show greater variation from the J_{MSC} and J_{AE} fit values, but we note that J_3 is now a more reasonable -9.0 cm⁻¹. Its stronger -13.2 cm⁻¹ in the calculated J_{GF} , making it comparable with J_2 (-14.8 cm⁻¹), is probably the main reason the simulation using J_{GF} values was poor, since the J_3 would not be completely frustrated in this case. Notwithstanding such small discrepancies between the values, the overall picture that emerges is that the three methods – DFT computations, MSC calculations, and experimental fits – give excellent agreement in the relative magnitude of the J_{ij} as strong (J_1, J_4), intermediate (J_2), and weak (J_3), and thereby rationalizing the experimental ground state of **1** by identifying the resulting spin vector alignments. To support our statement that the J_{MSC} , J_{AE} and J_{GF} are similar, we include in Table 5 the result of control fits of the experimental data using $J_1 - J_4$ input values of 0, -10 , and -20 cm⁻¹. The resulting J_0, J_{-10} , and J_{-20} are extremely different to each other and to the J_{MSC} , J_{AE} and J_{GF} ; the large F couplings are particular unrealistic for high-spin Fe^{III}. This supports the benefits of the synergistic use of MSC and DFT as both an internal check on each other and as a route to reliable approximations of J_{ij} values as inputs for fits of experimental data that will lead to believable J_{ij} fit values.

4. Conclusions

We are finally able to provide a publishable crystal structure of complex **1** to complement the previously published EPR spectral data [10], and we have also taken the opportunity to carry out a three-pronged study of its magnetic properties. The C_3 symmetry of the Fe₇ topology comprising a central octahedral Fe^{III} within a non-planar Fe₆ loop results in this being a 4- J system. The application of the three-pronged analysis has provided a synergistic means to minimize over-parameterization problems in fitting of experimental magnetism data by providing credible J_{ij} values to use as inputs. These have also allowed identification of spin frustration effects in **1**, and thus identification of spin vector alignments that lead to the experimentally-determined $S = 5/2$ ground state. The power of DFT methods coupled with the simplicity of the MSC has proven beneficial and supports the utility of this approach in the analysis of the magnetic properties of other Fe^{III}/O clusters of various metal nuclearities. Such studies are in progress.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2022.116045>.

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