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Salicylaldoxime-Supported Nona- and Tetrametallic FeIII Cages

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Abstract: The syntheses, structures and magnetic properties of seven new iron complexes, [Fe4O2(sao)4(tacn)2]·2MeOH·H2O (1), [Fe4O2(Me-sao)4(tacn)2]·2MeCN (2), [Fe4O2(Ph-sao)4(tacn)2]·2MeCN (3), [Fe6NaO4(Et-sao)6(hmp)8]·3MeCN·Et2O (4), [Fe4(Ph-sao)4(hmp)4]·Et-saoH2 (5), [Fe8NaO4(Et-sao)6(hmp)8]·3MeCN (6), and [Fe9NaO4(Et-sao)6(hmp)8(N3)7(H2O)] (7), stabilised with salicylaldoxime (saoH2) or derivatised salicylaldoxime (R-saoH2) ligands in conjunction with either 1,4,7-triazacyclononane (tacn), 2-(hydroxymethyl)pyridine (hmpH) or 2,6-pyridinedimethanol (pdmH2) are discussed.

INTRODUCTION

Polynuclear clusters of iron are currently being studied for a variety of reasons [1, 2]. For example, bioinorganic chemists are synthesising cages in the hope of further understanding the role they play in the iron containing protein Ferritin that stores and regulates Fe within living organisms and can contain up to approximately 4500 metal centres [3-5]. The relatively large spin of the FeIII ion also provides the possibility of these cluster molecules possessing large spin ground states and/or interesting magnetic properties [6]. The predominantly antiferromagnetic exchange between neighbouring FeIII ions can result in geometric frustration, which can result in spin glass behaviour or the appearance of unusual jumps or plateaus in field dependent magnetisation measurements [6, 7]. Extended frustrated lattices such as the Kagome lattice [6] exhibit these phenomena, but they can also be seen on the molecular scale in antiferromagnetic [Fe3] triangles [7], [Fe13] Keggin ions [8] and [Fe35] icosidodecahedra [9, 10]. The ground states in such species are degenerate and/or have low lying excited states owing to the relatively low energy differences between different orientations of the spins [11]. These properties are also ideal for low-temperature magnetic refrigeration, with recent results demonstrating that molecules such as [Fe4I] can outperform any conventionally employed solid state or intermetallic complexes by at least an order of magnitude [12].

Our work with FeIII has been concerned principally with the pro-ligand salicylaldoxime (saoH2, Fig. 1) and its derivatives [13-17]. When mono-deprotonated, (saoH), the ligand forms a pseudomacrocyclic ring which has the perfect cavity size to accommodate a CuII ion [18-20]. This has led to extensive research within extractive hydrometallurgy as it is extremely selective over other metal ions, and is now responsible for extracting approximately 25% of the world’s copper [21, 22]. Our interest also lies partly in its role as an anti-corrosive in protective coatings when treating lightly oxidised Fe surfaces, where it has been postulated that the protection occurs via polynuclear cluster formation on the surface [23]. A greater understanding of such clusters would therefore result in a more thorough understanding of the modes-of-action of the corrosion inhibition ability of the ligand [23].

To date we have explored the effects of systematically altering the reaction conditions within the rather simple FeIII/R-saoH2 reaction scheme, and have garnered a plethora of cages ranging in nuclearity from two to eight [13-17, 23-29]. Common to all the metallic skeletons are the triangular [FeO]12+ and tetrahedral [FeO]10+ building blocks. In the present work we employ co-ligands such as tacn, hmpH and pdmH2 (Fig. 1) in an attempt to introduce molecules that can compete with the phenolic oximes for the metal coordination sites and in the hope that novel coordination cages would form. The co-ligands were chosen based on their previous success in synthisising FeIII clusters, as reported in the literature [30-39]. For example, the ligand tacn was used in the synthesis of the first recognised FeIII Single-Molecule Magnet (SMM), [Fe3] [40, 41], and hmpH and pdmH2 have both been used extensively in metal cluster synthesis [30-32, 35, 36, 42-51].

EXPERIMENTAL SECTION

Syntheses

All manipulations were performed under aerobic conditions using chemicals as received, unless otherwise stated. 2-hydroxyacetophenone oxime (Me-saoH2) and 2-
hydroxypropiophenone oxime (Et-saoH2) were synthesised via the reaction of the appropriate ketone with hydroxylamine and sodium acetate as described in the literature [52]. tacn was prepared as previously described [53].

\[
\text{[Fe}_4\text{O}_2\text{(tacn)}_4\text{(sao)}_4\text{]}\cdot2\text{MeOH}\cdot\text{H}_2\text{O (1·2MeOH·H}_2\text{O)}
\]

FeCl2·4H2O (198 mg, 1 mmol) and saoH2 (205 mg, 1.5 mmol) were stirred in a 1:1 mixture of MeOH and CH2Cl2 (25 ml). In a separate flask tacn·3HBr (279 mg, 0.75 mmol) and NEt3 (6 ml, 54 mmol) were stirred in 5 ml of a 1:1 MeOH/CH2Cl2 mix. After 30 minutes the two independent solutions were added together and stirred for a further 18 hours, after which time the solution was filtered and left to evaporate slowly. X-ray quality crystals were present after 2 days in ~40% yield. Elemental analysis: found (calc. %) for C40H50Fe4N10O10: C 45.23 (45.57), H 4.67 (4.78), N 13.21 (13.29).

\[
\text{[Fe}_4\text{O}_2\text{(Me-sao)}_4\text{(tacn)}_4\text{]}\cdot2\text{MeCN (2·2MeCN)}
\]

Procedure as for 1, replacing saoH2 with Me-saoH2 (226 mg, 1.5 mmol) and MeOH with MeCN. Yield ~40%. Elemental analysis found (calc. %) for C44H58Fe4N10O10: C 47.46 (47.59), H 5.03 (5.26), N 12.25 (12.61).

\[
\text{[Fe}_4\text{O}_2\text{(Et-sao)}_4\text{(tacn)}_4\text{]}\cdot\text{MeOH (3·MeOH)}
\]

Procedure as for 1, replacing saoH2 with Et-saoH2 (165 mg, 1 mmol). X-ray quality crystals were grown by Et2O diffusion into the MeOH solution in ~40% yield after 1 week. Elemental analysis: found (calc. %) for C48H66Fe4N10O10: C 49.11 (49.42), H 5.52 (5.70), N 11.47 (12.01).

\[
\text{[Fe}_5\text{NaO}(\text{Et-sao})_8\text{(hmp)}_6\text{]}\cdot3\text{MeCN·Et}_2\text{O (4·3MeCN·Et}_2\text{O)}
\]

FeCl2·4H2O (298 mg, 1.5 mmol), Et-saoH2 (165 mg, 1 mmol), hmpH (163 mg, 1.5 mmol) and NaOMe (135 mg, 2.5 mmol) were stirred in MeCN for 18 hours. The solution was filtered and then diffused with Et2O. X-ray quality crystals grew during 5 days in approximately 30% yield. Elemental analysis: found (calc. %) for C91H10Fe6N12O23: C 49.21 (49.61), H 3.92 (4.27), N 7.25 (7.56).

\[
\text{[Fe}_4\text{(Et-sao)}_4\text{(hmp)}_4\text{]}\cdot\text{Et-saoH}_2\text{(5·Et-saoH}_2\text{)}
\]

FeCl2·4H2O (298 mg, 1.5 mmol), Et-saoH2 (165 mg, 1 mmol), hmpH (163 mg, 1.5 mmol) and Ca(OMe)2 (255 mg, 2.5 mmol) were stirred in MeCN for 18 hours. After filtration the solution was left to evaporate slowly, producing X-ray quality crystals after 5 days. Yield ~25%. Elemental analysis: found (calc. %) for C90H17Fe4N14O14: C 56.16 (56.23), H 4.64 (4.86), N 8.31 (8.55).

\[
\text{[Fe}_4\text{(Ph-sao)}_4\text{(hmp)}_4\text{]}\cdot6\text{MeCN (6·6MeCN)}
\]

FeCl2·4H2O (397 mg, 2 mmol), Ph-saoH2 (416 mg, 2 mmol), hmpH (327 mg, 3 mmol) and NaOMe (162 mg, 3 mmol) were stirred in MeCN for 18 hours. The solution was filtered and left to evaporate slowly for 3 days, during which time X-ray quality crystals grew in ~25% yield. Elemental analysis: found (calc. %) for C80H60Fe4N8O12: C 62.43 (62.04), H 4.02 (3.90), N 7.40 (7.23).

\[
\text{[Fe}_9\text{NaO}_3\text{(sao)}_6\text{(pdm)}_6\text{(N}_3)_7\text{(H}_2\text{O)}\text{] (7)}
\]

Fe(BF4)2·6H2O (337 mg, 1 mmol), saoH2 (68 mg, 0.5 mmol), pdmH2 (278 mg, 2 mmol) and NaOMe (130 mg, 2 mmol) were stirred in a 1:1 mix of MeCN/MeOH (30 ml). The solution was heated to 50°C and stirred for a further 3 hours. After filtering off a brown precipitate, the solution was allowed to evaporate slowly. X-ray quality crystals grew during three days in ~20% yield. Elemental analysis: found (calc. %) for C91H10Fe9N13O25.2: C 49.21 (49.61), H 3.09 (2.71), N 7.60 (7.23).

**PHYSICAL MEASUREMENTS**

Elemental analyses were performed by the EaStChem microanalysis service. Direct current magnetic susceptibility measurements were carried out on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7T magnet. Eicosane was used to restrain the microcrystalline samples and diamagnetic corrections were applied using Pascal’s constants. Single crystal X-ray crystallography for complexes 1, 2, 6, and 3, 4, 5, 7 was performed using a Bruker Smart Apex II CCD diffractometer equipped with an Oxford
RESULTS AND DISCUSSION

Synthesis

The general synthetic strategy adopted in this work was the introduction of co-ligands into our previously successful reaction schemes that examined the coordination chemistry of R-saoH2 ligands with Fe II/III salts, in order to understand the effect of these co-ligands on the structural identity of the resultant cluster compound [13-17, 23-29]. The reaction of FeCl2·4H2O, saoH2 and tacn in MeOH/CH2Cl2 with an excess of NEt3 affords the tetrametallic ‘butterfly’ complex 1. It is interesting to note that the only previously reported Fe clusters stabilised purely by R-saoH2 ligands are the tetrametallic cubes, [Fe4(Me-sao)4(Me-saoH)4]·MeOH and [Fe4(sao)4(saoH)4]·saoH2·C8H10 [13,23]. The same reaction, employing Me-saoH2 and Et-saoH2 instead of saoH2 and with the CH2Cl2 replaced with MeCN affords the structurally analogous complexes 2 and 3, respectively. It is therefore clear to see that the change in the phenolic oxime, the change of solvent and indeed any change to the ratio of reactants employed, has no effect on the identity of the product, suggesting that the rigid, triangular face-capping tacn ligand is the dominant structural player. This contrasts sharply to reactions performed in the absence of tacn, in which all these reaction variables do have prominent effects on the identity of the product [13-17, 23-29]. The reaction of FeCl2·4H2O, Et-saoH2, hmpH and NaOMe in MeCN yields the large and unusual nonametallic complex 4. The reaction can be considered similar to that which produced the butterfly complexes 1-3, but in which the tacn has been replaced by hmpH. The molecule, 4, therefore represents the difference between employing a rigid chelating ligand with one dominant coordination mode, versus a flexible ligand which can possess numerous coordination modes — both chelating and bridging. The presence of a single Na+ ion at the centre of the cluster suggested that the identity of the alkali metal ion used in the base would also have an important structure-directing role. Unfortunately we failed to isolate crystalline...
material from the use of other group 1 alkali metal cations (Li⁺, K⁺, Cs⁺); however we were successful with Ca(OMe)₂, isolating the tetranuclear square complex 5 in which there is no Ca²⁺ present. Interestingly, although highly unusual, the [Fe₃] square topology is reminiscent of another oxime-based, F-bridged square we published recently (vide infra) [17]. Repetition of the reaction which produces complex 5, but replacing Et-saoH₂ with other R-saoH₂ family members does not produce any crystalline material, but perhaps somewhat oddly, repetition of the reaction which produces complex 4, but replacing Et-saoH₂ with Ph-saoH₂ does produce the [Fe₄] square, 6. In this instance we presume that it is the steric bulk of the oximic Ph-group that is the dominant structural factor. Indeed a close inspection of nonametallic complex 4 suggests that the replacement of the Et-group with a Ph-group would likely be problematic from a simple steric consideration. This therefore gives us two routes to change from the large [Fe₉] complex to the smaller [Fe₄] complex: changing the charge on the cation, and/or increasing the bulk of the ketoxime group. Switching from the hmpH ligand to the closely related pdmH₂ produces a second nonametallic cage: the reaction of Fe(BF₄)₂·6H₂O, saoH₂, pdmH₂ and NaN₃ in MeOH/MeCN yields complex 7. A direct comparison of the formulae of 4 and 7 suggests the pdm⁻² ligand to be more dominant than the hmp⁻ ligand; the pdm⁻²:R-sao²⁻ ratio being 6:1 and the hmp⁻:R-sao²⁻ ratio being 1.33:1. All of these complexes were synthesised from ferrous salts and could not be reproduced with ferric salts.

**Description Of Structures**

The molecular structures of complexes 1-3 are analogous, differing only in the identity of the R-sao⁻² ligand, and so for the sake of brevity we describe only complex 1. Centrosymmetric complex 1 (Fig. 2) crystallises in the triclinic space group P-1 with two (analogous) [Fe₄] molecules present in the unit cell. The metallic skeleton describes two edge-sharing [Fe₃] triangles or, perhaps more conventionally, a [Fe₄] ‘butterfly’. Each triangle is scalene by strict definition, but isosceles based on ligand bridging modes. Central to each triangle is one μ₃-O₂⁻ ion, forming the common [Fe₃O]⁷⁺ moiety (or the [Fe₃O₂]⁶⁺ butterfly), with the two unshared edges of the triangle bridged by sao⁻² ligands in a familiar μ⁻ mode. These lie alternately above and below the [Fe₄] plane. The two μ⁻-[tacn] ligands each chelate a ‘wing-tip’ Fe⁺³ ion completing the [O₃N₃] donor set at this ion. These ions lie in distorted octahedral geometries that are
perhaps best described as trigonal-antiprismatic; the face-capping tacn ligands forcing a trigonal distortion (Fe…N, ~2.2 Å; Fe…O, ~1.9 Å). The ‘body’ FeIII ions have [O4N2] donor sets and lie in distorted octahedral environments with the four equatorial Fe…O distances measuring ~2.0 Å, and the two ‘axial’ Fe…N distances being ~2.2 Å.

There are four intra-molecular H-bonds between the monodentate phenolic O-atoms of the sao2- ligands and the N-atoms of the tacn ligands (O ···N, 2.850(5)-3.035(5) Å). The closest cluster…cluster interactions occur between C-atoms in the phenolic oxime ligands (2.754(4) – 3.062(7) Å). The closest intermolecular H-bonds, with bond lengths of ~2.3 Å to the two O2- ions, ~2.4 Å to the two O2- ions and ~2.6 Å to the phenolic O-atoms of the Et-sao2- ligand. There are no intramolecular interactions occurring between phenolic O-atoms and the FeIII ions: [O5N] for Fe4, Fe2, Fe6 and Fe8, and [O4N2] for Fe5, Fe3, Fe1, Fe7 and Fe9. The Na+ ion is six coordinate and in a very distorted environment, coordinated to six O-atoms, with bond lengths of ~2.3 Å to the two O2- ions, ~2.4 Å to the two O2- ions and ~2.6 Å to the two O2- ions.

Complex 4 crystallises in the triclinic space group P-1 (Fig. 3). The metallic skeleton (Fig. 3c) comprises a series of edge- and vertex-sharing [FeIII] triangles. When also considering the four O2- ions (2 x μ4, 2 x μ2) the core of the molecule can be described as two central [FeIII][O4NaO] tetrahedra sharing an edge, with both corners (at Fe6 and Fe2) connected to a peripheral [FeIII][O4NaO] tetrahedron (Fig. 3d). The triangular units contain the [FeIII][O(sao)]3 group, commonly observed in M4+/-R-sao2- coordination chemistry. Each triangle is linked to a tetrahedron through a η2:μ-in-μ-bridging mode and one η1:μ-hmp-bridging ligand (Fe2-Fe3 and Fe6-Fe7) ligand and one η1:μ-hmp-bridging ligand (Fe3-Fe4 and Fe7-Fe8). The additional edges on each triangle (Fe8-Fe9 and Fe4-Fe5) are bridged via one η1:η1:μ-Et-sao2- and one η1:η1:μ-hmp- All remaining bridging within the central tetrahedra are via η1:η1:μ-hmp- ligands (Fe3-Na1, Fe1-Fe2, Fe1-Fe6 and Fe7-Na1). All the FeIII ions lie in distorted octahedral geometries with cis angles in the range 73.54-114.17° and trans angles in the range 152.17-176.60°.

\[ [\text{Fe}^{III} \text{O}_2 \text{tacn}_2 \text{sa}o_2 \text{O}_2 \text{CR}_2] \]

The largest nuclearity FeIII cluster to be synthesised containing any R-saoH2 ligand and joins a relatively small family of iron complexes of nuclearity nine: a search of the CCDC database (Version 5.33, Nov 2011) reveals only 73 FeIII molecules in comparison with the 535 characterised FeIII molecules, for example.

Complex 5 (Fig. 4) crystallises in the triclinic space group P-1 with one Fe cluster and one Et-sao2H2 ligand in the asymmetric unit. The metallic core of 5 describes a distorted [FeIII] square with Fe…Fe lengths of 3.459(1)-3.474(1) Å and Fe-Fe-Fe angles of 86.97(2)-88.53(2)°. Each edge is bridged by a combination of one Et-sao2- ligand bridging in a η1:η1:η1:μ-fashion and one hmp- bridging in a η1:η1:μ-fashion. These lie alternately above and below the [FeIII] plane. In fact the [FeIII] square is very distorted and non-planar as can be seen from Fig. 4c. Each iron ion is in the 3+ oxidation state and lies in an octahedral geometry with a [O4Na2] donor set, with cis angles of 75.55(1)-105.18(1)° and

\[ [\text{Fe}^{III} \text{O}_2 \text{Et-sao}_2] \]
trans angles of 152.32(1)-175.39(1)°. There is an intermolecular H-bond to the co-crystallised Et-saoH₂ molecule in the lattice, between the phenolic O-atom of the coordinated oxime ligand and the oximic O-atom of the non-coordinated Et-saoH₂ molecule (O…O, 2.691(4) Å). The closest cluster…cluster interactions are of the order of 3.4 Å between C-atoms on neighbouring Et-sao²⁻ ligands. Complex 6 crystallises in the tetragonal space group \( I4_{1}/a \) with one molecule in the asymmetric unit and four within the unit cell (Fig. 4). The cluster is isostructural with complex 5, differing only in the identity of the R-saoH₂ ligand. Symmetry now forces all of the Fe…Fe distances to be equivalent (3.451(1) Å) and the Fe-Fe-Fe angles are 86.33(2)° - again describing a distorted, non-planar \([\text{Fe}^\text{III}]_{4}\) square. The octahedral Fe³⁺ ions have cis angles in the range 80.25(1)-104.6(1)° and trans angles in the range 154.89(1)-173.52(1)°. There are a number of inter-molecular interactions within the crystal lattice, most notably \( \pi-\pi \) stacking between two neighbouring hmp’ ligands (C...C, ~3.3 Å), with the shortest inter-molecular distance being between a phenolic O-atom and the pyridyl C-atoms of an hmp’ ligand (O...C 3.208(6) Å). Clusters with the \([\text{Fe}^\text{III}]_{4}\) square topology are very rare – indeed a search of the CCDC database returns only 8 hits when all bridges are the same (47 total). Interestingly however, complexes 5 and 6 are very similar to the complex \([\text{Fe}^\text{III}]_{4}(\text{Ph-sao})_{4}(\text{py})_{4}\) which we reported recently [15]. A comparison of the structures is given in Fig. (4). It is easy to see that the \( \mu\)F and the terminally bonded pyridine in the latter complex have simply been replaced by the hmp’ ligand in 5 and 6 which combines both coordination modes.

Complex 7 crystallises in the orthorhombic space group \( Pna2_{1} \) (Fig. 5). The metallic skeleton consists of six fused \([\text{Fe}^\text{III}]_{4}\) tetrahedra with each tetrahedron sharing a face with...
its neighbour. Central to the molecule are three $\text{O}^2-$ ions, two bonding in a $\mu_4$-fashion and one bonding in a $\mu_3$-fashion (Fig. 5b). The core can thus be described as two [Fe$^{III}_4\text{O}_7$]$^{10+}$ tetrahedra sharing a vertex (at Fe4) with an additional [Fe$^{III}_2\text{O}_3$]$^7+$ triangle sharing a vertex at Fe2. Only one sao$^2-$ ligand is present in the molecule, bridging in a $\eta^1:\eta^1:\eta^1:\mu^1$-mode between Fe5 and Fe6. The more prevalent ligand is the pdm$^2-$ ligand, with six present in the molecule, all bridging in a $\eta^1:\eta^1:\eta^1:\mu^1$-mode, except for the one bridging Fe7-Fe8 which bridges only two metals in a $\eta^1:\eta^1:\mu^1$-mode. The four remaining edges are bridged by end-on $\text{N}_2^-$ ligands, with three terminally bonded $\text{N}_2^-$ ligands filling the remaining coordination sites on the Fe centres. The end-on bridging azide is particularly rare in Fe$^{III}$ chemistry; a CCDC search revealing only two diiron complexes, each of which displays ferromagnetic exchange [54, 55]. Our previous efforts to incorporate azide bridges resulted in only a partial displacement (15%) of a $\mu$-OMe$^-$ bridge in the molecule [FeO$_2$(OMe)$_{1.85}$(N$_2$)$_{1.15}$(Me-sao)$_{3}$(py)$_2$] [16]. This makes 7 the first Fe$^{III}$ cluster to contain end-on azide bridges of nuclearity greater than two. Eight of the Fe$^{III}$ ions lie in distorted octahedral geometries with cis angles of 73.63(4)-128.39(4)$^\circ$ and trans angles of 138.45(4)-177.71(4)$^\circ$. The remaining Fe$^4$ ion (Fe4) is in a pentagonal bipyramidal geometry; equatorial angles between adjoining points on the pentagon are in the range 69.22(4)-79.16(4)$^\circ$, angles between axial and equatorial sites are in the range 73.44(4)-105.20(4)$^\circ$ and the angle between the axial-axial sites is 176.79(4)$^\circ$. All of the octahedral Fe$^{III}$ centres have a [O$_4$N$_2$] donor set and the pentagonal bipyramidal Fe$^{III}$ centre has a [O$_5$N$_2$] donor set. There are no inter-molecular hydrogen bonds, with the shortest contacts between neighbouring molecules being between a bridging azide ion and the pyridyl ring of a pdm$^2-$ ligand (C...N 3.03(3) Å).

**Magnetic Properties**

Direct current (dc) magnetic susceptibility studies were performed for complexes 2, 4, 6 and 7 between 5-300 K in an applied field of 0.1 T. These are plotted as the $\chi_M T$ product versus $T$ in Fig. (6). Complex 2 has a room temperature $\chi_M T$ value of 2.1 cm$^3$ K mol$^{-1}$ which is considerably lower than the expected value for four non-interacting Fe$^{III}$ centres (17.5 cm$^3$ K mol$^{-1}$) with $g = 2.00$, suggestive of strong antiferromagnetic exchange. The value of $\chi_M T$ continues to drop with decreasing temperature, reaching 0 cm$^3$ K mol$^{-1}$ at ~25 K. The data can be fitted to the isotropic spin-Hamiltonian (1):

$$\hat{H} = -2J(\hat{S}_i \cdot \hat{S}_j + \hat{S}_j \cdot \hat{S}_k + \hat{S}_k \cdot \hat{S}_l + \hat{S}_l \cdot \hat{S}_m + \hat{S}_m \cdot \hat{S}_n + \hat{S}_n \cdot \hat{S}_o) + \mu_B B \sum_{i=1}^{N} \hat{S}_i$$

where $J$ is the isotropic magnetic exchange interaction, $\hat{S}$ is a spin operator, $\mu_B$ is the Bohr magneton, $g = 2$ is the isotropic $g$-factor, $B$ is the external magnetic field, the index $i$ runs from 1 to 4 and we assume that all Fe$^{III}...Fe^{III}$ interactions are equivalent. This affords $J = -61$ cm$^{-1}$. The $S = 0$ ground spin state is separated from the first excited ($S = 1$) state by 122 cm$^{-1}$ (Fig. 7). For comparison, the very similar complex [L$_2$Fe$_2$(µ$_4$-O)$_2$(salox), (diphenylglycolocate),Fe$_2$](ClO$_4$)$_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) reported by Chaudhuri et al [25] has $J = -41.4$ cm$^{-1}$ and all published $J$ values of molecules with the Fe$_4$ butterfly topology fall in the range -33 to -46 cm$^{-1}$ [56, 57]. Complexes 4 and 7 are described together as both display similar properties. Complexes 4 and 7 have room temperature $\chi_M T$ values of 12.43 cm$^3$ mol$^{-1}$ K and 14.9 cm$^3$ mol$^{-1}$ K, respectively, which are lower than the spin-only expected value (g = 2) for nine non-interacting Fe$^{III}$ centres (39.375 cm$^3$ mol$^{-1}$ K). This indicates the presence of dominant and relatively strong antiferromagnetic exchange between the metal centres. As the temperature is decreased the magnetic susceptibility decreases to values of 4.49 cm$^3$ mol$^{-1}$ K for 4 and 4.1 cm$^3$ mol$^{-1}$ K for 7 at 5 K. This suggests a small spin ground state (perhaps $S = 5/2$) for both, as one would expect for an odd-membered, antiferromagnetically coupled Fe$^{III}$ cluster. The size of the metallic core and number of different exchange pathways preclude fitting of the susceptibility data. However, in order to shed further...
light on the nature and identity of the ground state for complexes 4 and 7 field dependant magnetisation data (T = 2-7 K, B = 0.5-7.0 T) were collected (Fig. 8), and the so-obtained data fitted to spin-Hamiltonian (2):

$$\hat{H} = D_S \left( \hat{S}_z^2 \right) - S(S+1)/3 + \mu_B g B \hat{S}$$

where $S$ is the total spin of the ground spin-state, $D_S$ is the uniaxial anisotropy of the ground spin-state, $g = 2$, and we assume that only the ground spin-state is populated. This affords the following spin-Hamiltonian parameters: $S = 5/2$, $D_{S-5/2} = +0.653 \text{ cm}^{-1}$ (4), and $S = 5/2$, $D_{S-5/2} = +0.301 \text{ cm}^{-1}$ (7).

Complex 6 has a room temperature $\chi M T$ value of 7.8 cm$^3$ mol$^{-1}$ K, lower than the spin-only expected value ($g = 2$) for four non-interacting Fe$^{III}$ centres (17.5 cm$^3$ K mol$^{-1}$). The $\chi M T$ value decreases with decreasing temperature reaching 0 cm$^3$ K mol$^{-1}$ by 10 K, indicative of comparatively strong antiferromagnetic interactions, resulting in a diamagnetic ground state. The data can again be fitted to the isotropic spin-Hamiltonian (1), in the same way as previously described. This affords an exchange interaction $J = -13.6 \text{ cm}^{-1}$ with the first excited ($S = 1$) state located 27.2 cm$^{-1}$ above the $S = 0$ ground state (Fig. 7). It is interesting to compare the exchange interactions for complexes 2 (mediated by oxime -N-O- and O$_2^-$) and 6 (mediated by oxime -N-O- and OR), with the former almost five times stronger than the latter [58]. We can also compare the data for 6 to that previously reported for the complex [Fe$_4$F$_4$(Ph-sao)$_4$(py)$_4$]. The presence of more than one [Fe$_4$] molecule in the unit cell of the latter complex precluded any fitting of the data, but a simple qualitative comparison of the data in Fig. (6) suggests that the exchange mediated by the F-bridges is somewhat weaker than that mediated by the alkoxides.

CONCLUSION

Seven new clusters have been added to the ever-growing family of polymetallic Fe$^{III}$ clusters stabilised by salicylaldoxime-based ligands. The clusters have been synthesised by employing co-ligands (namely tacn, hmpH and pdmH$_2$) that are able to compete with the oxime ligands for the Fe coordination sites. This has resulted in a set of tetranuclear ‘butterfly’ clusters with the ligand tacn that display very strong antiferromagnetic exchange interactions and diamagnetic ground states. The pro-ligand hmpH produced three clusters:
two tetranuclear squares formed via two entirely different routes, and an unusual nonametallic cage. The related proligand pdmH₂ stabilized another intriguing [Fe₈] cluster containing some similar structural oddities. These include a rare example of Fe³⁺ ions being bridged by end-on azides - previously observed in only two dinuclear clusters, and the first occurrence of a pentagonal bipyramidal Fe⁺⁺ centre in Fe-salicylaldoxime chemistry.

CONFLICT OF INTEREST
The authors confirm that this article content has no conflicts of interest.

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