Building Fe(III) clusters with derivatised salicylaldoximes[†]

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Received 17th November 2009, Accepted 6th January 2010 First published as an Advance Article on the web 3rd February 2010 DOI: 10.1039/b924143d

The syntheses, structures and magnetic properties of nine new iron complexes containing salicylaldoxime (saoH₂) or derivatised salicylaldoximes (R-saoH₂), [Fe₃O(OMe)(Ph-sao)₂ Cl₂(py)₃]·2MeOH (1·2MeOH), [Fe₃O(OMe)(Ph-sao)₂Br₂(py)₃]·Et₂O (**2**·Et₂O), [Fe₄(Ph-sao)₄F₄(py)₄]·1.5MeOH (**3**·1.5MeOH), [Fe₆O₂(OH)₂(Et-sao)₂(Et-saoH)₂(O₂CPh)₆] (**4**), [HNEt₃]₂[Fe₆O₂(OH)₂(Et-sao)₄(O₂CPh(Me)₂)₆]·2MeCN (**5**·2MeCN), [Fe₆O₂(O₂CPh)₁₀(**3**-'But-5-NO₂-sao)₂(H₂O)₂]·2MeCN (**6**·2MeCN), [Fe₆O₂(O₂CCH₂Ph)₁₀(**3**-'But-sao)₂(H₂O)₂]·5MeCN (**7**·5MeCN), {[Fe₆Na₃O(OH)₄(Me-sao)₆(OMe)₃(H₂O)₃(MeOH)₆]·MeOH}n (**8**·MeOH) and [HNEt₃]₂[Fe₁₂Na₄O₂(OH)₈(sao)₁₂(OMe)₆-(MeOH)₁₀] (**9**) are discussed. The predominant building block appears to be the triangular [Fe₃O(R-sao)₃]⁺ species which can self-assemble into more elaborate arrays depending on reaction conditions. An interesting observation is that the R-saoH⁻/R-sao²⁻ ligand system tends to adopt coordination modes similar to carboxylates. The most unusual molecule is the [Fe₄F₄] molecular square, **3**. While Cl⁻ and Br⁻ appear to act only as terminal ligands, the F⁻ ions bridge making a telling impact on molecular structure and topology.

Introduction

Salicylaldoxime ligands have been studied extensively for their use in extractive hydrometallurgy.¹ They show great selectivity for Cu(II) in particular and account for a quarter of the world's copper production.^{2,3} This selectivity is due to the size of the cavity created by two singly deprotonated phenolic oximes hydrogen bonding to form a pseudomacrocyclic arrangement (Chart 1) which provides an almost ideal fit for the square planar Cu²⁺ ion. Once a phenolic oxime has been doubly deprotonated however, it has the possibility to bind through the phenolate oxygen, the oxime nitrogen and the oximato oxygen, giving great potential for polynuclear complex formation and, as a consequence, a large number of complexes of metals such as Mn,⁴⁻¹² Co,^{4,13,14} Ni,^{4,13} and Fe have been reported.^{4,15-24}



Chart 1 The pseudo-macrocyclic structure formed by mono-deprotonated phenolic oxime copper extractants.

The coordination chemistry of Mn^{III} with such ligands has been extensively studied for its relevance to the field of single molecule magnetism, resulting in many structures with remarkable properties. The coordination chemistry of salicylaldoximates with Fe^{III} has been less extensively reported - a CCDC search reveals only nineteen Fen+-salicylaldoximate complexes with nuclearities ranging from 2-8.15-24 Our interest in Fe-salicylaldoximate complexes is in part due to their role as anti-corrosives in protective coatings. Phenolic oximes have been used to treat lightly oxidised Fe surfaces and it is postulated that the corrosion inhibition is due to the formation of polynuclear complexes on the surface.²⁴ An extensive knowledge of the coordination of such ligands with Fe would tell us more about possible modes-of-action of the corrosion inhibition ability of the ligands. There is also potential for the complexes to have large spin ground states due to the relatively large spin of the Fe^{III} ion (s = 5/2) which could have application in molecular magnetism. The aim of this work therefore is to expand the current family of Fe-salicylaldoxime structures and investigate the coordination modes and magnetism of the complexes based on the ligands shown in Scheme 1.



Scheme 1 General structure of derivatised salicylaldoximes where for $saoH_2$, Me-saoH₂, Et-saoH₂, Ph-saoH₂ ($R_1 = H$, Me, Et and Ph respectively and $R_2 = H$); and for 'But-saoH₂ ($R_1 = H$ and $R_2 =$ 'But).

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[†] Electronic supplementary information (ESI) available: Additional data. CCDC reference numbers 755035, 755036, 755037, 755038, 755039, 755040, 755041, 755042 and 755043. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b924143d

Syntheses

All manipulations were performed under aerobic conditions using chemicals as received, unless otherwise stated.

Caution

Care should be taken when using the potentially explosive perchlorate salts. 2-Hydroxyacetophenone oxime (Me-saoH₂), 2-hydroxypropiophenone oxime (Et-saoH₂) and 2-hydroxybenzophenone oxime (Ph-saoH₂) were synthesised *via* the reaction of the appropriate ketone with hydroxylamine and sodium acetate in EtOH, as described in the literature.²⁵

[Fe₃O(OMe)(Ph-sao)₂Cl₂(py)₃]·2MeOH (1·2MeOH)

FeCl₃·6H₂O (405 mg, 1.50 mmol) and Ph-saoH₂ (213 mg, 1.00 mmol) were dissolved in a mixture of MeOH (25 ml) and pyridine (5 ml). After 120 mins stirring the solution was filtered and left to evaporate slowly, producing X-ray quality crystals after 3 days in approximately 50% yield. The dried sample analysed as 1·MeOH. Found (calc.%): $C_{43}H_{40}Cl_2Fe_3N_5O_7$; C 52.39 (52.85), H 3.91 (4.13), N 7.45 (7.17). IR data (KBr pellet; cm⁻¹): 1593 s, 1557 m, 1514 m, 1487 s, 1429 s, 1314 s, 1249 m, 1148 m, 1037 s, 959 s, 855 m, 758 s, 699 s, 665 s, 582 m, 462 m.

[Fe₃O(OMe)(Ph-sao)₂Br₂(py)₃]·Et₂O (2·Et₂O)

FeBr₃ (296mg, 1.00 mmol) and Ph-saoH₂ (213 mg, 1.00 mmol) were dissolved in a mixture of MeOH (25 ml) and pyridine (5 ml). After 120 mins stirring the solution was filtered and diffused with Et₂O, producing X-ray quality crystals after 2 weeks in approximately 30% yield. The dried sample analysed as **2**. Found (calc.%): $C_{42}H_{36}Br_2Fe_3N_5O_6$; C 49.15 (48.78), H 3.94 (3.51), N 6.55 (6.77). IR data (KBr pellet; cm⁻¹): 1592 s, 1558 m, 1514 m, 1487 s, 1428 s, 1310 s, 1248 m, 1148 m, 1037 s, 958 s, 854 m, 758 s, 700 s, 665 s, 582 m, 462 m.

[Fe4(Ph-sao)4F4(py)4]-1.5MeOH (3-1.5MeOH)

FeF₃·3H₂O (167 mg, 1.00 mmol) and Ph-saoH₂ (213 mg, 1.00 mmol) were dissolved in a mixture of MeOH (25 ml) and pyridine (5 ml). After 180 mins stirring, the solution was filtered and left to evaporate slowly, producing X-ray quality crystals after 1 week, in approximately 30% yield. The dried sample analysed as **3**. Found (calc.%): $C_{72}H_{56}F_4Fe_4N_8O_8$; C 58.95 (59.21), H 3.47 (3.86), N 7.45 (7.67). IR data (KBr pellet; cm⁻¹): 1592 s, 1560 m, 1521 m, 1488 m, 1433 s, 1319 s, 1255 m, 1147 m, 1039 s, 957 s, 855 m, 750 s, 696 s, 660 s, 546 m, 460 m.

$[Fe_6O_2(OH)_2(Et-sao)_2(Et-saoH)_2(O_2CPh)_6] (4)$

FeCl₃·6H₂O (135 mg, 0.5 mmol), Et-saoH₂ (82.5 mg, 0.5 mmol), NaO₂CPh (216 mg, 1.5 mmol) were dissolved in MeCN (25 ml) in the presence of NEt₃ (0.25 ml, 0.2 mmol) and heated to 50 °C. After 90 mins stirring the solution was filtered and then layered with Et₂O to produce X-ray quality crystals in 2 weeks. The crystals were collected by filtration and dried *in vacuo*. The yield was approximately 55%. The dried sample analysed as **4**.

Found (calc.%): $C_{84}H_{85}Fe_6N_5O_{24}$; C 53.87 (53.56), H 4.72 (4.55), N 3.96 (3.72). IR data (KBr pellet; cm⁻¹): 1599 s, 1560 s, 1400 s, 1313 m, 1254 m, 1070 m, 1016 m, 935 m, 839 m, 752 m, 717 s, 671 m, 638 m, 586 m, 513 m, 467 s.

[HNEt₃]₂[Fe₆O₂(OH)₂(Et-sao)₄(O₂CC₆H₃(Me)₂)₆]·2MeCN (5· 2MeCN). FeCl₃·6H₂O (270 mg, 1.0 mmol), Et-saoH₂ (165 mg, 1.0 mmol) and NaO₂CC₆H₃(Me)₂ (sodium 3,5-dimethylbenzoate, 158 mg, 1.0 mmol) were dissolved in MeCN (30 ml) in the presence of NEt₃ (1.0 ml, 8.0 mmol) and heated to 50 °C. After 120 mins stirring the solution was filtered and the solution left to evaporate slowly at room temperature. X-ray quality crystals formed in 2 weeks. The crystals were collected by filtration and dried *in vacuo*. The yield was approximately 30%. The dried sample analysed as 5·MeCN. Found (calc.%): $C_{104}H_{127}Fe_6N_7O_{24}$; C 56.49 (56.93), H 5.81 (5.83), N 4.72 (4.47). IR data (KBr pellet; cm⁻¹): 1568 s, 1431 s, 1398 s, 1309 m, 1267 m, 1076 m, 1053 m, 931 m, 841 m, 789 m, 752 s, 648 m, 598 m, 509 m, 465 s.

$[Fe_6O_2(O_2CPh)_{10}(3-^tBut-5-NO_2-sao)_2(H_2O)_2]$ ·4MeCN (6·4MeCN)

 $[Fe_3O(O_2CPh)_6(H_2O)_3]NO_3 (500 mg, 0.48 mmol) and 'But-saoH_2 (94 mg, 0.48 mmol) were dissolved in MeCN (25 ml). After 120 min stirring the solution was filtered and left to evaporate slowly producing X-ray quality crystals after 1 week in approximately 30% yield. The dried sample analysed as$ **6** $·MeCN. Found (calc.%): <math>C_{92}H_{78}Fe_6N_4O_{32}$; C 52.69 (52.95), H 3.74 (3.77), N 2.87 (2.68). IR data (KBr pellet; cm⁻¹): 1599 s, 1554 s, 1493 s, 1408 s, 1306 s, 1176 m, 1113 m, 1026 m, 843 m, 717 s, 673 m, 615 m, 480 s.

[Fe₆O₂(O₂CCH₂Ph)₁₀(3-^tBut-sao)₂(H₂O)₂]·5MeCN (7·5MeCN)

 $[Fe_3O(O_2CCH_2Ph)_6(H_2O)_3]NO_3 (100 mg, 0.09 mmol) and 3-¹But$ $saoH_2 (18 mg, 0.09 mmol) were dissolved in MeCN (25 ml). After$ 180 mins stirring the solution was filtered and left to evaporateslowly producing X-ray quality crystals after 1 week in approximately 30% yield. The dried sample analysed as 7·MeCN. Found(calc.%): C₁₀₂H₁₀₀Fe₆N₂O₂₈; C 56.98 (57.33), H 4.25 (4.72), N 1.68(1.31). IR data (KBr pellet; cm⁻¹): 1576 s, 1496 m, 1410 s, 1298 m,1194 m, 999 m, 962 m, 876 m, 752 m, 727 m, 642 m, 575 m, 546 m,501 m.

Method 1. Fe(ClO₄)₂·6H₂O (182.5 mg, 0.5 mmol), Me-saoH₂ (151 mg, 1.0 mmol) and NaO₂CHCl₃ (185 mg, 1.0 mmol) were dissolved in MeOH (25 ml) in the presence of NEt₃ (1.0 ml, 8 mmol). After 180 mins stirring the solution was filtered and then left to evaporate slowly, producing X-ray quality crystals in 4 days. The crystals were collected by filtration and dried *in vacuo*. The yield was approximately 65%. The dried sample analysed as **8**. Found (calc.%): C₅₇H₈₄Fe₆Na₃N₆O₂₉; C 39.43 (39.77), H 4.54 (4.92), N 5.18 (4.88). IR data (KBr pellet; cm⁻¹): 1630 m, 1593 m, 1568 m, 1531 m, 1473 m, 1435 s, 1306 s, 1250 m, 1130 m, 1024 s, 962 m, 856 m, 752 s, 665 s, 611 m, 449 m, 415 m.

Method 2. $Fe(O_2CMe)_2 \cdot 6H_2O(174 \text{ mg}, 1.0 \text{ mmol})$, Me-sao H_2 (151 mg, 1.0 mmol) and NaOMe (324 mg, 6.0 mmol) were dissolved in MeOH (25 ml). After 120 mins stirring the solution was filtered and then left to evaporate slowly, producing X-ray

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	1.2MeOH	$2 \cdot Et_2O$	3.1.5MeOH	4	5.2MeCN	6.4MeCN	7	8	9	
M, g mol ⁻¹	1009.29	1108.25	1508.71	1835.66	2235.32	2250.90	2342.26	1753.41	3262.67	
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Hexagonal	Monoclinic	
Space group	$P 2_1/c$	$P 2_1/c$	$P 2_1/c$	P-1	$P 2_1/c$	P-1	$P 2_1/c$	P63/m	$P2_1/c$	
a/Å	14.2027(3)	14.6095(5)	26.0878(16)	12.8061(8)	14.6892(6)	12.272(5)	13.8956(6)	12.40610(10)	23.1511(7)	
b/Å	18.0542(4)	18.2293(6)	20.7755(12)	13.5584(9)	19.6643(9)	14.458(4)	18.6592(8)	12.40610(10)	13.5740(4)	
c/Å	18.0473(4)	18.2766(6)	27.5991(17)	14.0247(9)	19.2762(9)	16.754(7)	21.4730(9)	28.8478(6)	23.7570(8)	
α (°)	90	90	90	71.209(4)	90	69.97(8)	90	90	90	
β (°)	98.0570(10)	98.945(2)	115.9810(10)	78.955(4)	104.153(2)	71.74(8)	96.520(2)	90	95.223	
γ (°)	90	90	90	78.812(4)	90	69.68(6)	90	120	90	
$V/Å^3$	4581.98(17)	4808.2(3)	13446.6(14)	2239.6(3)	5399.0(4)	2554.5(16)	5531.5(4)	3845.16(9)	7434.7(4)	
T/K	150	150	150	150	150	173(2)	150	150	150	
Ζ	4	4	8	1	2	1	2	2	2	
$ ho_{ m calc}/ m g~cm^{-3}$	1.463	1.531	1.490	1.322	1.37	1.436	1.406	1.51	1.45	
Crystal shape and colour	Black rod	Black block	Black plate	Black block	Black block	Red rod	Black block	Red block	Dark red block	
Crystal	$0.48 \times 0.15 \times$	$0.66 \times 0.37 \times$	$0.44 \times 0.13 \times$	$0.24 \times 0.11 \times$	$0.20 \times 0.15 \times$	$0.50 \times 0.20 \times$	$0.41 \times 0.17 \times$	$0.38 \times 0.28 \times$	$0.21 \times 0.20 \times$	
size/mm	0.15	0.32	0.07	0.10	0.12	0.50	0.16	0.15	0.15	
μ/mm^{-1}	1.110	2.608	0.923	1.015	0.859	7.366	0.844	1.199	1.227	
unique data	42560	41924	72924	7881	11117	34298	44591	3379	15221	
unique data,	7742	7249	14464	4615	6311	8714	8893	2110	6186	
$(I > 2\sigma(F))$										
R_1 , ^{<i>a</i>} $wR2^b$	0.0636,	0.0421,	0.0803,	0.0617,	0.0536,	0.1084,	0.0935,	0.0297,	0.0753,	
	0.1527	0.1073	0.1741	0.1741	0.1660	0.2984	0.1936	0.0322	0.2685	
goodness of fit	1.142	1.030	1.118	0.9039	0.6354	1.056	1.1351	0.9647	1.4701	
^{<i>a</i>} R1) $\sum (Fo - Fc) / \sum (Fo)$ for observed reflections. ^{<i>b</i>} wR2) { $\sum [w(Fo^2 - Fc^2)_2] / \sum [w(Fo^2)_2]$ } ^{1/2} for all data.										

quality crystals in 3 days. The crystals were collected by filtration and dried *in vacuo*. The yield was approximately 50%. The dried sample analysed satisfactorily as solvent-free **3**.

Method 3. FeCl₃·6H₂O (270 mg, 1.0 mmol), Me-saoH₂ (302 mg, 2.0 mmol) and NaOMe (216 mg, 4.0 mmol) were dissolved in MeOH (25 ml). After 120 mins stirring the solution was filtered and then left to evaporate slowly, producing X-ray quality crystals in 4 days. The crystals were collected by filtration and dried *in vacuo*. The yield was approximately 50%. The dried sample analysed satisfactorily as solvent-free **3**.

Method 4. Fe(ClO₄)₂·6H₂O (182.5 mg, 0.5 mmol), Me-saoH₂ (151 mg, 1.0 mmol) and NaO₂CHBr₃ (319 mg, 1.0 mmol) were dissolved in MeOH (25 ml) in the presence of NEt₄OH (1.0M in water; 0.125 ml, 0.125 mmol). After 120 mins stirring the solution was filtered and then left to evaporate slowly, producing X-ray quality crystals in 3 days. The crystals were collected by filtration and dried *in vacuo*. The yield was approximately 55%. The dried sample analysed satisfactorily as solvent-free **3**.

[HNEt₃]₂[Fe₁₂Na₄O₂(OH)₈(sao)₁₂(OMe)₆(MeOH)₁₀] (9)

Fe(ClO₄)₂·6H₂O (365 mg, 1.0 mmol), saoH₂ (137 mg, 1.0 mmol) and NaO₂CCBr₃ (319 mg, 1.0 mmol) were dissolved in MeOH in the presence of NEt₃ (0.125 ml, 1 mmol). After 180 mins stirring the solution was filtered and then left to evaporate slowly producing X-ray quality crystals in 3 days. The crystals were collected by filtration and dried *in vacuo*. The yield was approximately 30%. The dried sample analysed as **9**. Found (calc.%): C₁₁₂H₁₅₆Fe₁₂Na₄N₁₄O₅₀; CHN; C 40.92 (41.26), H 4.46 (4.82), N 5.83 (6.01). IR data (KBr pellet; cm⁻¹): 1593 s, 1543 m, 1473 m, 1437 m, 1321 m, 1290 s, 1200 m, 1153 m, 1120 m, 1018 m, 916 s, 818 m, 764 s, 665 m, 607 m.

X-Ray crystallography and structure solution

Diffraction data were collected on a Bruker Smart Apex CCD diffractometer equipped with an Oxford Cryosystems LT device, using Mo radiation. Data collection parameters and structure solution and refinement details are listed in Table 1. Full details can be found in the CIF files provided in the supporting information, along with lists of bond lengths and angles.

Physical measurements

Elemental analyses (C, H, N) were performed by the EaStCHEM microanalysis service. IR spectra were recorded as KBr pellets in the 4000-400 cm⁻¹ range on a JASCO FT/IR-410 spectrometer. Variable temperature magnetic susceptibility measurements were made on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. Data were collected on powdered samples restrained in eicosane to prevent torquing. Diamagnetic corrections were applied using Pascal's constants.

Results and discussion

Synthesis

The reaction of FeCl₃·6H₂O with Ph-saoH₂ in a 3:2 molar ratio in a MeOH/pyridine solution yields the trinuclear complex [Fe₃O(OMe)(Ph-sao)₂Cl₂(py)₃] (1). Repeating the reaction with FeBr₃ in place of FeCl₃·6H₂O affords the bromide analogue [Fe₃O(MeO)(Ph-sao)₂Br₂(py)₃] (2), but the use of FeF₃·3H₂O in the same reaction leads to the tetranuclear complex [Fe₄(Phsao)₄F₄(py)₄] (3), in which the halide ions bridge between metals rather than bonding terminally as in 1 and 2. A combination of the bulky Ph-sao²⁻ ligand and the coordinating pyridine appears to favour the production of low nuclearity complexes, but the introduction of carboxylates tends to favour larger species. For example reaction of FeCl₃·6H₂O with Et-saoH₂ and NaO₂CPh in the presence of NEt₃ yields the hexanuclear complex [Fe₆O₂(OH)₂(Etsao)₂(Et-saoH)₂(O₂CPh)₆] (4). The low ratio of base employed results in 4 containing two singly deprotonated Et-saoH⁻ ligands. Increasing this ratio allows us to fully deprotonate all four ligands yielding the hexanuclear complex [HNEt₃]₂[Fe₆O₂(OH)₂(Et $sao_4(O_2CC_6H_3(Me)_2)_6$ (5). The increase in the amount of base employed also leads to the presence of two bridging hydroxides which link the two triangles (vide infra). This type of structure has been seen in previously reported carboxylate-only [Fe^{III}₆] clusters, suggesting that oximes could potentially be employed as direct replacements for carboxylates in many other known polymetallic Fe-carboxylate clusters.^{19,20} The similarity between the carboxylate coordination in 4 and 5 and the basic Fe(III) carboxylates of general formula $[Fe_3O(O_2CR)_6L_3]^+$ (L = solvent) led to the idea that we could start with pre-made iron carboxylate triangles and replace the carboxylates with oximes, to create similar complexes. Indeed treatment of [Fe₃O(O₂CPh)₆(H₂O)₃]NO₃ with 3-^tBut-saoH₂ yields the complex [Fe₆O₂(O₂CPh)₁₀(3-^tBut-5-NO₂-sao)₂(H₂O)₂] (6). Four carboxylates have been replaced with two oximes which crosslink the two triangles (vide infra), in a manner identical to work previously reported by Boudalis et al.²⁰ A peculiar anomaly in this instance is that the 3-'But-sao²⁻ ligand has undergone an in situ nitration at the 5 position. Although never seen before in our work there is precedent for this in organic literature.^{26,27} Repeating this reaction with [Fe₃O(O₂CCH₂Ph)₆(H₂O)₃]NO₃ yields the analogous complex $[Fe_6O_2(O_2CCH_2Ph)_{10}(3-^tBut-sao)_2(H_2O)_2]$ (7) in which there is no ligand nitration.

The reaction of $Fe(ClO_4)_2 \cdot 4H_2O$ with Me-saoH₂ and NaO₂CCBr₃ and NEt₃ yields the polymeric ([Fe₆Na₃O(OH)₄(Me-sao)₆(OMe)₃(H₂O)₃(MeOH)₆]·MeOH)_n (8·MeOH), in which carboxylate does not feature. This is presumably a result of its highly acidic nature, acting solely as a source of Na. Indeed the complex can also be obtained by introducing the Na⁺ using excess NaOMe. Repeating the reaction but reducing the bulk of the oxime produces the related, but unusual, molecular complex [HNEt₃]₂[Fe₁₂Na₄O₂(OH)₈(sao)₁₂(OMe)₆(MeOH)₁₀] (9).

Description of structures

Complexes 1-9 are shown in Fig. 1-6. Full details of the bond lengths and angles are given in the supplementary information.[†] 1 and 2 are isostructural, differing only in the identity of the halide and so here we describe only complex 1 (Fig. 1) in detail. This crystallises in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. It consists of a $[Fe^{III}_{3}(\mu_{3}-$ O)] triangular unit where the Fe1-Fe2 and Fe1-Fe3 edges are each bridged by a fully deprotonated Ph-sao²⁻ ligand in a $\eta^1:\eta^1:\mu_2$ fashion. The Fe2-Fe3 edge is bridged by one µ-MeO⁻ ion (Fe2-O1F-Fe3, 98.84(13)°). The remaining coordination sites on Fe1 are occupied by three pyridine molecules. Fe2 and Fe3 are five coordinate and the remaining site in each is occupied by a halide (1 = Cl, 2 = Br). The Fe \cdots Fe separations and Fe- μ_3 -O-Fe angles are unequal (3.3552(8) Å, 3.3834(8) Å, 3.0133(8) Å, 128.1(2)°, $126.6(2)^{\circ}$, $105.3(1)^{\circ}$) and so the triangle is truly scalene rather than isosceles. Fel is in a distorted octahedral geometry with cis angles in the range 81.7(1)-97.4(1)°, and trans angles in the range 166.5(1)-176.6(1)°. Fe2 and Fe3 are both in a distorted



Fig. 1 The molecular structure of 1. Colour code: Fe = olive green; O = red; N = blue; C = gold; Cl = bright green.



Fig. 2 The molecular structure of **3** (top) and its magnetic core (bottom). Colour code: Fe = olive green; O = red; N = blue; C = gold; F = yellow.

square based pyramidal geometry with a τ value of 0.190 (where $\tau = (\beta - \alpha)/60$),²⁸ their oxidation states were assigned using charge balance considerations, bond lengths and BVS calculations.^{29,30} In the crystal lattice there are no intermolecular hydrogen bonds, with the closest contacts being between a pyridine ligand and the phenolic O-atom (C···O, 3.347(7) Å); Cl and the solvent MeOH (Cl···O, 3.365(6) Å); MeOH and a phenyl ring of the Ph-sao²⁻ ligand (O···C, 3.457(8) Å). Complex **3** (Fig. 2) crystallises in the monoclinic space group $P2_1/c$ with eight molecules in the unit cell, it contains two independent molecules in the asymmetric unit



Fig. 3 The molecular structures of 4 (left) and 6 (right). Colour code as previous Figures.

which vary slightly in bond lengths and angles but are structurally equivalent. The Fe^{III} ions are connected by a combination of four fully deprotonated Ph-sao²⁻ ligands in a η^1 : η^1 : η^1 : μ_2 -fashion and four μ_2 -F⁻ ions creating an unusual [Fe₄] square. The remaining coordination site on each Fe^{III} is occupied by a pyridine molecule. Each Fe^{III} ion is in a distorted octahedral geometry (*cis*, 82.1(2)-102.1(2)°; *trans*, 166.9(2)-178.3(2)°). The structure is unique in that it is the first case of a Fe^{III} square bridged through fluoride, and to the best of our knowledge is one of only five fluoride-bridged first row transition metal squares.³¹⁻³⁴ In the crystal lattice there are no intermolecular hydrogen bonds, with the closest contacts being between pyridine ligands and phenolic O-atoms (C ··· O, 3.008(8)-3.380(1) Å).

Complex 4 was obtained as triclinic crystals, space group $P\overline{1}$ with one molecule in the unit cell (Fig. 3). The molecule contains a $[Fe^{III}{}_6(\mu_3\text{-}O)_2(\mu\text{-}OH)_2]^{12+}$ core, whose topology consists of two centrosymmetrically related off-set [Fe^{III}₃(μ_3 -O)] triangular units linked at one Fe₂ edge (Fe1-Fe3) by two µ-OH⁻ ions and two oximate O atoms from two $\eta^1:\eta^2:\mu_3$ -Et-saoH⁻ ligands. Two Fe_2 edges (Fe2-Fe3) are each bridged by one oximate oxygen atom from one $\eta^1:\eta^1:\mu_2$ -Et-sao²⁻ and one PhCO₂⁻ ligand in its familiar syn, syn, μ_2 -mode. The remaining two Fe₂ edges (Fe1-Fe2) are bridged by two PhCO₂⁻ ligands. Each Fe^{III} ion lies in a distorted octahedral geometry (cis, 81.47(16)-105.51(17)°; trans, 161.79(16)- $178.37(18)^{\circ}$). In the crystal lattice there are no intermolecular hydrogen bonds, with the closest contacts being between two Etsao^{2–} ligands and two phenolic O- atoms (C···O, 3.406(7) Å) which result in the formation of pseudo 1D chains in the bc-plane (Fig. SI1).

5 has a similar structure to **4** with the following differences: the two singly deprotonated Et-saoH⁻ ligands in **4** are replaced by two fully (doubly) deprotonated Et-sao²⁻ ligands, which is perhaps to be expected given the larger amount of base used in the synthesis, with charge balance being maintained by the presence of two [HNEt₃]⁺ cations. Again, the Fe^{III} ions lie in distorted octahedral geometries with *cis* angles in the range 80.46(15)-103.24(15)° and *trans* angles in the range 164.76(16)-177.27(15)°). In the crystal

lattice there are inter-molecular hydrogen bonding interactions between two phenolic O-atoms and the two cations (N···O, 2.793(8) Å) and close contacts between a phenolic O-atom and the cation (C···O, 3.533(8) Å) and between a (Me)₂PhCO₂⁻ ligand and the cation (C···O, 3.271(11) Å). This results in the formation of 2D sheets lying in the *bc* plane, with the closest intermolecular Fe ··· Fe distance being 8.925(10) Å.

The molecule in complex **6** (Fig. 3) is similar in structure to that in **4** except that the bridging between the two $[Fe^{III}_3(\mu_3-O)_2]$ triangular units occurs only through the two oximate O atoms, *i.e.* there are no μ -OH⁻ ions present, as in **4**. The oxime used in **6** was 3-'But-saoH₂, but under the reaction conditions the benzene ring has become nitrated at the 5 position giving 3-'But-5-NO₂-sao²⁻.^{26,27} There are only two oximes present in **6** compared to the four in **4**, the edges that were bridged by one $\eta^1:\eta^1:\eta^1:\mu_2$ -Et-sao²⁻ and one PhCO₂⁻ ligand in **4**, are now bridged by two PhCO₂⁻ ligands in their familiar, *syn*, *syn*, μ -mode in **6**. In the crystal lattice there are intermolecular hydrogen bonds between the NO₂ salicylaldoxime and the H₂O (O···O, 2.803(1) Å) and between the H₂O and the MeCN solvent (N···O, 2.924(2) Å).

The molecule in 7 has a similar structure to 6 with the exception that there has been no nitration of the benzene ring. In the crystal lattice there are again intermolecular hydrogen bonds between the H₂O and the MeCN solvent (N···O, 2.875(9) Å) and also between the H₂O and a carboxylate O-atom (O···O, 2.963(6) Å).

8 crystallises in the hexagonal space group *P*63/m with two molecules in the unit cell and has a 2D framework structure (Fig. 4-5). The metallic skeleton of the [Fe₆] unit (composed of two linked [Fe₃(μ_3 -O)_{0.5}(μ_3 -OH)_{0.5}]^{7.5+} triangles) (Fig. 4) within the 2D framework describes a trigonal prism of Fe^{III} ions connected along the square faces *via* three μ_3 -OH⁻ ions and three μ -MeO⁻ ions to form an [Fe^{III}₆(μ_3 -O)(μ_3 -OH)₄(μ -OMe)₃]⁹⁺ core. BVS calculations on O3 and symmetry equivalent (s.e) of the [Fe₃(μ_3 -O)_{0.5}(μ_3 -OH)_{0.5}]^{+7.5} triangles reveal values that lie between those expected for O²⁻ and OH⁻ suggesting that a proton is shared between O3 and s.e. This is reasonable considering the short O···O distance of 2.472(3) Å between O3 and s.e indicative of a hydrogen bonding



Fig. 4 The $[Fe_6]$ trigonal prismatic unit present in **8**, viewed parallel to the $[Fe_3]$ planes. Colour code: Fe = green; O = red; N = blue; C = gold.

interaction. The six Fe₂ edges (Fe1-Fe1' and s.e) of the triangular faces of the trigonal prism are each linked by a fully deprotonated Me-sao^{2–} ligand bridging in a $\eta^1:\eta^1:\eta^1:\mu_2$ fashion. Each Fe ion has a distorted octahedral geometry (*cis*, 76.94(6)-97.07(7)°; *trans*, 169.42(6)-172.01(6)°) with a 3+ oxidation state assigned using charge balance considerations, bond lengths and BVS calculations.

The triangle of Na⁺ ions in the [Na₃] unit (Fig. 5) within the framework is connected *via* three μ -H₂O molecules on each edge. Each Na⁺ ion is linked to the [Fe₆] unit *via* a μ_3 -OH⁻ ion; with six terminal methanol molecules completing the coordination sphere. The Na⁺ ions define a distorted trigonal bipyramid with a τ value of 0.955.²⁸ Each [Fe^{III}₆O(OH)₄(Me-sao)₆(OMe)₄] unit is linked to three [Na₃(μ_2 -H₂O)₃(MeOH)₆] units forming a non interpenetrated 2D network (Fig. SI2⁺) with the centroid of O3 and s.e of the [Fe^{III}₆O(OH)₄(Me-sao)₆(OMe)₄] unit forming two 3-connecting nodes of a (6,3) 2D net in the *ab*-plane. In the crystal lattice there are significant numbers of

complementary hydrogen bonds: two between the terminally bound MeOH molecules and the oximato O-atoms (O···O, 2.742(3) Å); two between the phenolic O-atoms and bridging H_2O molecules; and one between a OH⁻ ion and a bridging MeO⁻ ion.

9 (Fig. 6) contains two [Fe₆Na] units linked by a single central [Na₂] unit forming an unusual S-shaped molecule. This is structurally very similar to **8** except that a single Na⁺ is connected



Fig. 6 The molecular structure of 9 viewed perpendicular (top) and parallel to the [Fe₃] planes. The lower picture shows only the [Fe₆Na] unit. Colour code: Fe = green; Na = cyan O = red; N = blue; C = gold.



Fig. 5 The structure of the [Fe₃Na₃] unit in 8 (left) and the respective packing in the crystal as viewed down *c*-axis (right). Colour code: Fe = green; Na = cyan O = red; N = blue; C = gold.

to one edge of the trigonal prism via one μ_3 -OH⁻ and two sao²⁻ ligands bridging in a η^2 : η^1 : η^1 : μ_3 -fashion forming the [Fe₆Na] unit. Three Fe₂ edges (Fe1-Fe2, Fe2-Fe3, Fe5-Fe6) of the triangular faces of the trigonal prism are linked by fully deprotonated sao2ligands bridging in a $\eta^1:\eta^1:\mu_2$ -fashion, while the remaining three Fe₂ edges (Fe1-Fe3, Fe4-Fe5, Fe4-Fe6) are linked by a fully deprotonated sao^{2–} ligand bridging in a η^2 : η^1 : μ_3 -fashion. Each Fe^{III} ion has a distorted octahedral geometry (cis, 76.4(3)-100.6(3)°; trans, 166.4(3)-173.9(3)°). In 8 the [Fe₆] units are connected by [Na₃] units whereas in 9 the linkers are [Na₂] units. These are connected via two µ-MeOH molecules which are then connected to each of the two [Fe₆Na] units via one μ_3 -OH⁻ ion and the phenolate oxygen of a $\eta^2:\eta^1:\eta^1:\mu_3$ sao²⁻ ligand (Fig. 6). Terminal MeOH molecules complete the coordination of the Na⁺ ions in the [Na₂] unit forming a discrete molecular complex in contrast to the coordination polymer found in 9. The Na⁺ ions in the [Fe₆Na] unit have a distorted octahedral geometry (cis, 68.1(3)- $117.7(11)^{\circ}$; trans, 147.66(3)-170.57(3)°), while the Na⁺ ions in the [Na₂] unit are square pyramidal with a τ value of 0.119.²⁸ In the crystal lattice there are significant numbers of intra-molecular hydrogen bonds: two between oximic O-atoms and bridging MeOH molecules $(O \cdots O, 2.615(0) \text{ Å})$; two between phenolate O-atoms and terminal MeOH molecules $(O \cdots O, 2.814(11) \text{ Å});$ four between μ_3 -OH⁻ ions and bridging OMe⁻ ions (O···O, 2.693(7), 2.633(0) Å); and two between μ_3 -OH⁻ ions and μ_3 -O²⁻ ions ($O \cdots O$, 2.526(7) Å). The packing of **9** in the crystal can be found in Fig SI3. The closest intermolecular Fe ··· Fe distance is 8.751(2) Å.

Magnetic properties

Direct current (dc) magnetic susceptibility studies were performed on microcrystalline samples of **1**, **3-6**, **8**, **9** in the 5-300 K range under an applied field of 0.1 T. For **1** (Fig. 7) the room temperature $\chi_{\rm M}T$ value of approximately 4.8 cm³ K mol⁻¹ is lower than expected for three non-interacting Fe^{III} ions (~13 cm³ K mol⁻¹). Upon cooling, the value of $\chi_{\rm M}T$ initially decreases to approximately ~4.3 cm³ K mol⁻¹ at 125 K before increasing to a value of ~4.5 cm³ K mol⁻¹ at 25 K. Below this temperature there is a rapid decrease to approximately 4.1 cm³ K mol⁻¹ at 5 K - presumably due to inter-molecular interactions and/or Zeeman effects. This



Fig. 7 Plot of $\chi_M T vs. T$ for complex 1. The solid red line represents the simulation of the experimental data - see text for details.

behaviour is indicative of antiferromagnetic exchange between the metal centres and an S = 5/2 ground state. The 300-25 K data for 1 were simulated employing the spin-Hamiltonian $\hat{H} = -2J_1(\hat{S}_1 \cdot \hat{S}_2 +$ $\hat{S}_1 \cdot \hat{S}_3$ -2 $J_2(\hat{S}_2 \cdot \hat{S}_3)$ affording the parameters S = 5/2, g = 2.02, $J_1 = -40.0 \text{ cm}^{-1}$, $J_2 = -5.5 \text{ cm}^{-1}$. Magnetic measurements were not made on 2 as it is isostructural with 1 differing only in the nature of the coordinating halides. For complex 3 (Fig. 8) the room temperature $\chi_{\rm M} T$ value of approximately 15 cm³ K mol⁻¹ is lower than expected for four non-interacting Fe^{III} ions (~17.5 cm³ K mol⁻¹). Upon cooling, the value of $\chi_{\rm M}T$ decreases almost linearly to approximately ~2 cm3 K mol-1 at 5 K, indicative of relatively strong antiferromagnetic exchange with a diamagnetic ground state. Despite appearing to be a very simple molecule, each of the Fe-Fe interactions is unique and there are in fact two different [Fe₄] clusters per unit cell, requiring a total of eight separate J-values. Attempts to fit the data employing simple 1, 2 and 3 J models all failed to produce a satisfactory result.



Fig. 8 Plot of $\chi_{\rm M} T$ vs. T for complex 3.

For complexes **4-6** and **8-9** (Fig. 9) the room temperature $\chi_M T$ values of approximately 6.4, 6.1, 5.2, 11.0 and 10.2 cm³ K mol⁻¹ respectively are lower than that expected for six non-interacting Fe^{III} ions (26.25 cm³ K mol⁻¹). On cooling, the values of $\chi_M T$ decrease to approximately 0.3, 1.1, 0.6, 0.26 and 0.22 cm³ K mol⁻¹ at 5 K respectively. This behaviour is consistent with antiferromagnetic exchange between the metal centres and small (probably S = 0) ground states.



Fig. 9 Plot of $\chi_M T vs. T$ for complexes **4** (magenta); **5** (red); **6** (green); **8** (blue); and **9** (olive).

The complexity of structures of **4-6**, **8** and **9** precludes the fitting of the susceptibility data by standard procedures.

Conclusions

The nine new iron(III) cluster compounds assembled using salicylaldoxime derivatives range in nuclearity from three to twelve. The results support the proposition that salicylaldoximates favour the formation of polynuclear complexes with higher oxidation state transition metal ions, whilst the coordination chemistry with M(II) ions is dominated by mononuclear complexes.⁴ The predominant building block in the new clusters - as also seen in Mn(III) chemistry⁵⁻⁸ - appears to be the triangular [Fe₃O(R- $(sao)_3$]⁺ species, which can assemble into more elaborate arrays depending on reaction conditions. An interesting observation is that R-saoH-/R-sao2- ligand system tends to adopt coordination modes similar to carboxylates, and given that the latter have been deployed successfully in making magnetically interesting molecules, it is timely to extend that range of oximate-based Fe(III) clusters. The most unusual molecule is 3 which contains the [Fe₄F₄] molecular square. Whilst Cl⁻ and Br⁻ appear to act only as terminal ligands, the F- ions bridge thus making a major impact on molecular structure and topology-affording the square rather than the "expected" (oxo-centered) triangles. F- bridges have been used with great success in recent Cr(III) chemistry³⁵⁻³⁶ but their use in building Fe(III) clusters is extremely rare,³⁷ again suggesting potential future routes to novel Fe molecules.

Acknowledgements

The authors would like to thank SHEFC for a SPIRIT studentship (KM) and EaStCHEM for fellowships (AC and FJW).

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