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# Syntheses, structural, spectroscopic and magnetic properties of polynuclear Fe(III) complexes containing N and O donor ligands

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#### Abstract

Syntheses, X-ray structural and spectroscopic properties are reported for  $[{Fe(L)_2}_3Fe]$  (1),  $[Fe_2(L)_2(ClCH_2COO)_2(H_2O)]$  (2) and  $[Fe(L)(HL)]_2$  (3)  $[H_2L = a \text{ tridentate ONO-donor ligand } N-$ (2-hydroxyphenyl)salicylidenimine]. For (2) and (3), variable temperature magnetic susceptibilities have been measured and modelled. Both are antiferromagnetic overall. Compound 1 has a tetranuclear  $Fe_4O_6$  core with Fe(III) species at the vertices of a triangle and the fourth Fe(III) at the center of the triangle. The central Fe(III) is surrounded by six phenoxo bridges that connect it to the three peripheral Fe(III) centres. In complex 2, the two sixcoordinate Fe(III) centers are bridged by a chloroacetate and two phenoxy oxygens. The remaining three coordination sites on each iron are occupied by a terminal phenoxy oxygen, an imino nitrogen and, in one case, by a water oxygen while in the other by a terminal chloroacetate oxygen. Comparison of 2 with compounds of similar core structure reveals transition between antiferromagnetic and ferromagnetic coupling occurs at a bridgehead angle between ~97 and ~102 degrees. The asymmetric unit of compound 3 consists of two symmetry-independent mononuclear species (Z' = 2) joined by two statistically equivalent short (2.429(2) and 2.432(2)) Å) O<sup>•••</sup>H<sup>•••</sup>O bridges, each involving two phenolic oxygens and a strongly bound H atom. Unprecedented weak antiferromagnetic coupling between the two high spin Fe(III) species via these very strong hydrogen bonds was detected.

*Keywords:* Dinuclear; Tetranuclear; Iron(III); Carboxylate bridge; Phenoxo bridge; Magnetochemistry

#### **1. Introduction**

Iron is one of the most important microelements in nature and it is an essential element in the majority of biological systems. For example, oxo- hydroxo- and carboxylato-bridged polynuclear iron(III) units have been found in many non-heme metalloproteins and metalloenzymes [1-12]. Hemerythrin (a dioxygen carrier) and ribonucleotide reductase (a tyrosyl radical generator) contain an oxo- and carboxylato-bridged diiron(III) unit, and methane monooxygenase (a catalyst for the conversion of methane to methanol) in its oxidized resting state contains a dihydroxy- and carboxylato-bridged diiron(III) unit. Observation of these and other roles of iron(III) in biology has stimulated examination of the structural, magnetic, spectroscopic and redox properties of oxo- and carboxylato-bridged polynuclear iron(III) complexes as model compounds of biological systems [13-28].

The paramagnetic nature of iron in its common oxidation states generates interesting magnetic properties in its polynuclear clusters. As a result, these are attracting magnetochemists to study structure–magnetism relationships in non–heme iron–containing enzymes [29, 30], interactions in spin–coupled systems [31], possibilities for generating polynuclear clusters with large spin values in their ground state [21, 32] and new examples of single molecule magnets. Although interactions between Fe(III) ions are generally antiferromagnetic, some clusters experience spin frustration or display particular Fe<sub>x</sub> topological arrangements that can result in ground states with reasonably large spins. Previous reports concerning di- and higher nuclearity iron(III) systems have shown that organic oxygen bridge atoms of all types provide weak antiferromagnetic coupling between irons whereas oxo bridges provide stronger coupling, but other details of the influence of structure remain poorly defined. There is, therefore, a continuing

search for synthetic procedures that yield new types of polynuclear iron compounds having novel chemical and physical properties.

In this work, we report preparations for new chloroacetato- and phenoxo- bridged polynuclear Fe(III) compounds with ONO donor ligands based on the species H<sub>2</sub>L shown below as well as structural, spectroscopic and variable temperature magnetic studies of these complexes.



#### 2. Experimental

#### 2.1. Chemicals and Materials

All chemicals were of reagent grade and were used without further purification. Salicylaldehyde and 2-aminophenol were purchased from Sigma-Aldrich. Chloroacetic acid, NaHCO<sub>3</sub>, anhydrous ferric chloride, Fe(ClO<sub>4</sub>)<sub>3</sub>.6H<sub>2</sub>O and perchloric acid (70%) were supplied by Spectrochem Pvt. Ltd. (India). Solvents were used as received. We have previously reported preparation of the precursor oxo-centered trinuclear iron(III) complex, [Fe<sub>3</sub>( $\mu_3$ -O)(O<sub>2</sub>CCH<sub>2</sub>Cl)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]ClO<sub>4</sub>, [33].

#### 2.2. Synthesis of N-(2-hydroxyphenyl)salicylidenimine (H<sub>2</sub>L):

The ligand, H<sub>2</sub>L, was prepared by modification of the procedure of Westland et al. [34]. A solution of 2–aminophenol (1.10 g, 10.1 mmol) in methanol (20 ml) was added slowly to a

solution of salicylaldehyde (1.22 g, 9.99 mmol) in the same solvent (20 ml) with stirring. The resulting mixture was stirred for 3 hours. During this time an orange–red microcrystalline precipitate gradually separated. This was removed by filtration, washed several times with ethanol then diethyl ether and dried in air. Yield: 1.54 g (72.3 %), *Anal. Calc.* for  $C_{13}H_{11}NO_2$ : C, 73.23; H, 5.20, N, 6.57. Found: C, 73.02; H, 5.04, N, 6.42. MS: (*m/z*) 214 ([M+1]<sup>+</sup>, 100%).

#### 2.3. Synthesis of iron(III)complexes

#### 2.3.1. [ $\{Fe(L)_2\}_3Fe$ ] (1) and [ $Fe_2(L)_2(ClCH_2COO)_2(H_2O)$ ] (2)

To a stirred solution of the precursor complex  $[Fe_3(\mu_3-O)(O_2CCH_2Cl)_6(H_2O)_3]ClO_4$  (450 mg, 0.501 mmol) in CH<sub>3</sub>CN (30 ml), a solution of the ligand H<sub>2</sub>L (160 mg, 0.750 mmol) in the same solvent (20 ml) was added drop-wise. The color of the solution changed from orange to dark reddish-brown during the addition. The solution was stirred for 30 min and filtered to remove undissolved solids and the filtrate was allowed to evaporate 30% of its volume over two days at room temperature during which a black crystalline precipitate of (1) was deposited. The precipitate was collected by filtration, washed with Et<sub>2</sub>O and dried in air. Yield: 310 mg (55.4% based on Fe). Layering a 40 mg sample of 1 dissolved in CH<sub>3</sub>CN (15 ml) with diethyl ether gave, after sitting undisturbed for several days, X-ray quality black crystals.

The filtrate from which the black crystals had initially been obtained was again, at room temperature, allowed to evaporate slowly a further 40% of its initial volume. This resulted in precipitation of a mixture of **1** and **2** that was separated by filtration and discarded. The remaining filtrate was again, at room temperature, allowed to evaporate very slowly a further 20% of its initial volume. A precipitate of X–ray quality dark brown crystals of **2** was deposited and then collected by filtration, washed with Et<sub>2</sub>O, and dried in air. Yield: 90 mg (16.2% based on Fe). *Anal. Calc.* for  $C_{78}H_{54}Fe_4N_6O_{12}$  (**1**): C, 62.84; H, 3.65; N, 5.64. C: Found: 62.65; H:

3.49; N: 5.48 %. IR (KBr, cm<sup>-1</sup>): 3427 (w, br), 1604 (s), 1580 (s), 1538 (s), 1463 (s), 1440 (m), 1379 (s), 1299 (w, br), 1146 (w, br), 839 (s), 751 (s), 612 (w), 524 (m) (for **1**). UV–Vis [CH<sub>3</sub>CN,  $\lambda_{max}$ , nm ( $\varepsilon$ , dm<sup>3</sup> mole<sup>-1</sup> cm<sup>-1</sup>)]: 223 (sh), 296 (86,639), 340 (sh), 388 (83,310) and 495 (12,635) (for **1**). *Anal. Calc.* for C<sub>30</sub>H<sub>24</sub>Cl<sub>2</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>9</sub> (**2**): C, 48.75; H, 3.27; N, 3.79; Cl, 9.59. Found: C: 48.24; H: 3.20; N: 4.15; Cl, 9.54 %. IR (KBr, cm<sup>-1</sup>): 3427 (w, br), 1604 (s), 1580 (s), 1570 (s), 1538 (s), 1463 (s), 1440 (m), 1379 (s), 1303 (s), 1256 (s), 1151 (m), 839 (s), 751 (s), 620 (m), 524 (m) (for **2**). UV–Vis [CH<sub>3</sub>CN,  $\lambda_{max}$ , nm ( $\varepsilon$ , dm<sup>3</sup> mole<sup>-1</sup> cm<sup>-1</sup>)]: 227 (sh), 315 (58,424), 345 (sh), 379 (51,120) and 490 (15,420) nm (for **2**).

#### 2.3.2. $[{Fe(HL)_2}{Fe(L)_2}]$ (3)

To a solution of Fe(ClO<sub>4</sub>)<sub>3</sub> 6H<sub>2</sub>O (463 mg, 1.00 mmol) in CH<sub>3</sub>CN (10 ml), a solution of H<sub>2</sub>L (426 mg, 2.00 mmol) in CH<sub>3</sub>CN (10 ml) was added with stirring. The resulting solution turned deep red immediately and a dark brown microcrystalline precipitate appeared within a few minutes. The mixture was stirred for 3 hours during which the color of the precipitate gradually changed to yellowish brown. The precipitate was collected by filtration, washed with acetonitrile and diethyl ether and dried in air. Yield: 450 mg (93.8%). Crystals for X–ray analysis were obtained by recrystallization from acetonitrile. *Anal. Calc.* for C<sub>52</sub>H<sub>38</sub>Fe<sub>2</sub>N<sub>4</sub>O<sub>8</sub> (**3**): C, 65.15; H, 3.99; N, 5.84. Found: C: 65.02; H: 3.87; N: 6.08 %. IR (KBr, cm<sup>-1</sup>): 3436 (w, br), 3057 (w), 1605 (s), 1580 (s), 1536 (s), 1465 (s), 1438 (s), 1311 (m), 1149 (m), 826 (m), 881 (s), 743 (s), 609 (m), 516(m), 471 (m). UV–Vis [CH<sub>3</sub>CN,  $\lambda_{max}$ , nm ( $\varepsilon$ , dm<sup>3</sup> mole<sup>-1</sup> cm<sup>-1</sup>)]: 230 (sh), 295 (17,500), 345 (sh), 408 (16,500) and 500 (5,100).

#### 2.4. Physical measurements

Elemental analyses were performed by Canadian Microanalytical Service Ltd. (2) or by using a Perkin-Elmer 2400 Series II elemental analyzer (H<sub>2</sub>L), (1) and (3). Fourier Transform Infrared (FTIR) spectra (4000-400 cm<sup>-1</sup>) were recorded using KBr disks on a JASCO FTIR-460 Plus spectrometer. Electronic absorption spectra were recorded at a concentration of 1 x 10<sup>-5</sup> mol L<sup>-1</sup> in acetonitrile on a JASCO V-530 spectrophotometer. Variable temperature (2–300 K) magnetic susceptibility measurements were obtained by using a Quantum Design MPMS SQUID magnetometer at a fixed field strength of 1.00 Tesla. Diamagnetic corrections were estimated by using Pascal's constants [35].

#### 2.5. X-ray crystallography

Single crystals of (1) and (3) were mounted on glass fibres and coated with perfluoropolyether oil, while (2) was coated in oil and mounted on a low temperature MiTeGen loop. Intensity data were collected at 100 K (for 1), 120 K (for 2) and 150 K (for 3) on a Bruker-AXS SMART APEX II diffractometer (1 and 3) or a Rigaku Saturn 70 diffractometer (2) equipped with a CCD detector and using graphite-monochromated Mo-Ka radiation ( $\lambda = 0.71073$  Å). The data were processed with SAINT [36a] and absorption corrections were made with SADABS [36a] software packages (1 and 3), while 2 was processed *via* the Crystal Clear software suite [36b]. The structures were solved by direct methods and refined by full-matrix least-squares analysis based on  $F^2$  using WINGX software of SHELXTL [37a] and SHELX-97 [38] (1 and 3), while 2 was also refined using SHELX-97 [38], but *via* the Crystal Structure [37b] graphical interface. For 1, 2 and 3, non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were placed at their geometrically calculated positions with fixed isotropic parameters. 1 and 3 were treated via the Platon SQUEEZE [39] routine. For 1, 86

electrons were recovered from two voids (total volume 422 Å<sup>3</sup>), while for **3**, 28 electrons were recovered from one void with volume 113 Å<sup>3</sup>. Contents of these void spaces were not included in the reported formulas. Crystals of **2** were tiny and diffracted weakly and so after processing and inspection of intensity statistics, reflections were truncated at  $47^{\circ}$  in 20 for refinement. The high values of R1 and wR2 for **2** reflect this weak data set. Details of crystallographic parameters, data collection and refinements are given in Table 1.

Parameter	$[{Fe(L)_2}_3Fe](1)$	$[Fe_2(L)_2(ClCH_2COO)_2(H_2O)]$ (2)	$[{Fe(HL)_2}{Fe(L)_2}]$ (3)
Empirical Form.	$C_{78}H_{54}Fe_4N_6O_{12}$	$C_{30}H_{24}Cl_2Fe_2N_2O_9$	$C_{26}H_{18}FeN_2O_4$
Formula Wt.	1490.67	739.13	478.27
<i>Т</i> , К	100(2)	163(2)	150(2)
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	P-1	P-1	P-1
a /Å	12.455(5)	9.8771(14)	11.391(5)
b /Å	13.162(5)	11.4238(17)	12.501(5)
c /Å	21.514(5)	14.590(2)	16.480(5)
α/deg	93.114(5)	72.454(5)	75.047(5)
$\beta$ /deg	98.019(5)	78.906(6)	76.264(5)
γ/deg	98.099(5)	69.046(5)	78.640(5)
$V/Å^3$	3,448(2)	1,459.2(4)	2,179.3(15)
Ζ	2	2	4
$\mu$ /mm <sup>-1</sup>	0.893	1.236	0.729
$\lambda/Å$	0.71073	0.71075	0.71703
F(000)	1528	752	984
Crystal size / mm <sup>3</sup>	0.28x0.22x0.16	0.11x0.07x0.02	0.35x0.23x0.18
$D_{calc} / g cm^{-3}$	1.436	1.682	1.458
No. of data /	12,113 / 0 / 901	9,342 / 0 / 407	7,930 / 0 / 595
restraints /	0		
parameters			
No. of Reflns	5 ,547	4,259	5,921
$[I>2\sigma(I)]$			
GOF on F <sup>2</sup>	0.782	1.100	0.891
Final R indices	$R1^a = 0.0638$	$R1^a = 0.1155$	$R1^a = 0.0424$
$[I>2\sigma(I)]$	$wR2^{b} = 0.1412$	$wR2^{b} = 0.2096$	$wR2^{b} = 0.1230$
<i>R</i> indices (all data)	$R1^a = 0.1462$	$R1^a = 0.1582$	$R1^a = 0.0596$
	$wR2^{b} = 0.1713$	$wR2^{b} = 0.2335$	$wR2^{b} = 0.1344$

Table 1	Crystallographic Data
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 ${}^{a} \operatorname{R1}(F) = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. {}^{b} \operatorname{wR2}(F^{2}) = \left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}\right]^{\frac{1}{2}}.$ 

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The ligand, H<sub>2</sub>L, was prepared by condensation (Scheme 1) of 2–aminophenol and salicylaldehyde in methanol. Syntheses of the iron(III) complexes are illustrated in Schemes 2 and 3.



When trinuclear  $[Fe_3(\mu_3-O)(O_2CCH_2Cl)_6(H_2O)_3]ClO_4$  is treated with 1.5 equivalents of H<sub>2</sub>L in acetonitrile, two products, tetranuclear **1**, and binuclear **2** are obtained (Scheme 2). The reaction must be performed in acetonitrile because in methanol the  $[Fe_3O]^{+7}$  framework is decomposed. Both **1** and **2** are obtained from the same reaction medium by virtue of their different solubilities as described in the Experimental section.





An attempt to obtain **1** directly by reacting  $Fe(ClO_4)_3.6H_2O$  with  $H_2L$  led however to **3** (Scheme 3) in which two closely similar but non-identical iron species in the X-ray structural asymmetric unit are associated through two very strong O- - -H- - -O bridges as revealed by the X-ray crystal structure (*vide infra*).



Scheme 3

In addition to X-ray crystallography and quantitative elemental analysis, compounds **1**, **2** and **3** have been characterized by IR and UV-Vis spectroscopy. In the IR spectra of the complexes, the C=N stretching vibration, observed at 1632 cm<sup>-1</sup> in the ligand, is shifted toward lower wave-numbers (1604 (**1**), 1608 (**2**) and 1605 (**3**) cm<sup>-1</sup>) indicating coordination of the imino-nitrogen to the iron(III) centers. In the oxo-bridged complexes **1** and **2**, the  $v_{as}$ Fe-O-Fe vibration appears as a medium intensity band at 839 (**1**) and 835 (**2**) cm<sup>-1</sup>. In general, for oxo-bridged Fe(III) compounds, this band occurs between 885 and 725 cm<sup>-1</sup> with the band position depending on the Fe-O-Fe bridge angle [40]. The carboxylate ion C=O vibration in the spectrum of **2** is observed at 1570 cm<sup>-1</sup> and, as expected, this band is absent from spectra of **1**.

Cmpd	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	N→Fe		O→Fe
_	(phenolic)	(phenolic)	(C=N)	(CT)		(CT)
$H_2L$	225 (sh)	262	351		437	
		(53,266)	(49,732)		(12,719)	
(1)	223 (sh)	296	340 (sh)	388		495
		(86,639)		(83,310)		(12,635)
(2)	227 (sh)	315	345 (sh)	379		490
		(58,424)		(51,120)		(15,420)
(3)	230 (sh)	295	345 (sh)	408		500 (5,100)
		(17,500)		(16,500)		

Table 2Electronic Spectra and Band Assignments<sup>a</sup>

<sup>a</sup>In CH<sub>3</sub>CN,  $\delta$  in nm ( $\epsilon$  in L mol<sup>-1</sup> cm<sup>-1</sup>) **Note:** CT, charge transfer; sh, shoulder

Electronic spectral details of the ligand and its three complexes are presented in Table 2. The spectrum of H<sub>2</sub>L displays absorptions centred at 225 (sh), 262 ( $\varepsilon = 53,266 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), 351 ( $\varepsilon = 49,732 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and 437 nm ( $\varepsilon = 12,719 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) that can be assigned to two  $\pi \rightarrow \pi^*$  transitions of the aromatic system [41-45] and to a  $\pi \rightarrow \pi^*$  transition of the –C=N- system [41, 43, 46] while the remaining band at 437 nm is of unknown origin although ligands of related

structure have been observed to show an unassigned band of variable intensity near this wavelength [41]. The electronic spectrum of **1** exhibits absorptions at 223 (sh) 296 ( $\varepsilon$  = 86,639 L mol<sup>-1</sup> cm<sup>-1</sup>), 340 (sh), 388 ( $\varepsilon$  = 83,310 L mol<sup>-1</sup> cm<sup>-1</sup>) and 495 nm ( $\varepsilon$  = 12,635 L mol<sup>-1</sup> cm<sup>-1</sup>). By comparison to the spectrum of the free ligand, it is plausible to assign the two highest energy bands in the spectrum of the complex as  $\pi \rightarrow \pi^*$  transitions of the ligand's aromatic system and the shoulder at 340 nm as a  $\pi \rightarrow \pi^*$  transition of the ligand's –C=N- system, the last having been shifted somewhat from its wavelength in the free ligand as a result of coordination. The bands at 388 and 495 nm may then be assigned to an N $\rightarrow$ Fe(III) LMCT and an O $\rightarrow$ Fe(III) LMCT, respectively as observed in related species [47-49]. The spectra of **2** and **3** are similar to that of **1**, as might be expected on the basis of structure (*vide infra*), and their bands are assigned similarly.

#### 3.2. Description of crystal structures

#### $3.2.1. [{Fe(L)_2}_3Fe] (1)$

An ORTEP representation of **1** along with a partial atom labelling scheme is shown in Fig. 1 while selected bond lengths are listed in Table 3. In this tetranuclear entity, three iron(III) atoms occupy the vertices of a roughly equilateral triangle while the fourth occupies its centre. The non-bonded Fe···Fe distances are 5.629(1) (Fe(1)<sup>...</sup>Fe(2)), 5.643(1) (Fe(2)<sup>...</sup>Fe(3)) and 5.709(1) (Fe(3)<sup>...</sup>Fe(4)) Å. Distances from the central to the peripheral irons are Fe(1)····Fe(4) (3.269(1)), Fe(2)····Fe(4) (3.265(1)) and Fe(3)····Fe(4) (3.271(1)) Å. The Fe–Fe(4)–Fe angles fall in the range  $118.96(1)-121.62(1)^{\circ}$ . Each iron(III) at a vertex is coordinated by two ONO donor ligands forming three [Fe(L)<sub>2</sub>]<sup>-</sup> crystallographically distinct moieties. Among the Fe–O bonds of **1**, the Fe–O(bridging) distances are larger than the Fe–O(terminal) ones (Table 3). The central Fe(III) is connected to the three peripheral irons by pairs of phenoxo bridges in each case. These Fe(4)–O(phenoxo) bond distances lie between 1.992(4) and 2.024(4) Å and the Fe(4)–O–Fe angles vary between  $106.35(18)^{\circ}$  and  $107.09(17)^{\circ}$ . This leads to the formation of a propeller-like

tetranuclear Fe(III) species containing a central FeO<sub>6</sub> core. As such, it is a member of a class of compounds known as "stars" that are of interest for their single molecule magnetic (SMM) and other properties [50-52]. Internal structural parameters within the Fe<sup>III</sup><sub>4</sub>O<sub>12</sub> cores of **1** and a related Fe<sup>III</sup><sub>4</sub> star, [{Fe(L<sup>2</sup>)<sub>2</sub>}<sub>3</sub>Fe] (H<sub>2</sub>L<sup>2</sup> = N-(2-hydroxybenzyl-L-leucinol) reported by Singh et al. [50], are similar. For example, differences in Fe-O distances between the two species are on average <0.05 Å, in Fe … Fe distances < 0.06 Å and in Fe-N distances <0.14 Å. Likewise, in **1** the three angles at Fe(4) are on average 74.89°, those at peripheral iron atoms Fe(1), Fe(2) and Fe(3) are on average 71.99° and the six angles at oxygens 2, 4, 5, 7, 8 and 12 are on average 106.55°. Comparable angles in the star described by Singh et al. are on average 72.28°, 71.69° and 107.71°, respectively.



Fig. 1 ORTEP representation of  $[{Fe(L)_2}_3Fe]$  (1) showing 50% probability displacement ellipsoids. H-atoms omitted for clarity.

**Table 3.** Selected interatomic distances (Å) for  $[{Fe(L)_2}_3Fe]$  (1).

Interatomic Distances		Interatomic	Distances	
Fe(1)····Fe(4)	3.269(1)	Fe(2) - N(2)	2.120(5)	
Fe(2)····Fe(4)	3.265(1)	Fe(3) - O(8)	2.090(4)	
Fe(3)••••Fe(4)	3.270(1)	Fe(3)–O(9)	1.889(4)	

Fe(1)–O(5)	2.067(4)	Fe(3)–O(10)	1.920(4)	
Fe(1)–O(6)	1.924(4)	Fe(3)–O(12)	2.090(4)	
Fe(1)–O(7)	2.073(4)	Fe(3) - N(7)	2.138(5)	
Fe(1)–O(11)	1.897(5)	Fe(3) - N(8)	2.146(5)	
Fe(1) - N(3)	2.144(5)	Fe(4) - O(2)	1.997(4)	
Fe(1) - N(4)	2.111(5)	Fe(4) - O(4)	2.024(4)	
Fe(2)–O(1)	1.912(4)	Fe(4) - O(5)	2.010(4)	
Fe(2)–O(2)	2.062(4)	Fe(4) - O(7)	2.006(4)	
Fe(2)–O(3)	1.907(5)	Fe(4) - O(8)	1.995(4)	
Fe(2)–O(4)	2.055(4)	Fe(4)–O(12)	1.992(4)	
Fe(2)–N(1)	2.111(5)			

An ORTEP representation for 2 with atom labels is in Fig. 2 while selected bond distances are given in Table 4. The neutral complex consists of two iron(III) centers bridged asymmetrically by two phenolate oxygens, O(1) and O(3), of two ONO donor ligands derived from H<sub>2</sub>L. The resulting Fe-O distances are Fe(1)–O(1) 2.033(7) Å, Fe(1)–O(3) 2.010(7) Å and Fe(2)-O(1) 2.015(7) Å, Fe(2)-O(3) 2.056(7) Å. Each iron(III) is surrounded by one nitrogen and five oxygen atoms in a distorted octahedral geometry. The atoms O(1)O(3)O(2)N(1) (for Fe(1)) and O(1)O(3)N(2)O(4) (for Fe(2)) are nearly planar with maximum deviations from their leastsquares planes being 0.102 and 0.051 Å, respectively while the Fe atoms are displaced from those planes by 0.048 and 0.022 Å, respectively. A fifth coordination site of each Fe is occupied by the oxygens of an asymmetrically bridging chloroacetato group in syn, syn mode while the sixth coordination sites of Fe(1) and Fe(2) are occupied by one oxygen of a terminally bound chloroacetate ion (Fe(1)) and a water molecule (Fe(2)). The monodentate carboxylate Fe-O distance of 2.044(7) Å is shorter than one of the bridging carboxylate distances of 2.090(7) Å (Fe(1)-O(5)) and longer than the other of 2.019(7) Å (Fe(2)-O(6)). None of these distances are strikingly different from the corresponding Fe-O distances found in the precursor complex  $[Fe_3(\mu_3-O)(O_2CCH_2Cl)_6(H_2O)_3]ClO_4$  [33].

Comparison may be made between core structural parameters from **2** and from dinuclear phenoxy bridged species such as those described by Yahsi et al. [53] and by Mikuriya et al. [54]. In the former, Fe-O(bridging phenoxy) distances are 1.996(10) and 2.244(11)Å. In the latter, they are 2.107(3) and 2.021(3)Å. In **2**, comparable bonds have lengths of 2.010(7) and 2.033(7)Å. Likewise, terminal Fe-N distances in the former are 2.133(13) and 2.166(12)Å and in the latter 2.083(4)Å whereas in **2**, these lengths are 2.106(8) and 2.115(9)Å. In the former, Fe-O-Fe angles are 103.83(4) and in the latter  $91.5(1)^{\circ}$  whereas in **2** these angles are Fe(1)-O(1)-Fe(2) 102.2(3) and Fe(1)-O(3)-Fe(2)  $101.6(3)^{\circ}$ . Angles at the Fe(III) atoms in the former are

76.17(4) and in the latter are  $88.5(1)^\circ$  whereas in 2, the angles are O(3)–Fe(1)–O(1) 76.5(3) and O(1)–Fe(2)–O(3) 75.9(3)°. Differences in bridge angles in the compound reported by Mikuriya et al. are probably the consequence of two additional acetate bridges as well as the phenoxy bridges in that compound whereas in 2, there is only one additional chloroacetate bridge and in the compound reported by Yahsi et al. there are no additional bridges.



Fig. 2 ORTEP representation of the binuclear complex [Fe<sub>2</sub>(L)<sub>2</sub>(ClCH<sub>2</sub>COO)<sub>2</sub>(H<sub>2</sub>O)] (2) showing 50% probability displacement ellipsoids. H-atoms omitted for clarity.

Interatomic I	Distances	Interatomi	c Distances	
		Fe(1)–O(5)	2.090(7)	
Fe(1)····Fe(2)	3.152(7)	Fe(1) - N(1)	2.106(8)	
		Fe(2) - O(4)	1.872(7)	
		Fe(2)-O(1)	2.015(7)	
Fe(1)-O(2)	1.885(7)	Fe(2)–O(6)	2.019(7)	
Fe(1)-O(3)	2.010(7)	Fe(2) - O(3)	2.056(7)	
Fe(1) - O(1)	2.033(7)	Fe(2)–O(9)	2.096(7)	
Fe(1)–O(7)	2.044(7)	Fe(2) - N(2)	2.115(9)	

**Table 4.**Selected interatomic distances (Å) for  $[Fe_2(L)_2(ClCH_2COO)_2(H_2O)]$  (2).

#### 3.2.3. $[Fe(L)(HL)]_2$ (3)

An ORTEP representation for **3** with atom labels is in Fig. 3 while selected bond distances are in Table 5. The asymmetric unit consists of two symmetry-independent mononuclear FeN<sub>2</sub>O<sub>4</sub> cores linked together by two statistically equivalent short (2.429(2) and 2.432(2) Å) O<sup> $\cdots$ </sup>H<sup> $\cdots$ </sup>O bridges, each involving two phenolic oxygens and a strongly bound hydrogen. These hydrogens were not found in the difference map, and consequently were omitted from the structure model, but their presence is required for charge balance, and is implied by the short separation between the phenolic oxygens. This structure can be compared to that of [{Ni(H<sub>2.5</sub>L)}<sub>2</sub>](ClO<sub>4</sub>).2H<sub>2</sub>O (H<sub>4</sub>L = a phenol-based tetrapodal Schiff base ligand) [55] in which three such hydrogen bonds with equal O<sup> $\cdots$ </sup>H<sup> $\cdots$ </sup>O distances of 2.481(7) Å hold a nickel dimer together.

Precise X-ray and neutron diffraction studies of a series of hydrogen bonds has established a continuum of O<sup>···</sup>O and O<sup>···</sup>H distances that can be used to describe such bonds as "weak" on one hand (O<sup>···</sup>O >2.80 Å) to "very strong" on the other (O<sup>···</sup>O) <2.50 Å) [56] On this continuum, the O<sup>···</sup>O distances of the hydrogen bonds in **3** are very short suggesting the hydrogen bonds are very strong. It has also been observed that the H atom in Z<sup>···</sup>H<sup>···</sup>Z hydrogen bonded systems becomes increasingly symmetrically positioned between the electron-rich atoms, Z, as Z<sup>···</sup>Z distances become increasingly shortened. When Z = O, shortening of O<sup>···</sup>O from 2.80

to 2.40 Å (cf. ~2.43 Å in **3**) parallels a shift from asymmetric and electrostatic hydrogen bonding to symmetric and covalent O<sup>--</sup>H<sup>--</sup>O bonding. Thus, while the H atoms in the two hydrogen bonds of **3** were not located in the X-ray crystal study, it is reasonable to predict their placement approximately equidistant from, and on a line between, the appropriate phenolate oxygens. Furthermore, because the bonds are so short, their bonding is probably best described as 3-centre four electron covalent [57]. In both halves of **3**, the metal centers are coordinated to two ONO donor ligands derived from H<sub>2</sub>L and adopt a distorted octahedral geometry (Fig. 4). The atoms O(1), O(3), O(2) and O(4) deviate from their least-squares plane by  $\leq \pm 0.25$  Å whereas O(5), O(7), O(6) and O(8) deviate by  $\leq \pm 0.30$  Å. The atoms Fe(1) and Fe(2) lie in their respective planes and the imino nitrogens N(1), N(2) and N(3), N(4) occupy sites perpendicular to the planes.



Fig. 3 ORTEP representation of  $[Fe(L)(HL)]_2$  (3) showing 50% probability displacement ellipsoids and short hydrogen bond O<sup>++</sup>O distances. H-atoms omitted for clarity.

Interatomic	Distances
Fe(1)–O(1)	1.926(2)
Fe(1)–O(2)	2.078(2)
Fe(1)–O(3)	1.912(2)
Fe(1) - O(4)	2.083(2)
Fe(1) - N(1)	2.108(3)
Fe(1) - N(2)	2.105(2)
Fe(2)–O(5)	1.915(2)
Fe(2)–O(6)	2.091(2)
Fe(2)–O(7)	1.919(2)
Fe(2)–O(8)	2.067(2)
Fe(2) - N(3)	2.133(2)
Fe(2) - N(4)	2.127(3)
O(4)••••O(8)	2.429(2)
O(2)••••O(6)	2.432(2)
Fe(1)••••Fe(2)	5.251(3)

Table 5. Selected interatomic distances (A)	Ă)	for	[Fe(L)(	$(HL)]_2$	(3).
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#### 3.3. Magnetic properties

vents a: Variable temperature magnetic susceptibility measurements and simulations are displayed in Figures 4 and 5. Magnetic moments for compounds 2 and 3 at 300 K are 8.22 and 8.37 BM, respectively. At room temperature, the spin-only moment for an uncoupled binuclear high-spin Fe(III) compound would be 8.37 BM. Therefore, the coupling between the iron atoms in these compounds is weak, or even zero in 3, at room temperature. However, as can be seen qualitatively from the curves in Figures 4 and 5, both show characteristic antiferromagnetic shapes with low temperature maxima indicative of weak antiferromagnetic coupling. The value of  $\chi$  at the inflection point in the curve of **3** is larger than the value in the curve of **2** and the maximum for 3 occurs at lower temperature than for 2. Both indicate that antiferromagnetic coupling in 3 is significantly weaker than in 2. These observations pose a question related to mathematical modeling of these systems. Pavlishchuk et al. [58] have shown that for binuclear iron(III) systems with very small intramolecular coupling constants, it is not possible to obtain physically meaningful parameters from curve fitting processes that neglect zero field splitting (ZFS) effects. In fact, if ZFS is neglected for 3, a visually pleasing fit can be obtained, but with a

g value less than 2, which has no physical reality, and with intermolecular coupling that is significantly larger than intramolecular coupling when there is no basis to expect this from the X-ray structural determination. On the other hand, when ZFS is included in the fitting process for **3**, sensible parameters are obtained. As shown by Pavlishchuk et al., ZFS does not need to be included in cases such as **2** where J is somewhat larger and, in fact, the results for **2** are not significantly different when fitting is done with or without a term for ZFS included.

Fitting was based on the isotropic Heisenberg spin Hamiltonian,  $H = -2JS_1S_2$ , which has been shown to be acceptable for d<sup>5</sup>, S = 5/2 binuclear species in an octahedral ligand field such as exists in these compounds [59]. Suitable equations for both cases are available in the literature [53, 58, 60]. In the present work, non-linear least squares fitting of calculated susceptibilities to the experimental data in order to estimate the magnetic parameters was carried out using the program MAGMUN 4.1 [61]. For **2**, J = -5.64  $\pm$  0.02 cm<sup>-1</sup>, g = 2.032  $\pm$  0.001,  $\rho$  = 0.005, TIP = 0.00037 cgsu/mol and  $\theta$  = 0 with R = [ $\Sigma \chi_{obs} - \chi_{calc}$ )<sup>2</sup>]/ $\Sigma$ ( $\chi_{obs}$ )<sup>2</sup>] = 1.63 x 10<sup>-3</sup>. For **3**, J = -0.99  $\pm$ 0.02 cm<sup>-1</sup>, g = 2.000  $\pm$  0.002,  $\rho$  = 0, TIP = 0.000375 cgsu/mol,  $\theta$  = -0.5 K and D = 2.04 cm<sup>-1</sup> with R = 1.62 x 10<sup>-2</sup>. The parameters obtained have their usual meanings, namely, g is the Lande factor, J is the coupling constant,  $\theta$  is the Curie-Weiss correction for intermolecular exchange interactions,  $\rho$  is the mole fraction of a magnetic impurity obeying Curie's Law and having the same molar mass and g as the main component in the mixture, TIP is temperature independent paramagnetism and D is zero field splitting.



Fig. 4(b) Chi x T vs T for  $[Fe_2(L)_2(ClCH_2COO)_2(H_2O)]$  (2)





Intramolecular exchange, as expected, is small in both cases with that in 3 being the smaller. In 2, there is no discernible intermolecular coupling while in 3, an antiferromagnetic component is suggested through the fitting process. In 2, superexchange coupling involves a pair of bridging phenoxy oxygens and a single bidentate bridging chloroacetate between the iron This compound involves comparable coordination by L to that found in atoms.  $[Fe_2(L)_2(CH_3CO_2)_2]$  reported by Mikuriya et al. [62] in which, in addition to L, two acetates bridge the iron atoms. In 2 however, a chloroacetate forms a single corresponding bridge and instead of a second bridging acetate as in  $[Fe_2(L)_2(CH_3CO_2)_2]$  the remaining coordination sites in 2 are filled by a terminal chloroacetate and a terminal H<sub>2</sub>O. In [Fe<sub>2</sub>(L)<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>], the reported value for J is 1.56(15) cm<sup>-1</sup> indicating a ferromagnetic ground state whereas in 2 the ground state is antiferromagnetically coupled with J = -5.64(2) cm<sup>-1</sup>. In centrosymmetric [Fe<sub>2</sub>(L)<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>], the Fe•••Fe separation and phenoxo Fe-O-Fe bridge angles are 2.9301(1) Å and 90.9(1)° whereas the corresponding dimensions in 2 are 3.152(7) Å and 102.2(3)° and 101.6(3)° at O(1) and O(3), respectively. Thus, replacing the second oxygen donor acetate bridge in [Fe<sub>2</sub>(L)<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>] with two terminal oxygen donor ligands has a substantial impact on the geometry of the molecule's core and thereby on the nature of any magnetic coupling between the iron atoms. The latter occurs because the quality of orbital overlap between bridgehead oxygen and bridged iron atoms is angle dependent and because any through space effects will be strongly distance dependent. In percentage terms, the difference in bridgehead angles between [Fe<sub>2</sub>(L)<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>] and 2 is much larger than the difference in interatomic distances between their iron atoms and therefore, as a first approximation, the angle at the bridgehead should be examined first for its impact on the coupling.

Comparison of  $[Fe_2(L)_2(CH_3CO_2)_2]$  and **2** reveals that a bridgehead angle close to 90° is associated with ferromagnetic behavior whereas a larger angle of approximately 102°, as found in **2**, is associated with antiferromagnetic behavior. Adding the phenoxo-oxygen bridged compounds  $[Fe_2(salmp)_2]$  (H<sub>2</sub>salmp = 2-bis(salicylidenamino)methylphenol) [63] and  $[Fe_2(chphn)_2Cl_2]$  (H<sub>2</sub>chphn = N-(4-chloro-2-hydroxyphenyl)-3-hydroxy-2-napthaldimine) [64] to the comparison reveals a bridgehead angle sequence of 90.9(1)°, 97.06(9)°, 101.9(3)° (avge from **2**) and 105.64(4)° with accompanying J values of 1.56 cm<sup>-1</sup>, 1.21 cm<sup>-1</sup>, -5.64(2) cm<sup>-1</sup> and -10.9 cm<sup>-1</sup>. The sequence reveals a bridgehead angle dependence upon whether these dinuclear Fe(III) species exhibit ferromagnetic or antiferromagnetic behavior and that the transition in behavior occurs between ~97° and ~102°.

There being no detectable through-space ferromagnetic coupling in 2 at an Fe<sup>•••</sup>Fe separation of 3.152(7) Å makes it unlikely there would be any in 3 at a separation of 5.251(3) Å and indeed none was found. In 3 however, unprecedented antiferromagnetic superexchange coupling of two high spin Fe(III) species via two very strong hydrogen bonds is observed. The coupling is weak (J = -0.99(2) cm<sup>-1</sup>) and occurs through what can be thought of as three-centre (O-H-O) four electron bonds (*vide supra*). It may be noted that antiferromagnetic coupling via hydrogen bonds, while not unknown, is relatively uncommon. One reported example is a binuclear Ni(II) species with three hydrogen bonds [55]. In that case, J = -0.23 cm<sup>-1</sup> and the O•••O distances across the hydrogen bonds are  $2.48 \pm .01$  Å or more than 0.052 Å longer, on average, than those in 3. Another example involves spin and charge transfer through hydrogen bonding in [Co(NH<sub>3</sub>)<sub>5</sub>(OH<sub>2</sub>)][Cr(CN)<sub>6</sub>] in which a polarized neutron diffraction experiment and local density functional calculations both suggest a strong involvement of the protons in the hydrogen bond [65]. A review of hydrogen bonds as structural and magnetic design elements

using hydroxylated phenyl  $\alpha$ -nitronyl nitroxide radicals as model systems has also been published and provides insight into the role of the hydrogen bond in transmission of magnetic effects [66]. In particular, spin density mapping can reveal the sign of the spin density on various atoms in odd electron species and if nuclei with the same sign of their spin density are in close contact any coupling between them would be antiferromagnetic. This is understandable as akin to spin pairing that accompanies bond formation from overlap of orbitals with the same sign to their wave functions.

Due to the paucity of examples in the literature of compounds exhibiting magnetic coupling exclusively via hydrogen bonds it is difficult to draw meaningful magnetostructural correlations other than to propose that such evidence as is available suggests that, at least in the case of strong hydrogen bonds like those in **3** that can be viewed as symmetrical three-centre two-electron bonds [57], coupling occurs by mechanisms little different than those through conventional electron pair  $\sigma$  bonds. Coupling in species like **3** is nonetheless weaker than that in those with a simple phenolic oxygen bridge between two Fe(III) centres. Coupling in the former is attenuated by passage through four bonds whereas in the latter it occurs through only two bonds.

#### 4. Conclusion

Three Fe(III) compounds, [{Fe(L)<sub>2</sub>}<sub>3</sub>Fe] (1), [Fe<sub>2</sub>(L)<sub>2</sub>(ClCH<sub>2</sub>COO)<sub>2</sub>(H<sub>2</sub>O)] (2) and [Fe(L)(HL)]<sub>2</sub> (3), have been synthesized. Synthesis of 1 and 2 proceeds through the intermediate [Fe<sub>3</sub>( $\mu_3$ -O)(O<sub>2</sub>CCH<sub>2</sub>Cl)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]ClO<sub>4</sub> yielding a mixture of both products that are separated by a process based upon their solubility differences while that of 3 is obtained directly from Fe(ClO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O and H<sub>2</sub>L. X-ray structures of 1 and 2 are unremarkable whereas that of 3 reveals a dimer of two monomers held together by two very strong hydrogen bonds. Spectroscopic features of the three

compounds are consistent with their solid state structures. Intramolecular superexchange in 2 and 3 is small and antiferromagnetic. No intermolecular coupling was detected in 2 but a small antiferromagnetic interaction was found in 3. Comparison of the magnetostructural characteristics of 2 with those of related compounds in the literature suggests the angle at the bridgehead between the two coupled iron atoms is a dominant factor affecting the magnitude of superexchange in compounds of similar core structure. Furthermore, there is a transition between antiferromagnetic and ferromagnetic coupling that occurs in these compounds at a bridgehead angle between ~97 and ~102 degrees. In 3, unprecedented weak antiferromagnetic coupling of two high spin Fe(III) species via two very strong hydrogen bonds was detected.

#### **Supplementary material**

CCDC 767221, 875401 and 772571 contain the supplementary crystallographic data for 1, 2 and 3. respectively. These obtained data can be free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data tables 1, 2 and 3 contain selected bond (and torsion for 3) angles, respectively.

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Magnetostructural properties of two compounds are reported. From one, a range of bridgehead angles within which coupling changes from ferromagnetic to antiferromagnetic is established. From the other (below), antiferromagnetic coupling between high spin Fe(III) centres via two very strong hydrogen bonds is observed. Acctiontic



- [{Fe(L)<sub>2</sub>}<sub>3</sub>Fe] **1**, [Fe<sub>2</sub>(L)<sub>2</sub>(ClCH<sub>2</sub>COO)<sub>2</sub>(H<sub>2</sub>O)] **2** and [Fe(L)(HL)]<sub>2</sub> **3** are synthesized •
- Intramolecular superexchange in 2 and 3 is small and antiferromagnetic •
- Cores like 2 go from antiferro- to ferromagnetic at bridge angles between ~97 & ~102° •
- **3** is a dimer held together by two very strong hydrogen bonds •
- Antiferromagnetic coupling in 3 occurs via the hydrogen bonds •

Acctinition