Properties and Reactivity of Unusual Diiron Complexes of a Linear Tetradentate Ligand. Crystal Structures of Diiron-(II) and -(III) Complexes†

Rita Hazell,[a] **Kenneth B. Jensen,**[b] **Christine J. McKenzie***,[b] **and Hans Toftlund**[b]
[a] *Department of Chemistry, Aarhus University, DK-8000 Århus C, Denmark*
[b] *Department of Chemistry, Odense University, DK-5230 Odense M, Denmark*

Dinuclear iron complexes containing the tetradentate N_4 ligand *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-ethane-1,2-diamine (L) have been prepared. The diiron(II) complex $[LFe(O_2CMe)_2FeL][ClO_4]_2$ **1** has been characterized by X-ray crystallography: triclinic, space group $P\bar{1}$, with $a = 13.756(3)$, $b = 15.033(3)$, $c = 13.637(3)$ Å, $\alpha = 97.82(1)$, $\beta = 108.95(1)$, $\gamma = 118.07(1)°$ and $Z = 2$. The structure refined to a final *R* value of 0.046 for 3556 reflections. The complex contains two iron(II) ions bridged by two acetate groups, Fe ··· Fe 4.382(2) Å. Each acetate bridges the iron atoms in an *O,O'* mode using the *syn* lone pair of one carboxylate oxygen atom and the *anti* lone pair of the other. The ligand shows a *cis*-α conformation about the iron(II) centres. Complex **1** is readily oxidized in solution by air and from these solutions a diiron(III) complex containing a μ-oxo-μ-acetato core, $[LFeO(O_2CMe)FeL][ClO_4]_3$, was recovered. Another diiron(III) complex, prepared in the absence of other possible bridging groups, is formulated as $[LFeO(OH)FeL][ClO_4]_3 \cdot 2H_2O$, **2**. The spectroscopic data for it are consistent with the unusual formulation of a doubly bridged μ-oxo-μ-hydroxo-diiron(III) core, only the second reported example of a small molecule with this core structure. In solution, **2** is sensitive towards carbon dioxide, reacting to give $[LFeO(CO_3)FeL][ClO_4]_2 \cdot 2H_2O$, **3**. The structure of **3** has been solved by X-ray crystallography and shows a dibridged μ-oxo-μ-carbonato-*O,O'* core: monoclinic, space group *C*2/*c*, $a = 19.565(8)$, $b = 13.427(2)$, $c = 13.722(9)$ Å, $\beta = 94.31(3)°$ and $Z = 8$. The structure refined to a final *R* value of 0.066 for 4575 reflections. The average Fe–(μ-O) is 1.804(5) Å, Fe–O–Fe is 126.1(3)° and Fe ··· Fe 3.216(1) Å. Again L shows a *cis*-α conformation. Complex **2** was used to prepare other complexes containing the $[LFeOFeL]^{4+}$ core: $[LFeO(O_2CMe)FeL][ClO_4]_3$, $[LFeO(O_2CH)FeL][ClO_4]_3$ and $[LFeO(SO_4)FeL][ClO_4]_2$, by addition of acetic acid, formic acid and sodium hydrogensulfate respectively; and $[L(Cl)FeOFe(Cl)L][ClO_4]_2$ by addition of chloride ions.

In recent years substantial progress has been made in modelling the diiron centres in haemerythrin, ribonucleotide reductase and methane monooxidase.[1] Conversely, few examples of stable diiron(II) and iron(II)iron(III) complexes have appeared in the literature. Low-oxidation-state diiron complexes have the potential to simulate some of the reactivity towards dioxygen shown by these metalloenzymes in their active reduced states. Of the few examples reported, some are based on terminal capping ligands,[2] and others are complexes of dinucleating ligands containing a hingeing alkoxo oxygen atom.[3] We are interested in the preparation of the former class of complexes.

Dinuclear complexes of metal ions with a preference for octahedral co-ordination using the archetypal tripodal tetradentate capping ligand tris(2-pyridylmethyl)amine (tpa) have been reported showing that both mono- and di-bridged M(μ-oxo)M core structures (M = V, Cr, Mn or Fe) are accessible.[4] The dibridged diiron complexes are model compounds for the active metallocentre in the fully oxidized B2 subunit of *Escherichia coli* ribonucleotide reductase which shows a dibridged (μ-oxo)(μ-acetato) core in its recently reported structure.[5] Que and co-workers[4d–h] have employed tpa in some of their work on diiron(III) complexes. This has proved a flexible system in which the μ-oxo atom in the diiron(III) systems can be supported by a variety of bidentate bridging ligands with a range of 'bite' distances [*i.e.* generating Fe ··· Fe distances in the range 3.196(2)–3.402(2) Å and Fe–O–Fe 125.4(3)–143.4(3)]. Part of the motivation for the work presented here was to synthesize complexes of N_4 ligands which are less capable than tpa in stabilizing higher oxidation states, due to their weaker ligand-field strengths. Dimeric iron(II) complexes of these ligands may therefore be more accessible.

We have investigated the diiron complexes of a linear tetradentate N_4 capping aminopyridyl ligand based on *N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine (bpen). Our previous work with iron(II) spin cross-over systems of the type $Fe(N_4)(NCS)_2$ showed that the *N*-alkylated linear N_4 compounds formed high-spin iron(II) complexes below 70 K whereas the iron(II) complex of tpa and bpen remains low spin.[6] The evidently weaker ligand-field strengths of the *N*-alkylated bpen ligands suggested to us their suitability in the preparation of low-oxidation-state diiron complexes. In the present study we use the methyl-substituted ligand *N,N'*,dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine (L). Replacement of the NH groups of bpen with NMe groups offers the further advantage of eliminating the possibility of formation of very stable low-spin iron(II) diimine complexes *via* the oxidative dehydrogenation of the co-ordinated bpen. We suspected this type of reaction during our work on the iron(II) complexes of bpen[6b] where the formation of deep purple oxidation products was observed on exposure of the solutions to air. Raleigh and Martell[7] have observed analogous reactions of amine ligands in related cobalt(II) systems.

Iron,[6b] manganese[8] and cobalt[9] complexes of linear tetradentate N_4 chelating ligands based on bpen apparently have a high preference for a *cis*-α co-ordination geometry. This geometry is ideal for the construction of singly and doubly bridged diiron core units. We have recently prepared a stable

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

dibridged (μ-oxo)(μ-acetato)dimanganese(III) complex of L which lends support to the feasibility of obtaining stable low-oxidation-state complexes of this ligand.[10]

The crystal structure of methaemerythrin shows, as well as the (μ-oxo)bis(μ-acetato)diiron(III) core and terminal co-ordination by five histidines, an available site for exogenous ions. Under physiological conditions, molecular oxygen binds at this site as HO_2^-.[11] The structure of fully oxidized R2 subunit of ribonucleotide reductase shows one co-ordinated water molecule at each iron atom.[12] The recently reported structure of the apoprotein form of this reductase saturated with Mn^{2+} shows a water ligand bound to one of the manganese centres.[13] The very recent crystal structure of methane monooxidase[14] shows likewise a terminal water molecule bound to one of the iron(III) atoms. Besides this an acetate ligand (originating from the crystallization buffer media) bridging the two iron(III) atoms indicates the availability of exchangeable sites on each iron atom. The vacant co-ordination site and substitution labile aqua ligands in the structures of these diiron enzymes are presumably of fundamental importance for their biological activities. A second objective of the present work, which may be particularly relevant in modelling naturally occurring metalloenzymes, has been the synthesis of dinuclear iron complexes containing labile water ligands, in attempts to produce compounds with exchangeable and/or reactive sites. The discovery of complexes which show reactivity towards dioxygen and/or catalyse oxidation reactions is a desirable outcome of these efforts. We have previously isolated μ-oxo-diiron(III) complexes of tripodal tetradentate ligands with additional terminal water ligands[15] and with a hydrogen-bonded aqua–hydroxo ($H_3O_2^-$) bridging group.[15b] The complexes $[(bpp)(H_2O)FeOFe(H_2O)(bpp)][ClO_4]_2$ {Hbpp = 3-[bis(2-pyridylmethyl)amino]propionic acid} and $[(tpa)FeO(H_3O_2)Fe(tpa)][ClO_4]_3$ have been structurally characterized by X-ray crystallography; the latter shows interesting reactivity in that it is capable of promoting the hydrolysis of acetonitrile and triphenyl phosphate.[15b]

Experimental

Infrared spectra were measured as KBr discs using a Hitachi 270-30 spectrometer, NMR spectra with a Bruker AC 250 FT spectrometer, and UV/VIS absorption spectra on a Shimadzu UV-3100 spectrophotometer. Electrospray (ES) mass spectra were obtained using a Finnigan TSQ 710 spectrometer with a combined electrospray and atmospheric pressure chemical ionization source. Samples were 0.1 mmol dm^{-3} in acetonitrile. Elemental analyses were carried out at the microanalytical laboratory of the H.C. Ørsted Institute, Copenhagen.

CAUTION: The following compounds were isolated as perchlorate salts and were treated as potential explosives.

N,N'-Dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine dihydroperchlorate ($L{\cdot}2HClO_4$) was prepared according to the method of Toftlund *et al.*[6b]

Di-μ-acetato-bis{[N,N'-*dimethyl*-N,N'-*bis*(2-*pyridylmethyl*)-*ethane*-1,2-*diamine*]*iron*(II)} *Perchlorate*, $[LFe(O_2CMe)_2FeL][ClO_4]_2$ **1**.—The synthesis was carried out under Ar using standard Schlenk techniques. A mixture of $L{\cdot}2HClO_4$ (0.680 g, 1.45 mmol) and triethylamine (0.330 g, 3.27 mmol) dissolved in dry methanol (10 cm^3) was added to a stirred suspension of freshly prepared $Fe(O_2CMe)_2$ (0.250 g, 1.45 mmol) in dry methanol (5 cm^3). On warming, the $Fe(O_2CMe)_2$ dissolved to give a yellow solution from which a yellow precipitate was deposited within minutes. The precipitate was separated and dissolved immediately in dry acetonitrile. Diffusion of diethyl ether into the acetonitrile solution gave yellow block-shaped crystals of complex **1**. These were collected and washed with a mixture of acetonitrile and diethyl ether, yield 0.456 g, 65% (Found: C, 44.35; H, 5.10; Cl, 7.45; N, 11.50. $C_{36}H_{50}Cl_2Fe_2N_8O_{12}$ requires C, 44.60; H, 5.20; Cl, 7.30; N, 11.55%). λ_{max}/nm (MeCN) 274 (ε/dm^3 mol^{-1} cm^{-1} 14 600), 325 (1770), and 383 (2700). *m/z* 385.2 (M^{2+}, 100%); other species observed in the mass spectra are described in the Results and Discussion section.

μ-*Hydroxo*-μ-*oxo-bis*{[N,N'-*dimethyl*-N,N'-*bis*(2-*pyridylmethyl*)*ethane*-1,2-*diamine*]*iron*(III)} *Perchlorate*, $[LFeO(OH)FeL][ClO_4]_3{\cdot}2H_2O$ **2**.—A mixture of $L{\cdot}2HClO_4$ (0.376 g, 0.8 mmol) and sodium hydroxide (0.094 g, 2.35 mmol) dissolved in ethanol–water (1:1, 10 cm^3) was added to $Fe(ClO_4)_3{\cdot}6H_2O$ (0.529 g, 1.1 mmol) dissolved in ethanol (2 cm^3). The colour changed to a deep maroon within seconds. The product crystallized as maroon crystals over several days. The crystals were collected and washed with ethanol, yield 0.133 g, 34% (Found: C, 37.45; H, 4.65; Cl, 10.70; N, 10.90. $C_{32}H_{49}Cl_3Fe_2N_8O_{16}$ requires C, 37.70; H, 4.85; Cl, 10.40; N, 11.00%). The ES mass spectrum is described in the Results and Discussion section.

μ-*Carbonato*-μ-*oxo-bis*{[N,N'-*dimethyl*-N,N'-*bis*(2-*pyridylmethyl*)*ethane*-1,2-*diamine*]*iron*(III)} *Perchlorate*, $[LFeO(CO_3)FeL][ClO_4]_2{\cdot}2H_2O$ **3**.—A mixture of $L{\cdot}2HClO_4$ (1.024 g, 2.2 mmol) and sodium hydroxide (0.276 g, 6.9 mmol) dissolved in ethanol–water (1:1, 15 cm^3) was added to $Fe(ClO_4)_3{\cdot}6H_2O$ (1.589 g, 3.4 mmol) dissolved in ethanol (15 cm^3). Over a few days green crystals of the product were deposited along with a flocculent precipitate of iron oxide. The bulk of the latter was removed by decanting. The green crystals were dissolved in acetonitrile, and the remaining undissolved iron oxide was filtered off. The acetonitrile solution slowly evaporated to produce complex **3** as green needles which were collected and washed with acetonitrile, yield 0.120 g, 11% (Found: C, 41.05; H, 4.90; Cl, 7.25; N, 11.65. $C_{33}H_{48}Cl_2Fe_2N_8O_{14}$ requires C, 41.15; H, 5.00; Cl, 7.35; N, 11.65%). *m/z* 364.2 (M^{2+}, 100) and 827.1 ($[M + ClO_4]^+$, 1.4%). The crystals were suitable for X-ray diffraction studies. Crystal data and details of the structure determination are collected in Table 2. A full description of the structure refinement will not be given here since the crystal structure was also reported by Arulsamy *et al.*[16] during the preparation of this manuscript.

The authenticity of this complex was checked also by its preparation *via* standard self-assembly procedures: a mixture of $L{\cdot}2HClO_4$ (0.302 g, 0.60 mmol) and sodium carbonate (0.289 g, 2.7 mmol) dissolved in methanol–water (1:1, 15 cm^3) was added to $Fe(ClO_4)_3{\cdot}6H_2O$ (0.308 g, 0.66 mmol) dissolved in methanol (4 cm^3). The resulting green solution was filtered to remove traces of iron oxide and allowed slowly to evaporate. Green crystals of **3** were deposited over a few days. They were collected and washed with methanol, yield 0.071 g, 12%. The spectral characteristics of this product were identical to those above.

μ-*Acetato*-μ-*oxo-bis*{[N,N'-*dimethyl*-N,N'-*bis*(2-*pyridylmethyl*)*ethane*-1,2-*diamine*]*iron*(III)} *Perchlorate*, $[LFeO(O_2CMe)FeL][ClO_4]_3$ **4**.—Complex **4** can be prepared by three different methods: (*i*) the air oxidation of **1** in solution; (*ii*) the reaction of **2** with acetate ions; (*iii*) the standard self-assembly reaction described. The spectral characteristics of the products obtained by these different methods are identical.

A mixture of $L{\cdot}2HClO_4$ (0.5291 g, 1.1 mmol) and sodium acetate (0.2352 g, 2.86 mmol) dissolved in methanol (3 cm^3) and water (1 cm^3) was added to $Fe(ClO_4)_3{\cdot}6H_2O$ (0.6086 g, 1.3 mmol) dissolved in methanol (2 cm^3). The colour changed to green and the product precipitated as fine olive-green/brown crystals. After standing for several hours complex **4** was collected and washed with methanol. It was recrystallized from either acetonitrile or acetone–water, yield 0.330 g, 57% (Found: C, 39.80; H, 4.65; Cl, 10.30; N, 11.00. $C_{34}H_{47}Cl_3Fe_2N_8O_{15}$ requires C, 39.80; H, 4.60; Cl, 10.35; N, 10.90%). *m/z* 242.5 (M^{3+}, 100) and 413.1 ($[M + ClO_4]^{2+}$, 18%).

μ-Formato-μ-oxo-bis{[N,N'*-dimethyl-*N,N'*-bis*(2*-pyridylmethyl*)*ethane-*1,2*-diamine*]*iron*(III)} *Perchlorate*, $[LFeO(O_2CH)FeL][ClO_4]_3$ **5**.—Formic acid (0.015 g, 0.32 mmol) in acetonitrile (1 cm^3) was added to $[LFeO(OH)FeL][ClO_4]_3$ **2** (0.04 g, 0.04 mmol) dissolved in acetonitrile (5 cm^3) The resulting green solution was heated at 50 °C for 1 h. The product was deposited as a brown microcrystalline product, collected and washed with cold methanol, yield 0.026 g, 64% (Found: C, 38.50; H, 4.15; Cl, 10.25; N, 11.05. $C_{33}H_{45}Cl_3Fe_2N_8O_{15}$ requires C, 39.45; H, 4.55; Cl, 10.65; N, 11.20%). *m*/*z* 237.7 (M^{3+}, 100%) and 406.3 ($[M + ClO_4]^{2+}$, 18%).

μ-Oxo-μ-sulfato-bis{[N,N'*-dimethyl-*N,N'*-bis*(2*-pyridylmethyl*)*ethane-*1,2*-diamine*]*iron*(III)} *Perchlorate*, $[LFeO(SO_4)FeL][ClO_4]_2$ **6**.—An aqueous solution of sodium sulfate (0.036 g, 0.31 mmol) was added to $[LFeO(OH)FeL][ClO_4]_3$ **2** (0.1 g, 0.1 mmol) dissolved in water (5 cm^3). The resulting green solution was filtered and left to stand. The product was deposited as green plate-like crystals which were collected and washed with cold methanol, yield 0.068 g, 69% (Found: C, 39.20; H, 4.50; Cl, 7.20; N, 11.40; S, 3.25. $C_{32}H_{44}Cl_2Fe_2N_8O_{13}S$ requires C, 39.90; H, 4.60; Cl, 7.35; N, 11.65; S, 3.35%). *m*/*z* 382.2 (M^{3+}, 100) and 863.1 ($[M + ClO_4]^{2+}$, 0.75).

μ-Oxo-bis{*chloro*[N,N'*-dimethyl-*N,N'*-bis*(2*-pyridylmethyl*)*ethane-*1,2*-diamine*]*iron*(III)} *Perchlorate*, $[L(Cl)FeOFe(Cl)L][ClO_4]_2 \cdot 0.5H_2O$ **7**.—An aqueous solution of sodium chloride (0.2 cm^3 of 2 mol dm^{-3}) was added to $[LFeO(OH)FeL][ClO_4]_3$ **3** (0.1 g, 0.1 mmol) dissolved in water (5 cm^3). The resulting red solution was filtered and left to stand. The product was deposited as red crystals over 2 d. The crystals were collected and washed with cold methanol, yield 0.040 g, 43% (Found: C, 40.60; H, 4.70; Cl, 14.85; N, 11.65. $C_{32}H_{45}Cl_4Fe_2N_8O_{9.5}$ requires C, 40.60; H, 4.80; Cl, 15.00; N, 11.85%). *m*/*z* 369.2 (M^{2+}, 100) and 837.1 ($[M + ClO_4]^+$, 2%).

Dichloro[N,N'*-dimethyl-*N,N'*-bis*(2*-pyridylmethyl*)*ethane-*1,2*-diamine*]*iron*(III) *Perchlorate*, $[FeCl_2L]ClO_4 \cdot 3H_2O$ **8**.—To a mixture of $L \cdot 2HClO_4$ (0.196 g, 0.42 mmol) and $FeCl_3 \cdot 6H_2O$ (0.117 g, 0.43 mmol) dissolved in water (2 cm^3) was added triethylamine (*ca.* 0.06 g, 0.6 mmol) to bring the solution to pH *ca.* 4. The product separated as a bright yellow microcrystalline product and was collected and washed with water, yield 0.075 g, 34% (Found: C, 35.10; H, 4.10; Cl, 19.50; N, 10.05. $C_{16}H_{28}Cl_3FeN_4O_4$ requires C, 34.90; H, 5.10; Cl, 19.30; N, 10.15%). λ_{max}/nm (MeCN) 294 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 4007) and 367 (3325).

Magnetic Studies.—Magnetic susceptibility measurements were performed by the Faraday method in the temperature range 4–300 K at a field strength of 1.3 T using instrumentation described elsewhere.[17] The variation of susceptibility with temperature can be described by the equations derived from the Heisenberg–Dirac–Van Vleck model for isotropic binuclear magnetic exchange interactions ($H = -2JS_1 \cdot S_2$).[18] The molar susceptibility was corrected for underlying diamagnetism by the use of Pascal's constants and fitted by a least-squares method, in the case of iron(III) dimers, by use of equation (1) where

$$\chi_M = (1 - p)\frac{Ng^2\mu_B{}^2}{kT} \times \frac{2e^{2x} + 10e^{6x} + 28e^{12x} + 60e^{20x} + 110e^{30x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x}} + \frac{35p}{8T} + \text{t.i.p.} \quad (1)$$

$x = J/kT$, p = mole fraction of paramagnetic impurities, and t.i.p. = temperature-independent paramagnetism. For the iron(II) dimer **1** an analogous equation, taking account of the different spin multiplicity, was used.

Resonance-Raman Studies.—Raman spectra were recorded on a Czerny-Turner scanning spectrometer. The samples were prepared as discs containing 300 mg of KBr, 20 mg of the complex and 20 mg of K_2SO_4 for use as internal standard [referenced to $\nu_1(SO_4{}^{2-})$ 983 cm^{-1}]. Spectra were recorded at three excitation wavelengths, 457.9, 487.9 and 514.5 nm.

X-Ray Crystallography.—A crystal of complex **1** of dimensions 0.2 × 0.2 × 0.1 mm was used for the collection of X-ray diffraction data. Crystal data and details of the structure determinations of **1** and **3** are collected in Table 2. Data were corrected for dead-time losses, background, Lorentz, polarization, and absorption effects (minimum and maximum transmission 0.91 and 0.94). The structure was solved by direct methods,[19] and refined by the full-matrix least-squares technique.[20] Refinement on F with weights $w = \{[\sigma(F^2) + 1.03F^2]^{\frac{1}{2}} - F\}^{-2}$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions after verification by means of a Fourier-difference synthesis. The positions as well as thermal parameters were refined for hydrogen atoms of the bridging acetate group; the other hydrogen atoms were constrained to have one common thermal parameter. The perchlorate groups show large thermal movement and other signs of disorder. Attempts at refining two orientations of each perchlorate with idealized geometry and a common TLX model for the thermal motion resulted in significantly higher R values. No extinction effects were found. The final shift/e.s.d. was 0.24. Scattering factors including anomalous dispersion for Fe were taken from ref. 21. Fractional atomic coordinates are listed in Table 3, and the co-ordination geometry[22] in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The syntheses of an unusual diiron(II) and six new μ-oxo-diiron(III) complexes of *N*,*N'*-dimethyl-*N*,*N'*-bis(2-pyridylmethyl)-ethane-1,2-diamine (L) are described in the Experimental section. Spectroscopic and magnetic properties for the diiron(III) complexes are listed in Table 1. The integrities of all the diiron complexes were verified using electrospray ionization (ES) mass spectrometry. The μ-oxo-diiron(III) complexes **3**–**7** all show clean mass spectra with a peak for the triply or doubly charged cationic complex $[LFeO(X)FeL]^{n+}$ as the most intense. A peak for the doubly or singly charged ion pair $\{[LFeO(X)FeL](ClO_4)\}^{n+}$ is also observed as a much less-intense peak. Molecular ion peaks are listed in the Experimental section.

μ-Acetato-bridged Diiron-(II) and -(III) *Complexes of* L.—An unusual di-μ-acetato-diiron(II) complex $[LFe(O_2CMe)_2FeL][ClO_4]_2$ **1** was isolated as yellow crystals from the reaction of L with iron(II) acetate. The structure solved by X-ray crystallography shows a doubly bridged μ-acetato-*O*,*O'* core, see below. The variation of the magnetic susceptibility *versus* temperature shows the two iron(II) centres to be very weakly antiferromagnetically coupled. The room-temperature magnetic moment per dimer is 7.5 μ_B, which drops to 3.8 μ_B at 5 K. Fitting of the data by the Heisenberg–Dirac–Van Vleck model for isotropic binuclear magnetic exchange interactions where $S_1 = S_2 = 2$ and, without taking zero-field splitting into account, leads to a $-J$ value of 1.5 cm^{-1}.

Complex **1** is readily oxidized in solution: to an oxo-bridged iron(III) complex, which can be observed in the UV/VIS and ES mass spectra. The UV/VIS spectrum of **1** (Experimental section) is relatively featureless, however if the acetonitrile solution is allowed to stand it becomes green and features above 400 nm appear in the spectrum. These features are characteristic for a diiron(III) complex containing a bent Fe–O–Fe unit.[1a] The

Table 1 Properties of μ-oxo-diiron(III) complexes $[LFeO(X)FeL][ClO_4]_n$

	2 X = OH^-	**3** CO_3^{2-}	**4** $MeCO_2^-$	**5** HCO_2^-	**6** SO_4^{2-}	**7** $2Cl^-$
Electronic Spectra[a]						
λ_{max}/nm	339 (5995)	337(sh) (7588)	340 (9780)	340 (7500)	319 (10 852)	330(sh) (8963)
(ε dm^3 mol^{-1} cm^{-1})	374 (5085)	368(sh) (6070)	367(sh) (7180)	372(sh) (4900)		375 (7584)
	438(sh) (1821)	437 (1270)	422(sh) (1100)	428(sh) (800)	427 (1124)	
	460(sh) (993)		464 (1310)	467 (1000)	493 (484)	
	490(sh) (619)	505 (662)	495(sh) (860)	495(sh) (720)	504 (453)	505(sh) (193)
	539 (290)		512 (800)	514 (600)		
	562 (601)	578(sh) (113)	543(sh) (230)	545(sh) (200)	530 (190)	
	800(sh) (97)	667 (140)	670 (160)	670 (150)	629 (159)	535(sh) (164)
ν(FeOFe) Data (cm^{-1})[b]						
ν_{asym}		728	740	743	740	
ν_{sym}	593	495	487	487	474	335
Magnetic properties						
$-J$/cm^{-1}	42	104	112	104	93	70
t.i.p./cm^3 mol^{-1}	0.000 900	0.000 140	0.000 080	0.000 000	0.000 060	0.000 000
p/mol fraction	0.004 2	0.002 4	0.006 0	0.003 7	0.005 6	0.025 0
g	2.00	2.01	2.01	2.10	1.99	2.01

[a] In MeCN solution. [b] ν_{asym} from IR spectrum, identified by comparison to the 'fingerprint' pattern of the IR spectrum of the mononuclear iron(III) complex of L, $[FeCl_2L]ClO_4$ **8**; not assigned for complexes **2** and **7**; ν_{sym} from the resonance-Raman spectrum.

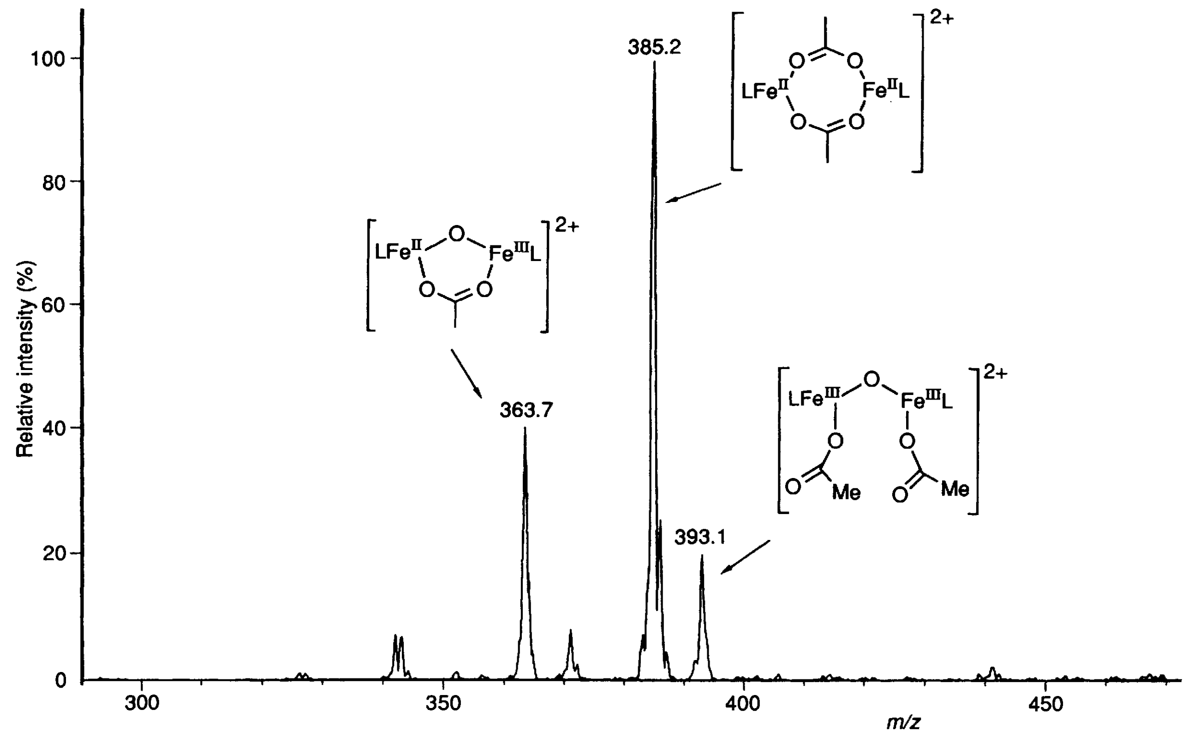

Fig. 1 Electrospray ionization mass spectrum of complex **1** in acetonitrile together with a structural assignment for the major peaks

ES mass spectrum, part of which is shown in Fig. 1, clearly shows a peak corresponding to the molecular ion, $[LFe(O_2CMe_2)_2FeL]^{2+}$, as the most intense feature. However significant peaks are assigned to the various fully and partially oxidized derivatives of **1** with the core structures as illustrated.

An oxidized derivative of complex **1**, the dibridged $[LFeO(O_2CMe)FeL][ClO_4]_3$ **4**, was isolated, as green crystals, from solutions of **1** exposed to air. Its identity was verified by preparation by the simpler self-assembly method starting with Fe^{3+}, L and sodium acetate, described in the Experimental section. The UV/VIS spectral characteristics are very similar to those reported for the acetato-oxo-bridged tpa analogue of complex **4**. The value of 487 cm^{-1} for ν_{sym} in the Raman spectrum is consistent with a Fe–O–Fe angle close to 130°, typical for acetato-oxo-bridged diiron(III) complexes.[23]

Synthesis, Spectroscopic and Magnetic Characterization of the Complex $[LFeO(OH)FeL][ClO_4]_3 \cdot 2H_2O$ **2**.—The reaction of L with Fe^{3+}, in the absence of other possible supporting bridging ligands, was carried out with varying amounts of base, in attempts to prepare a complex based on the $[LFe–O–FeL]^{4+}$ unit and comprising substitution labile terminal ligands. The procedure described in the Experimental section gives maroon crystals which we have formulated as $[LFeO(OH)FeL][ClO_4]_3\cdot$

$2H_2O$ **2**. Although unable to determine the crystal structure of this complex due to the lack of suitable crystals, we propose that it contains the unique doubly bridged $Fe^{III}_2(\mu\text{-}O)(\mu\text{-}OH)$ core for the reasons presented below.

At the outset of the present work with the linear N_4 ligand L we had anticipated that the preparation of a μ-oxo-diiron(III) complex in aqueous solutions in the absence of possible bridging ligands would lead to the formation of species of the type $[L(H_2O)Fe\text{–}O\text{–}Fe(H_2O)L]^{4+}$ or $[L(H_2O)Fe\text{–}O\text{–}Fe(OH)L]^{3+}$, similar to those we have characterized previously with different terminal tetradentate ligands.[15] The formulation of **2** as a μ-oxo-diiron(III) complex of the type $[L(H_2O)Fe\text{–}O\text{–}Fe(H_2O)L]^{4+}$ could be eliminated on the basis of the elemental analysis which is consistent with three perchlorate counter anions. The presence of a hydroxide was necessary to balance the charge, however the spectroscopic characteristics suggested that the complex, although composed chemically similarly to $[(tpa)(H_2O)FeOFe(OH)(tpa)][ClO_4]_3$, contains a fundamentally different core structure; the Fe–O–Fe unit is apparently much more bent. Hence the formulation of a $Fe^{III}(\mu\text{-}O)(\mu\text{-}OH)Fe^{III}$ core for **2**.

The isolation of a complex in which two iron(III) atoms are bridged by an oxo and a hydroxo group, although postulated in iron(III)–oxo–hydroxo aggregation, is extremely rare in diiron(III) chemistry. This is only the second example reported. The first structurally characterized (X-ray crystallography and extended X-ray absorption fine structure, EXAFS) example of a complex containing this core was reported during the writing of this manuscript by Zang *et al.*[24] for the structure of $[(tmpa)Fe(\mu\text{-}O)(\mu\text{-}OH)Fe(tmpa)][ClO_4]_3$[24] {tmpa = tris[(6-methyl-2-pyridyl)methyl]amine}. Their structure gives us confidence that our assignment of this structure is valid. Related four-atom, edge-shared structures are known in iron(III) chemistry.[25] For example, dinuclear complexes with the $Fe(\mu\text{-}OR)_2Fe$ core (R = H, alkyl or aryl) have been reported.[1b] Other edge-shared structures contain oxygen atoms bridging more than two iron atoms and form the skeleton framework of polynuclear complexes.[2] Since none of these core structures contains an *unsubstituted* μ-oxo atom, the magnetic and spectroscopic characteristics of complexes containing these core structures do not aid in the interpretation of the spectral and magnetic properties of **2**.

The M(μ-O)(μ-OH)M moiety (M = transition-metal ion) is, in fact, surprisingly rare. It has been found in dichromium(III) complexes,[17b,26] with only one structurally characterized example.[26] There are, however, several structurally characterized examples of the conjugate acid and base of this core, $M(\mu_2\text{-}OH)_2M$ and $M(\mu\text{-}O)_2M$ respectively, in transition-metal chemistry. The $[M(\mu\text{-}OH)_2M]^{4+}$ core is well known in chromium(III) and cobalt(III) chemistry and several complexes containing the $[Fe(\mu\text{-}OH)_2Fe]^{4+}$ core have been reported[1a] and two such cores structurally characterized by Thich *et al.*[25f] and Borer *et al.*[27] in neutral complexes of anionic terminal ligands. The so-called aqua dimer $[(H_2O)_4Fe(\mu\text{-}OH)_2Fe(H_2O)_4]^{4+}$ has been proposed also to contain a di-μ-hydroxo core.[28] The acid–base equilibria involving the $Fe(\mu\text{-}OH)_2Fe$ unit and its mono- and di-deprotonated counterparts Fe(μ-O)(μ-OH)Fe and $Fe(\mu\text{-}O)_2Fe$ have not been studied. No stable small molecule containing a $Fe(\mu\text{-}O)_2Fe$ is so far known and may be difficult to obtain due to the propensity of Fe^{III} to form higher-nuclearity oxo aggregates and finally rust in basic media. The $M(\mu\text{-}OH)_2M$ core is well known in early transition-metal chemistry. Linear N_4 ligands based on bpen have been utilized previously to prepare dimanganese complexes containing $Mn^{III}(\mu\text{-}O)_2Mn^{IV}$ cores.[8] The kinetics of the protonation reaction of one of the μ-oxo bridges of a $Mn(\mu\text{-}O)_2Mn$ complex has been studied and found to be slow.[29]

A diiron(III) complex in which a μ-oxo atom is supported by another one-atom bridge represents an extreme case for the Fe–(μ-O)–Fe angles in oxo-bridged complexes. By comparison to a dichromium(III) complex containing a $[Cr(\mu\text{-}O)(\mu\text{-}OH)Cr]^{3+}$ core,[26] a Fe–(μ-O)–Fe angle close to 100.6(2)° is expected for **2**. This is *ca.* 20° more acute than in any previously reported μ-oxo-diiron(III) complex,[1a] apart from the very recently reported structure of $[(tmpa)Fe(\mu\text{-}O)(\mu\text{-}OH)Fe(tmpa)][ClO_4]_3$ by Zang *et al.*,[24] where, although the μ-oxo and μ-hydroxo bridges were not distinguished in the crystal structure and the Fe–O–Fe and Fe–OH–Fe angles averaged to 98.7(6) Å, their results using EXAFS inferred a Fe–(μ-O)–Fe angle of 106°. Sanders-Loehr *et al.* have used resonance-Raman spectroscopy to predict the Fe–O–Fe angle in a series of μ-oxo-diiron(III) complexes containing none, one and two supporting bridging groups. As the Fe–O–Fe angle decreases in the mono- through to di- and tri-bridged complexes, the frequency of the symmetric stretch, observable in the Raman spectrum, increases. A linear relationship between the square of this frequency and the cosine of the Fe–O–Fe angle has been predicted from theory.[30] The resonance-Raman spectrum of **2** shows a strong band at 593 cm^{-1},* which, in the absence of other appropriate bands above 300 cm^{-1}, we assign to the symmetric stretch, ν_{sym}(Fe–O–Fe). This band occurs at a higher frequency than the ν_{sym}(Fe–O–Fe) for any other μ-oxo-diiron(III) complexes reported.[23] In fact, if the plot of Fe–O–Fe angle *versus* ν_{sym}(Fe–O–Fe) reported by Sanders-Loehr *et al.*[23] is extrapolated to ν_{sym}(Fe–O–Fe) 593 cm^{-1} a Fe–O–Fe angle of around 100° is predicted. Hence the resonance-Raman spectrum for **2** is consistent with a Fe(μ-O)(μ-OH)Fe core structure. In contrast, the symmetric Fe–O–Fe stretch recorded for the chemically similar $[(tpa)(H_2O)FeOFe(OH)(tpa)][ClO_4]_3$,[15b] 453 cm^{-1}, falls in the range recorded by Sanders-Loehr *et al.*[23] appropriate for the Fe–O–Fe angle of 138.9(4)° found in its crystal structure (the Fe–O–Fe unit is forced to bend as a consequence of a hydrogen-bonding interaction between the *cis* aqua and hydroxo groups).

The magnetic moment recorded for complex **2** decreases with temperature, showing antiferromagnetic coupling as is usually the case in μ-oxo diiron(III) complexes. The fit by an isotropic Heisenberg–Dirac–Van Vleck model, although not completely satisfactory, gives the coupling constant, $-J = 42\ cm^{-1}$, which is very low compared to $-J$ for other μ-oxo-diiron(III) complexes.[1a] In all of these complexes it is the μ-oxo bridge that is aniticipated to provide the major magnetic exchange pathway.[31] A μ-hydroxo bridge is a poor mediator of electronic coupling[32] and is not expected to contribute a significant pathway between the metal centres in the putative Fe(μ-O)(μ-OH)Fe core of **2**.

In general, μ-oxo-bridged iron(III) dimers have $-J$ values of around 100 cm^{-1} and this coupling constant is found not to be correlated with the Fe–O–Fe angle.[32,33] Although diiron(III) complexes containing an Fe–O–Fe angle as acute as that postulated for **2**, are not included in these studies, we believe the low value for $-J$ of 42 cm^{-1} is not inconsistent with this lack of correlation (*i.e.* that the strong antiferromagnetic coupling usually found in μ-oxo-diiron(III) complexes is not found for **2**). A very acute Fe–O–Fe angle is likely to effect a decrease in the π bonding between the iron atoms resulting in a reduced magnetic exchange coupling. An analogy can be drawn from the oxo-bridged dichromium(III) complexes: the linear oxo-bridged basic rhodo ion $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$ shows a very high coupling constant, $-J$, of 225 cm^{-1}.[34] However the coupling constant for $[(bipy)_2Cr(\mu\text{-}O)(\mu\text{-}OH)Cr(bipy)_2][ClO_4]_3\cdot 4H_2O$ (bipy = 2,2′-bipyridyl) is much less, 30 cm^{-1}.[17b]

The electronic spectrum of complex **2** in acetonitrile shows distinctive differences in comparison to the other μ-oxo-diiron(III) complexes of L, **3**–**7** (Table 1), and of other capping

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* The intensity of this band is enhanced ten times by the λ = 457.9 nm laser line as compared to the λ = 514.5 nm line. The enhancement profile for **2** is the reverse of the resonance enhancement found for the other complexes in this series which show the most enhancement from the lowest-energy laser line (λ = 514.5 nm) of the three used.

ligands [1a] and lends further support for the structural proposal. Previously bands in the 550–700 nm region of the electronic spectra of multiply bridged μ-oxo-diiron(III) complexes (where the supporting bridges are oxo acids, *i.e.* are three-atom bridging groups) have been attributed to an oxo-to-iron charge-transfer transition, the energy of which depends on the Fe–O–Fe angle. These bands are expected to be blue shifted as the Fe–O–Fe angle increases.[4g,35] The blue shift can be attributed to an increased π bonding between the iron atoms and the μ-oxo atom as the Fe–O–Fe angle approaches 180°, thereby decreasing the basicity of the oxo bridge and the Lewis acidity of the iron centres. Consequently the gap between the ligand donor and metal acceptor orbitals widens. We assign a shoulder at 800 nm in the spectrum of an acetonitrile solution of **2** to this oxo-to-iron charge-transfer transition. The considerable red shift of this band, compared to the λ_{max} assigned for this transition for the other μ-oxo-diiron(III) complexes in Table 1 (667 nm for the μ-O-μ-CO_3-bridged **3**, 670 nm for the μ-O-μ-O_2CR-bridged **4** and **5**; 629 nm for the μ-O-μ-SO_4-bridged **6**; 535 nm for the μ-oxo-bridged **7**) is consistent with a much more acute Fe–O–Fe angle. Of particular note is a band at 562 nm (ε 601 $dm^3\ mol^{-1}\ cm^{-1}$) in the spectrum of **2**. We believe this is assignable to one of the bands usually observed in the 400–550 nm region of the electronic spectra of multiply bridged μ-oxo-diiron(III) complexes. These features are blue shifted and/or lose intensity as the Fe–O–Fe angle increases. The red shift to above 550 nm of this λ_{max}, and a gain in intensity, is, therefore, consistent with a decrease of the Fe–O–Fe angle. As with other μ-oxo-diiron(III) complexes, there is a band in the 400–550 nm region of medium intensity at 490 nm. This has been assigned to a $^6A_1 \longrightarrow (^4E, {}^4A_1)$ transition, which is independent of the Fe–O–Fe angle.[35]

Reactivity of $[LFeO(OH)FeL][ClO_4]_3\cdot 2H_2O$ **2** *towards Nucleophiles*.—The ES mass spectrum of complex **2** supports the structural proposal for a Fe(μ-O)(μ-OH)Fe core. A spectrum is shown in Fig. 2. Assignments are indicated. The peak at *m/z* 228.3 is assigned to the molecular ion, $[LFeO(OH)FeL]^{3+}$ and that at *m/z* 392.2 to the ion pair $\{[LFeO(OH)FeL]ClO_4\}^{2+}$. The peak at *m/z* 342.2 is assigned to the deprotonated derivative of **2**, namely $[LFe(\mu\text{-}O)_2FeL]^{2+}$. The facile removal of one proton suggests a unique environment for that proton, *i.e.* that the hydrogen atom of the postulated μ-OH bridge has been lost (removal of a ligand proton under the mild conditions of the experiment is extremely unlikely). In fact, in other spectra, the peak for the doubly charged $[LFe(\mu\text{-}O)_2FeL]^{2+}$ was usually more intense than for that for the triply charged $[LFeO(OH)FeL]^{3+}$ ion. However the relative intensities of the peaks in the mass spectra do not reflect the concentration of the species in an equilibrium mixture, and lower charged species usually give more intense peaks. Perhaps most notable is the 100% peak at *m/z* 242.2 which we assign to the acetamide-bridged complex, $[LFeO(HNOCMe)FeL]^{3+}$. Although we have not isolated this complex in the solid state we have precedence for its formation by hydrolysis of the solvent acetonitrile promoted by complex **2**: we have previously observed this type of reaction with $[(tpa)(H_2O)FeOFe(OH)(tpa)][ClO_4]_3$.[15b] The assignment is supported by the absence of this peak in the spectrum of **2** recorded in methanol. This result is an indication of the reactivity of complex **2** in solution.

In order to record the spectrum in Fig. 2 it was necessary to prepare the sample under Ar. If this precaution was not taken the spectra usually showed an intense peak at *m/z* 364.0 which we assign to the product of the reaction between complex **2** and carbon dioxide. The sensitivity of **2** towards carbon dioxide, evident in the mass spectra, had been forecasted by attempted recrystallizations of **2**. Products, which proved to be mixtures, showing bands in their IR spectra recognized to be carbonate-derived were usually isolated from attempted recrystallizations. On some occasions green crystals of the pure μ-oxo-μ-carbonato bridged complex $[LFeO(CO_3)FeL][ClO_4]_2\cdot 2H_2O$ **3** were recovered. It appears that **2** reacts readily with carbon dioxide to give **3**. The formulation of the latter was verified by its synthesis by the self-assembly reaction of L, Fe^{3+} and CO_3^{2-} which gives a product with identical spectral features to those of the product derived from the reaction of **2** with carbon dioxide. The ES mass spectrum of **3** is clean and corroborates the assignment of a peak due to contamination by $[LFeO(CO_3)FeL]^{2+}$ in the spectrum of **2**. The structure of **3** has been

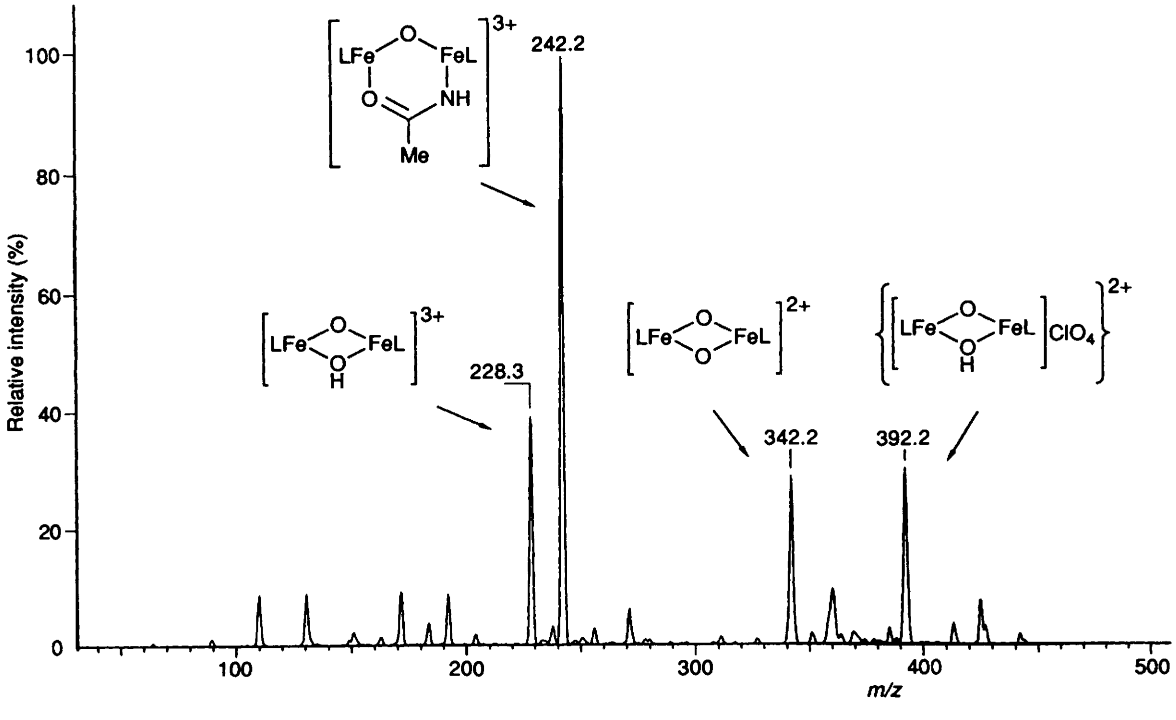


Fig. 2 Electrospray ionization mass spectrum of complex **2** in acetonitrile together with a structural assignment for the major peaks

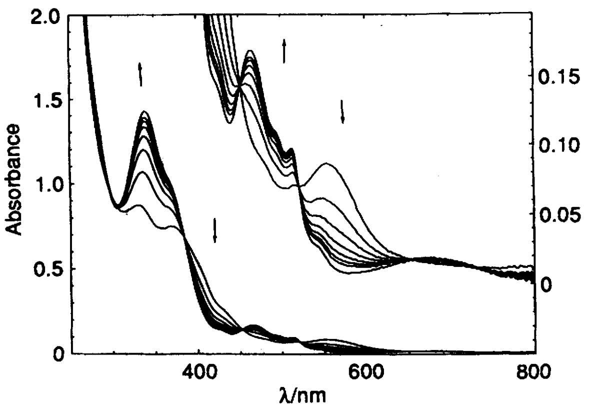


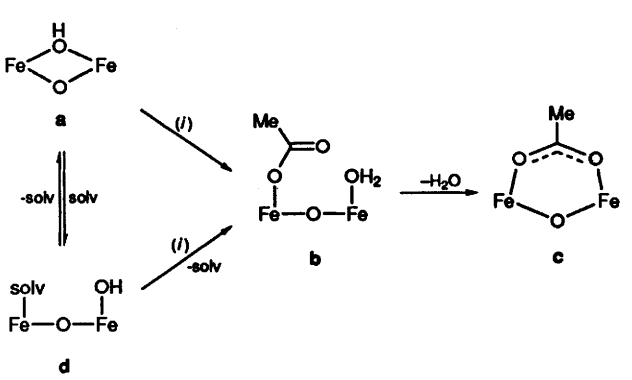
Fig. 3 The UV/VIS spectra of a solution of complex **2** and 1 equivalent of acetic acid in MeCN. Successive spectra were recorded with 8 min intervals except for the final spectrum which was recorded after 3 h. The spectra on the right have been magnified ten times. Initial and final parameters for **2** and **4** are given in Table 1

solved by X-ray crystallography and shows a doubly bridged μ-oxo-μ-carbonato-*O*,*O′* core, see below.

Substitution of the Bridging μ-OH *in* [LFeO(OH)FeL]-$[ClO_4]_3$·$2H_2O$ **2**.—One objective of the work here in synthesizing diiron complexes containing water and/or hydroxo ligands is to provide exchangeable sites in preformed Fe–O–Fe cores. Hence, we utilized complex **2** as a starting material for other μ-oxo-diiron(III) complexes of L. We have succeeded in substituting the μ-hydroxo group to give both mono- and di-bridged complexes in the present study.

The addition of acetic or formic acid to a solution of complex **2** in acetonitrile gives the acetato-bridged [LFeO(O_2CMe)-FeL]$[ClO_4]_3$, **4**, or the formato-bridged [LFeO(O_2CH)FeL]-$[ClO_4]_3$ **5**. The addition of sodium hydrogensulfate to a solution of **2** gives the sulfato-bridged complex, [LFeO-(SO_4)FeL]$[ClO_4]_2$ **6**. The substitution reactions were monitored in solution by the changes in the UV/VIS spectrum. The acetate-substitution reaction in acetonitrile over 3 h, is shown in Fig. 3. Interestingly, the reaction of **2** with acetic acid is slow compared to that of [(tpa)(H_2O)FeOFe(OH)(tpa)]$[ClO_4]_3$ to give [(tpa)FeO(O_2CMe)Fe(tpa)]$[ClO_4]_3$ which occurs within seconds.[15b] The differences in the rates of the acetate-substitution reactions of **2** and the two complexes probably reflect the structural differences in their diiron cores. A plausible mechanism for the acetate-substitution reaction is illustrated in Scheme 1. The μ-hydroxo bridge in **2** is required to undergo a bridge-cleavage step **a** ⟶ **b**, to generate the labile species represented by **b**, which rapidly eliminates water to give the acetate-bridged complex **c**. The bridge-cleavage step may first involve a protonation of the bridging hydroxide group which ends up as a terminal water ligand. An alternative pathway, particularly in aqueous solvent, may be *via* the transient formation of a solvated species **d**. This is probably not the case in the reaction followed spectrophotometrically in Fig. 3 in which the concentration of water is negligible and the co-ordination of acetate ion is apparently favoured over the co-ordination of acetonitrile. The formation of the acetamide-bridged complex is much slower than the formation of the acetate-bridged complex, as no sign of the acetamido-complex is apparent from electronic spectra of solutions of **2** in acetonitrile after 3 h.

The formation of an aqua-hydroxo species **d** in Scheme 1, solv = H_2O, is probably the reason that solutions of complex **2** in acetonitrile lose their characteristic UV/VIS spectrum when water is added and the characteristic features above 500 nm disappear. This effect is consistent with a disruption of the μ-hydroxo bridge by the co-ordination of a water ligand to one of the iron atoms and the hydroxide ligand becoming a terminal ligand on the adjacent iron atom, *i.e.* the Fe–O–Fe unit approaches linearity resulting in a less detailed electronic spectrum. Clearly this type of aquahydroxo species is accessible in μ-oxo-diiron(III) complexes since we have isolated and structurally characterized one in the tpa series.[15b] The fact that we are unable to isolate this core structure using L as the capping ligand under the same preparative conditions for which it can be isolated with tpa, suggests that the different steric requirements of the capping ligand is an important factor in determining which core structure is formed. An influencing factor evident in a space-filling model for **2** is that a four-atom core may be particularly favoured over a linear μ-oxo core due to π-stacking interactions of the pyridyl groups of adjacent ligands in the *cis*-α conformation. The pyridyl groups are forced into a severe and repulsive interaction if the μ-OH is cleaved and the Fe–O–Fe angle is opened up. A time-consuming rearrangement of the linear N_4 ligands may be enforced in order to accommodate a terminal ligand on each iron centre. The fact that the aqua and hydroxo groups in [(tpa)(H_2O)FeOFe-(OH)(tpa)]$[ClO_4]_3$ are *cis* to each other and strongly hydrogen bonded is probably necessary for the stabilization of the terminal hydroxide ligand, which until the characterization of [(tpa)(H_2O)FeOFe(OH)(tpa)]$[ClO_4]_3$ was unknown in iron(III) chemistry. The *cis* arrangement of the aqua and hydroxide ligands with core structure **d**, solv = H_2O, using L as a capping ligand may be unfavourable due to the steric requirements of the ligand.



Scheme 1 Proposed reaction mechanism for the substitution of the μ-OH in complex **2** by μ-$MeCO_2^-$. solv = Solvent. (*i*) $MeCO_2H$

We can envisage several factors to explain a slow bridge-cleavage reaction. From space-filling models of complex **2**, assuming a *cis*-α-conformation for both ligands {similar to the conformation found for most complexes of bpen-derived ligands[8,9] and notably for [LMn(μ-O)$_2$MnL]$[ClO_4]_3$,[36] which contains a four-atom Mn_2O_2 core unit] it can be seen that an attack by an incoming ligand will be severely impeded by the sterically demanding *N*-methyl groups of each ligand. A similar steric hindrance by bulky *N*-methyl groups has been noted by Wieghardt *et al.*[37] in a study of hydroxo-bridge cleavage in the triply bridged dicobalt triol complexes of 1,4,7-triazacyclononane (tacn) and its 1,4,7-trimethylated derivative. Apparently cleavage of one of the μ-OH bridges to give the corresponding diaquabis(μ-hydroxo) species is possible only when unsubstituted tacn is the capping ligand.

Complex **2** can also be used to prepare a complex containing an unsupported μ-oxo bridge. The addition of chloride ions to solutions containing **2** gives [L(Cl)FeOFe(Cl)L]$[ClO_4]_2$ **7**, which was isolated as a red crystalline solid. The spectroscopic evidence suggests a linear μ-oxo-bridged core structure for **7**. The ES mass spectrum shows that, in solution, the chloride ions are co-ordinated, rather than as counter anions, consistent with terminal chloro ligation, similar to the structure found for the corresponding tpa complex, [(tpa)ClFeOFeCl(tpa)]$[ClO_4]_2$ for which we have determined the crystal structure.[15b]

There are distinctive differences in the UV/VIS and Raman spectra of singly and doubly bridged μ-oxo-diiron(III) complexes. As discussed above with reference to complex **2**, the position of ν_{sym}(Fe–O–Fe) in the Raman spectra gives an indication of the Fe–O–Fe angle. The band assigned to ν_{sym}(Fe–O–Fe) of **7** occurs at the lowest frequency of the complexes listed in Table 1, consistent with an expected Fe–O–Fe angle close to 180°. The UV/VIS spectrum of **7**, in comparison to those for the dibridged complexes **2**–**6**, is relatively featureless, consistent also with an almost linear Fe–O–Fe unit.

The magnetic exchange coupling constant, $-J = 70$ cm^{-1}, is lower than expected for a linear μ-oxo bridge. In the absence of a crystal structure determination for complex **7** we do not wish to comment extensively on this result. However intuition tells us that the source of the reduced coupling may be due to the strain evident in space-filling models of a linear oxo-bridged complex, not only with regard to the possible clashes between adjacent pyridyl groups, but also particularly close repulsive interactions between the bulky *cis* chloro and *N*-methyl groups at each iron atom. A possible outcome of these steric demands may be an elongation of the Fe–(μ-O) bonds, consequently reducing the π overlap between the π-bonding orbitals of the μ-oxo and iron atoms. This should effect a reduction in the magnetic exchange interaction. A lower bond order and consequently lower force constants for each Fe–(μ-O) bond is consistent also with the low ν_{sym} assigned from the Raman spectrum of **7**. The value of 335 cm^{-1} is lower than for any of the mono oxo-bridged complexes reported by Sanders-Loehr *et al.*[23]

Crystal and Molecular Structure of $[LFe(\mu\text{-}O_2CMe)_2FeL][ClO_4]_2$ **1**.—The crystal structure of the complex consists of $[LFe(\mu O_2CMe)_2FeL]^{2+}$ cations and perchlorate anions. A view of the cation is shown in Fig. 4. The iron atoms, linked by two acetato-*O,O′* bridges, are approximately octahedrally co-ordinated to the four nitrogen atoms of L and two acetato oxygen atoms. Important interatomic distances and angles are given in Table 4. The ligand shows the *cis*-α configuration about both iron centres, in which the axial ligation is provided by the pyridine groups and the equatorial ligation by the amine nitrogens and the bridging acetato oxygen atoms. The compound is isomorphous to $[LMn(\mu\text{-}O_2CMe)_2MnL][ClO_4]_2$ though described in a different cell.[38] Each acetate group bridges the iron atoms in an *O,O′* mode using the *syn* lone pair on one carboxylate oxygen and the *anti* lone pair on the other. The Fe$^{II}\cdots$Fe^{II} distance is 4.382(2) Å. A similar arrangement for the μ-acetato bridges was observed in a diiron(II) complex of tpa.[29g] Interestingly, a structural hypothesis for the diiron centre of reduced B2 from *E. coli* ribonucleotide reductase has been proposed recently, based on multifield saturation magnetization measurements, to contain a di(μ-carboxylato) core unit similar to that in **1**.[39] The recent structural determination of the corresponding manganese(II)-substituted reductase shows a doubly bridged dimanganese(II) core where the two bridging carboxylates are derived from Glu-238 and Glu-115.[13] The short Mn$^{II}\cdots$Mn^{II} separation of 3.6 Å[13] compared to the Fe$^{II}\cdots$Fe^{II} distance in **1** probably indicates a *syn-syn* bidentate bridging by the bridging carboxylate groups in the Mn-substituted apoprotein.

Crystal and Molecular Structure of $[LFeO(CO_3)FeL][ClO_4]_2\cdot 2H_2O$ **3**.—The crystal structure of the complex consists of $[LFe(\mu\text{-}O)(\mu\text{-}CO_3)FeL]^{2+}$ cations, perchlorate anions and solvent water. A view of the cation is shown in Fig. 5. The iron atoms, linked by the μ-oxo and μ-carbonato-*O,O′* bridging groups, are octahedrally co-ordinated to the four nitrogen atoms of L, a carbonate oxygen atom, and the bridging oxygen atom. Important interatomic distances and angles are given in Table 5. Again the ligand shows the *cis*-α conformation about both iron centres, in which the axial ligation is provided by the pyridine groups and the equatorial ligation by the amine nitrogens and the bridging oxo and acetato groups. A comparison by means of half-normal probability plots[40] to the recently published crystal structure determination of the same compound[16] shows that the bond lengths found in the two investigations agree as could be expected within the standard deviations given. However, the coordinates agree less well, the *y* values being systematically 0.0045 different. The other differences seem random but about three times as large as expected from the standard deviations. The structure is built of layers normal to the *c* direction with water between, and changes in water content may possibly cause the layers to shift slightly.

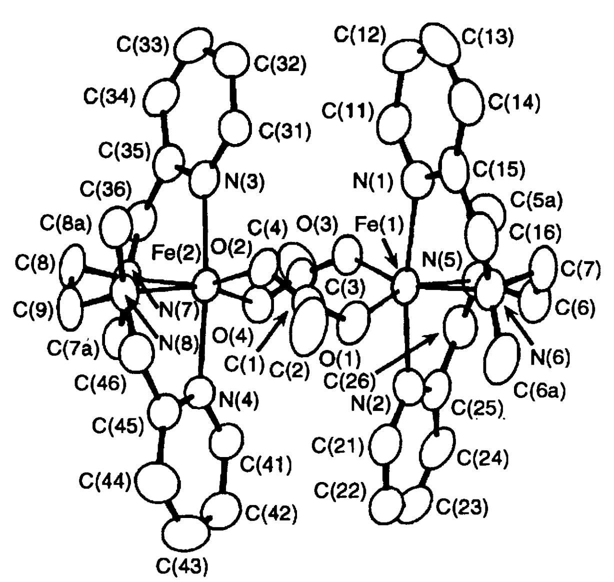


Fig. 4 Drawing of $[LFe(O_2CMe)_2FeL]^{2+}$ **1** showing the numbering scheme. Hydrogen atoms are omitted for clarity

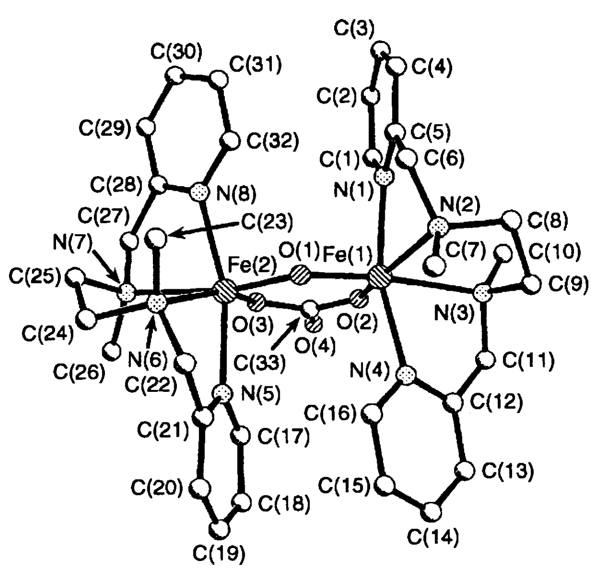


Fig. 5 Drawing of $[LFeO(CO_3)FeL]^{2+}$ **3** showing the numbering scheme. Hydrogen atoms are omitted for clarity

Conclusion

Perhaps the most significant result of this work is the successful isolation and characterization of a simple diiron(III) complex containing a $[Fe(\mu\text{-}O)(\mu\text{-}OH)Fe]^{3+}$ core. This core may represent an important link in the formative process of large iron oxohydroxo aggregates such as rust and the core of ferritin.[25d,41] The present work with the linear N_4 ligand L together with our earlier work with other tetradentate capping

Table 2 Crystal data and details of structure determinations for $[LFe(\mu\text{-}O_2CMe)_2FeL][ClO_4]_2$ **1** and $[LFe(\mu\text{-}O)(\mu\text{-}CO_3)FeL][ClO_4]_2{\cdot}2H_2O$ **3**

	1	**3**
Formula	$C_{36}H_{50}Cl_2Fe_2N_8O_{12}$	$C_{33}H_{48}Cl_2Fe_2N_8O_{14}$
M	969.475	963.403
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a/Å	13.756(3)	19.565(8)
b/Å	15.033(s)	13.427(2)
c/Å	13.637(3)	32.722(9)
α/°	97.82(1)	
β/°	108.95(1)	94.31(3)
γ/°	118.07(1)	
U/Å^3	2208.6(5)	8571(5)
Z	2	8
D_c/g cm^{-3}	1.46	1.35
Crystal dimensions/mm	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.3
Diffractometer	HUBER four-circle	Enraf–Nonius CAD-4
F(000)	1008	4000
h, *k*, *l* ranges	0–16, −14 to 12, −16 to 14	−24 to 24, 0–14, 0–42
μ/cm^{-1}	8.40	8.6
Scan type	ω–2θ	ω
$2\theta_{max}$/°	46.0	56.0
Reflections	6157	9756
	3556 [$I > 3\sigma(I)$]	4575 [$I > 2\sigma(I)$]
R	0.046	0.066
R′	0.052	0.069

* Details in common: 295 K; Mo-Kα radiation (λ = 0.710 69 Å); graphite monochromator.

Table 3 Atomic coordinates for $[LFe(\mu\text{-}O_2CMe)_2FeL][ClO_4]_2$ **1**

Atom	*x*	*y*	*z*
Fe(2)	−0.741 63(8)	−0.749 06(7)	−0.484 10(7)
Fe(1)	−0.476 22(8)	−0.739 02(7)	−0.190 64(7)
O(1)	−0.583 0(4)	−0.859 0(3)	−0.343 3(4)
O(2)	−0.763 1(4)	−0.882 3(3)	−0.438 3(4)
C(1)	−0.692 5(6)	−0.914 2(5)	−0.414 9(5)
C(2)	−0.740 9(10)	−1.028 6(7)	−0.476 3(10)
O(4)	−0.572 4(4)	−0.610 9(3)	−0.369 7(4)
O(3)	−0.508 1(4)	−0.618 7(3)	−0.200 5(4)
C(3)	−0.520 2(6)	−0.570 3(5)	−0.266 7(6)
C(4)	−0.461 6(14)	−0.450 4(7)	−0.215 8(9)
N(1)	−0.608 8(5)	−0.808 3(4)	−0.124 2(4)
C(11)	−0.668 7(6)	−0.766 9(5)	−0.097 4(6)
C(12)	−0.751 8(7)	−0.817 0(8)	−0.056 3(6)
C(13)	−0.773 6(7)	−0.911 8(8)	−0.043 0(6)
C(14)	−0.712 5(7)	−0.954 5(6)	−0.068 6(6)
C(15)	−0.630 5(6)	−0.900 9(6)	−0.108 2(6)
C(16)	−0.559 5(7)	−0.943 0(5)	−0.138 4(6)
N(2)	−0.321 7(5)	−0.665 0(5)	−0.230 9(5)
C(21)	−0.319 6(7)	−0.701 6(6)	−0.325 1(7)
C(22)	−0.220 8(8)	−0.647 0(8)	−0.348 1(7)
C(23)	−0.120 8(8)	−0.552 3(7)	−0.269 4(9)
C(24)	−0.119 6(6)	−0.514 6(6)	−0.173 2(8)
C(25)	−0.220 5(6)	−0.571 9(5)	−0.153 8(6)
C(26)	−0.227 7(6)	−0.534 0(5)	−0.050 3(6)
N(3)	−0.832 0(4)	−0.718 3(4)	−0.394 4(4)
C(31)	−0.873 4(6)	−0.773 6(5)	−0.333 3(6)
C(32)	−0.934 4(6)	−0.755 1(6)	−0.280 0(6)
C(33)	−0.956 8(6)	−0.676 5(7)	−0.292 2(6)
C(34)	−0.916 6(7)	−0.619 0(6)	−0.357 1(6)
C(35)	−0.851 2(6)	−0.639 3(5)	−0.404 1(5)
C(36)	−0.795 6(6)	−0.575 0(5)	−0.469 0(6)
N(4)	−0.663 5(4)	−0.781 9(4)	−0.586 2(4)
C(41)	−0.544 2(6)	−0.722 1(5)	−0.563 6(6)
C(42)	−0.497 9(7)	−0.745 1(6)	−0.631 1(7)
C(43)	−0.577 6(8)	−0.833 2(7)	−0.727 6(7)
C(44)	−0.700 3(7)	−0.895 5(6)	−0.750 6(6)
C(45)	−0.741 2(6)	−0.867 8(5)	−0.680 0(5)
C(46)	−0.871 6(6)	−0.934 3(5)	−0.698 2(5)
N(7)	−0.789 7(5)	−0.638 6(4)	−0.555 9(5)
C(7a)	−0.700 0(6)	−0.569 6(6)	−0.590 6(6)
C(8)	−0.914 0(6)	−0.709 0(6)	−0.650 8(6)
C(9)	−0.926 6(6)	−0.805 6(5)	−0.717 5(6)
N(8)	−0.907 3(4)	−0.868 6(4)	−0.648 5(4)
C(8a)	−1.018 1(6)	−0.937 3(5)	−0.636 2(6)
N(5)	−0.311 5(5)	−0.623 2(4)	−0.026 4(4)
C(5a)	−0.340 4(7)	−0.581 0(6)	0.056 6(6)
C(6)	−0.257 4(6)	−0.684 4(6)	0.011 9(6)
C(7)	−0.354 2(6)	−0.795 8(6)	−0.005 3(6)
N(6)	−0.440 5(5)	−0.855 6(4)	−0.124 1(4)
C(6a)	−0.389 7(7)	−0.901 0(6)	−0.179 4(7)
Cl(1)	−1.016 9(2)	−0.784 9(2)	−0.011 9(2)
O(11)	−0.892 6(5)	−0.713 4(4)	0.064 3(6)
O(12)	−1.091 7(6)	−0.801 5(6)	0.040 2(5)
O(13)	−1.032 5(7)	−0.877 8(6)	−0.060 0(9)
O(14)	−1.045 4(7)	−0.735 4(8)	−0.086 7(7)
Cl(2)	−0.787 3(2)	−0.287 8(2)	−0.320 0(2)
O(21)	−0.799 3(12)	−0.302 3(14)	−0.418 8(8)
O(22)	−0.890 6(7)	−0.368 9(7)	−0.316 1(10)
O(23)	−0.688 4(8)	−0.287 0(10)	−0.256 5(7)
O(24)	−0.789 3(9)	−0.202 8(7)	−0.275 8(10)

ligands[15] show that the core arrangements of μ-oxo-iron(III) complexes containing terminal hydroxo and water ligands can be tuned by an appropriate choice of capping ligand, and this in turn controls/prevents the growth of larger polyoxohydroxo-iron(III) species.

The differences in the reactivities of the chemically similar complexes $[LFeO(OH)FeL][ClO_4]_3$ **2** and $[(tpa)(H_2O)FeO\text{-}Fe(OH)(tpa)][ClO_4]_3$[15b] is noteworthy. Both complexes are able to promote the hydration of acetonitrile to give acetamide-bridged complexes, however the latter shows no sensitivity towards carbon dioxide and undergoes rapid acetate substitution. In contrast, complex **2** reacts readily with carbon dioxide and undergoes relatively slow substitution reactions with carboxylic acids. These differences, along with spectroscopic differences, lead us to the assignment of fundamentally different core structures in these two otherwise chemically similar complexes. An outcome of these different core arrangements will be that the Lewis acidity of the iron atoms as well as the Lewis basicity of the μ-oxo atom will be greater in the μ-O-μ-OH complex **2**, compared to the μ-O-μ-HOHOH

Table 4 Important distances (Å) and angles (°) for [LFe(μ-$O_2CMe)_2LFe][ClO_4]_2$ **1**

Fe(1) · · · Fe(2)	4.382(2)		
Fe(1)–O(1)	2.061(4)	Fe(2)–O(2)	2.095(4)
Fe(1)–O(3)	2.064(4)	Fe(2)–O(4)	2.092(4)
Fe(1)–N(1)	2.185(5)	Fe(2)–N(3)	2.152(5)
Fe(1)–N(2)	2.181(6)	Fe(2)–N(4)	2.150(5)
Fe(1)–N(5)	2.261(5)	Fe(2)–N(7)	2.283(5)
Fe(1)–N(6)	2.256(5)	Fe(2)–N(8)	2.277(5)
O(1)–Fe(1)–O(3)	108.4(2)	O(2)–Fe(2)–O(4)	109.5(2)
O(1)–Fe(1)–N(1)	96.0(2)	O(2)–Fe(2)–N(3)	93.1(2)
O(1)–Fe(1)–N(2)	90.7(2)	O(2)–Fe(2)–N(4)	89.3(2)
O(1)–Fe(1)–N(5)	159.4(2)	O(2)–Fe(2)–N(7)	160.3(2)
O(1)–Fe(1)–N(6)	86.9(2)	O(2)–Fe(2)–N(8)	86.8(2)
O(3)–Fe(1)–N(1)	90.8(2)	O(4)–Fe(2)–N(3)	90.7(2)
O(3)–Fe(1)–N(2)	93.2(2)	O(4)–Fe(2)–N(4)	92.5(2)
O(3)–Fe(1)–N(5)	87.8(2)	O(4)–Fe(2)–N(7)	87.5(2)
O(3)–Fe(1)–N(6)	160.7(2)	O(4)–Fe(2)–N(8)	160.1(2)
N(1)–Fe(1)–N(2)	170.7(2)	N(3)–Fe(2)–N(4)	175.1(2)
N(2)–Fe(1)–N(5)	75.4(2)	N(3)–Fe(2)–N(7)	76.3(2)
N(2)–Fe(1)–N(6)	98.4(2)	N(3)–Fe(2)–N(8)	100.1(2)
N(1)–Fe(1)–N(5)	96.4(2)	N(4)–Fe(2)–N(7)	100.2(2)
N(1)–Fe(1)–N(6)	75.6(2)	N(4)–Fe(2)–N(8)	75.8(2)
N(5)–Fe(1)–N(6)	80.3(2)	N(7)–Fe(2)–N(8)	78.9(2)

Table 5 Important distances (Å) and angles (°) for [LFe(μ-O)(μ-$CO_3)FeL][ClO_4]_2\cdot 2H_2O$ **3**

Fe(1) · · · Fe(2)	3.216(1)	Fe(2)–O(1)	1.807(5)
Fe(1)–O(1)	1.800(5)	Fe(2)–O(3)	1.929(5)
Fe(1)–O(2)	1.932(5)	Fe(2)–N(5)	2.149(6)
Fe(1)–N(1)	2.154(6)	Fe(2)–N(6)	2.215(6)
Fe(1)–N(2)	2.224(5)	Fe(2)–N(7)	2.279(6)
Fe(1)–N(3)	2.255(7)	Fe(2)–N(8)	2.165(7)
Fe(1)–N(4)	2.160(7)		
Fe(1)–O(1)–Fe(2)	126.1(3)	O(1)–Fe(2)–O(3)	102.7(2)
O(1)–Fe(1)–O(2)	102.4(2)	O(1)–Fe(2)–N(5)	96.6(2)
O(1)–Fe(1)–N(1)	97.1(2)	O(1)–Fe(2)–N(6)	95.4(2)
O(1)–Fe(1)–N(2)	96.5(2)	O(1)–Fe(2)–N(7)	168.1(2)
O(1)–Fe(1)–N(3)	168.6(2)	O(1)–Fe(2)–N(8)	96.4(2)
O(1)–Fe(1)–N(4)	96.1(2)	O(3)–Fe(2)–N(5)	91.8(2)
O(2)–Fe(1)–N(1)	90.9(2)	O(3)–Fe(2)–N(6)	159.3(2)
O(2)–Fe(1)–N(2)	157.9(2)	O(3)–Fe(2)–N(7)	85.5(2)
O(2)–Fe(1)–N(3)	84.0(2)	O(3)–Fe(2)–N(8)	92.8(2)
O(2)–Fe(1)–N(4)	95.0(2)	N(5)–Fe(2)–N(6)	76.0(2)
N(1)–Fe(1)–N(2)	75.4(2)	N(5)–Fe(2)–N(7)	91.7(2)
N(1)–Fe(1)–N(3)	92.2(2)	N(5)–Fe(2)–N(8)	164.9(2)
N(1)–Fe(1)–N(4)	164.0(3)	N(6)–Fe(2)–N(7)	78.3(2)
N(2)–Fe(1)–N(3)	79.3(2)	N(6)–Fe(2)–N(8)	95.1(2)
N(2)–Fe(1)–N(4)	94.2(3)	N(7)–Fe(2)–N(8)	74.4(2)
N(3)–Fe(1)–N(4)	73.8(2)		

complex $[(tpa)(H_2O)FeOFe(OH)(tpa)][ClO_4]_3$. This will be particularly important to their respective reactivities. The apparent reactivity of **2** towards carbon dioxide illustrates this point. The mechanism of this reaction may involve either an attack by the very basic μ-oxo atom on the carbon atom of carbon dioxide or nucleophilic attack by an oxygen atom of carbon dioxide at one of the Lewis-acidic iron centres. The steric constraints of the capping ligands have apparently prevented the further nucleation to give species with an oxygen bridging between three iron(III) atoms, but on the other hand have allowed a reaction with carbon dioxide to occur.

Peaks that can be assigned to various species formed from the oxidation of $[LFe^{II}(\mu\text{-}O_2CMe)_2Fe^{II}L]^{2+}$ **1** in solution have been identified by ES mass spectrometry. These include one mixed-valence oxo-bridged $Fe^{II}Fe^{III}$ complex. However it was only possible to isolate the μ-oxo-μ-acetato-diiron(III) complex **4** from these solutions. Complex **4** as well as other doubly and singly bridged μ-oxo-diiron(III) complexes was prepared also by substitution of the μ-hydroxo bridge of **2**.

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