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## Fe(III) clusters built with tripodal alcohol ligands

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Dedicated to Prof. Malcolm Chisholm on the occasion of his 60th birthday.

### Abstract

Reaction of the tripodal ligand 1,1,1-tris(hydroxymethyl)ethane (H<sub>3</sub>thme) with a variety of Fe(III) precursors under both ambient and solvothermal conditions has led to the isolation of a number of new complexes ranging in nuclearity from 4 to 16. These include the rhomb or diamond-like clusters [Fe<sub>4</sub>(thme)<sub>2</sub>Cl<sub>4</sub>(O<sub>2</sub>CR)<sub>2</sub>(R'OH)<sub>2</sub>] (**1**, R = Me, R' = Et; **2**, R = Ph, R' = Me; **3**, R = CMe<sub>3</sub>, R' = Me); the related nonanuclear and undecanuclear clusters [Fe<sub>9</sub>O<sub>4</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>13</sub>(thme)<sub>2</sub>] (**4**) and [NEt<sub>4</sub>][Fe<sub>11</sub>O<sub>4</sub>(O<sub>2</sub>CPh)<sub>10</sub>(thme)<sub>4</sub>(dmhp)<sub>2</sub>Cl<sub>4</sub>] (**5**) (dmhp = 4,6-dimethyl-2-hydroxypyrimidine) and the octametallic and hexadecametallic wheels [Fe<sub>8</sub>(O<sub>2</sub>CR)<sub>12</sub>(thme)<sub>4</sub>] (**6**, R = Ph; **7**, R = CMe<sub>3</sub>) and [Fe<sub>16</sub>(EtO)<sub>4</sub>(O<sub>2</sub>CPh)<sub>16</sub>(Hthme)<sub>12</sub>](NO<sub>3</sub>)<sub>4</sub> (**8**). Magnetic studies reveal the presence of dominant antiferromagnetic interactions between the Fe centres in all eight complexes which results in the presence of small spin ground states for complexes **1**–4 and **6**–8. For **5** however, these stabilise an S = 11/2 spin ground state with an axial zero-field splitting parameter of D = -0.46 cm<sup>-1</sup>. Single crystal hysteresis loops in magnetisation versus external magnetic field measurements show the temperature and sweep rate dependence indicative of single-molecule magnetism behaviour.

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## 1. Introduction

Polymetallic cluster complexes of paramagnetic transition metal ions have attracted intense study since the discovery that such molecules can display the phenomenon of single-molecule magnetism (SMM) [1]. There is a barrier to relaxation of magnetisation in SMMs due to the combination of a large ground state spin multiplicity and a significant negative zero-field splitting of that ground state and this imparts a molecular magnetic memory effect that can be observed as hysteresis loops in M versus H studies. All SMMs made to date only exhibit this memory effect at very low temperatures and there is therefore an intense effort in synthesizing larger clusters in an attempt to generate larger spin ground states and higher energy barriers to loss of magnetization [2]. Here, we describe the synthesis of some new Fe<sup>III</sup> clusters with the tripodal ligand 1,1,1tris(hydroxymethl)ethane (H<sub>3</sub>thme). Tripodal ligands such as H<sub>3</sub>thme have previously been used in the solvothermal synthesis of oxo-vanadium and oxo-molybdenum clusters but until recently, very rarely in the synthesis of paramagnetic 3d transition metal clusters [3]. To date most cluster

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synthesis has involved "conventional" coordination chemistry techniques, i.e., solution chemistry under atmospheric pressure and at temperatures limited to the boiling points of common solvents. Solvothermal techniques allow the application of high temperatures to reactions in low boiling solvents and are also an excellent method for the preparation of pure, crystalline products [4]. In this work, we have explored reactions of Fe<sup>III</sup> precursors with H<sub>3</sub>thme under both ambient and solvothermal conditions and we observe a very wide range of cluster topologies and nuclearities depending on subtle changes in the reaction conditions.

## 2. Experimental

## 2.1. Synthesis

The complexes  $[Fe_3O(O_2CR)_6(H_2O)_3]X$  (R = Me, CMe<sub>3</sub>, Ph; X = Cl, NO<sub>3</sub>, O<sub>2</sub>CMe<sub>3</sub>) and  $[NEt_4]_2[Fe_2OCl_6]$  were made as previously described [5].

## 2.1.1. $[Fe_4(thme)_2Cl_4(O_2CMe)_2(EtOH)_2]$ (1)

FeCl<sub>3</sub> · 6H<sub>2</sub>O (2.0 g, 7.39 mmol), H<sub>3</sub>thme (0.30 g, 2.46 mmol) and NaO<sub>2</sub>CMe (0.61 g, 7.39 mmol) were dissolved in acetonitrile (30 ml) with stirring. The resultant yellow solution was stirred for 8 h, filtered and taken to dryness under reduced pressure. The resulting residue was then re-dissolved in MeOH (15 ml) and filtered. Yellow crystals grew upon diffusion of ethanol during three weeks. Yield: ~17%. Elemental *Anal.* Calc. for 1: C, 45.86; H, 7.60; Fe, 15.99. Found: C, 45.91; H, 7.68; Fe, 16.02%. IR (KBr;  $v/\text{cm}^{-1}$ ): 2997 (w), 2953 (m), 2912 (w), 2862 (w), 1527 (s), 1461 (w), 1433 (s), 1399 (w), 1321 (m), 1208 (w), 1119 (m), 1016 (s), 979 (s), 917 (w), 866 (m), 722 (w), 663 (m), 608 (m), 551 (w), 502 (s), 413 (w).

### 2.1.2. $[Fe_4(thme)_2Cl_4(O_2CPh)_2(MeOH)_2]$ (2)

FeCl<sub>3</sub> · 6H<sub>2</sub>O (2.0 g, 7.39 mmol), H<sub>3</sub>thme (0.30 g, 2.46 mmol) and NaO<sub>2</sub>CPh (1.06 g, 7.39 mmol) were dissolved in methanol (30 ml) with stirring. The yellow solution was stirred for 8 h, filtered and taken to dryness under reduced pressure. The resulting residue was redissolved in methanol (15 ml) and filtered. Yellow-brown crystals grew upon diffusion of diethyl ether during three weeks. Yield: ~20 %. Elemental *Anal.* Calc. for **2**: C, 37.00; H, 4.14; Cl, 14.56; Fe, 22.94. Found: C, 37.69; H, 3.61; Cl, 14.59; Fe, 22.25%. IR (KBr;  $v/\text{cm}^{-1}$ ): 2976 (w), 2934 (w), 2867 (w), 1600 (m), 1562 (m), 1519 (m), 1493 (w), 1406 (s), 1178 (m), 1121 (m), 1070 (m), 1017 (s), 918 (w), 834 (w), 790 (w), 721 (m), 676 (w), 607 (w), 488 (s), 406 (w).

## 2.1.3. $[Fe_4(thme)_2Cl_4(O_2CCMe_3)_2(MeOH)_2]$ (3)

FeCl<sub>3</sub>  $\cdot$  6H<sub>2</sub>O (2.0 g, 7.39 mmol), H<sub>3</sub>thme (0.30 g, 2.46 mmol) and NaO<sub>2</sub>CCMe<sub>3</sub> (0.92 g, 7.39 mmol) were dissolved in methanol (30 ml) with stirring. The yellow solution was stirred for 8 h, filtered and taken to dryness under reduced pressure. The resulting residue was

re-dissolved in methanol (15 ml) and filtered. Yellowbrown crystals grew upon diffusion of diethyl ether after 2–3 weeks. Yield: ~17 %. Elemental *Anal*. Calc. for **3**: C, 32.47; H, 4.77; Cl, 15.97; Fe, 25.16. Found: C, 31.89; H, 4.46; Cl, 16.50; Fe, 24.39%. IR (KBr)  $v / \text{cm}^{-1}$ ): 2932 (w), 2863 (w), 1587 (m), 1561 (w), 1514 (s), 1445 (w), 1401 (s), 1177 (w), 1119 (m), 1037 (m), 1017 (s), 985 (w), 913 (w), 723 (s), 677 (m), 607 (m), 487 (s).

## 2.1.4. $[Fe_9O_4(O_2CCMe_3)_{13}(thme)_2]$ (4)

[Fe<sub>3</sub>O(O<sub>2</sub>CCMe<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](O<sub>2</sub>CCMe<sub>3</sub>) (0.30 g, 0.32 mmol) and H<sub>3</sub>thme (0.038 g, 0.32 mmol) were dissolved in acetonitrile (6 ml) and placed in a 23 ml Teflon-lined autoclave. This was then heated at a rate of 1.0 °C min<sup>-1</sup> to 150 °C and maintained at this temperature for 12 h. Cooling to room temperature at a rate of 0.05 °C min<sup>-1</sup> resulted in the formation of large orange/brown crystals. These were washed with several portions of fresh acetonitrile and air dried. Yield: ~50 %. Elemental *Anal*. Calc. for **4**: C, 44.75; H, 6.63; Fe, 20.80. Found: C, 45.13; H, 7.26; Fe, 20.93%. IR (KBr  $\nu/cm^{-1}$ ): 29.62 (s), 2931 (m), 2903 (m), 2873 (m), 1567 (s), 1538 (s), 1484 (s),1459 (m) 1428 (s), 1393 (w), 1379 (s), 1362 (m), 1230 (s), 1153 (m), 1073 (s), 1015 (s), 966 (w), 939 (w), 919 (w), 896 (w), 788 (m), 608 (s), 441 (s).

## 2.1.5. $[NEt_4][Fe_{11}O_4(O_2CPh)_{10}(thme)_4(dmhp)_2Cl_4]$ (5)

[NEt<sub>4</sub>][Fe<sub>2</sub>OCl<sub>6</sub>] (0.5 g, 0.83 mmol), NaO<sub>2</sub>CPh (0.24 g, 1.66 mmol) dmhp (0.103 g, 0.83 mmol) and H<sub>3</sub>thme (0.1 g, 0.83 mmol) were added to MeCN (30 ml) and stirred for 12 h and then filtered. The resulting orange solution was allowed to evaporate yielding complex **5** in approximately 20% yield after one week. Elemental *Anal*. Calc. for **5**: C, 45.86; H, 4.24; N, 2.43. Found: C, 45.15; H, 4.23; N, 2.57%. IR (KBr  $\nu/cm^{-1}$ ): 1590 (w), 1533 (s), 1480 (m), 1447 (w), 1394 (s), 1171 (w), 1123 (w) , 1047 (m), 1021 (m), 996 (m), 778 (w), 721 (m), 677 (w), 608 (w), 477 (m).

## 2.1.6. $[Fe_8(O_2CPh)_{12}(thme)_4]$ (6)

(a)  $[Fe_3O(O_2CPh)_6(H_2O)_3]C1$  (0.30 g, 0.30 mmol) and  $H_3$ thme (0.036 g, 0.30 mmol) were dissolved in acetonitrile and placed in a 23 ml Teflon-lined autoclave. This was then heated at a rate of 1.0 °C min<sup>-1</sup> to 150 °C and maintained at this temperature for 12 h. Cooling to room temperature at a rate of 0.05 °C min<sup>-1</sup> resulted in the formation of large orange/brown crystals. These were washed with several portions of fresh acetonitrile and air dried. Yield: ~50%. (b)  $[Fe_3O(O_2CPh)_6(H_2O)_3](NO_3)$  (0.5 g 0.49 mmol) and  $H_3$ thme (0.06 g, 0.49 mmol) were stirred in MeCN (30 ml) for 12 h. The resulting precipitate was filtered, air-dried and re-dissolved in CH<sub>2</sub>Cl<sub>2</sub>. Crystals formed in two days after diffusion of diethyl ether into the solution in approximately 30% yield.

Elemental *Anal.* Calc. for **6**: C, 52.74; H, 4.09; Fe, 18.75. Found: C, 52.73; H, 4.10; Fe, 18.86%. IR (KBr  $\nu/cm^{-1}$ ): 3055 (w), 1598 (m), 1555 (m), 1530 (m), 1521 (m), 1429 (s), 1307 (w), 1177 (m), 1152 w), 1065 (m), 1023 (w), 1011 (m), 838 (w), 718 (s), 676 (m), 623 (m), 588 (m), 477 (s), 442 (w).

## 2.1.7. $[Fe_8(O_2CCMe_3)_{12}(thme)_4]$ (7)

 $[Fe_3O(O_2CCMe_3)_6(H_2O)_3]Cl (0.30 g, 0.34 mmol)$  and H<sub>3</sub>thme (0.041 g, 0.34 mmol) were dissolved in acetonitrile and placed in a 23 ml Teflon-lined autoclave. This was then heated at a rate of 1.0 °C min<sup>-1</sup> to 150 °C and maintained at this temperature for 12 h. Cooling to room temperature at a rate of 0.05 °C min<sup>-1</sup> resulted in the formation of large orange/brown crystals. These were washed with several portions of fresh acetonitrile and air dried. Yield:  $\sim 50$  %. Elemental Anal. Calc. C, 45.15; H, 6.82; Fe, 20.95. Found: C, 45.13; H, 7.07; Fe, 20.99%. IR (KBr)  $\nu/cm^{-1}$ : 2962 (m), 2931 (w), 1567 (s), 1536 (s), 1484 (s), 1427 (s), 1379 (m), 1362 (m), 1231 (s), 1153 (w), 1071 (s), 1015 (m), 897 (w), 789 (w), 606 (m), 442 (s).

## 2.1.8. $[Fe_{16}(EtO)_4(O_2CPh)_{16}(Hthme)_{12}](NO_3)_4$ (8)

 $[Fe_3O(O_2CPh)_6(H_2O)_3](NO_3)$  (0.5 g, 0.49 mmol) and H<sub>3</sub>thme (0.06 g, 0.49 mmol) were stirred in MeCN (30 ml) for 12 h. The resulting precipitate was filtered, air-dried and re-dissolved in a 1:1 mixture of CH<sub>2</sub>Cl<sub>2</sub> and EtOH. Crystals formed after two days in approximately 15% yield. Elemental Anal. Calc. C, 46.22; H, 4.74; N, 1.20. Found: C, 46.08; H, 4.41; N, 1.14%. Selected IR data (KBr pellet,  $cm^{-1}$ ): 1554 (s), 1528 (s) 1493 (m), 1409 (s), 1307 (w), 1176 (m), 1158 (w), 1069 (w), 1045 (m), 1025 (m), 877 (w), 717 (s).

## 2.2. X-ray crystallography and structure solution

All structures were solved by direct methods. The data are summarised in Table 1.

For complexes 1, 2, and 6 all the non-hydrogen atoms were refined anisotropically and the H atoms were included in calculated positions. 3: the asymmetric unit contains half a molecule and two disordered MeOH molecules. The CMe<sub>3</sub> group of the pivalates was disordered. All non-H atoms were refined anisotropically except those of the disordered atoms of the solvent at lower occupancy. H atoms were included in calculated positions except those bonded to C1T and C2T which were omitted. 4: a number of the CMe<sub>3</sub> groups were disordered over two sites whose occupancies were constrained to sum to 1.0 with restraints on the geometric parameters. All non-H atoms were refined anisotropically except the disordered atoms. H atoms were included in calculated positions. 5: the asymmetric unit contains half the molecule together with a number of solvent fragments; there are two CH<sub>2</sub>Cl<sub>2</sub> molecules and three highly disordered fragments which were not recognisable so the atoms were all defined as C with some at occupancy 0.5. The non-H atoms were refined anisotropically. H atoms were included in calculated positions except those of the disordered solvent. 7: the atoms C23-C25 and C42, C43, C45 were disordered over two sites each whose

Table 1								
Crystallographic details for	or complexes 1-8							
	$1[Fe_4]$	$2[Fe_4]$	$3[Fe_4]$	4[Fe9]	5[Fe <sub>11</sub> ]	6[Fe <sub>8</sub> ]	$7[Fe_8]$	8[Fe <sub>16</sub> ]
Formula	$C_{18}H_{36}Cl_4Fe_4O_{12}$	$C_{34}H_{44}Cl_4Fe_4O_{14}$	$C_{26}H_{58}Cl_4Fe_4O_{16}$	$C_{75}H_{135}Fe_9O_{36}$	$C_{131}H_{130}Cl_4Fe_{11}N_{14}O_{38}$	$C_{117}H_{96}Fe_8O_{38}$	$C_{81}H_{145.5}Fe_8N_{0.50}O_{36}$	C <sub>196</sub> H <sub>204</sub> Cl <sub>8</sub> Fe <sub>16</sub> O <sub>82</sub>
$M  ext{ (g mol}^{-1})$	809.67	1041.89	991.92	2115.48	3264.64	2556.74	2149.28	5048.81
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	tetragonal
Space group	P2(1)/n	Pbca	P2(1)/c	P2(1)/c	P2(1)/c	P2(1)	C2/c	P4(2)/n
a (Å)	8.3469(11)	9.6283(10)	12.583(7)	15.350(3)	13.9889(9)	16.490(15)	27.147(2)	24.7413(16)
$b(\mathbf{\hat{A}})$	16.265(2)	16.8943(18)	16.947(12)	28.114(3)	21.5807(15)	22.51(2)	17.3115(12)	24.7413(16)
c (Å)	10.6978(15)	27.275(3)	9.820(10)	24.484(2)	23.9145(16)	18.531(7)	44.931(3)	20.6068(19)
α (°)	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
$\beta$ (°)	96.873(2)	90.00	96.41(7)	108.025(11)	94.753(1)	115.563(1)	91.6430(10)	90.00
γ (°)	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
$V(\dot{A}^3)$	1441.9(3)	4436.7(8)	2081(3)	10047(2)	7194.7(8)	6204(10)	21 107(3)	12614.1(16)
$T(\mathbf{K})$	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Z	2	4	2	4	2	2	8	2
$P_{ m calc}~({ m g~cm^{-3}})$	1.865	1.560	1.583	1.398	1.507	1.369	1.353	1.358
Crystal shape/colour	yellow prism	brown cuboid	brown block	brown plate	brown prism	yellow plate	yellow plate	yellow plate
$\mu \ (mm^{-1})$	2.398	1.582	1.685	1.335	1.229	0.985	1.142	1.057
Unique data	3405	5366	4224	20458	14643	21439	21 549	11123
Unique data $(I > 2\sigma(F))$	2838	4705	3855	13963	11583	14358	15951	8547
$R_1, wR_2$	0.0401, 0.0755	0.0422, 0.0957	0.0417, 0.1072	0.0920, 0.1449	0.040, 0.1105	0.097, 0.2369	0.0565, 0.1375	0.0952, 0.2717

occupancies were constrained to sum to 1.0. There were two partially occupied MeCN solvent molecules one of which was incomplete. All non-H atoms were refined anisotropically except the disordered atoms and those of the solvent. H atoms were included in calculated positions except those of the solvent. 8: initially, the R value was very high and twinning was suspected. A twin matrix which exchanges the h and k axes was applied (01010000-1), and the twin fraction was found to be 0.44788. Accounting for the twinning reduced the *R* value from over 30% to under 10%. The asymmetric unit contains one quarter of the molecule together with a nitrate and a disordered solvent fragment, assumed to be CH<sub>2</sub>Cl<sub>2</sub>, and some water molecules. The phenyl rings were constrained to ideal geometry. Most of the non-H atoms were refined anisotropically except those of the solvent fragments, using restraints. H atoms were included in calculated positions except for the solvent H atoms.

#### 3. Crystal structure description

3.1. Structure of  $[Fe_4(thme)_2Cl_4(O_2CR)_2(R'OH)_2]$ (1, R = Me, R' = Et; 2, R = Ph, R' = Me; 3,  $R = CMe_3$ , R' = Me)

The core structures of complexes 1-3 (Fig. 1) are isostructural and consist of a central [Fe<sub>4</sub>O<sub>6</sub>]<sup>6+</sup> planar rhomb or diamond in which each of the oxygen atoms is derived from bridging [thme]<sup>3-</sup> ligands. These sit one-above and one-below the [Fe<sub>4</sub>] plane and each provide one  $\mu_3$ -oxygen arm that bridges between the two central Fe<sup>III</sup> ions and one outer  $Fe^{III}$  ion, and two  $\mu_2$ -oxygen arms that each bridge between an outer and central Fe<sup>III</sup> ion. These ions are also bridged by the two carboxylates which adopt their common syn, syn µ-mode. Each of the four Fe<sup>III</sup> ions contains a terminal chloride ion, while the coordination spheres of each of the two terminal Fe ions is completed by one R'OH molecule. The Fe centres are in distorted octahedral geometries and all are in the +3 oxidation state as confirmed by a combination of charge balance and bond length considerations and BVS calculations.

## 3.2. Structure of $[Fe_9O_4(O_2CCMe_3)_{13}(thme)_2]$ (4)

Complex 4 (Fig. 2) has a near planar rhomb-like array of nine Fe<sup>III</sup> ions linked via a combination of oxide and alkoxide ions to give a  $[Fe_9(O^{2-})_4(RO^{1-})_6]^{13+}$  core. Closer inspection reveals that the complex contains the identical  $[Fe_4O_6]^{6+}$  rhomb (Fe6–Fe9, O25–O30) seen in complexes 1–3. To this rhomb are now attached four  $[Fe_3O]^{7+}$  triangular units which each share one Fe ion (Fe8, Fe9 or Fe6) with the  $[Fe_4O_6]^{6+}$  rhomb. The two central  $[Fe_3O]^{7+}$ triangular units (containing Fe2, Fe3, Fe9 and O6 and Fe3, Fe4, Fe9 and O11) edge share to form a  $[Fe_4O_2]^{8+}$ rhomb. The two peripheral  $[Fe_3O]^{7+}$  triangles (containing Fe4, Fe5, Fe6 and O16, and Fe1, Fe2, Fe8 and O1) each share one vertex with the  $[Fe_4O_2]^{8+}$  rhomb and one vertex



Fig. 1. The structure of complex 1 viewed perpendicular (top) and parallel (bottom) to the  $[{\rm Fe}_4]$  plane.

with the  $[Fe_4O_6]^{6+}$  rhomb. The  $[Fe_4O_6]^{6+}$  unit and the  $[Fe_3O]^{7+}$  triangles are linked to each other through the thirteen carboxylate ligands that bind in three different modes: the usual  $\mu$ ,  $\eta_1$ ,  $\eta_1$ , mode, the less common  $\mu$ ,  $\eta_2$ ,  $\eta_1$  mode



Fig. 2. The structure of complex 4 viewed perpendicular to the  $[{\rm Fe}_9]$  'plane'.

(e.g., between Fe1 and Fe2), and as simple chelates (completing the coordination geometries of Fe(5) and Fe(7)).

All the Fe ions are in the +3 oxidation state and exhibit distorted octahedral geometries, with the exception of Fe(4), which is five-coordinate and in a distorted square based pyramidal geometry.

# 3.3. Structure of $[NEt_4][Fe_{11}O_4(O_2CPh)_{10}(thme)_4-(dmhp)_2Cl_4]$ (5)

The structure of complex 5 (Fig. 3) closely resembles that observed in 1-3 and 4. This time the structure contains two identical [Fe<sub>4</sub>O<sub>6</sub>]<sup>6+</sup> rhombs (containing Fe2, Fe4, Fe5 and Fe6 and symmetry equivalents), one at each 'end' of the molecule, linked to a central linear  $[Fe_3O_4]^{1+}$  unit (containing Fe1, Fe3 and Fe1A). Alternatively the core can be thought of as four vertex sharing  $[Fe_4]^{n+}$  units in which the two peripheral  $[Fe_4O_6]^{6+}$  rhombs are connected to two central  $[Fe_4O_2]^{8+}$  rhombs (comprising Fe1, Fe2 and symmetry equivalents) which themselves share one vertex (Fe3) forming a  $[M_7O_4]^{13+}$  sub-unit. The 10 PhCO<sub>2</sub><sup>-</sup> ligands bridge in their familiar syn, syn µ-mode both within and between the various [Fe<sub>4</sub>] units. The coordination geometries of Fe2 and Fe4 are completed by a combination of terminal Cl<sup>-</sup> ions and neutral dmhp ligands. These latter ligands are protonated with the nitrogen atom hydrogen bonding to a  $\mu_2$ -oxygen of a thme<sup>3-</sup> ligand. The [M<sub>4</sub>] units seen in all of the above complexes are common building blocks in the structures of  $Fe^{III}$  and  $Mn^{III}$  clusters and the  $[M_7O_4]^{13+}$  sub-unit is also a common feature in larger clusters, including [Fe<sub>17</sub>]/[Fe<sub>19</sub>] [6], [Mn<sub>8</sub>] [7], and [Fe<sub>11</sub>] clusters [8]. In fact the  $[Fe_{11}]$  core is similar to a  $[Mn_{11}]$  cluster reported by Christou and co-workers [9], but in this case the peripheral units are  $[Mn_4]$  cubes not rhombs.

While there are many examples of tetranuclear Fe aggregates, complex 4 is only the fifth nonanuclear Fe cluster reported [10] and complex 5 is only the second undecanuclear Fe complex reported. The original [Fe<sub>11</sub>] has no structural resemblance to 5 being based on a penta-capped trigonal prism [5].

## 3.4. Structure of $[Fe_8(O_2CR)_{12}(thme)_4]$ (6, R = Ph; 7, $R = CMe_3$ )

The structure of both complex **6** and complex **7** (Fig. 4) can be described as a wheel of eight Fe<sup>III</sup> ions bridged by a combination of  $\text{RCO}_2^-$  and thme<sup>3-</sup> ligands. The  $\text{RCO}_2^-$  ligands bridge neighbouring Fe<sup>III</sup> ions in the usual *syn, syn*  $\mu$ -manner while the triply-deprotonated thme<sup>3-</sup> ligands show much greater flexibility in each bridging four iron centres – each arm providing a  $\mu_2$ -oxygen for adjacent metals. The iron ions all lie in distorted octahedral geometries and are of four types: Fe1, Fe3, Fe5 and Fe7 are bridged to three  $\text{RCO}_2^-$  and two thme<sup>3-</sup> ligands; Fe2 and Fe6 are bound to four  $\text{RCO}_2^-$  and two thme<sup>3-</sup> ligands; and Fe4 and Fe8 bond to two  $\text{RCO}_2^-$  and two thme<sup>3-</sup> ligands. The "Fe<sub>8</sub>" wheel is non-planar and perhaps best described as ladle-shaped with a diameter of approximately 8 Å.

# 3.5. Structure of $[Fe_{16}(EtO)_4(O_2CPh)_{16}-(Hthme)_{12}](NO_3)_4$ (8)

The size of the wheel seen in complex 7 is doubled by the addition of a coordinating alcohol in the crystallisation step – use of EtOH produces the hexadecametallic wheel  $[Fe_{16}(EtO)_4(O_2CPh)_{16}(Hthme)_{12}](NO_3)_4$ . Complex 8 (Fig. 5) can be described as a wheel of sixteen Fe<sup>III</sup> ions bridged by PhCO<sub>2</sub><sup>-</sup>, Hthme<sup>2-</sup> and EtO<sup>-</sup> ligands. The



Fig. 3. The structure of complex 5 viewed perpendicular to the  $[Fe_{11}]$  'plane'.



Fig. 4. The structure of complex 6 viewed parallel to the [Fe8] 'plane'.



Fig. 5. The structure of complex  ${\bf 8}$  viewed perpendicular to the  $[Fe_{16}]$  'plane'.

 $PhCO_2^{-}$  ligands again bridge in their familiar  $\mu$ -mode: above, below and in the 'plane' of the [Fe<sub>16</sub>] wheel. The Hthme<sup>2-</sup> ligands are of two types. Eight ligands use their two deprotonated arms as  $\mu_2$ -bridges forming a nearly linear chain of three metals, with the third protonated arm bonded only to the central iron center. Four Hthme<sup>2-</sup> li-

gands occupy the central cavity of the wheel: the deprotonated arms again acting as  $\mu_2$ -bridges, with the protonated arm hydrogen bonding to the monodentate arm of an adjacent Hthme<sup>2-</sup> ligand (for example, O11–O15B 2.591(6) Å) and to a water molecule above the central cavity of the wheel (O11-O1S, 2.804(6)) Å. The four EtO<sup>-</sup> ligands each bridge two iron centres on the outside edge of the wheel. The iron ions are all in distorted octahedral geometries and bound to six oxygen atoms. For Fe(1) these are derived from three  $PhCO_2^{-}$ , two Hthme<sup>2-</sup> ligands and one EtO<sup>-</sup>. For Fe(2) from two  $PhCO_2^{-}$ , three  $Hthme^{2-}$  ligands and one EtO<sup>-</sup>. For Fe(3) from one  $PhCO_2^-$  and five  $Hthme^{2-}$ ligands, and for Fe(4) from two PhCO<sub>2</sub><sup>-</sup> and four Hthme<sup>2-</sup> ligands. Again the wheel is non-planar and best described as bowl-shaped with an approximate diameter of 16 Å.

#### 4. Magnetic measurements

## 4.1. Magnetism of $[Fe_4(thme)_2Cl_4(O_2CR)_2(R'OH)_2]$ (1-3)

Solid state DC susceptibility measurements of complexes 1-3 were taken in the range of 2-300 K in a field of 3 kG. The data for all three complexes is essentially identical and here we limit our discussion to complex 1. The  $\chi_m T$  value of 10.61 cm<sup>3</sup> mol<sup>-1</sup> K at 300 K gradually decreases with decreasing temperature to a minimum of  $1.24 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 6 K before increasing slightly to  $1.52 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 2 K. The spin only (g = 2) value expected for four non-interacting Fe<sup>III</sup> centres is approximately  $17.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ . This behaviour is indicative of antiferromagnetic exchange between the Fe<sup>III</sup> centres with the  $\chi_m T$  value at low temperature consistent with a ground state spin of S = 0 or S = 1. Magnetisation data were collected in the range of 0-5.0 T at 2 K. The magnetisation increases beyond the expected saturation value for S = 1, most likely because higher multiplicity states become more stable as the magnetic field is increased due to the close proximity of these states to the ground state. Because of this no fit of the data was attempted.

## 4.2. Magnetism of $[Fe_9O_4(O_2CCMe_3)_{13}(thme)_2]$ (4)

Solid state DC susceptibility measurements of complex 4 were taken in the range 2–300 K in a field of 5 kG. The  $\chi_m T$ value of 28.3 cm<sup>3</sup> mol<sup>-1</sup> K at 300 K gradually decreases with decreasing temperature approaching a value of approximately 0.40 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K. The room temperature  $\chi_m T$  value is smaller than the spin only value for nine non-interacting high spin Fe<sup>III</sup> centres (39.38 cm<sup>3</sup> mol<sup>-1</sup> K) indicating the presence of antiferromagnetic interactions. The low temperature value is close to that expected for a complex exhibiting a S = 1/2 spin ground state. Magnetisation data collected in the range of 0–5.0 T at 2 K are consistent with a small spin ground state with the presence of low-lying excited states of larger multiplicity that become populated with increasing field - as indicated by an inflexion point (at ca. 2.2 T) and the continual rise in magnetization with applied field.

## 4.3. Magnetism of $[NEt_4][Fe_{11}O_4(O_2CPh)_{10}(thme)_4-(dmhp)_2Cl_4]$ (5)

Solid state dc magnetization measurements were performed on 5 in the range 2–300 K in a field of 0.2 T between 300 and 50 K and 0.05 T between 50 and 2.0 K. (Fig. 6). The room temperature  $\chi_m T$  value of approximately  $18.7 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  decreases to a minimum of  $12.4 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 70 K and then rises to a maximum of  $15.4 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 12 K. This indicates that 5 has a non-zero spin ground state and that the ground spin state is higher than S = 9/2. In order to obtain the ground state spin value magnetization data were collected in the ranges of 2.0-6.0 K and 0.01-5.5 T (Fig. 6). The fits were made simultaneously on the four different temperatures (2, 3, 4 and 6 K), assuming only the ground state is populated, giving a best fit of S = 11/2, g = 2.03 and D = -0.46 cm<sup>-1</sup>. The maximum value of  $\chi_m T$  at low temperature (15.4 cm<sup>3</sup> mol<sup>-1</sup> K) and the fact that the magnetization data at 2 and 6 K can be fit with one set of parameters is a strong indication that the ground state is indeed S = 11/2 and that the first excited state is rather high in en-



Fig. 6. Thermal variation of  $\chi_m T$  in ranges 300–50 K at 0.2 T and 50–2 K at 0.05 T (top) and magnetization vs. H/T plot at 2 ( $\Box$ ), 3 ( $\bigcirc$ ), 4 ( $\triangle$ ) and 6 ( $\bigtriangledown$ ) K (bottom) for complex **5**.



Fig. 7. Magnetisation (*M*) of **5** plotted as a fraction of maximum  $M_s$  vs. applied magnetic field ( $\mu_0 H$ ). The loops are shown at different field sweep rates (top) and different temperatures (bottom).

ergy. The previously reported [Fe<sub>11</sub>] complex has an S =1/2 spin ground state [5]. Given the nature of S and sign of D, measurements were taken to see if 5 acts as a SMM. Low-temperature (1.2–0.04 K) single crystal magnetic measurements were performed on 5 using a micro-SQUID instrument equipped with three orthogonal field that allow the magnetic field to be scanned in all directions [11]. Below 1.2 K hysteresis loops are seen in magnetization versus field studies whose coercivities increase with decreasing temperature (Fig. 7). A detailed study of the field sweep rate dependence of the hysteresis loops showed that the hysteresis at non-zero fields is not due to a phonon bottleneck but due to slow relaxation because of the anisotropy barrier. Slow relaxation is seen at H = 0 but the presence of strong tunnelling does not allow for a reliable Arrhenius plot. For all SMMs the barrier is reduced at H = 0 because of the presence of tunnelling. Even for half-integer spin systems which in theory should not tunnel do so because of coupling with the environment – dipolar coupling between molecules, hyperfine coupling, spin-spin cross relaxation, and other multibody quantum processes. For a system with S = 11/2 and D = -0.46 cm<sup>-1</sup> for example, and assuming an internal transverse field of approximately 10 mT, one can estimate a tunnel splitting of ca.  $2.8 \times$  $10^{-6}$  K and thus a tunnel probability of P = 0.68 for a sweep rate of  $0.1 \text{ T s}^{-1}$  in good agreement with our

measurements. This has also been observed in a [Mn<sub>4</sub>] cluster with S = 9/2 [7].

4.4. Magnetism of  $[Fe_8(O_2CR)_{12}(thme)_4]$  (6, R = Ph; 7,  $R = CMe_3$ ) and  $[Fe_{16}(EtO)_4(O_2CPh)_{16}(Hthme)_{12}]$ - $(NO_3)_4$  (8)

The magnetic behaviour of compounds 6 and 7 are essentially identical and thus here we limit the discussion to complex 6. Magnetic studies of both 6 and 8 indicate antiferromagnetic exchange between the metal centres. For both **6** and **8** the value of  $\chi_m T$  declines rapidly from room temperature (~19, ~28 cm<sup>3</sup> K mol<sup>-1</sup>, respectively) to a value approaching 0 cm<sup>3</sup> K mol<sup>-1</sup> at 1.8 K indicative of S = 0 ground states for both complexes. The room temperature  $\chi_m T$  value is approximately half the expected value for 8 ( $\sim$ 35 cm<sup>3</sup> K mol<sup>-1</sup>) and 16 ( $\sim$ 70 cm<sup>3</sup> K mol<sup>-1</sup>) non-interacting iron centres, indicating the existence of strong antiferromagnetic interactions even at room temperature. This is commonly found for iron-oxo clusters with Fe–O–Fe angles between 100° and 120° [12]. Both 6 and 8 can be broken down into simple units of two metal ions and the bridging ligands that connect them (Scheme 1). In this scheme,  $J_1$ ,  $J_2$  and  $J_3$  are the magnetic coupling constants between two Fe<sup>III</sup> ions for each of the three different bonding interactions found. These are: one alkoxo and two carboxylate bridging ligands  $(J_1)$ ; two alkoxo and one carboxylate bridging ligands  $(J_2)$ ; and two alkoxo bridging ligands  $(J_3)$ . In order to analyse the magnetic behaviour of **6** and 8 we have found exact analytical equations for the  $\chi T$ product as a function of the temperature using the interaction topologies shown in Scheme 1. These equations have been developed following the classical spin approach and the methodology previously described by Fischer for onedimensional systems [13]. This methodology can be applied since the spin correlation paths generated by the interac-



Scheme 1. The different bonding interactions  $(J_1, J_2, J_3)$  present in complexes **6–8**.



Fig. 8. Experimental and theoretical (solid lines)  $\chi$  vs. *T* curves for [Fe<sub>16</sub>] (squares) and [Fe<sub>8</sub>] (circles).

tion schemes shown in Scheme 1 are large enough to neglect spin auto-correlation contributions through an entire loop [14]. The obtained analytical law is:

$$\chi T = \chi T_{\text{freeion}} \sum_{i,j,k} c_{i,j,k} u^i v^j w^k, \qquad (1)$$

where u,v and w are the Langevin functions for  $J_1$ ,  $J_2$  and  $J_3$ , respectively, and  $c_{i,j,k}$  are the coefficients of each term.

The best fits of the  $\chi$  versus *T* curves (Fig. 8) in the 300– 10 K temperature range are obtained with the following parameters: g = 2.0,  $J_1 = -22.2$  cm<sup>-1</sup> and  $J_2 = -8.5$  cm<sup>-1</sup> for **6**; and g = 2.0,  $J_1 = -16.0$  cm<sup>-1</sup>,  $J_2 = -9.1$  cm<sup>-1</sup> and  $J_3 = -74.4$  cm<sup>-1</sup> for **8**.

## 5. Conclusions

The tripodal ligand H<sub>3</sub>thme has led to the isolation of a series of new Fe<sup>III</sup> clusters. A simple combination of FeCl<sub>3</sub>, NaO<sub>2</sub>CR and H<sub>3</sub>thme in a mixture of MeCN and MeOH under ambient temperature and pressure gives rise to a series of rhomb- or diamond-like  $[Fe_4]$  clusters. The identical [Fe<sub>4</sub>] units are seen as building blocks in the formation of related [Fe<sub>9</sub>] and [Fe<sub>11</sub>] clusters, appearing once in the [Fe<sub>9</sub>] cluster and twice in the [Fe<sub>11</sub>] cluster. The [Fe<sub>9</sub>] cluster was made via the solvothermal reaction of [Fe<sub>3</sub>O(O<sub>2</sub>CR)- $(H_2O)_3$ ]O<sub>2</sub>CR with H<sub>3</sub>thme in MeCN – the same reaction at room temperature produces no isolable products. Repeating this reaction but simply replacing the RCO<sub>2</sub><sup>-</sup> counter ion with NO<sub>3</sub><sup>-</sup> or Cl<sup>-</sup> under the same conditions produces dramatically different compounds with the formation of octametallic wheel-like clusters. The benzoate (R = Ph) form of this cluster can also be made under ambient conditions, albeit in much lower yields and in lower purity due to a tendency to co-crystallise with unreacted starting material [Fe<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]NO<sub>3</sub>. The solvothermal reaction gives much higher yield and pure crystalline product directly. The pivalate analogue ( $R = CMe_3$ ) could only be isolated by a solvothermal route. The size of the wheel formed can be doubled via the introduction of alcohol to the reaction mixture to give a [Fe<sub>16</sub>] wheel. Previously reported cyclic  $[Fe_8]$  compounds have contained alkali metal ions within the central cavity of the wheel and the  $[Fe_{16}]$  complex is unprecedented. The above reactions highlight the very wide range of product cluster nuclearities and topologies that can result from subtle changes in reaction conditions – for example, changes in counter-ion, or solvothermal versus lower temperature routes.

All of the Fe species display dominant antiferromagnetic exchange interactions, but in the case of  $[Fe_{11}]$  this stabilises a rather large S = 11/2 spin ground state. Negative zero-field splitting within this ground state gives rise to single-molecule magnetism behaviour that is manifested in the presence of temperature and sweep rate dependent hysteresis loops.

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