

# Unusual Fe<sub>9</sub> and Fe<sub>18</sub> structural types from the use of 2,6-pyridinedimethanol in Fe<sup>III</sup> cluster chemistry†

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The syntheses, crystal structures and magnetochemical characterization are reported for two new Fe<sup>III</sup> complexes [Fe<sub>18</sub>O<sub>6</sub>(OH)<sub>8</sub>(pdm)<sub>10</sub>(pdmH)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>](ClO<sub>4</sub>)<sub>10</sub> (**3**) and [Fe<sub>9</sub>O<sub>4</sub>(OH)<sub>2</sub>(O<sub>2</sub>CMe)<sub>10</sub>(pdm)-(pdmH)<sub>4</sub>](NO<sub>3</sub>) (**4**). They were synthesized from the use of the potentially O,N,O tridentate chelate, 2,6-pyridinedimethanol (pdmH<sub>2</sub>), in the presence or absence of carboxylate groups. Octadecanuclear complex **3** was obtained during reactivity studies on previously-reported [Fe<sub>8</sub>O<sub>3</sub>(OEt)(pdm)<sub>4</sub>(pdmH)<sub>4</sub>(EtOH)<sub>2</sub>](ClO<sub>4</sub>)<sub>5</sub> (**2**), the latter undergoing hydrolysis to **3** on recrystallization from undried MeCN. The reaction of pdmH<sub>2</sub> with preformed [Fe<sub>3</sub>O(O<sub>2</sub>CMe)<sub>6</sub>(py)<sub>3</sub>](NO<sub>3</sub>) in CH<sub>2</sub>Cl<sub>2</sub> gave enneanuclear complex **4**. Both complexes **3** and **4** are unprecedented structural types. The core of **3** comprises a central [Fe<sub>4</sub>O<sub>6</sub>] defective-dicubane attached on either side to a [Fe<sub>7</sub>O<sub>11</sub>] unit, which can be described as two [Fe<sub>4</sub>(μ<sub>4</sub>-O)] tetrahedra fused at a common Fe atom. The core of **4** can be considered as four vertex-fused triangular [Fe<sub>3</sub>(μ<sub>3</sub>-O)] units. Variable-temperature (*T*) and -field (*H*) solid-state dc and ac magnetization (*M*) studies were carried out on complexes **3** and **4** in the 1.8–300 K range. Analysis of the obtained data revealed that complexes **3** and **4** possess an *S* = 4 and *S* = 5/2 ground state spin, respectively.

## Introduction

The systematic development of iron cluster chemistry over many years has led to a remarkable variety of species that have been of interest from several viewpoints, including structural aesthetics and spectroscopic and physical properties. From a biological viewpoint, the active sites of a variety of proteins such as hemerythrin, methane monooxygenase and ribonucleotide reductase have been shown to contain di-iron cores bridged by oxo or hydroxo ligands.<sup>1</sup> The protein ferritin has also received attention, owing to the biological importance of the role of this protein in the storage and recycling of iron, and a variety of compounds of high metal nuclearity that model the storage of iron in the protein have been synthesized.<sup>2</sup> Another interesting aspect of large polynuclear iron clusters is the potential for these clusters to possess large spin (*S*) values in their ground states due to a relatively large number of unpaired electrons of high-spin Fe<sup>III</sup> ions: the exchange interactions between these Fe<sup>III</sup> ions are normally antiferromagnetic, but with high enough Fe<sub>*x*</sub> nuclearities and appropriate topologies, such compounds can sometimes possess large ground-state spin values as a result of spin frustration effects among the various Fe<sub>2</sub> pairwise exchange pathways,<sup>3–5</sup> and can even occasionally function as single-molecule magnets (SMMs).<sup>6–9</sup> The latter are molecules that display slow magnetization relaxation rates and which, below a certain (blocking) temperature (*T*<sub>B</sub>), can function as single-domain magnetic particles of nanoscale dimensions.

For the above reasons, we have long been interested in the synthesis of polynuclear Fe<sub>*x*</sub> clusters. One approach to their synthesis is the hydrolysis or alcoholysis of either a ferric salt

in the presence of carboxylate groups, or of a preformed small nuclearity Fe<sub>*x*</sub> carboxylate cluster, with or without other potentially chelating/bridging ligands. In line with this methodology, a wide variety of potential ligands have been explored, and a large number of high nuclearity products, with nuclearities up to 168,<sup>10</sup> have been isolated.<sup>11–14</sup> The hydrolysis and alcoholysis reactions of ferric salts with appropriately chosen ligands in the absence of carboxylates are also a common approach to the synthesis of oxide/hydroxide/alkoxide-containing iron complexes, and have yielded various Fe<sub>*x*</sub> clusters, with nuclearities up to 17.<sup>4a,15–17</sup> We have been recently exploring the extension of this non-carboxylate Fe<sup>III</sup> chemistry as a synthetic route to high nuclearity products, with a particular interest in using pyridyl alcohols as potential chelates. Pyridyl alcohols have proven to be extremely versatile chelating and bridging groups that have yielded a number of 3d metal clusters with various structural motifs, large *S* values and SMM behavior.<sup>18–21</sup> In a previous report, we described the synthesis and properties of Fe<sub>4</sub>, Fe<sub>6</sub>, and Fe<sub>8</sub> complexes obtained from the initial employment of the pyridyl-alcohol 2,6-pyridinedimethanol (pdmH<sub>2</sub>) in homometallic Fe<sup>III</sup> chemistry.<sup>22</sup> This initial success and the interesting products obtained encouraged us to extend these studies further, and this we have done in a number of directions, including exploring reactions in the presence of carboxylates. These efforts have led us to even higher nuclearity Fe<sub>9</sub> and Fe<sub>18</sub> products, and ones that have particularly interesting structural features, especially the Fe<sub>18</sub> cluster. In the present report, we describe the syntheses, structures, and magnetochemical properties of these new Fe<sub>9</sub> and Fe<sub>18</sub> clusters obtained from the use of pdmH<sub>2</sub>.

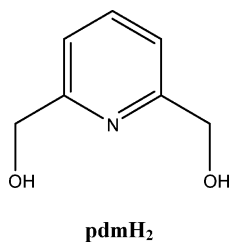
## Experimental

### Syntheses

All manipulations were performed under aerobic conditions using chemicals and solvents as received, unless otherwise

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stated.  $[\text{Fe}_3\text{O}(\text{O}_2\text{CMe})_6(\text{py})_3](\text{NO}_3)$  was prepared as reported elsewhere.<sup>23</sup>

**Safety note:** Perchlorate salts are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with utmost care at all times.

**$[\text{Fe}_8\text{O}_3(\text{OEt})(\text{pdm})_4(\text{pdmH})_4(\text{EtOH})_2](\text{ClO}_4)_5$  (2).** This compound was made by a slight modification to the published procedure for the methoxide analogue  $[\text{Fe}_8\text{O}_3(\text{OMe})(\text{pdm})_4(\text{pdmH})_4(\text{MeOH})_2](\text{ClO}_4)_5$  (1).<sup>22</sup> To a stirred solution of pdmH<sub>2</sub> (0.14 g, 1.0 mmol) and  $\text{NEt}_3$  (0.14 mL, 1.0 mmol) in EtOH (30 mL) was added solid  $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  (0.46 g, 1.0 mmol). The resulting light brown solution was left stirring overnight, during which time a light brown precipitate was obtained. The latter was collected by filtration, washed with copious amount of EtOH and  $\text{Et}_2\text{O}$ , and dried under vacuum; the yield was ~65%. Found: C, 32.74; H, 3.72; N, 4.61. Calc. for **2**·H<sub>2</sub>O: C, 33.12; H, 3.54; N, 4.98%. Selected IR data ( $\text{cm}^{-1}$ ): 3405 (mb), 1607 (m), 1582 (w), 1470 (w), 1438 (w), 1346 (w), 1266 (w), 1218 (w), 1145 (s), 1111(s), 1088 (s), 786 (m), 754 (w), 723 (m), 677 (m), 627 (m), 592 (m), 541 (m), 508 (m), 470 (w), 436 (w).

**$[\text{Fe}_{18}\text{O}_6(\text{OH})_8(\text{pdm})_{10}(\text{pdmH})_4(\text{H}_2\text{O})_4](\text{ClO}_4)_{10}$  (3).** Complex **2**·H<sub>2</sub>O (0.28 g, 0.13 mmol), prepared and dried as described above, was dissolved in MeCN (30 mL). The resulting brown solution was filtered, and the filtrate was carefully layered with  $\text{Et}_2\text{O}$ /hexanes (1 : 1 v/v). After several days, brown crystals had grown and were collected by filtration, washed with cold MeCN (2 × 5 mL) and  $\text{Et}_2\text{O}$  (2 × 5 mL), and dried under vacuum; the yield was ~10%. The dried solid analyzed as solvent-free. Found: C, 27.66; H, 2.79; N, 4.46. Calc. for **3**: C, 27.84; H, 2.81; N, 4.64%. Selected IR data ( $\text{cm}^{-1}$ ): 3420 (mb), 1609 (m), 1582 (w), 1472 (w), 1438 (w), 1361 (w), 1346 (w), 1266 (w), 1216 (w), 1144 (s), 1190 (s), 1041 (s), 786 (w), 721 (m), 677 (m), 627 (m), 550 (m), 520 (m), 474 (m), 419 (m).

**$[\text{Fe}_9\text{O}_4(\text{OH})_2(\text{O}_2\text{CMe})_{10}(\text{pdm})(\text{pdmH})_4](\text{NO}_3)$  (4).** To a stirred solution of pdmH<sub>2</sub> (0.035 g, 0.25 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) was added  $[\text{Fe}_3\text{O}(\text{O}_2\text{CMe})_6(\text{py})_3](\text{NO}_3)$  (0.46 g, 0.25 mmol). The resulting brown solution was stirred for 2 h and filtered, and the filtrate was left to slowly concentrate by evaporation. X-Ray quality crystals of **4** slowly formed over a week. These were collected by filtration, washed with cold  $\text{CH}_2\text{Cl}_2$  and  $\text{Et}_2\text{O}$ , and dried under vacuum; the yield was ~40%. Found: C, 33.40; H, 3.58; N, 4.06. Calc. for **4**·H<sub>2</sub>O: C, 33.69; H, 3.75; N, 4.29%. Selected IR data ( $\text{cm}^{-1}$ ): 3417 (mb), 1584 (s), 1541 (s), 1435 (s), 1385 (s), 1348 (m), 1268 (w), 1236 (w), 1219 (w), 1162 (w), 1114 (m), 1086 (m), 1050 (m), 1021 (m), 981 (w), 790 (w), 713 (m), 657 (s), 617 (m), 534 (m), 503 (m), 448 (m).

**Table 1** Crystallographic data for **3**·7MeCN·3H<sub>2</sub>O and **4**·7CH<sub>2</sub>Cl<sub>2</sub>

Parameter	<b>3</b>	<b>4</b>
Formula <sup>a</sup>	$\text{C}_{112}\text{H}_{145}\text{Cl}_{10}\text{Fe}_{18}\text{N}_{21}\text{O}_{89}$	$\text{C}_{62}\text{H}_{79}\text{Cl}_{14}\text{Fe}_9\text{N}_6\text{O}_{39}$
Fw, g mol <sup>-1</sup>	4569.29	2531.26
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C_2$
$a/\text{\AA}$	26.3129(17)	25.150(2)
$b/\text{\AA}$	13.9984(9)	15.3942(13)
$c/\text{\AA}$	27.3080(18)	14.1502(12)
$\alpha/^\circ$	90	90
$\beta/^\circ$	116.9220(10)	115.8900(10)
$\gamma/^\circ$	90	90
$V/\text{\AA}^3$	8968.5(10)	4928.7(7)
Z	2	2
T/K	173(2)	173(2)
Radiation/ $\text{\AA}^b$	0.71073	0.71073
$\rho_c/\text{g cm}^{-3}$	1.692	1.706
$\mu/\text{mm}^{-1}$	1.657	1.747
$R_1^{c,d}$	0.0850	0.0422
$wR_2^e$	0.2196	0.1161

<sup>a</sup> Including solvate molecules. <sup>b</sup> Graphite monochromator. <sup>c</sup>  $I > 2\sigma(I)$ . <sup>d</sup>  $R_1 = \sum(|F_o| - |F_c|)/\sum F_o$ . <sup>e</sup>  $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ ,  $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$ , where  $p = [\max(F_o^2, 0) + 2F_c^2]/3$ .

### X-Ray crystallography†

Data were collected on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Suitable crystals of **3**·7MeCN·3H<sub>2</sub>O and **4**·7CH<sub>2</sub>Cl<sub>2</sub> were attached to glass fibres using silicone grease and transferred to a goniostat where they were cooled to 173 K for data collection. An initial search of reciprocal space revealed a monoclinic cell for both compounds, and the choices of space groups  $P2_1/n$  and  $C_2$  were confirmed by the subsequent solution and refinement of their structures. Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the  $\omega$ -scan method (0.3° frame width). 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 structures were solved by direct methods in *SHELXTL6*,<sup>24</sup> and refined on  $F^2$  using full-matrix least-squares. The non-H atoms were treated anisotropically, whereas the H atoms were placed in calculated, ideal positions and refined as riding on their respective C atoms. Unit cell parameters and structure solution and refinement data are listed in Table 1.

For **3**·7MeCN·3H<sub>2</sub>O, the asymmetric unit consists of half a Fe<sub>18</sub> cluster located on an inversion centre, five  $\text{ClO}_4^-$  anions,  $3\frac{1}{2}$  MeCN solvent molecules and  $1\frac{1}{2}$  water molecules; three half MeCN molecules are disordered against  $\text{ClO}_4^-$  anions. Two  $\text{ClO}_4^-$  anions are fully disordered and each was refined in two parts. The third had only its O atoms disordered and also was refined in two parts. All hydroxyl and water protons were obtained from a difference Fourier map and refined as riding on their parent atoms. A total of 1100 parameters were included in the final cycle of refinement using 8269 reflections with  $I > 2\sigma(I)$  to yield  $R_1$  and  $wR_2$  of 8.50 and 21.96%, respectively.

For **4**·7CH<sub>2</sub>Cl<sub>2</sub>, the asymmetric unit consists of a half Fe<sub>9</sub> cluster cation, a  $\frac{1}{2}$   $\text{NO}_3^-$  anion, and  $3\frac{1}{2}$  CH<sub>2</sub>Cl<sub>2</sub> solvent molecules; all half fragments are located on two-fold rotation axes. The  $\text{NO}_3^-$ , the  $\frac{1}{2}$

CH<sub>2</sub>Cl<sub>2</sub>, and one CH<sub>2</sub>Cl<sub>2</sub> in a general position are all disordered and each was refined in two parts. A total of 628 parameters were included in the final cycle of refinement using 10 062 reflections with  $I > 2\sigma(I)$  to yield  $R_1$  and  $wR_2$  of 4.22 and 11.61%, respectively.

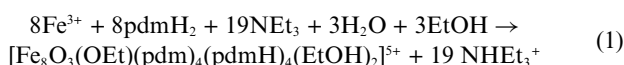
### Physical studies

Infrared spectra were recorded in the solid state (KBr pellets) on a Nicolet Nexus 670 FTIR spectrometer in the 400–4000 cm<sup>-1</sup> range. Elemental analyses (C, H, and N) were performed by the in-house facilities of the University of Florida Chemistry Department. Variable-temperature dc and ac magnetic susceptibility data were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 tesla magnet and 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.<sup>25</sup> Pascal's constants were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibilities to give the molar paramagnetic susceptibilities ( $c_M$ ). A correction for the sample holder (plus eicosane) was obtained experimentally in the absence of sample.

## Results and discussion

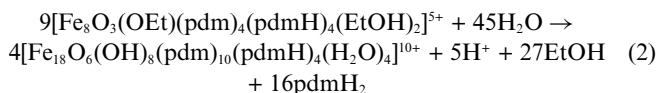
### Syntheses

The previous use of pdmH<sub>2</sub> in non-carboxylate Fe<sup>III</sup> chemistry involved the reaction of Fe(ClO<sub>4</sub>)<sub>3</sub> and pdmH<sub>2</sub> in MeOH and led to isolation of [Fe<sub>8</sub>O<sub>3</sub>(OMe)(pdm)<sub>4</sub>(pdmH)<sub>4</sub>(MeOH)<sub>2</sub>](ClO<sub>4</sub>)<sub>5</sub> (**1**).<sup>22</sup> This possesses a prototypical [Fe<sub>8</sub>(μ<sub>4</sub>-O)(μ<sub>3</sub>-O)<sub>2</sub>]<sup>18+</sup> core consisting of the fusion of a central [Fe<sub>4</sub>(μ<sub>4</sub>-O)]<sup>10+</sup> oxide-centred tetrahedron with two triangular, oxide-centred [Fe<sub>3</sub>(μ<sub>3</sub>-O)]<sup>7+</sup> units. In the present work, we investigated the corresponding reaction in EtOH and obtained a light brown precipitate whose IR spectral similarities with **1** and elemental analysis data established that the product was the analogous [Fe<sub>8</sub>O<sub>3</sub>(OEt)(pdm)<sub>4</sub>(pdmH)<sub>4</sub>(EtOH)<sub>2</sub>](ClO<sub>4</sub>)<sub>5</sub> (**2**), and a crystal structure was not pursued. The formation of the cation is summarized in eqn (1).

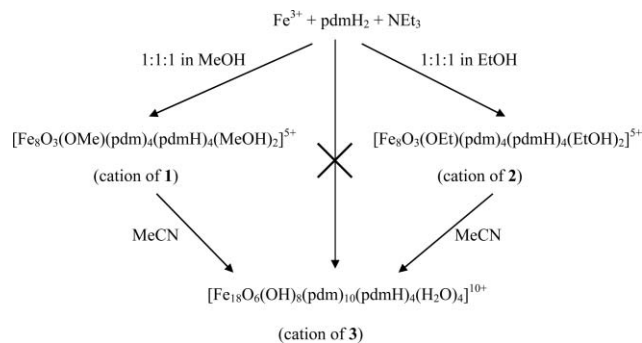


We have carried out a variety of investigations of the reaction that leads to **1** and **2**. When the reaction mixtures were heated to reflux, light brown precipitates were formed in both MeOH and EtOH. Infrared spectra and elemental analysis data indicated the solids to contain pdmH<sup>-</sup> and/or pdm<sup>2-</sup> groups and to be different from **1** or **2**. We have not been able to characterize these products further, but believe their insolubility is indicating a polymeric structure. When the reaction medium was changed to MeCN, MeCN–alcohol or MeCN–water (without reflux), we were unable to isolate any pure, crystalline products. We therefore turned to exploring the reactivity properties of preformed **1** and **2**, and found them to be very sensitive to hydrolysis, which is consistent with their bridging alkoxide groups. Thus, dissolution of complex **2** in MeCN and layering with Et<sub>2</sub>O/hexanes gave well-formed brown crystals of [Fe<sub>18</sub>O<sub>6</sub>(OH)<sub>8</sub>(pdm)<sub>10</sub>(pdmH)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>](ClO<sub>4</sub>)<sub>10</sub> (**3**) in low (10%) yield. This is clearly a complicated hydrolysis and rearrangement reaction caused by the small amount of water in the MeCN; deliberate addition of more water did not give **3**, perhaps due to further hydrolysis. Nor, as implied above, did we

obtain **3** directly by carrying out the preparative reaction for **2** in MeCN, MeCN–alcohol or MeCN–water. We thus settled for the low but reproducible yield of **3** obtained from preformed **2**. The overall transformation is summarized in eqn (2).

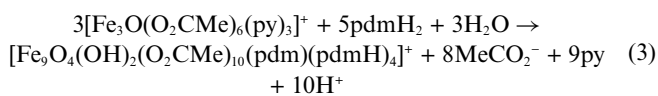


Complex **1** in MeCN was found to undergo the same transformation to **3**, as confirmed by IR spectral comparisons. The above reactions are summarized in the Scheme 1. Other solvents were also explored for the transformation of preformed **2**, and acetone was found to give complex **3** in comparable yield.



**Scheme 1** The reactions described in the text.

In earlier studies of the reactions of Fe<sup>III</sup> sources with related 2-hydroxymethylpyridine (hmpH),<sup>22,26</sup> the presence or absence of carboxylate groups had a profound effect on the product identity, giving structurally very different [Fe<sub>6</sub>O<sub>2</sub>(O<sub>2</sub>CBu')<sub>6</sub>(hmp)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub> and [Fe<sub>6</sub>O<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(hmp)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> products, for example, from the reaction in MeCN of hmpH with [Fe<sub>3</sub>O(O<sub>2</sub>CBu')<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](NO<sub>3</sub>) or simple Fe<sup>III</sup> nitrate, respectively. We thus investigated this point in the present Fe<sup>III</sup>/pdmH<sub>2</sub> chemistry. Indeed, after investigating several reaction conditions and solvents, we found that the reaction of pdmH<sub>2</sub> with [Fe<sub>3</sub>O(O<sub>2</sub>CMe)<sub>6</sub>(py)<sub>3</sub>](NO<sub>3</sub>) in CH<sub>2</sub>Cl<sub>2</sub> gave the enneanuclear Fe<sup>III</sup> cluster [Fe<sub>9</sub>O<sub>4</sub>(OH)<sub>2</sub>(O<sub>2</sub>CMe)<sub>10</sub>(pdm)(pdmH)<sub>4</sub>](NO<sub>3</sub>) (**4**). Complex **4** was the only isolable product, in lower or comparable yield, from a number of reactions in which we varied the solvent, the Fe<sup>III</sup> starting material, and the reagent ratio. The formation of the cation of **4** is summarized in eqn (3).



Finally, since **3** and **4** both contain bridging hydroxide ions, we explored the analogous reactions also containing azide to see if azide groups might be incorporated in their place, as seen by Perlepes<sup>27</sup> and coworkers for some Fe, Ni and Co clusters where bridging hydroxide groups could be replaced with end-on bridging azide. However, under our conditions, the only isolable products were again **3** and **4**.

### Description of structures

The structure and a stereoview of [Fe<sub>18</sub>O<sub>6</sub>(OH)<sub>8</sub>(pdm)<sub>10</sub>(pdmH)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>](ClO<sub>4</sub>)<sub>10</sub> (**3**) are presented in Fig. 1, together with its labelled core. Selected interatomic distances and angles are

**Table 2** Selected interatomic distances (Å) for complex **3**

Fe1–O3	1.921(7)	Fe5–N4	2.066(10)
Fe1–O10	1.994(7)	Fe5–O10	2.093(6)
Fe1–O13	2.000(7)	Fe6–O2	1.932(7)
Fe1–O17'	2.022(6)	Fe6–O19	1.960(7)
Fe1–O23	2.045(6)	Fe6–O11	1.967(7)
Fe1–O23'	2.117(6)	Fe6–O20	1.986(7)
Fe2–O3	1.906(6)	Fe6–O21	2.104(8)
Fe2–O6	1.947(6)	Fe6–O22	2.147(7)
Fe2–O12	1.994(7)	Fe7–O5	1.969(6)
Fe2–O1	2.073(6)	Fe7–O15	1.975(6)
Fe2–N5	2.074(10)	Fe7–O8	1.981(6)
Fe2–O13	2.130(6)	Fe7–O2	1.981(7)
Fe3–O3	1.857(6)	Fe7–N6	2.131(9)
Fe3–O4	1.987(7)	Fe7–O14	2.162(7)
Fe3–O16	1.998(7)	Fe8–O18	1.937(7)
Fe3–O17	2.068(6)	Fe8–O15	1.979(7)
Fe3–N7	2.072(8)	Fe8–O6	2.060(7)
Fe3–O23'	2.162(6)	Fe8–O7	2.126(6)
Fe4–O19	1.970(7)	Fe8–O2	2.170(6)
Fe4–O1	1.981(7)	Fe8–N2	2.175(8)
Fe4–O12	2.034(7)	Fe8–O1	2.254(6)
Fe4–O4	2.069(6)	Fe9–O7	1.908(6)
Fe4–O5	2.086(6)	Fe9–O20	1.918(7)
Fe4–N1	2.100(9)	Fe9–O8	1.985(8)
Fe5–O1	1.965(7)	Fe9–N3	2.111(8)
Fe5–O16	2.004(6)	Fe9–O2	2.169(6)
Fe5–O18	2.013(6)	Fe9–O9	2.177(8)
Fe5–O11	2.054(7)		

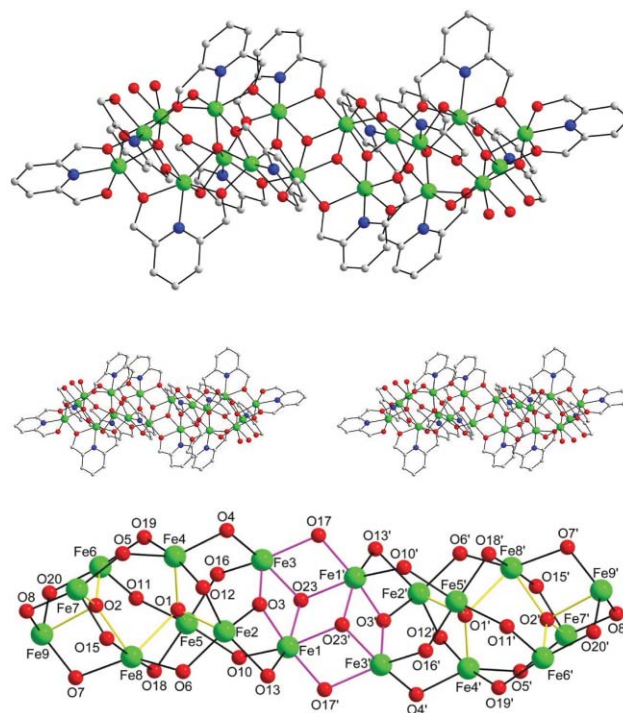
**Table 3** Bond valence sums for selected O atoms in complex **3**<sup>a</sup>

Atom	BVS	Assgt	Atom	BVS	Assgt
O1	1.79	O <sup>2-</sup>	O20	1.19	OH <sup>-</sup>
O2	1.82	O <sup>2-</sup>	O21	0.39	H <sub>2</sub> O
O3	2.11	O <sup>2-</sup>	O22	0.34	H <sub>2</sub> O
O18	1.11	OH <sup>-</sup>	O23	1.16	OH <sup>-</sup>
O19	1.14	OH <sup>-</sup>			

<sup>a</sup> The oxygen atom is an O<sup>2-</sup> if the BVS is ~1.8–2.0, an OH<sup>-</sup> if the BVS is ~1.0–1.2, and a H<sub>2</sub>O if the BVS is ~0.2–0.4.

listed in Table 2. Complex **3** possesses a centrosymmetric [Fe<sub>18</sub>(μ<sub>4</sub>-O)<sub>4</sub>(μ<sub>3</sub>-O)<sub>2</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(μ-OH)<sub>6</sub>(μ-OR)<sub>24</sub>] core containing four μ<sub>4</sub>-O<sup>2-</sup> (O1, O2), two μ<sub>3</sub>-O<sup>2-</sup> (O3), two μ<sub>3</sub>-OH<sup>-</sup> (O23) and six μ-OH<sup>-</sup> (O18, O19, O20) ions, whose protonation levels were confirmed by bond-valence-sum (BVS) calculations (Table 3). The Fe atoms are additionally bridged by the alkoxide arms of ten pdm<sup>2-</sup> and four pdmH<sup>-</sup> groups. The pdm<sup>2-</sup> groups are doubly-deprotonated and tridentate-chelating to an Fe atom, with each of their alkoxide arms also bridging to adjacent Fe atoms; these groups are thus η<sup>1</sup>:η<sup>3</sup>:η<sup>1</sup>:μ<sub>3</sub>. The pdmH<sup>-</sup> groups are singly-deprotonated and again tridentate-chelating to an Fe atom, but only the deprotonated alkoxide arm bridges to an adjacent Fe atom; these groups are thus η<sup>1</sup>:η<sup>3</sup>:μ. The ligation is completed by four terminal H<sub>2</sub>O groups (O21, O22; and their symmetry partners) on Fe6 and Fe6'. All Fe atoms are six-coordinate with distorted octahedral geometries except for Fe8 and Fe8' which are seven-coordinate with distorted pentagonal bipyramidal geometry. The Fe–N and Fe–O bond lengths are as expected for high-spin Fe<sup>III</sup>.<sup>28</sup>

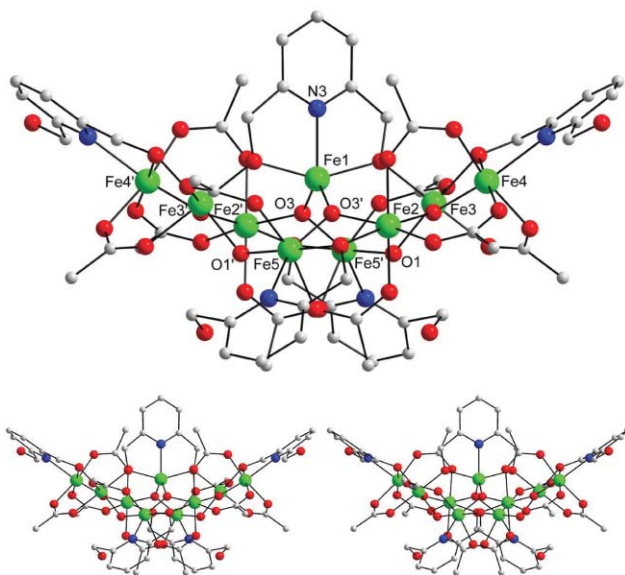
The core of **3** can be described as a central [Fe<sub>6</sub>O<sub>6</sub>] defective dicubane-like subunit (Fe1, Fe3, Fe1' and Fe3') which contains μ<sub>3</sub>-OH<sup>-</sup> (O23 and O23'), μ<sub>3</sub>-O<sup>2-</sup> (O3 and O3') and μ-alkoxide arms of μ<sub>3</sub>-pdm<sup>2-</sup> (O17 and O17') (Fig. 1, bottom). On both sides of the central unit, the μ<sub>3</sub>-O<sup>2-</sup> is linked to [Fe<sub>7</sub>O<sub>11</sub>] units, which can



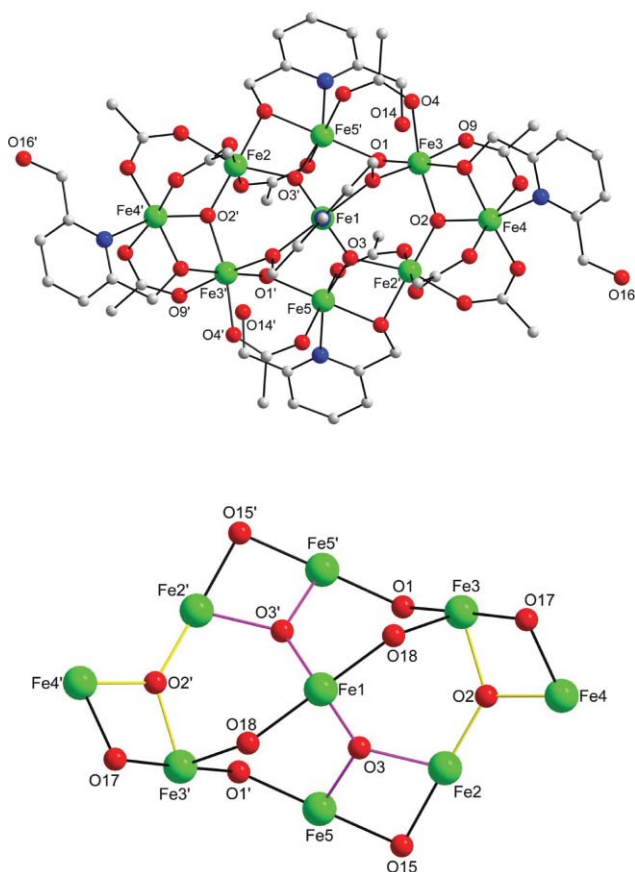
**Fig. 1** The structure of **3** (top), a stereopair (middle), and the labelled core. H atoms have been omitted for clarity. Colour code: Fe<sup>III</sup> green; O red; N blue; C grey.

be described as two [Fe<sub>4</sub>(μ<sub>4</sub>-O)] tetrahedra (O1, Fe2, Fe4, Fe5, Fe8, and O2, Fe6, Fe7, Fe8, Fe9) fused at Fe8. The Fe–μ<sub>4</sub>-O<sup>2-</sup>–Fe angles within these tetrahedra range from 96.1 to 132.8°, deviating significantly from the 109.5° ideal values of a tetrahedron. The two [Fe<sub>3</sub>(μ<sub>3</sub>-O)] triangular units (Fe1, Fe2, Fe3) are essentially isosceles (Fe1...Fe2 = 3.066 Å, Fe1...Fe3 = 2.996 Å, Fe2...Fe3 = 3.555 Å), the long separation corresponding to the one not bridged by a pdm<sup>2-</sup> or OH<sup>-</sup> group. This is also reflected in the geometry at the μ<sub>3</sub>-O<sup>2-</sup> ions, O3, which have Y-shaped geometry (largest Fe–O–Fe angle of 141.7) rather than trigonal planar as usually seen in triangular metal carboxylates;<sup>29</sup> O3 is also 0.272 Å above its Fe<sub>3</sub> plane. Complex **3** joins a small family of only three previous Fe<sub>18</sub> clusters, two of which are molecular wheel complexes and one a ‘molecular chain’, *i.e.* with a discrete, serpentine-like extended structure.<sup>30</sup> Complex **3** is also the highest nuclearity non-carboxylate Fe<sup>III</sup> cluster discovered to date.

The structure and a stereoview of the cation of [Fe<sub>9</sub>O<sub>4</sub>(OH)<sub>2</sub>(O<sub>2</sub>CMe)<sub>10</sub>(pdm)(pdmH)<sub>4</sub>(NO<sub>3</sub>) (**4**) viewed along the *a*-axis are presented in Fig. 2. A labelled view along the *b*-axis and its core are shown in Fig. 3. Selected interatomic distances and angles are listed in Table 4. Complex **4** has imposed C<sub>2</sub> symmetry and contains a [Fe<sub>9</sub>(μ<sub>3</sub>-O)<sub>4</sub>(μ-OH)<sub>2</sub>(μ-OR)<sub>6</sub>] core held together by four μ<sub>3</sub>-O<sup>2-</sup> (O2, O3, O2', O3') and two μ-OH<sup>-</sup> (O1 and O1') ions, as confirmed by BVS calculations (Table 5). The Fe atoms are additionally bridged by the alkoxide arms of one pdm<sup>2-</sup> and four pdmH<sup>-</sup> groups, as well as ten acetates in the common η<sup>1</sup>:η<sup>1</sup>:μ bridging mode. The unbound pdmH<sup>-</sup> alcohol oxygen atoms (O14) are statically disordered between (a) forming a H-bond to the nearby hydroxide (O1) (O14...O1 = 2.708(7) Å) and the unbound pdmH<sup>-</sup> alcohol oxygen atoms of the neighbouring molecules (O16) (O14...O16 = 2.702(7) Å) or (b) forming a H-bond to the nearby



**Fig. 2** The structure of **4** (top), and a stereopair (bottom), viewed along the *a*-axis. H atoms have been omitted for clarity. Colour code: Fe<sup>III</sup> green; O red; N blue; C grey.



**Fig. 3** The structure of complex **4** (top), and its labelled core (bottom), viewed along the *b*-axis. H atoms have been omitted for clarity. Colour code: Fe<sup>III</sup> green; O red; N blue; C grey.

carboxylate oxygen atoms (O4 and O9) ( $O14 \cdots O4 = 2.829(12) \text{ \AA}$ ,  $O14 \cdots O9 = 2.857(16) \text{ \AA}$ ) and the unbound pdmH<sup>-</sup> alcohol oxygen atoms of the neighbouring molecules (O14). The core can

**Table 4** Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **4**

Fe1–O3'	1.844(3)	Fe3–O4	2.041(3)
Fe1–O3	1.844(2)	Fe3–O9	2.077(3)
Fe1–O18'	2.051(3)	Fe4–O2	1.890(2)
Fe1–O18	2.051(3)	Fe4–O10	1.989(3)
Fe1–N3	2.084(5)	Fe4–O17	1.996(3)
Fe2–O2	1.866(3)	Fe4–O13	2.026(4)
Fe2–O3'	1.960(3)	Fe4–O8	2.053(3)
Fe2–O15'	2.034(3)	Fe4–N2	2.208(3)
Fe2–O11	2.065(3)	Fe5–O3	1.935(3)
Fe2–O6	2.074(3)	Fe5–O1	1.948(3)
Fe2–O12	2.086(3)	Fe5–O15	1.982(3)
Fe3–O2	1.942(3)	Fe5–O5	2.029(3)
Fe3–O1	1.962(3)	Fe5–O7'	2.051(3)
Fe3–O18	2.008(3)	Fe5–N1	2.253(3)
Fe3–O17	2.028(3)	Fe5–Fe2'	2.9796(7)
Fe5–O1–Fe3	125.13(14)	Fe1–O3–Fe2'	134.41(14)
Fe2–O2–Fe4	121.95(14)	Fe5–O3–Fe2'	99.79(11)
Fe2–O2–Fe3	134.18(13)	Fe5–O15–Fe2'	95.76(11)
Fe4–O2–Fe3	100.19(12)	Fe4–O17–Fe3	93.84(11)
Fe1–O3–Fe5	125.80(13)	Fe3–O18–Fe1	124.44(13)

**Table 5** Bond valence sums for selected O atoms in complex **4**<sup>a</sup>

Atom	BVS	Assgt
O1	1.17	OH <sup>-</sup>
O2	2.08	O <sup>2-</sup>
O3	2.02	O <sup>2-</sup>

<sup>a</sup> See the footnote for Table 3.

be described as an array of four vertex-fused [Fe<sub>3</sub>O] triangular units. Two of these (Fe1–Fe2–Fe5, and its symmetry partner) are scalene ( $Fe1 \cdots Fe2 = 3.507(1) \text{ \AA}$ ,  $Fe1 \cdots Fe5 = 3.364(1) \text{ \AA}$ , and  $Fe2 \cdots Fe5 = 2.980(1) \text{ \AA}$ ), and their central O<sup>2-</sup> atoms (O3, O3') are essentially (0.004  $\text{\AA}$ ) in the Fe<sub>3</sub> plane. The other two triangular units (Fe2–Fe3–Fe4, and their symmetry partner) are also scalene ( $Fe2 \cdots Fe3 = 3.508(1) \text{ \AA}$ ,  $Fe2 \cdots Fe4 = 3.284(1) \text{ \AA}$ ,  $Fe3 \cdots Fe4 = 2.939(1) \text{ \AA}$ ), but with their O<sup>2-</sup> atoms distinctly out (0.206  $\text{\AA}$ ) of their Fe<sub>3</sub> plane. In each case, the shortest Fe  $\cdots$  Fe separation is the bridged by both a  $\mu_3$ -O<sup>2-</sup> and a deprotonated pdmH<sup>-</sup> alkoxide arm. All Fe atoms are six-coordinate with octahedral geometry except for the one Fe atom in the centre (Fe1), which is five-coordinate with distorted trigonal bipyramidal geometry, pdm<sup>2-</sup> O atoms O18 and O18' occupying the axial positions. The Fe–N and Fe–O bond lengths in complex **4** are as expected for high-spin Fe<sup>III</sup>.<sup>28</sup> There are several Fe<sub>n</sub> clusters known in the literature,<sup>4a,4b,13a,31,32</sup> but none of them have the same Fe<sub>n</sub> topology as **4**.

## Magnetochemistry

**Magnetic susceptibility studies on complex 3.** Variable-temperature magnetic susceptibility measurements were performed on powdered polycrystalline samples of **3**, restrained in eicosane to prevent torquing, in a 1 kOe (0.1 T) field and in the 5.0–300 K range. The  $\chi_M T$  decreases with decreasing temperature from 26.10 cm<sup>3</sup> K mol<sup>-1</sup> at 300 K to a minimum of 8.46 cm<sup>3</sup> K mol<sup>-1</sup> at 25 K and then increases slightly to 9.05 cm<sup>3</sup> K mol<sup>-1</sup> at 5.0 K (Fig. 4). The 300 K value is much less than the spin-only ( $g = 2$ ) value of 78.75 cm<sup>3</sup> K mol<sup>-1</sup> for eighteen non-interacting Fe<sup>III</sup> ions, indicating dominant antiferromagnetic exchange interactions, as expected for oxo-bridged Fe<sup>III</sup> systems. The 5.0 K value is close to

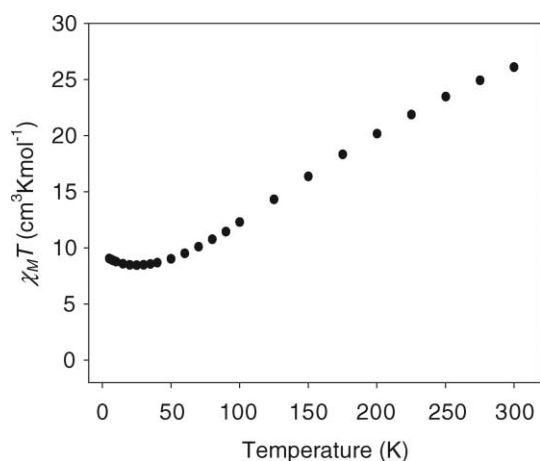


Fig. 4 Plot of  $\chi_M T$  vs.  $T$  for **3**.

the spin-only ( $g = 2.0$ ) value of a complex with an  $S = 4$  ground state ( $10.00 \text{ cm}^3 \text{ K mol}^{-1}$ ).

To confirm the indicated  $S = 4$  ground state, and to estimate the magnitude of the axial zero-field splitting (ZFS) parameter  $D$ , magnetization vs. dc field ( $H$ ) data were collected on restrained samples at applied magnetic fields and temperatures in the 0.1–7 T and 1.8–10.0 K ranges, respectively. The obtained magnetization ( $M$ ) data are plotted as reduced magnetization ( $M/N\mu_B$ ) vs.  $H/T$  in Fig. 5, where  $N$  is Avogadro's number and  $\mu_B$  is the Bohr magneton. They were fit using the program MAGNET<sup>25</sup> to a model that assumes only the ground state is populated at these temperatures and magnetic fields, includes axial zero-field splitting ( $DS_z^2$ ) and the Zeeman interaction, and incorporates a full powder average. The corresponding spin Hamiltonian is given by eqn (4), where  $\hat{S}_z$  is the easy-axis spin operator,  $g$  is the Landé  $g$  factor, and  $\mu_0$  is the vacuum permeability.

$$H = DS_z^2 + g\mu_B\mu_0\hat{S}\cdot H \quad (4)$$

Only data collected at fields up to 3 T were employed in the final fit, because satisfactory fits could not be obtained using data collected at higher fields. Such problems are typical for high nuclearity complexes that have low-lying excited states with  $S$  greater than that of the ground state and whose  $M_S$  levels thus approach those

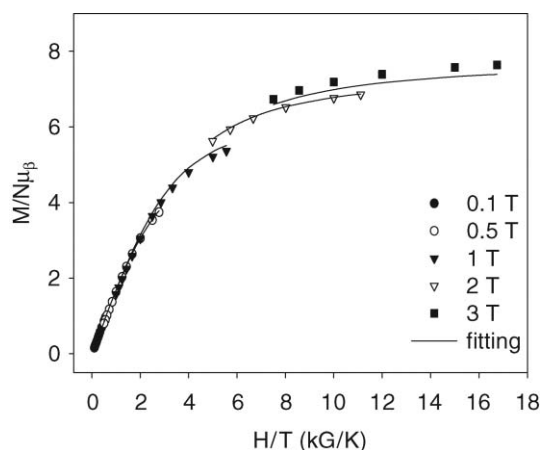


Fig. 5 Reduced magnetization ( $M/N\mu_B$ ) vs.  $H/T$  plot for **3**. The solid lines are the fit of the data; see the text for the fit parameters.

of the ground state with increasing applied fields. The resulting best fit is shown as the solid lines in Fig. 5 and was obtained with  $S = 4$ ,  $g = 1.97$ , and  $D = -0.25 \text{ cm}^{-1}$ . Alternative fits with  $S = 3$  or 5 were rejected because they gave unreasonable values of  $g$ . In order to examine the obtained fit quality, we calculated the root-mean-square  $D$  vs.  $g$  error surface using the program GRID,<sup>33</sup> which calculates the relative difference between the experimental  $M/N\mu_B$  data and those calculated for various combinations of  $D$  and  $g$ . The obtained error surface, plotted as a 2-D contour plot in Fig. 6, in fact exhibits two minima, one with positive  $D$  and the other with a negative one, as is typically found in such fits, which are not very sensitive to the sign of  $D$ . Nevertheless, the fit with  $D < 0$  clearly has the smaller relative error, suggesting the true sign of  $D$  is negative. Examination of the stretched nature of the contour lines around the best-fit, indicating to a somewhat soft minimum, allows the reliability in the fit parameters to be estimated as  $S = 4$ ,  $g = 1.97(1)$ , and  $D = -0.25(3) \text{ cm}^{-1}$ .

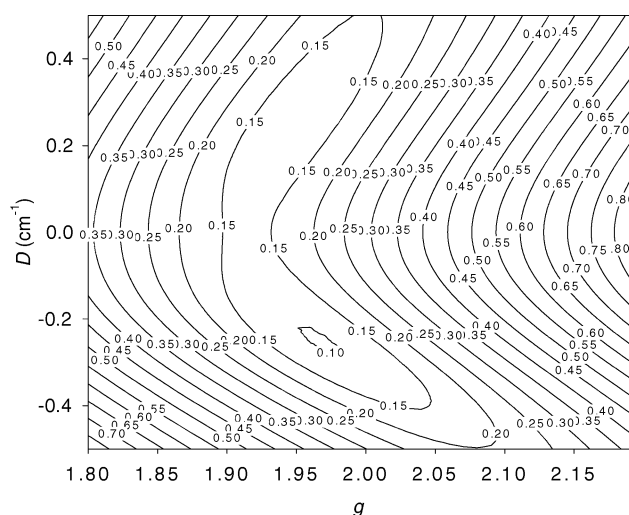


Fig. 6 Two-dimensional contour plot of the root-mean-square error surface for the  $D$  vs.  $g$  fit for **3**.

As we have described before,<sup>34</sup> ac susceptibility studies are a powerful complement to dc studies for determining the ground state of a system, because they preclude any complications arising from the presence of a dc field. In an ac experiment, a weak magnetic field (typically in the 1–5 Oe range) oscillating at some ac frequency is applied to a sample to investigate its magnetization relaxation dynamics. The ac data for complex **3** were collected in the 1.8–15 K range in a zero dc field and a 3.5 Oe ac field oscillating at frequencies in the 50–1000 Hz range. The in-phase ac susceptibility, plotted as  $\chi_M' T$  vs.  $T$ , is shown in Fig. 7. The  $\chi_M' T$  of **3** is  $8.86 \text{ cm}^3 \text{ K mol}^{-1}$  at 15 K, increases steadily to a plateau of  $\sim 10.0 \text{ cm}^3 \text{ K mol}^{-1}$  below 2.2 K as excited states are depopulated, and the plateau value is as expected for a  $S = 4$  ground state with  $g = 2.0$ . Complex **3** is thus confirmed to possess an  $S = 4$  ground state. There were no out-of phase ac signals down to 1.8 K, the operating limit of our SQUID magnetometer.

**Magnetic susceptibility studies on complex 4.** Data were collected on powdered polycrystalline samples of **4**· $\text{H}_2\text{O}$  under the same conditions as for **3**. The  $\chi_M T$  steadily decreases with decreasing temperature from  $12.06 \text{ cm}^3 \text{ K mol}^{-1}$  at 300 K to  $4.17 \text{ cm}^3 \text{ K mol}^{-1}$  at 5.0 K (Fig. 8). The 300 K value is again

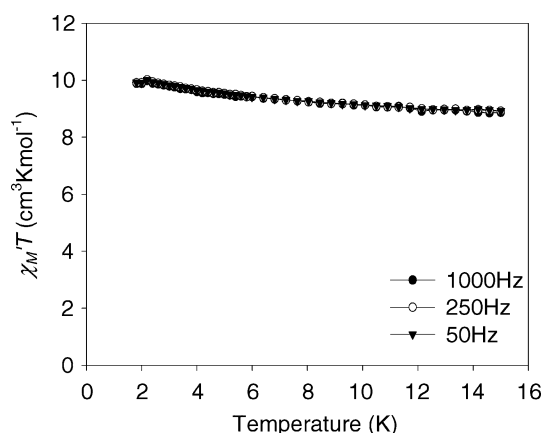


Fig. 7 In-phase ac susceptibility ( $\chi_M'$ , plotted as  $\chi_M' T$  vs.  $T$ ) of **3** in a 3.5 Oe ac field oscillating at the indicated frequencies.

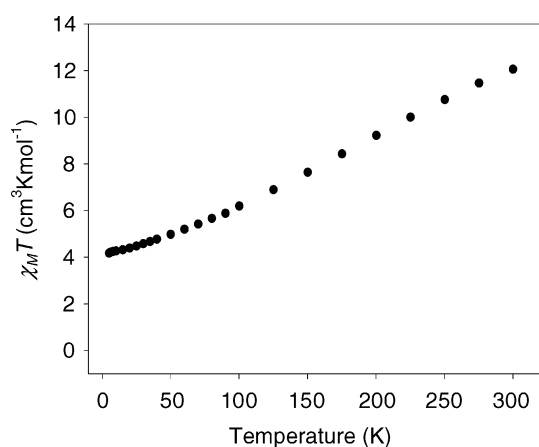


Fig. 8 Plot of  $\chi_M T$  vs.  $T$  for **4**.

less than the spin-only value of  $39.38 \text{ cm}^3 \text{ K mol}^{-1}$  for nine non-interacting  $\text{Fe}^{\text{III}}$  ions, indicating dominant antiferromagnetic interactions. The 5.0 K value is close to the spin-only ( $g = 2$ ) value of a complex with a  $S = 5/2$  ground state ( $4.38 \text{ cm}^3 \text{ K mol}^{-1}$ ). In order to investigate this further, and to estimate the magnitude of  $D$ , magnetization vs. dc field data were collected on restrained samples at applied magnetic fields and temperatures in the 0.1–7 T and 1.8–10.0 K ranges, respectively. The obtained  $M/N\mu_B$  vs.  $H/T$  plot is shown in Fig. 9, and we were able to obtain an excellent fit with the program MAGNET using all the data collected up to 7 tesla, suggesting that the ground state of **4** is relatively well isolated from the nearest excited states. The best fit is shown as the solid lines in Fig. 9 and was obtained with  $S = 5/2$  and either  $g = 1.96$  and  $D = 0.89 \text{ cm}^{-1}$ , or  $g = 1.94$  and  $D = -0.64 \text{ cm}^{-1}$ . The error surface for the fit (Fig. 10) again exhibits two minima, both of which are much softer (more poorly defined) than those for **3**: one has fit parameters of  $S = 5/2$ ,  $g = 1.94(1)$  and  $D = -0.64(8) \text{ cm}^{-1}$ , and another with positive  $D$  and fit parameters  $S = 5/2$ ,  $g = 1.96(2)$  and  $D = +0.89(18) \text{ cm}^{-1}$ . However, unlike for **3**, the two fits for **4** are essentially of equal quality, and it would thus require more sensitive techniques such as EPR spectroscopy or magnetization measurements on oriented single-crystals to confirm the sign of  $D$ .

Ac magnetic susceptibility studies were performed on **4** in the 1.8–15 K range using a 3.5 Oe ac field oscillating at frequencies

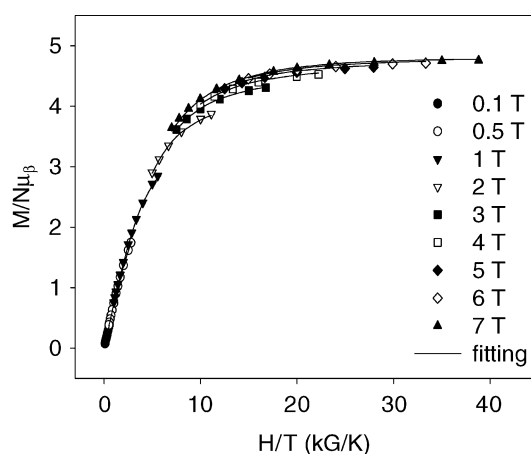


Fig. 9 Reduced magnetization ( $M/N\mu_B$ ) vs.  $H/T$  plot for **4**. The solid lines are the fit of the data; see the text for the fit parameters.

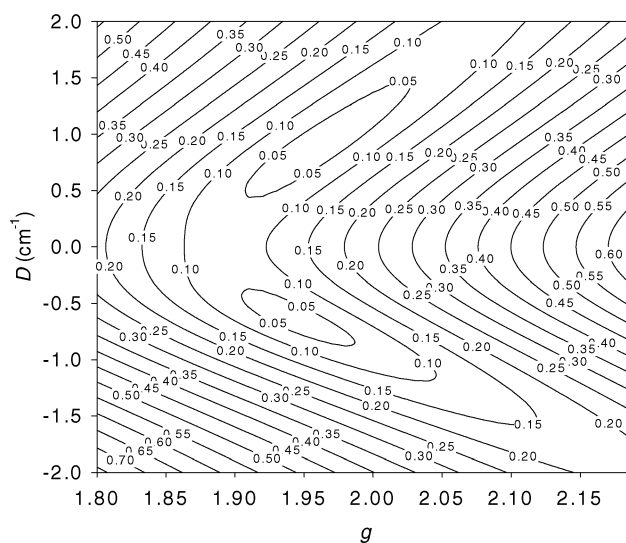


Fig. 10 Two-dimensional contour plot of the root-mean-square error surface for the  $D$  vs.  $g$  fit for **4**.

in the 50–1000 Hz range. The in-phase  $\chi_M' T$  vs.  $T$  plot is shown in Fig. 11, and it is essentially temperature-independent at  $\sim 4.4 \text{ cm}^3 \text{ K mol}^{-1}$ , except for a tiny decrease at the lowest temperatures assignable to very weak intermolecular interactions. The  $\chi_M' T$  vs.  $T$  plot thus supports the conclusion from the dc magnetization fit of a well isolated ground state for  $S = 4$ . The value of  $\sim 4.4 \text{ cm}^3 \text{ K mol}^{-1}$  is as expected for an  $S = 5/2$  ground state with  $g \sim 2$ ;  $S = 3/2$  and  $7/2$  would give  $\chi_M' T = 2.63$  and  $7.88 \text{ cm}^3 \text{ K mol}^{-1}$ , respectively.

**Rationalization of the  $S = 5/2$  ground state of complex **4**.** It is of interest to try to rationalize the observed  $S = 4$  and  $5/2$  ground states of **3** and **4**, respectively. However, the high nuclearity and low symmetry of **3** make it impossible for this compound. An  $S = 4$  ground state cannot result from simple spin-up/spin-down alignment of spins, and it is clear that many intermediate spin alignments must be present as a result of extensive spin frustration effects present in the many  $\text{Fe}_3$  triangular sub-units in the core.

The smaller size and  $C_2$  symmetry of **4** allow more satisfying conclusions to be reached. The nuclearity is still too high to allow

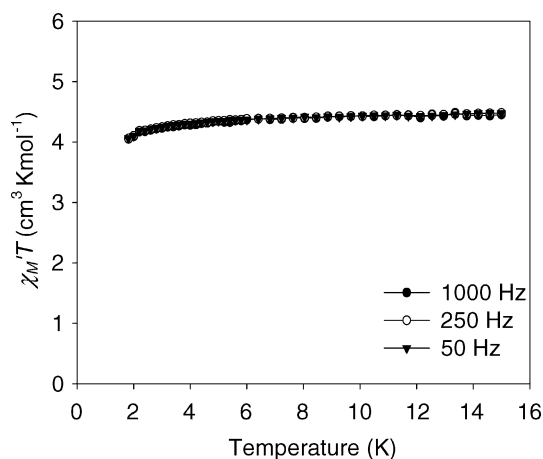


Fig. 11 In-phase ac susceptibility of **4** in a 3.5 Oe field oscillating at the indicated frequencies.

the experimental  $\chi_M T$  vs.  $T$  data to be fit by matrix diagonalization of the appropriate spin Hamiltonian involving the eight symmetry-independent nearest-neighbour Fe exchange interactions,  $J_{ij}$ ; this would involve diagonalizing a matrix of dimensions slightly greater than  $1 \times 10^7$  by  $1 \times 10^7$ . We thus estimated the  $J_{ij}$  values using the magnetostructural correlation of Gorun and Lippard,<sup>35</sup> which is based on the bridging Fe–O–Fe bond distances. The resulting  $J_{ij}$  values ( $H = -2J_{ij}S_i \cdot S_j$  convention) calculated for each  $Fe_i$ – $Fe_j$  interaction are shown in Fig. 12, where the viewpoint is that of Fig. 3 (bottom). As expected, all interactions are antiferromagnetic and span a range from  $-6.0$  to  $-41.2$   $cm^{-1}$ . Consideration of spin frustration (competing exchange interactions) within each  $Fe_3$  triangular sub-unit leads to the conclusions of the individual spin alignments shown in Fig. 12. In almost all cases, one of the interactions is significantly weaker (by a factor of two or more) than the other two interactions, allowing us to conclude that this interaction will clearly be frustrated and the spin alignments therefore determined by the other two. The weaker, frustrated interactions are shown in blue. The exception is  $J_{34}$  ( $-25.4$   $cm^{-1}$ ), which is within  $-4$   $cm^{-1}$  of  $J_{23}$  ( $-29.6$   $cm^{-1}$ ) but we propose the  $Fe_3$  spin is nevertheless locked parallel to the  $Fe_4$  spin by the combined stronger  $J_{23}$  and  $J_{35}$  interactions. We thus offer Fig. 12

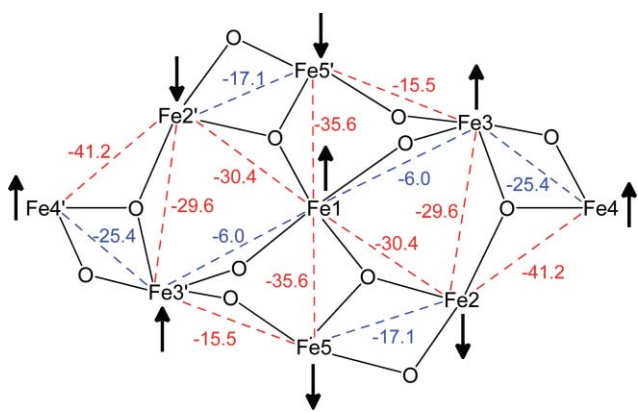


Fig. 12 Rationalization of the  $S = 5/2$  ground state of **4**, on the basis of the predicted magnitudes ( $cm^{-1}$ ) of the pairwise  $J_{ij}$  exchange constants and the resulting spin frustration effects; frustrated interactions are shown in blue. The viewpoint and atom labels are those of Fig. 3 (bottom).

as a rationalization of the  $S = 5/2$  ground state of **4**, which can be summarized as an outer  $S = 0$  loop of four antiparallel-aligned  $Fe_2$  pairs of  $S = 5$  spins, and an inner  $S = 5/2$   $Fe_1$  spin, giving the overall  $S = 5/2$  spin of the complete molecule. No doubt other spin alignments involving some spins in intermediate alignments also significantly contribute to the ground state spin wave function of the molecule, but we believe Fig. 12 describes the main component, on the basis of the calculated  $J_{ij}$  values at least.

## Summary and conclusions

Our continuing use of  $pdmH_2$  in  $Fe^{III}$  cluster chemistry has led to two interesting new  $Fe_{18}$  (**3**) and  $Fe_9$  (**4**) clusters, both of which are of an unprecedented structural type. The  $Fe_{18}$  complex **3** is the highest nuclearity complex to date in non-carboxylate  $Fe^{III}$  chemistry and can be obtained readily from hydrolysis of  $[Fe_8O_3(OEt)(pdm)_4(pdmH)_4(EtOH)_2](ClO_4)_5$  (**2**) or its  $MeO^-/MeOH$  analogue, but we have not been able to prepare it directly from simple  $Fe^{III}$  salts. It has an unusual cigar-like core, and we see no reason why longer, higher nuclearity analogues might not be accessible. The  $Fe_9$  complex **4**, on the other hand, has a basket-like topology. The complexes have  $S = 4$  (**3**) and  $5/2$  (**4**) ground states, both clearly arising from spin frustration effects within the many  $Fe_3$  triangular sub-units; the  $S$  value for **3** is impossible to rationalize but that for **4** can be rationalized on the basis of the exchange interactions predicted from published magnetostructural correlations.

The combined results demonstrate the usefulness of  $pdmH_2$ , which is still poorly explored in  $Fe^{III}$  chemistry, to give interesting new high nuclearity products, and shows once again that the presence or absence of carboxylates can have a marked effect on the obtained products. We also find it of interest that preformed alkoxide-containing clusters can undergo mild hydrolysis to yield clusters not accessible directly from simple starting materials, suggesting a possible means of targeted nuclearity increase of known compounds. Further studies are in progress.

## Acknowledgements

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## Notes and references

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