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Synthesis, structure and magnetism of a tetranuclear Fe(III) complex containing an $[Fe_4(\mu_3\text{-}O)_2]^{8+}$ core

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Abstract

The tetranuclear Fe(III) complex $[L_2Fe_2(\mu_3\text{-}O)_2(\mu_2\text{-}CH_3COO)_3(Sao)_2Fe_2]X$ (X = ClO_4 (**1**), PF_6 (**2**)), where L is the cyclic amine 1,4,7-trimethyl-1,4,7-triazacyclononane and Sao is the dianion of salicylaldoxime (H_2Sao), has been synthesized and characterized on the basis of elemental analysis, IR, electronic, Mossbauer spectroscopy and variable-temperature (4–285 K) magnetic susceptibility measurements. The molecular structure has been established by X-ray diffraction of **2**. The structure consists of an $[Fe_2^{wing}(\mu_3\text{-}O)_2Fe_2^{body}]^{8+}$-butterfly core. Each Fe(III) ion is in a distorted octahedral environment The two $Fe(Sao)^+$ units function as bridges between two terminal 'wing' iron ions through their deprotonated oximate oxygen and represent the 'body' iron ions in the tetranuclear core. Three acetate groups are singly bridging between the iron ions. Mossbauer spectra display two quadrupole doublets, consistent with two different high-spin ferric sites. Magnetic susceptibility measurements reveal a diamagnetic ground state with antiferromagnetic exchange interactions among the four high-spin ferric centers The exchange coupling constant J_{12} ('body–body' interaction) could not be determined due to prevailing spin frustration, but the 'wing–body' antiferromagnetic interaction, J, was evaluated to be -46 cm^{-1} $[\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2\ \hat{S}_3 + \hat{S}_1\ \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_4) - 2J_{12}\hat{S}_1\ \hat{S}_2]$.

Introduction

The current interest in the chemistry of polynuclear systems with two or more Fe(III) ions bridged by oxygen donor ligands is mainly due to the growing awareness of the existence of oxo-bridged iron units in a variety of iron metalloproteins [1–11]. Dinuclear metal sites with μ-oxo and μ-carboxylato bridges have been found or proposed in different iron–oxo proteins [1–11], such as hemerythrin, ribonucleotide reductase and purple acid phosphatase. The most remarkable polynuclear iron–oxo core is found in the mammalian iron storage protein, ferritin [12]. The protein can store up to 4500 ferric ions inside a single molecule. Planar tetranuclear oxo- and hydroxo-bridged iron(III) clusters also occur in nature, in at least two minerals, amarantite, $[Fe_4O_2(SO_4)_4]\cdot 14H_2O$ [13] and leucophosphite, $K_2[Fe_4(OH)_2(PO_4)_4(H_2O)_2]\cdot 2H_2O$ [14].

The pursuit of model complexes for the (μ-oxo)diiron protein sites has yielded several interesting polynuclear ferric complexes with Fe_3, Fe_4, Fe_6, Fe_8, Fe_{10} and Fe_{11} compositions [15–35] which have been structurally characterized. The oxo-bridged dinuclear complexes [1, 4–7, 38–40] are by far the most commonly isolated amongst these complexes of different nuclearity. The binuclear complexes seem to constitute a thermodynamic pit for numerous Fe(III)–ligand systems.

There are several intriguing features associated with oxo–hydroxo polynuclear iron complexes. First, these complexes can have unusual electronic structures. There is substantial evidence that the pairwise exchange interactions in these types of complexes cannot be totally explained by the Heisenberg-Dirac-van Vleck (HDvV) Hamiltonian, $\hat{H} = -2J_{ij} \cdot \hat{S}_i\hat{S}_j$. Biquadratic and antisym-

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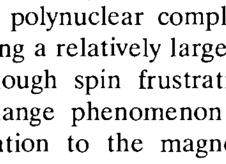
metric exchange as well as double exchange interactions have been considered to describe the magnetic properties of certain complexes [36]. A second general reason to study polynuclear metal complexes is that they may be building blocks for molecular-based magnetic materials. In general, molecules that have large numbers of unpaired electrons should serve, because of their topology, as good starting points for constructing magnetic molecular materials. Even though the pairwise exchange interactions in these complexes are found almost always to be antiferromagnetic, spin frustration in a polynuclear complex can result in ground states having a relatively large number of unpaired electrons. Although spin frustration is a well-known magnetic exchange phenomenon for extended lattices, its application to the magnetochemistry of discrete polynuclear complexes is not widely recognized [37].

Here we report the preparation and characterization of a tetranuclear iron(III) compound $[L_2Fe_4(Sao)_2(\mu_3\text{-}O)_2(\mu_2\text{-}CH_3COO)_3]ClO_4$ (**1**) and its -PF_6 salt (**2**); this molecule contains Fe(III) ion disposed in a 'butterfly' $[Fe_4O_2]^{8+}$ core, where bridging between the iron ions occurs via two μ_3-oxo anions. Apart from the here reported tetranuclear iron(III) complex, **1**, there have been several crystallographically characterized tetranuclear Fe(III) compounds [16–24] described in the literature that contain μ_2-oxo, μ_3-oxo, μ_2-hydroxo and/or μ_2-alkoxo bridges; but only four with the 'butterfly' core structure [18–22].

L =



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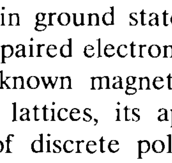


Experimental

$(C_9H_{21}N_3)FeCl_3$ was prepared as described in the literature [41]. All other reagents were used as received. Elemental microanalyses were performed by the Microanalytical Laboratory, Ruhr-Universität, Bochum. Iron was determined spectrophotometrically by using pyridine-2,6-dicarboxylic acid. The perchlorate anion was determined gravimetrically as tetraphenylarsonium(V) perchlorate. Physical measurements were performed as previously outlined [42]. The Mossbauer spectrometer worked in the conventional constant-acceleration mode with a $^{57}Co/Rh$ source of *c*. 1.8 GBq (Amersham Buchler). Isomer shifts are given relative to α-Fe at room temperature.

Preparation of compounds

$[(C_9H_{21}N_3)_2Fe_4(C_7H_5NO_2)_2(O)_2(CH_3COO)_3]ClO_4$ (1)

All operations were carried out under argon atmosphere. Ferrous acetate (0.33 g, 2.0 mmol) was added to a degassed solution of salicylaldoxime (0.27 g, 2.0 mmol) in 60 ml of methanol under vigorous stirring. The resulting suspension was stirred at room temperature for 0.5 h to yield a dark violet solution. The resulting solution was charged with a solid sample of $(C_9H_{21}N_3)FeCl_3$ (0.66 g, 2.0 mmol), sodium acetate (0.24 g, 3.0 mmol) and 2 ml of triethylamine. The suspension was refluxed for 1 h and then filtered in the air to get rid of some dark solid particles. Sodium perchlorate monohydrate (0.4 g) was added, and the dark brown solution was kept at ambient temperature. After 12 h, dark brown crystals were collected by filtration and air-dried. Yield 390 mg (34%).

Anal. Calc. for $C_{38}H_{61}N_8O_{12}Fe_4(ClO_4)$: C, 39.87; H, 5.37; N, 9.79; Fe, 19.51; ClO_4, 8.69. Found: C, 39.6; H, 5.4; N, 9.8; Fe, 19.3; ClO_4, 8.8%.

$[(C_9H_{21}N_3)_2Fe_4(C_7H_5NO_2)_2(O)_2(CH_3COO)_3]PF_6$ (2)

Complex **2** was obtained similarly to complex **1** with sodium hexafluorophosphate (400 mg) instead of sodium perchlorate used as the anion source. Dark brown crystals were obtained and used for the structure determination. Yield 500 mg (42%).

Anal. Calc. for $C_{38}H_{61}N_8O_{12}Fe_4(PF_6)$: C, 38.34; H, 5.17; N, 9.41; Fe, 18.77. Found: C, 38.2; H, 5.1; N, 9.4; Fe, 18.6%.

Caution. Although we experienced no difficulties with the perchlorate salt, the unpredictable behavior of perchlorate salts necessitates extreme caution in their handling.

Structure determination

Crystal data for **2** $[C_{38}H_{61}N_8O_{12}Fe_4](PF_6)$: cubic, space group *Pa*-3 (No. 205), $a = 32.712(4)$ Å, $V = 35004.3$ Å^3, $Z = 24$, $D_{calc} = 1.355$ g/cm^3, (Mo Kα) = 0.71073 Å, = 1.07 mm^{-1}, $F(000) = 14\,736$, $T = 298(1)$ K.

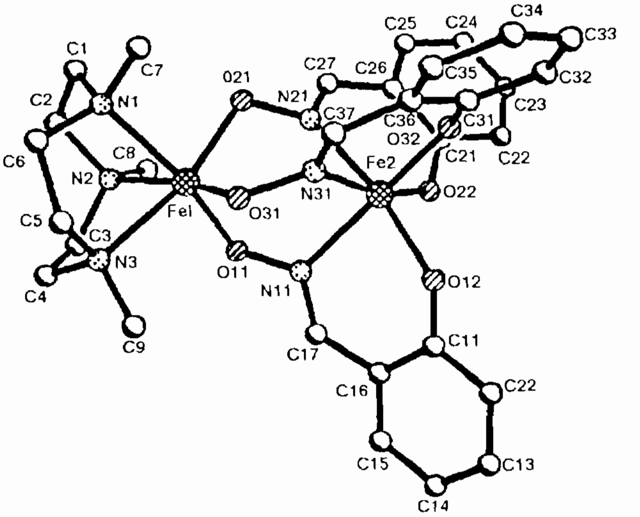
A large number of dark brown crystals had to be examined on a Weissenberg camera before a rather suitable specimen could be selected though it still suffered from poor diffraction quality and power. The crystal was then mounted on a Siemens R3m/V diffractometer; approximate dimensions were 0.22×0.43×0.45 mm. Cell parameters were refined from 25 reflections $10 \leqslant 2\theta \leqslant 26°$. 24 337 intensities were collected using ω–2θ scans in the range $2 \leqslant 2\theta \leqslant 45°$, *h*, *k*, *l* from 0 to 36. Four standard reflections were monitored every 400 measurements and showed only random deviations. Lp-correction and empirical absorption correction [43]* via ψ-scans were applied, min./max. transmission 0.83/1.00. Due to the very poor scattering only 2545 independent reflections were assigned observed with $F > 4\sigma(F)$. The systematic absences were consistent with space group *Pa*-3. Structure solution by direct methods revealed the Fe positions, remaining non-hydrogen atoms were located from subsequent ΔF maps. The PF_6 anion was found to be severely disordered over various sites which could only partially be determined, the remaining electron density was max. 2.2 e/Å^3 in height and too diffuse for further assignment. H atoms were fixed at idealized positions with common isotropic displacement parameters $U_{iso} = 0.08$ Å^2, Fe atoms refined anisotropically, refinement converged at $R = 0.14$, max. $(\Delta/\sigma) = 0.03$. All calculations were made with SHELXTL-Plus (Siemens 1990) [44].

Results and discussion

The deep violet solution obtained from ferrous acetate and salicylaldoxime (H_2Sao) in methanol under argon reacting with the LFe^{3+} unit (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) affords after addition of the perchlorate or hexafluorophosphate ion in the presence of air dark brown crystals of $[L_2Fe_4(Sao)_2(\mu_3\text{-}O)_2(\mu_2\text{-}CH_3COO)_3]X$ ($X = ClO_4$ (**1**), PF_6 (**2**)) in reasonable yield. The function of added triethylamine is to provide a basic medium needed for the deprotonation of the OH groups present in salicylaldoxime. A similar type of solvolysis reactivity of $LFeCl_3$ has been observed earlier several times [42].

Complexes **1** and **2** are sparingly soluble in water with decomposition (precipitation of insoluble brown solid $Fe(OH)_3 \cdot xH_2O$), but reasonably soluble in organic solvents such as acetone, alcohols, acetonitrile and nitromethane.

The yield of the preparation is very much dependent on the ratio of salicylaldoxime to $Fe(CH_3COO)_2$, the optimal ratio being 1:1. The amount of brown–black solid obtained by filtration in air (*vide infra*) steadily increases on increasing the amount of salicylaldoxime, with a consequent decrease in the yield of the tetranuclear complex **1** or **2**. The brown–black solid has been characterized, structurally and spectroscopically, to be the neutral dinuclear Fe(III) complex, $[LFe^{III}(Sao)_3Fe^{III}]$, with the following structure [45] and is the subject of a forthcoming paper.



We have also tried to optimize the amount of sodium acetate added. The maximum yield of **1** has been obtained with the following reactant stoichiometry: $LFeCl_3$ (1 equiv.), $Fe(CH_3COO)_2$ (1 equiv.), salicylaldoxime (1 equiv.), $NaOOCCH_3$ (3 equiv.).

It is worth noting that besides ligands and ClO_4 (or PF_6) absorptions, the IR spectra of **1** and **2** exhibit four sharp, medium intense bands in the region 690–610 cm^{-1} probably due to ν(Fe–O), $\nu(Fe_2\text{–}O)$ and $\nu(Fe_3O)$. The ν(CN) vibration is assigned to the medium intense band at ~1590 cm^{-1}. One of the characteristics in the IR spectra of the tetranuclear complexes is a very strong carbonyl stretching vibration found at 1560 cm^{-1}. The perchlorate salt shows a sharp strong band, whose intensity is comparable to that of ν(CO), at 1098 cm^{-1} (antisymmetric stretch), indicative of uncoordinated perchlorate anions. Complex **2** shows a strong sharp band at 843 cm^{-1} due to the hexafluorophosphate anions.

Figure 1 shows the electronic spectrum of **1** in acetonitrile. It consists principally of four maxima at 244 (57 600), 314 (29 300), 505 (6960), 1091 (18.2) nm and a shoulder at 400 nm (*c.* 9000); the extinction coefficients are given per tetranuclear complex in M^{-1} cm^{-1} within parentheses. The lowest energy absorption band in **1**, considered to arise from the $^6A_1 \rightarrow {}^4T_1(^4G)$ d–d transition, is red shifted by 60 nm from its position in the optical spectrum of $\{Fe_2O\}^{4+}$ unit present in $[L_2Fe_2O(\mu\text{-}CH_3COO)_2](ClO_4)_2$ [46]. The next highest energy transition (505 nm) presumably responsible for the dark brown color of **1**, is unusually intense for a high-spin Fe(III) d–d transition and is assigned to a phenolate-to-iron(III) transition. The expected ligand field transition $^6A_1 \rightarrow {}^4T_2(^4G)$ likely occurs in the 500–700 nm region, but is obscured by the more intense charge transfer phenolate-to-iron(III) transition. In the literature [47] this band has been assigned to a transition

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*Computations were carried out on a Microvax II Computer.

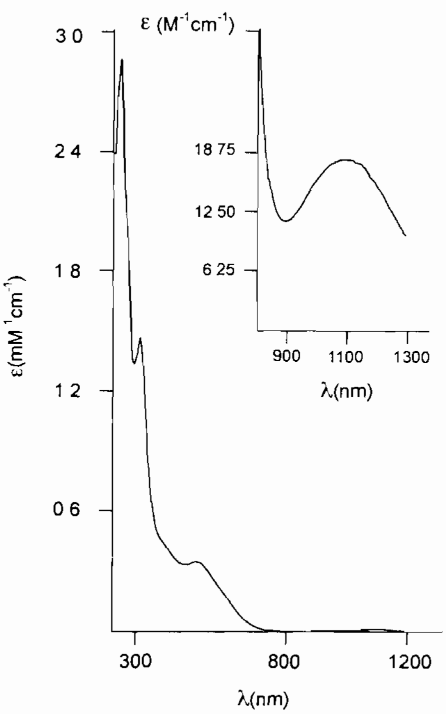


Fig. 1. Electronic spectrum of **1** in acetonitrile.

from pπ orbitals on the phenolate oxygen atoms to the half-filled dπ* orbitals on Fe(III). Interestingly the band at 505 nm has been found to be more intense (6960 M^{-1} cm^{-1}) than that expected on the basis of the proposal [48] of the additive absorptivity for phenolate binding ((1–2)×10^3 M^{-1} cm^{-1} per phenolate). The solution optical absorptions for the $\{Fe_4O_2\}^{8+}$ core in **1** are featureless in the ~400–500 nm region, where in general several transitions with oxo-to-iron(III) charge transfer character are observed in $\{Fe_2O\}^{4+}$ complexes with bent Fe–O–Fe units. The nature of the intense bands at 244, 314 and ~400 nm are thought to be principally charge transfer in origin.

Description of the structure

Although the analytical data, particularly the iron to perchlorate ratio, unambiguously showed the presence of four iron atoms as the smallest unit in the cation, an X-ray analysis was undertaken to remove the doubts regarding connectivity. Unfortunately, crystals of the cation obtained as its hexafluorophosphate salt diffract X-rays very weakly. Nevertheless, after several attempts we were able to collect a set of diffraction data of mediocre quality.

The structure of the cation in **2** is presented in Fig. 2. The cation possesses a $Fe_4(\mu_3\text{-}O)_2$ core. The metal geometry of the cluster may be described as a 'butterfly', based on two edge-sharing $Fe_3(\mu_3\text{-}O)$ triangular units with the oxygen atoms O1 below (0.111 Å) and O2 above (0.370 Å) the corresponding Fe_3 triangles. The Fe1···Fe2 distance is noticably short, 2.838 Å. The $[Fe_4O_2]^{8+}$ core has approximate C_2 symmetry. Selected distances and angles for the $[Fe_4O_2]^{8+}$ core and for the rest of the cation are given in Tables 1 and 2, respectively. The dispositions of the μ_3-oxides are almost symmetrical and are consistent with all metals being in the trivalent oxidation level, the differences being practically insignificant within the 3σ criterion. The dihedral angle between the planes Fe(1)Fe(2)Fe(3)O(1) and Fe(1)Fe(2)Fe(4)O(2) is 153.9°.

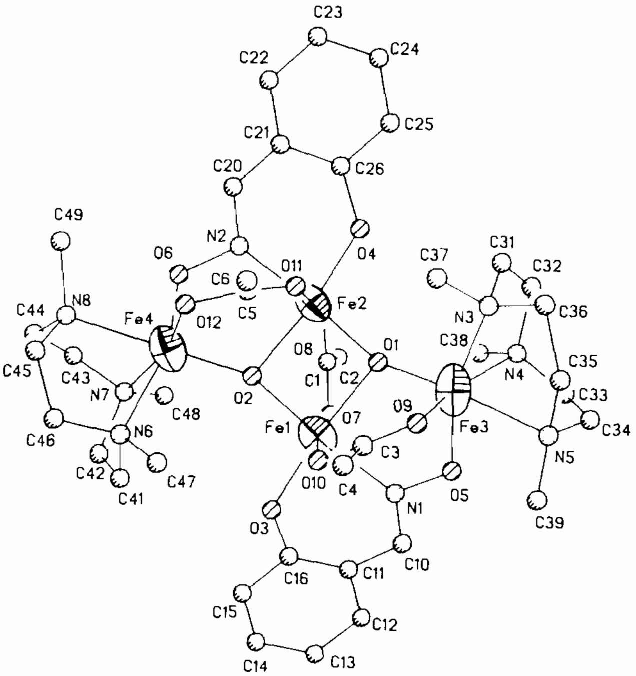
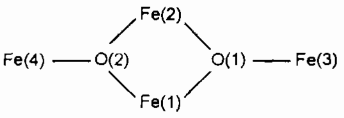


Fig. 2 Molecular structure of the monocation $[L_2Fe_4(\mu_3\text{-}O)_2(SaO)_2(CH_3COO)_3]^+$ in **2**.

TABLE 1. Bond distances (Å) and angles (°) within the $[Fe_4O_2]^{8+}$ core of **2**



Fe(4)–O(2)	1.891(26)
Fe(3)–O(1)	1.828(27)
Fe(1)–O(1)	2.067(26)
Fe(2)–O(1)	1.888(26)
Fe(2)–O(2)	2.019(26)
Fe(1)–O(2)	1.910(26)
Fe(2)–O(2)–Fe(1)	92.5(11)
Fe(2)–O(1)–Fe(1)	91.6(11)
O(2)–Fe(2)–O(1)	87.3(11)
O(2)–Fe(1)–O(1)	85.4(11)
Fe(4)–O(2)–Fe(2)	112.0(13)
Fe(4)–O(2)–Fe(1)	154.9(15)
Fe(3)–O(1)–Fe(2)	154.7(16)
Fe(3)–O(1)–Fe(1)	111.0(13)

TABLE 2. Selected bond distances (Å) and angles (°) for $[Fe_4O_2(Sao)_2(L)_2(CH_3COO)_3]PF_6$ (**1**)

Fel ..Fe2	2 839(9)	Fe2. Fe3	3.626(10)
Fel ... Fe3	3 214(10)	Fe2.. Fe4	3 242(9)
Fel ... Fe4	3 710(10)	Fe3 ..Fe4	6.101(10)
Bonds			
Fel–O3	1.937(34)	Fe2–O4	1.882(31)
Fel–O7	2.076(30)	Fe2–O8	2.076(29)
Fel–O10	2.080(32)	Fe2–O11	2.025(33)
Fel–N1	2.087(40)	Fe2–N2	2.058(37)
Fe3–O9	2.019(34)	Fe4–O12	2.057(33)
Fe3–O5	1.979(38)	Fe4–O6	1 936(32)
Fe3–N5	2 286(52)	Fe4–N8	2 266(46)
Fe2–N4	2.204(48)	Fe4–N7	2.149(42)
Fe3–N3	2.074(53)	Fe4–N6	2.239(44)
Angles			
O(2)–Fe(1)–O(3)	101.5(13)	O(1)–Fe(1)–O(3)	173.1(12)
O(2)–Fe(1)–N(1)	173.6(14)	O(1)–Fe(1)–N(1)	89 5(13)
O(1)–Fe(1)–O(7)	88.0(11)	O(3)–Fe(1)–N(1)	83.7(15)
O(3)–Fe(1)–O(7)	91 6(13)	O(2)–Fe(1)–O(7)	92 0(11)
O(1)–Fe(1)–O(10)	87.9(11)	N(1)–Fe(1)–O(7)	84.0(13)
O(3)–Fe(1)–O(10)	91 7(13)	O(2)–Fe(1)–O(10)	93 7(12)
O(7)–Fe(1)–O(10)	172.7(12)	N(1)–Fe(1)–O(10)	89.9(13)
O(1)–Fe(2)–O(4)	100.0(13)	O(2)–Fe(2)–O(4)	171.6(12)
O(1)–Fe(2)–N(2)	175.9(13)	O(2)–Fe(2)–N(2)	88.6(13)
O(4)–Fe(2)–N(2)	84.1(14)	O(1)–Fe(2)–O(8)	91 4(12)
O(2)–Fe(2)–O(8)	91.1(11)	O(4)–Fe(2)–O(8)	92 9(13)
N(2)–Fe(2)–O(8)	88 0(13)	O(1)–Fe(2)–O(11)	93 3(12)
O(2)–Fe(2)–O(11)	88.5(12)	O(4)–Fe(2)–O(11)	86.9(14)
N(2)–Fe(2)–O(11)	87 2(14)	O(8)–Fe(2)–O(11)	175.2(13)
O(1)–Fe(3)–O(5)	95.5(14)	O(1)–Fe(3)–O(9)	95.7(13)
O(5)–Fe(3)–O(9)	97.7(15)	O(1)–Fe(3)–N(3)	100.9(17)
O(5)–Fe(3)–N(3)	160 7(19)	O(9)–Fe(3)–N(3)	90 7(18)
O(1)–Fe(3)–N(4)	100.6(15)	O(5)–Fe(3)–N(4)	89.1(17)
O(9)–Fe(3)–N(4)	161 7(16)	N(3)–Fe(3)–N(4)	78.1(20)
O(1)–Fe(3)–N(5)	174.9(16)	O(5)–Fe(3)–N(5)	79.6(18)
O(9)–Fe(3)–N(5)	83.7(17)	N(3)–Fe(3)–N(5)	84.1(20)
N(4)–Fe(3)–N(5)	80.8(18)	O(2)–Fe(4)–O(6)	94.9(12)
O(2)–Fe(4)–O(12)	93.0(12)	O(6)–Fe(4)–O(12)	95.0(13)
O(2)–Fe(4)–N(6)	102.5(14)	O(6)–Fe(4)–N(6)	160 6(15)
O(12)–Fe(4)–N(6)	92.5(15)	O(2)–Fe(4)–N(7)	101.8(14)
O(6)–Fe(4)–N(7)	90.3(15)	O(12)–Fe(4)–N(7)	163.0(15)
N(6)–Fe(4)–N(7)	77.8(16)	O(2)–Fe(4)–N(8)	179 3(11)
O(6)–Fe(4)–N(8)	85.1(15)	O(12)–Fe(4)–N(8)	85.5(15)
N(6)–Fe(4)–N(8)	77.6(16)	N(7)–Fe(4)–N(8)	78.9(16)
Fe(2)–O(8)–C(1)	122.3(30)	Fe(1)–O(7)–C(1)	121.7(29)
Fe(3)–O(9)–C(3)	122.6(35)	Fe(1)–O(10)–C(3)	127.9(33)
Fe(4)–O(12)–C(5)	123.9(31)	Fe(2)–O(11)–C(5)	130.7(37)

In addition to the two μ_3-oxo groups, there are three bridging acetate groups in the tetranuclear structure, one each between iron atom pairs Fe(4)Fe(2), Fe(1)Fe(3) and Fe(1)Fe(2). Additionally two -[N–O] groups of the deprotonated oximes are coordinated to iron pairs Fe(4)Fe(2) and Fe(3)Fe(1) through their oxygen and nitrogen donor atoms, respectively.

It seems that the non-planarity of the $[Fe_4O_2]^{8+}$ unit is a consequence of the bridging carboxylate groups. Specifically, the iron atoms that are carboxylate bridged are apparently 'pulled' closer to one another (Fe(1)···Fe(3) 3.214, Fe(2)···Fe(4) 3.242 Å) than those that are without carboxylate bridging (Fe(1)···Fe(4) 3.710, Fe(2)···Fe(3) 3.626 Å). Just as there are two long and two short Fe···Fe separations, there are also two long (Fe(1)···O(1), Fe(2)···O(2)) and two short (Fe(1)···O(2), Fe(2)···O(1)) μ_3-oxo–iron bonds in the inner Fe_2O_2 core. The average Fe–(μ_3-O) bond distance of 1.93 Å is close to that observed for typical $Fe_3(\mu_3\text{-}O)$ species (1.90 Å).

Each iron ion is in a distorted octahedral environment, with Fe(1) and Fe(2) having $FeNO_5$, and Fe(3) and Fe(4) having FeN_3O_3 coordination spheres. Fe–N and Fe–O bond distances (see Tables 1 and 2) are typical of high spin Fe(III) coordination complexes. The Fe–N distances for the macrocyclic amine *trans* to the short Fe–(μ_3-O) bonds are marginally longer than those *cis* to it, an effect that is much less dramatic than in $[L_2Fe_2O(OOCCH_3)_2]^{2+}$ [46].

Very few tetranuclear Fe(III) complexes which have the same $[Fe_4O_2]^{8+}$-butterfly core have been reported [18–22] in the literature. The structural parameters for **2** fall in the range reported for the other $[Fe_4O_2]^{8+}$ complexes. Detailed comparisons for the previously reported $[Fe_4O_2]^{8+}$ complexes may be found elsewhere [19, 20]. We are refraining from discussing the structure of **2** in more detail because of its mediocre quality.

Mössbauer studies

The powder state Mössbauer spectrum at 77 K of **1** is displayed in Fig. 3. The isomer shifts (δ_{Fe}) and quadrupole splitting parameters (ΔE_Q) are listed in Table 3. The perchlorate salt shows two well-resolved doublets, in accord with the inequivalence of the 'body' (Fel, Fe2) and 'wing-tip' (Fe3, Fe4) iron sites in the solid state structure (Tables 1 and 2); but the spectrum of the PF_6 salt, **2**, is not that well-resolved. The reason for this ill-resolution is not yet clear to us. We are investigating in more detail the field-dependent and

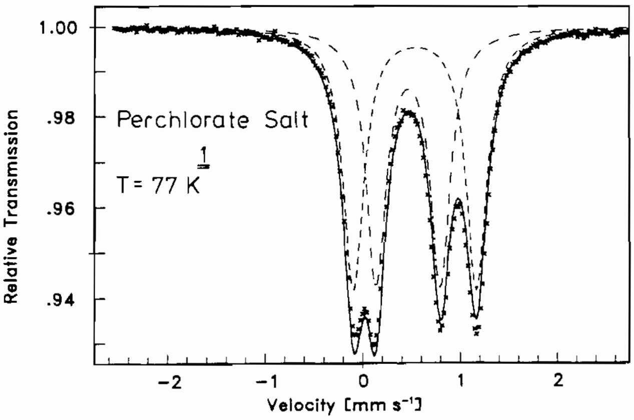


Fig 3. Mossbauer spectrum of **1** at 77 K.

TABLE 3 Mossbauer parameters of the complex as its perchlorate and hexafluorophosphate salt

Compound	T (K)	δ (mm/s)	ΔE_Q (mm/s)
1	77	0.54	1.26
		0.46	0.66
1	290	0.42	1.29
		0.36	0.66
2	77	0.52	1.20
		0.47	0.84
2	290	0.42	1.21
		0.36	0.86

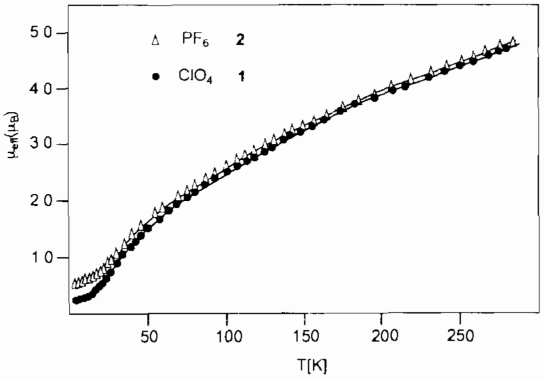


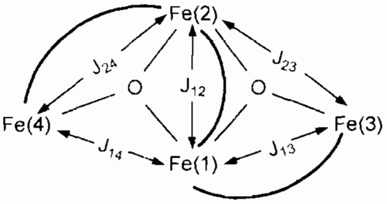
Fig 4 Plots of μ_{eff} vs. T for solid **1** and **2** The solid lines represent the best least-squares fits of the experimental data to the theoretical equation.

low-temperature Mossbauer spectra. Each spectrum was fitted to two nearly equal-area doublets, in accord with the symmetry of the tetranuclear core. The isomer shifts (δ_{Fe}) with slight temperature dependence for both doublets fall in the range 0.3–0.6 mm/s, typical for high-spin ferric complexes depending upon the nature of the coordination environment [49]. The δ value for a complex containing a similar [Fe_4O_2] unit, [$Fe_4O_2(O_2CCF_3)_8(H_2O)_6$], described by a Russian group [22], was reported to be 0.81 mm/s at 80 K, however. The two doublets do, however, exhibit differences in the ΔE_Q values that are consistent with a substantial distortion from octahedral symmetry for each site, since the valence electron contribution to ΔE_Q is negligible for a high-spin Fe(III). By comparing the bond lengths for the NO_5 coordination sphere about Fe1 and Fe2 (varying from 1.89 to 2.09 Å) with those for the N_3O_3 coordination sphere around Fe3 and Fe4 (ranging from 1.83 to 2.29 Å), the doublet with $\Delta E_Q < 1$ mm/s can be assigned to the 'body' irons (Fe1, Fe2), whereas the outer doublet is assignable to the 'wing-tip' irons (Fe3, Fe4) due to the more distorted ligation and the shortest Fe(3)–O(1) bond. That the principal distortion from octahedral symmetry is due to the length of the Fe–(μ_3-O) bond has been reported earlier [18–20] for two similar tetranuclear iron(III) complexes. We also arrive at the same conclusion by analyzing the structural data for **2**, although our data are of only mediocre quality.

Magnetic properties

Magnetic susceptibility data for polycrystalline samples of **1** and **2** were collected in the temperature range 4.2–285.7 K, and the data are displayed in Fig. 4 as μ_{eff} versus temperature. The shapes of the nearly identical plots reveal a behavior typical for antiparallel spin coupling. The values of μ_{eff}/complex are 4.81 μ_B at 285.7 K for the hexafluorophosphate salt, **2**, and 4.73 μ_B at 281.4 K for the perchlorate salt, **1**. These values are much lower than the value of $\mu_{eff} = 11.84\ \mu_B$ expected for four uncoupled 5/2 spins with $g = 2.0$ The magnetic moment decreases monotonically with decreasing temperature to an essentially diamagnetic value of 0.262 μ_B for **1** and 0.558 μ_B for **2** at 4.2 K; the residual non-zero moment is due to both temperature independent paramagnetism (TIP) and an amount of a paramagnetic impurity ($S = 5/2$). Thus the temperature-dependent behaviors of magnetic moments for **1** and **2** clearly indicate an $S_T = 0$ electronic ground state, in accord with what has been observed earlier for two other molecules of similar structure [18, 20]. A ground state of zero net spin can be qualitatively envisaged in terms of an antiparallel coupling of the four high-spin Fe(III) ions. The ground state $S_T = 0$ results from the anti-ferromagnetic coupling of $S_{34} = 5$ and $S_{12} = 5$ (*vide infra*). For a system of four ferric ions ($S = 5/2$) disposed in a butterfly-type arrangement, the overall degeneracy ($6^4 = 1296$) is distributed over 146 spin states with S_T values ranging from $S_T = 0$ to $S_T = 10$.

The bis-μ_3-oxo core of this butterfly complex is pictured below, where the arcs represent bridging carboxylate groups.



Assuming the exchange interaction between Fe(4) and Fe(3) to be negligible, there are three exchange coupling constants as defined above:

$J_{14} = J_{23}$; $J_{24} = J_{13}$ and J_{12}

But we have used a two J value magnetic exchange model, which is in conformity with the prevailing notion that acetate groups mediate very weak to negligible spin coupling [50]. The exchange coupling constants used by us to describe the magnetic interactions in **1** and **2** are

$$J = J_{14} = J_{23} = J_{24} = J_{13} \text{ and } J_{12}$$

Hence, the isotropic exchange interactions can be described by the Hamiltonian

$$\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_4) - 2J_{12}\hat{S}_1 \cdot \hat{S}_2$$

where $S_i = 5/2$ with $i = 1, 2, 3, 4$.

An equivalent operator expression to replace the above equation can readily be obtained by means of the Kambe method [51] with the following vector coupling scheme

$$\hat{S}_T = \hat{S}_{12} + \hat{S}_{34}$$

where $\hat{S}_{12} = \hat{S}_1 + \hat{S}_2$ and $\hat{S}_{34} = \hat{S}_3 + \hat{S}_4$.

The theoretical values of χ_M for the $[Fe_4(\mu_3\text{-}O)_2]^{8+}$ core were calculated by using the Kambe vector coupling scheme combined with the van Vleck susceptibility equation [52] which results from the above spin Hamiltonian. A correction for a small amount of paramagnetic impurity, P ($S = 5/2$), was also taken into account by adding a Curie law expression to the formula. The expression used is

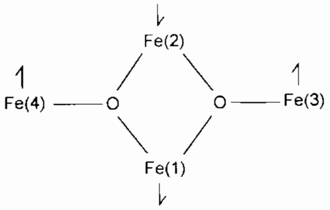
$$\chi_{\text{calc}}^{\text{Fe4 cluster}} = (1-P)\left[\frac{C}{T} f(J, J_{12}, T)\right] + P\frac{C}{T} + TIP$$

where P is the amount of paramagnetic impurity, $C = Ng^2\mu_B{}^2/k$, $f(J, J_{12}, T)$ is derived from the theoretical equation and $TIP = 630 \times 10^{-6}$ cm^{-3} mol^{-1} for each iron atom. The experimental values of χ (and μ_{eff} per molecule) have been fitted to this equation by treating J, J_{12} and P as adjustable parameters, and by holding $J_{12} = 0$ and allowing J and P to vary. The Zeeman interaction of the high-spin ferric ion in a $^6A_1$ ground state with practically no contribution from orbital angular momentum is isotropic; the observed g values are very close to the free-electron spin value of 2.0. Hence, we have fixed molecular g to 2.0. The quality of the fit is negligibly dependent on J_{12}. Variation J_{12} values from 0 to -25 cm^{-1} has got an insignificant effect on J values, which lie within the narrow range of -46.1 to -48.2 cm^{-1}. Hence the fits with $J_{12} = 0$ have been accepted to be more plausible. That J_{12} cannot be accurately determined from the susceptibility data in the temperature range *c.* 4–300 K, but J can be evaluated with a reasonable accuracy have been pointed out earlier [20]. The agreement between the calculated and observed magnetic susceptibilities above 30 K is very good and the best fits are shown as solid lines in Fig. 4. The best fit parameters obtained are: $J = -46.8$ cm^{-1}, $P = 0$ for **1** and $J = -46.1$ cm^{-1}, $P = 0.014$ for **2**. Preliminary attempts to fit the susceptibility versus temperature data below 30 K to the described spin-exchange coupling model indicated the need for more extensive theoretical analysis, currently being undertaken.

The evaluated J values for **1** and **2** do fall in the range which has been observed for trinuclear iron acetates [53], lending some credibility to the formulation of these $[Fe_4O_2]^{8+}$ complexes as edge-sharing μ_3-O trinuclear fragments. In other words, these $[Fe_4O_2]^{8+}$ complexes can be viewed as triangular $Fe^{III}{}_3O$ units to which has been added an Fe^{III}–O moiety. The observed J values are in good agreement with the reported exchange coupling constants for two similar compounds [20] and also consistent with the empirical correlations which have been made regarding Fe–μ-O bond lengths and the strength of magnetic exchange interactions in other polynuclear ferric complexes [54]. The terminal ligands thus appear not to exert a significant effect on the antiparallel spin coupling of these butterfly tetranuclear ferric cores $[Fe^{III}{}_4(\mu_3\text{-}O)_2]^{8+}$.

If J is appreciably more negative (i.e. stronger coupling) than J_{12}, then the energies of the $S_T = 0$ ground state and all thermally populated excited states are effectively only determined by J, making the nature of J_{12} interaction indeterminate in the $[Fe_4(\mu_3\text{-}O)_2]^{8+}$ core. This point has been elaborately discussed in a paper by McCusker *et al.* [20] and so we are refraining from discussing this further. The susceptibility data at very high temperatures may make it possible to determine J_{12}. We anticipate the thermal stability of **2**, a hexafluorophosphate salt, (but not of the perchlorate salt, **1**) might permit us such measurements at much higher temperatures, which will be carried out in the future.

The 'body–body' Fe(2)···Fe(1) interaction, J_{12}, is dominated by the 'wing–body' Fe···Fe exchange interactions, J, resulting in the overall favoured spin alignment as pictorially represented below:



The intrinsic character (i.e. antiparallel coupling) of the Fe(2)···Fe(1) interaction, J_{12}, can thus be totally negated resulting in spin frustration. The J_{12} interaction is frustrated with parallel spin alignment between the two body iron ions Fe(2) and Fe(1). This type of spin frustration in polynuclear manganese and iron complexes has been discussed recently by Hendrickson and coworkers [37] in detail.

Conclusions

(i) A tetranuclear ferric complex with an $[Fe_4(\mu_3\text{-}O)_2]^{8+}$ core structure has been prepared. This butterfly complex can be viewed as a triangular $Fe^{III}_3(\mu_3\text{-O})$ unit to which has been added an Fe^{III}–O moiety. In other words, the structure can be described as two triangular Fe^{III}_3O units sharing a common edge.

(ii) The evaluated exchange coupling constant (J) is very similar to those reported earlier for similar $[Fe_4O_2]^{8+}$ species, implying an insignificant effect of the terminal ligands on the antiparallel spin coupling in the butterfly core, $[Fe_4(\mu_3\text{-O})_2]^{8+}$.

(iii) A 'two-J' model seems to be sufficient to describe the magnetic properties of this core.

(iv) The ground state for the complex is $S_T = 0$, which results from the coupling of $S_{12} = 5$ and $S_{34} = 5$. The relative energies of the ground state and all of the thermally populated states depend only on J and not on J_{12}.

(v) Similar to reported analogous Fe^{III}_4 complexes, the 'wing–body' (J) antiferromagnetic interaction dominates over the 'body–body' (J_{12}) interaction, thus the intrinsic character of J_{12} can be totally negated. The J_{12} interaction is thus indeterminate, and also frustrated. It is interesting to note that in a similar heteronuclear $[Cr^{III}_2Fe^{III}_2(\mu_3\text{-O})_2]^{8+}$ complex [55], the 'wing–body' interaction (J_{CrFe}) does not dominate over the other interaction (J_{FeFe}), yielding a very complicated low-lying magnetic structure with a non-diamagnetic ($S_T \neq 0$) ground state.

Supplementary material

Further details of the crystal structure investigation may be obtained from U.F. and H.-J.H. (Paderborn).

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