Hexa- and octanuclear iron(III) salicylaldoxime clusters†

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The syntheses, structures and magnetic properties of six iron complexes stabilised with the derivatised salicylaldoxime ligands Me-saoH2 (2-hydroxyethanone oxime) and Et-saoH2 (2-hydroxypropiophenone oxime) are discussed. The four hexanuclear and two octanuclear complexes of formulae 

\[
[\text{Fe}_8\text{O}_2(\text{OMe})_4(\text{Me-sao})_6\text{Br}_4(\text{py})_4] \cdot 2\text{Et}_2\text{O} \cdot \text{MeOH} (1 \cdot 2\text{Et}_2\text{O} \cdot \text{MeOH}), [\text{Fe}_8\text{O}_2(\text{OMe})_{3.85}(\text{N}_3)_{4.15}(\text{Me-sao})_6(\text{py})_2] (2), [\text{Fe}_6\text{O}_2(\text{O}_2\text{CPh-4-NO}_2)_4(\text{Me-sao})_2(\text{OMe})_4\text{Cl}_2(\text{py})_2] (3), [\text{Fe}_6\text{O}_2(\text{O}_2\text{CPh-4-NO}_2)_4(\text{Et-sao})_2(\text{OMe})_4\text{Cl}_2(\text{py})_2] \cdot 2\text{Et}_2\text{O} \cdot \text{MeOH} (4 \cdot 2\text{Et}_2\text{O} \cdot \text{MeOH}), [\text{HNEt}_3][\text{Fe}_6\text{O}_2(\text{Me-sao})_4(\text{SO}_4)_2(\text{OMe})_4(\text{MeOH})_2] (5) \text{ and } [\text{HNEt}_3][\text{Fe}_6\text{O}_2(\text{Et-sao})_4(\text{SO}_4)_2(\text{OMe})_4(\text{MeOH})_2] (6) \]

all are built from a series of edge-sharing [Fe₄₁(μ₄-O)]²⁺ tetrahedra. Complexes 1 and 2 display a new μ₄-coordination mode of the oxime ligand and join a small group of Fe-phenolic oxime complexes with nuclearity greater than six.

Introduction

Polymetallic clusters of iron are being synthesised and studied for a host of reasons. In bioinorganic chemistry, for example, they have been employed as models for iron-containing enzymes such as methane monoxygenase and hemerythrin which both contain diiron cores, whilst the formation of larger oxy-hydroxy stabilised molecules can give insight into the formation and function of Ferritin, a protein containing up to ~4500 Fe centres that stores and regulates iron in living organisms.¹⁻³ The presence of five unpaired electrons in high spin Fe³⁺ ions also makes them attractive for making magnetically interesting complexes, and the triangular [Fe₃O]⁷⁺ and tetrahedral [Fe₄O]¹⁰⁺ building blocks common to the cores of many polymetallic Fe³⁺ cluster compounds are at the origin of a variety of phenomena such as spin glass behaviour or the appearance of unusual jumps and plateaus in the field-dependence of the magnetisation observed in antiferromagnetic [Fe₃] triangles, [Fe₆] Keggin ions and [Fe₉] icosidodecahedra – properties reminiscent of those observed in extended frustrated lattices such as the Kagomé lattice.⁴⁻⁵ An added effect of spin frustration is the presence of degenerate or low-lying excited spin states, a property that can be exploited in low-temperature magnetic refrigeration,⁸ with clusters such as [Fe₄] displaying an enhanced magnetocaloric effect.⁹⁻¹⁰

Salicylaldoxime ligands (Fig. 1) have been studied extensively for their use in extractive hydrometallurgy, showing great selectivity for Cu²⁺ and accounting for approximately 25% of the world’s copper production.¹¹⁻¹³ Our research into Fe-salicylaldoximate complexes is fuelled not only by an interest in their magnetic properties, but also due to their role as anti-corrosives in protective coatings, where phenolic oximes have been used to treat lightly oxidised Fe surfaces.¹⁴ It is postulated that the corrosion inhibition is due to the formation of polynuclear complexes on the surface and thus an extensive knowledge of the coordination chemistry of such ligands with Fe would tell us more about possible modes-of-action of the corrosion inhibition ability of the ligands. Herein we report the syntheses, structures and magnetic behaviour of four hexa- and two octametallic iron complexes built with the derivatised salicylaldoxime ligands Me-saoH₂ (2-hydroxyethanone oxime) and Et-saoH₂ (2-hydroxypropiophenone oxime).

Fig. 1 General structure of the (derivatised) salicylaldoxime ligands. Me-saoH₂, R¹ = Me and R², R’ = H; Et-saoH₂, R¹ = Et and R’ and R² = H.
Experimental

Syntheses

All manipulations were performed under aerobic conditions using chemicals as received, unless otherwise stated. 2-Hydroxyethanone oxime (Me-saoH₂) and 2-hydroxypropionophenone oxime (Et-saoH₂) were synthesised via the reaction of the appropriate ketone with hydroxylamine and sodium acetate in EtOH, as described in the literature. Complex 5 has been reported previously but is included here to aid discussion.

\[
\text{[Fe}_8\text{O}_2\text{(OMe)}_4\text{(Me-sao)}_6\text{Br}_4\text{(py)}_4\text{](1-2Et}_2\text{O-MeOH)}
\]

FeBr₃ (148 mg, 0.50 mmol) and Me-saoH₂ (226.5 mg, 1.50 mmol) were dissolved in MeOH (25 ml) in the presence of pyridine (2 ml). The dark red solution was stirred for 2 h, filtered and then diffused with Et₂O, producing X-ray quality crystals of 1 after 1 week, in approximately 20% yield. Elemental analysis found (calc.%) for C₄₁H₉₈Br₄Fe₈N₁₀O₂₁: C 41.73 (42.04), H 4.16 (4.27), N 5.97 (6.05).

\[
\text{[Fe}_8\text{O}_2\text{(OMe)}_4\text{(Me-sao)}_6\text{(Et-sao)}_2\text{(SO}_4)_2\text{(MeOH)}_2\text{](6)}
\]

The synthesis was identical to 5 using Et-saoH₂ (165 mg, 1.00 mmol) instead of Me-saoH₂. The yield was approximately 30%. Elemental analysis found (calc.%) for C₄₆H₆₁Cl₂Fe₆N₆O₇S₂: C 40.38 (40.42), H 5.24 (5.53), N 5.20 (5.24).

Physical measurements

Elemental analyses (C, H, N) were performed by the EaStCHEM microanalytical service. Variable temperature magnetic susceptibility measurements were made on powdered polycrystalline samples restrained in eicosane using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. Diamagnetic corrections were applied using Pascal's constants.

Results and Discussion

Synthesis

Reacting FeBr₃ with Me-saoH₂ in a 1 : 3 ratio in a MeOH–pyridine solution yields the octanuclear complex [Fe₈O₂(OMe)₄(Me-sao),Br₄(py)₄](1), which has a metallic skeleton of two edge-sharing [Fe₄O] tetrahedra, edge-capped by two additional Fe⁺⁺ ions. The oxime ligand displays a μ₄-bridging mode – the first time this has been observed. We can replace the terminal bromide ligands with terminal azides by simply introducing NaN₃ into the reaction mixture. This also has the effect of partially substituting the μ₄-bridging oximes with an end-on μ₃-azide bridge affording the complex [Fe₈O₂(OMe)₄(Me-sao),Cl₂(py)₂](2).

Further attempts to fully substitute the μ₄-bridging oximes have proved unsuccessful, even when employing a large excess of NaN₃. Attempts to repeat these reactions with other iron halide salts have proved unsuccessful, even when employing a large excess of NaN₃. It is interesting to note that (in Fe⁺⁺ chemistry) only two examples of end-on bridging azides appear in the CCDC database – and both display ferromagnetic exchange coupling between the Fe⁺⁺ centres.

Introducing carboxylates (in the form of Na₃O₃C₄H₄N₃O₆) to the reaction of FeCl₃·6H₂O and Me-saoH₂ in a 1 : 1 ratio in a MeOH–py solution leads to the related but lower nuclearity hexanuclear complex [Fe₆O₂(OMe)₄(C₄H₄O₄)₄(Me-sao),Cl₂(py)₂](3). The core again consists of two edge-sharing tetrahedra but the replacement of the μ₃-bridging oximes with μ₃-bridging carboxylates prevents the addition of two additional edge-capping Fe⁺⁺ ions. Repeating the same reaction with Et-saoH₂ instead of Me-saoH₂ simply gives the analogous compound, [Fe₆O₂(OMe)₄(C₄H₄O₄)₄(Et-sao),Cl₂(py)₂](4). Despite many attempts, we failed to isolate compounds with carboxylates other than 4-NO₂-benzoate. It is unclear why this should be so, but we presume it to be due to the steric bulk of the 4-substituent and/or the stabilising inter-molecular interactions propagated between neighbouring NO₂ groups (vide infra).

The introduction of co-ligands, such as carboxylates, thus appears to favour the formation of smaller clusters and...
The shared edge of the tetrahedra is equivalent (s.e.) with the Fe1–Fe3 and symmetry of two edge-sharing tetrahedra (Fe1–Fe2–Fe2 molecules in the unit cell (Fig. 2). The metallic skeleton consists of Me-sao2 bridges from the presence of NEt3 in MeOH produces the hexanuclear complex.

<table>
<thead>
<tr>
<th>Crystallographic details for complexes 1–4, 6</th>
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<td>M/g mol⁻¹</td>
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<td>R₁, wR₂</td>
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<td>Goodness of fit</td>
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* R1 = Σ(|Fobs| - |Fcalc|)/Σ(|Fobs|) for observed reflections. b wR2 = [Σ[w(F₂)² - |Fcalc|²])/Σ[w(F₂)²]¹/²] for all data.

μ-coordination of the phenolic oxime. This is corroborated when sulfate anions are introduced to the reaction mixture. The reaction of Fe₂(SO₄)₃·6H₂O with Me-saoH or Et-saoH in the presence of NEt₃ in MeOH produces the hexanuclear complexes [HNEt₃]₂[Fe₂O₅(Me-sao)₄(SO₄)₂](OMe)₂(MeOH)] (5) and [HNEt₃]₂[Fe₂O₅(Et-sao)₄(SO₄)₂](OMe)₂(MeOH)] (6). The metallic core of both (analogous) molecules again comprises two edge-sharing [Fe₅O₈] tetrahedra but on this occasion each tripodal SO₄²⁻ anion caps one of the triangular faces of the tetrahedron, preventing further growth.

Description of structures

Complex 1 crystallises in the trigonal space group R3 with nine molecules in the unit cell (Fig. 2). The metallic skeleton consists of two edge-sharing tetrahedra (Fe1–Fe2–Fe2–Fe3 and symmetry equivalent, s.e.) with the Fe1…Fe3 (and s.e.) vertices capped by another Fe³⁺ ion (Fe4). The shared edge of the tetrahedra is defined by Fe2–Fe2 molecules in the unit cell (Fig. 2). This tetranucleating motif of the salicylaldoxime may provide an explanation for how such ligands attach to lightly corroded iron surfaces when they are used as anti-corrosives.¹⁴

There are two symmetry inequivalent OMe⁻ ions: one bridges the edge-capping peripheral Fe³⁺ ion (Fe4) to the central tetrahedron (Fe3), and the other bridges across one edge of the central tetrahedron (Fe1–Fe2 and s.e.). Each Fe³⁺ ion is in a distorted octahedral geometry (cis, 74.3(1)-107.1(1°); trans, 156.4(1)-177.12(7)°) with FeO₅N (Fe2, Fe3), FeO₅Br (Fe1) and FeO₅N,Br (Fe4) coordination spheres. The remaining coordination sites on Fe1, Fe3 and Fe4 are filled with a combination of terminally bonded Br⁻ ions and/or pyridine molecules.

In the crystal, the molecules interact through two complementary C–H…π interactions [C5E–H5E…π] (C1A, C2A, C3A, C4A).
C4A, C5A, C6A), C⋯centroid 3.543 Å, C–H⋯centroid 124°] to form one-dimensional (1D) chains running along the c-axis (Fig. 3). Despite the absence of any other inter-molecular hydrogen bonds or π⋯π interactions [the closest inter-molecular contacts being between the phenyl ring of the μ1-Me-sao2− ligand and a neighbouring pyridine molecule (C⋯C, 3.321(7) Å) and between methyl and phenyl groups on opposing μ1-Me-sao2− ligands (C⋯C, 3.362(5) Å)], when viewed down the c-axis the chains of 1 pack in groups of three around the three-fold screw axes (either left or right handed) imposed by the rhombohedral lattice to create large hexagonal cavities approximately 11 Å in diameter (Fig. 3).

Complex 2 crystallises in the monoclinic space group P21/c with two molecules in the unit cell. The molecule differs only slightly from 1. Besides the small changes in bond lengths and angles, the obvious differences are the replacement of the terminal bromide ions with terminally bonded azide ligands and the partial replacement of a μ1-OMe− bridge with an end-on μ1-N3− bridge (15% on Fe1–Fe2). This is an interesting observation since the introduction of end-on bridging azides to Fe4+ cluster chemistry is likely to produce molecules exhibiting ferromagnetic nearest neighbour exchange.17,18 All Fe4+ ions have distorted octahedral geometries with cis angles in the range 74.09(9)–107.78(9)° and trans angles in the range 156.75(9)–179.4(1)°. There are no inter-molecular hydrogen bonds in the extended lattice with the closest contacts being between the phenyl ring of the μ1-Me-sao2− ligand and a neighbouring pyridine molecule (C⋯C, 3.370(5) Å).

Complex 3 (Fig. 4) crystallises in the triclinic space group P1 with three molecules in the asymmetric unit and two asymmetric units in the unit cell. The metallic core consists of two edge-sharing (Fe3–Fe4) tetrahedra (Fe1, Fe3, Fe4, Fe5 and Fe2, Fe3, Fe4, Fe6), each housing a central μ1-O2− ion (O134, O234). The two tetrahedral subunits are joined together by the two η1:η1:η1:μ1-Me-sao2− ligands bridging Fe1–Fe2 through their oximic NO moieties. The μ1-oximic O-atom of one then bridges Fe1–Fe4 while the other bridges Fe2–Fe3. The four μ1-O,CPh2-NO− ligands bridge the remaining vertices, the carboxylates bridging Fe2–Fe3, Fe3–Fe5, Fe4–Fe5 and Fe4–Fe6 in their familiar syn, syn, μ-mode and the μ1-OMe− bridging Fe1–Fe5, Fe2–Fe3, Fe3–Fe5 and Fe4–Fe6. The two remaining coordination sites on Fe5 and Fe6 are both occupied with one pyridine molecule and one halide ligand. Each Fe4+ ion is a distorted octahedral geometry (cis, 77.9(1)–103.9(1)°; trans, 157.6(1)–177.7(1)°) with FeO6 (Fe3, Fe4), FeO,N (Fe1, Fe2) and FeO,NCl (Fe5, Fe6) coordination spheres. In the crystal there are a number of inter-molecular interactions propagated through neighbouring 4-NO2 groups of the carboxylates (O⋯O, 3.011(4)–3.184(4) Å), as well as between the chloride ions and neighbouring pyridine molecules (Cl⋯C, 3.400(6) Å).

Complex 4 crystallises in monoclinic P21/c space group with four molecules in the unit cell. 4 differs from 3 only in the identity of the phenolic oxime, Et-sao2− replacing Me-sao2− and the intramolecular bond lengths and angles are very similar in both compounds. In the crystal lattice there are inter-molecular hydrogen bonds between the 4-NO2 group of carboxylate ligands and MeOH solvent molecules (O⋯C, 3.00(1) Å), with the shortest contact between neighbouring cluster molecules (3.40(1) Å) being between C-atoms on the phenyl rings of adjacent carboxylate and Me-sao2− ligands.

Complex 6 (Fig. 5) crystallises in the orthorhombic space group Pbca with four molecules in the unit cell. Its structure is analogous to that of 5 (but containing Et-sao2− rather than Me-sao2−), which we have reported in a previous paper.16 6 is another
example of an [Fe$^{III}$] cluster whose metallic core describes two edge sharing tetrahedra. The common edge is Fe1–Fe1' with an inversion centre at its midpoint. The tetrahedra are built upon edge sharing tetrahedra. The common edge is Fe1–Fe1.

An examination of the extended lattice reveals short contacts between the NEt$_4$ ions (O123 and s.e.) and connected via four μ-OMe ions (O1A, O14 and s.e.) creating a [Fe$_6$O$_2$(OMe)$_4$]$^{10+}$ core similar to that observed in 3 and 4. The μ:μ:μ:μ:μ-SO$_4$ ligands cap the Fe1–Fe2–Fe3 (and s.e.) triangular face of a tetrahedron, whilst the four μ:μ:μ:μ-Me-sao$_2$ ligands bridge the Fe1–Fe2 and Fe1–Fe3 (and s.e.) edges. The remaining coordination sites on Fe1 and Fe1' are filled by terminal MeOH molecules. The Fe$^{II}$ ions have FeO$_6$ (Fe1) or FeO$_5$N coordination spheres and lie in distorted octahedral geometries with cis angles in the range 76.9(2)–108.1(2)$^\circ$ and trans angles in the range 152.6(2)–175.4(2)$^\circ$. An examination of the extended lattice reveals short contacts between the NEt$_4^+$ cation and the SO$_4^{2-}$ (N···O, 2.82(1) Å), with the closest distances between neighbouring clusters being between the phenyl ring of the Et-sao$_2$ ligand and a SO$_4^{2-}$ O-atom (C···O, 3.412(8) Å). There are also intra-molecular H-bonds present – between a terminally bonded MeOH molecule and an oximic O-atom (O···O, 2.737(6) Å). A scheme depicting the observed bridging modes of the R-sao$_2$ ligands is given in Fig. 6.

Discussion

There are now a number of Fe$^{III}$/R-saoH$_2$ clusters in the literature (Table 2). They range in size ($\leq$ [Fe$_{12}$]) and structure, but there are undoubtedly some pervading themes. The body of published work in this area (Table 2) clearly shows that, akin to Mn$^{III}$/R-saoH$_2$ chemistry, the [Fe($\mu$-O)]$^{1+}$ triangle is the most frequently encountered building block. The related tetrahedral subunit [Fe$_6$(μ$_4$-O)]$^{20+}$ is the next most common, and this has no counterpart in Mn$^{III}$ chemistry. The variance in size of the [Fe$_x$] cluster can be attributed to a number of factors, including the presence or absence of co-ligand (here carboxylates and sulfates) and the steric bulk of the ketoxime group. This is another area in which we see a difference in comparison with the Mn$^{III}$ chemistry, where all of the above have little or no effect upon the products of the reaction.

The addition of (relatively large) bridging co-ligands tends to favour smaller nuclearity clusters (they edge- and face-cap preventing further growth) and encourages the μ-bridging mode of the phenolic oxime. In the absence of such co-ligands higher order bridging modes of R-sao$_2$ are seen (and higher nuclearity clusters as a consequence) and in complexes 1 and 2 the μ-bridging mode is seen for the very first time. The bridging modes depicted in Fig. 5 thus offer some insight into possible ligand bonding modes on lightly corroded iron surfaces when salicylaldoximes are used as anti-corrosives.

Variations in the bulk of the ketoxime group can also change the topology of the cluster greatly in Fe$^{III}$ chemistry, whereas in Mn$^{III}$ chemistry the [M$_3$O(R-sao)$_3$]$^{1+}$ unit is almost always retained and the only differences observed appear to be in the twisting of the Mn–N–O–Mn torsion angles. For example, both complex 1 and [Fe$_6$O(OMe)(Ph-sao)$_2$]Br$_3$(py)$_4$Et$_2$O$_{27}$ are made by reacting FeBr$_3$ with the appropriate R-saoH$_2$ pro-ligand in a MeOH–pyridine solvent mix. The bulky Ph-sao$_2$ ligand restricts the size of the cluster to an [Fe$_3$] entity, but the Me-sao$_2$ ligand allows the growth of an octametallic cluster, [Fe$_8$].

When employing carboxylates in Fe$^{III}$/R-saoH$_2$ chemistry one might expect the structures to resemble the basic Fe$^{II}$ carboxylates of general formula [Fe$_x$O$_y$(O$_{2}$CR)$_z$L$_y$]$^{1-}$ (L = solvent) in which μ$_{2,3}$-bridging R-sao$_2$ ligands simply replace the μ-bridging carboxylates. Indeed this is true in [Fe$_3$] clusters where the [Fe$_6$(μ$_4$-O)]$^{1+}$ building block predominates, and the μ$_3$-bridging oxime promotes oligomerisation of the basic triangles. Complexes 3 and 4 differ, the major change in reaction conditions being the introduction of pyridine. This results in the formation of a cluster adopting a metallic skeleton comprising two edge-sharing tetrahedra. Pyridine is present in excess and thus acts as base, ligand and co-solvent – a strategy that has been shown previously to aid the growth of very large mineral-like Fe$^{III}$ clusters.

Magnetism

Direct current (dc) magnetic susceptibility measurements were performed on microcrystalline samples of representative 1 and 3 in a field of 0.1 T and in the 5–300 K temperature range. The magnetic behaviour of complex 5 is analogous to that of complex 6 which we have reported before, so will not be repeated here. For 1 (Fig. 7) the room temperature $\chi_M$T value of 12.38 cm$^3$ K mol$^{-1}$ is significantly below the value of 35 cm$^3$ K mol$^{-1}$ expected for eight non-interacting high spin ($S = 5/2$) Fe$^{III}$ ions, indicative
The room temperature $\chi_m T$ value of complex 3 is $11.23 \text{ cm}^3 \text{ K mol}^{-1}$, lower than the expected value for six non-interacting Fe$^{3+}$ ions (26.25 cm$^3$ K mol$^{-1}$). The $\chi_m T$ value then decreases constantly with decreasing temperature to a value of 0.25 cm$^3$ K mol$^{-1}$. This is again indicative of antiferromagnetic exchange interactions between the Fe$^{3+}$ ions and the stabilisation of a diamagnetic ground state. A Curie–Weiss analysis of the $1/\chi_m$ vs. $T$ plot affords $\theta = -386$ K. The complex nature of the structures precludes fitting of the susceptibility data by standard procedures. Of the thirty two complexes listed in Table 2 only two structural types (and a total of eight molecules) have been reported to possess non-zero spin ground states – the [Fe$_3$] triangles and [Fe$_4$] tetrahedra. Both are the result of spin frustration effects. This paper
Conclusions

The two hexa- and four octa-metallic Fe$^{3+}$ salicylaldiminato clusters presented here all have a common building block, the tetrahedral [Fe$_2$O]$^{8+}$ moiety. Each contains a central core of two such edge-sharing tetrahedra, with 1 and 2 having two vertices additionally capped by Fe$^{3+}$ ions, as a result of a unique μ$_2$-Me-sao$^-$ coordination mode. In contrast to Mn$^{3+}$ complexes, the self-assembly of these Fe$^{3+}$ molecules – and the coordination mode of the phenolic oxime ligand – appears to be highly dependent upon the presence of co-ligands and the steric bulk of the ketoxime group. The magnetic behaviour of all complexes is [perhaps unsurprisingly] dominated by relatively strong antiferromagnetic exchange interactions, as seen for almost all reported Fe$^{3+}$/R- exchange interactions. It suggests targeting both azide-based clusters and highly symmetric assembly of these Fe$^{3+}$ molecules – and the coordination mode of the partial replacement of a μ$_2$-OMe$^-$ ion with an end-on μ-N$_3^-$ ion, and the symmetric cores of complexes 5 and 6, suggests targeting both azide-based clusters and highly symmetric complexes, since they may pave the way for isolating compounds displaying frustration effects, and/or ferro- or ferrimagnetic exchange interactions.

Notes and References

8 M. Evangelisti and E. K. Brechin, Dalton Trans., 2010, 39, 4672.
13 P. J. Mackey, CMM Mag., 2007, 2, 35.