The Reactions of Elemental Iron with Dipicolinic Acid (H_2dipic) and Quinaldic Acid (Hquin) – X-ray Crystal Structures of $[C_5H_5NH][Fe(Dipic)(Hdipic)(C_5H_5N)_2]\cdot 3C_5H_5N$, $[Fe_2(\mu\text{-}O)(Dipic)_2(C_5H_5N)_4]\cdot 2C_5H_5N\cdot 2H_2O$ and *trans*-$[Fe(Quin)_2(MeOH)_2]$

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Iron powder reacts with dipicolinic acid (H_2dipic) in pyridine at 110 °C to give the heptacoordinate iron(II) complex $[C_5H_5NH][Fe(dipic)(Hdipic)(C_5H_5N)_2]$; the $(Hdipic)^-$ ligand binds to the metal centre *solely* through the oxygen atoms of one carboxylate group, the first example of this coordination mode at iron. Upon dissolution in pyridine under aerobic conditions this complex transforms into the oxo-bridged diiron(III) species $[Fe_2(\mu\text{-}O)(dipic)_2(C_5H_5N)_4]$, which possesses a linear Fe–O–Fe axis. Quinaldic acid (Hquin) reacts with iron powder in pyridine at 110 °C to give $[Fe(quin)_2(C_5H_5N)_2]$, analogous to the corresponding reactivity of picolinic acid. This complex is converted into *trans*-$[Fe(quin)_2(MeOH)_2]$ or $[Fe_2(\mu\text{-}O)(quin)_4(dmf)_2]$ in methanol or DMF respectively. The formation of an iron(II) complex in the reaction with methanol differs markedly from the picolinate system.

Introduction

Picolinic acid (Hpic) is a highly efficient promoter of Gif-type catalytic oxygenation of methylene groups in cycloalkane substrates using iron complexes (GoAgg^{III} conditions).[1] The active catalyst in GoAgg^{III} is proposed to be an iron-hydroperoxy complex, although the processes involved in the construction of this species are poorly understood. Stavropoulos[2] has reported that iron powder reacted with Hpic at room temperature to give polymeric $[Fe(pic)_2]_n$ (in dichloromethane) or $[Fe(pic)_2(C_5H_5N)_2]$ (in pyridine), from which an array of mono- and bimetallic systems was readily generated by treatment with coordinating solvents (DMF, methanol, water) and/or aerobic oxidation. The catalytic oxygenation profiles of adamantane using these picolinate complexes lend valuable support to the radical-based mechanism believed to operate in Gif chemistry. Also, Shova et al. have reported that the reaction of iron powder with Hpic in water leads to $[Fe(pic)_2(H_2O)_2]$.[3]

The richness of the iron(0)-Hpic system prompted us to investigate the behaviour of dipicolinic and quinaldic acids (H_2dipic and Hquin respectively) with elemental iron. Ferrous and ferric complexes with dipicolinate[4–14] and quinaldinate[15–21] ligands have hitherto been prepared from iron salts, however the use of iron in elemental form as a substrate with the parent acids has not been explored. There is precedent for the use of iron-dipicolinate complexes as GoAgg^{III} oxygenation catalysts,[12] although doubts were later cast on the validity of these results,[10] since these complexes have a tendency to interconvert in solution. Access to a range of structurally and spectroscopically characterised iron derivatives containing dipicolinate and quinaldinate ligands is thus eminently desirable in order to evaluate their catalytic potential.

Results and Discussion

Dipicolinate Complexes

Initial attempts at the iron(0)-H_2dipic reaction in dichloromethane, both at room temperature and under reflux, showed no visual evidence for any reaction, as the supernatant solution remained colourless throughout, with insoluble H_2dipic and iron powder present c.f. Hpic reacts at room temperature with Fe^0 to give $[Fe(pic)_2]_n$ in 63 % yield after four days.[2] The use of pyridine as the reaction solvent proved to be more profitable.

Refluxing a mixture of H_2dipic and iron powder (molar ratio 2:1) in pyridine for 5 h under argon produces a deep red solution from which unreacted iron is removed by anaerobic filtration whilst hot. Upon cooling the filtrate to –20 °C for 24 h a red crystalline solid is deposited. The molecular structure of the complex was determined crystallographically to be $[C_5H_5NH][Fe(dipic)(Hdipic)(C_5H_5N)_2]\cdot$

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$3C_5H_5N$ ($1·3C_5H_5N$, Figure 1) in which $dipic^{2–}$ is coordinated in tridentate fashion to Fe(1) via the N(1), O(7) and O(8) atoms, while $(Hdipic)^–$ is bound via O(16) and O(17) of one carboxylate group to give a four-membered metallacycle with the N(11), O(18) and O(19) atoms oriented away from Fe(1). **1** is the first iron complex in which the 2,6 isomer of $(Hdipic)^–$ is solely *O,O′*-bidentate through one carboxylate group. Fe(1) has a pentagonal bipyramidal geometry, with equatorial $[NO_4]$ donor atoms being supplied by dipicolinate ligands and axial pyridines completing the coordination sphere. By analogy with Stavropoulos' iron(0)-Hpic system[2] and our own rigorous exclusion of dioxygen and moisture during the reaction, we assign a +2 oxidation state to the iron centre. Magnetic susceptibility measurements of powdered samples reveal $\mu_{eff} \approx 4.7$ B.M at room temperature, confirming a high-spin iron(II) species. The ^1H NMR spectrum of **1** in $[D_5]$pyridine at room temperature comprises broad singlets at $\delta_H = 75.5$, 52.7 and 4.7 ppm. The bond lengths and angles in **1** concur with other (dipicolinato)iron complexes,[8–11,13] with O(16)–Fe(1)–O(17) 58.11(7)°, the Fe(1)–O lengths span the range 2.1614(19)–2.2905(19) Å. The pyridinium counterion and one of the solvate pyridine molecules hydrogen-bond to the iron complex [H(51)···O(8) 1.81(2) Å, N(51)···O(8) 2.737(3) Å, N(51)–H(51)···O(8) 156(4)°; H(19)···N(41) 1.62(1) Å, O(19)···N(41) 2.598(4) Å, O(19)–H(19)···N(41) 177(4)°]. This interaction between O(8) and the pyridinium cation lengthens Fe(1)–O(8) by ca. 0.04 Å compared to Fe(1)–O(7).

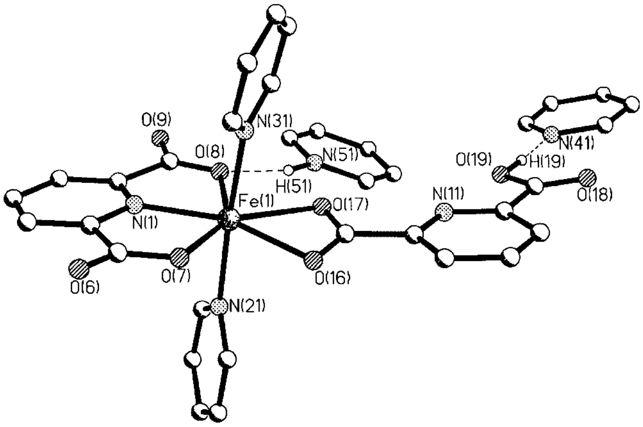

Figure 1. Molecular structure of $1·3C_5H_5N$ (hydrogen atoms and non-H bonded solvate molecules omitted for clarity); selected bond lengths (Å) and angles (°): Fe(1)–N(1) 2.133(2), Fe(1)–O(7) 2.1614(19), Fe(1)–O(8) 2.2095(18), Fe(1)–N(31) 2.218(2), Fe(1)–N(21) 2.234(2), Fe(1)–O(17) 2.246(2), Fe(1)–O(16) 2.2905(19), N(1)–Fe(1)–O(7) 73.49(8), N(1)–Fe(1)–O(8) 72.36(8), O(7)–Fe(1)–O(8) 145.71(7), N(1)–Fe(1)–N(31) 95.14(8), O(7)–Fe(1)–N(31) 90.12(8), O(8)–Fe(1)–N(31) 90.00(8), N(1)–Fe(1)–N(21) 88.21(8), O(7)–Fe(1)–N(21) 90.04(8), O(8)–Fe(1)–N(21) 91.80(8), N(31)–Fe(1)–N(21) 176.55(9), N(1)–Fe(1)–O(17) 147.06(8), O(7)–Fe(1)–O(17) 139.39(7), O(8)–Fe(1)–O(17) 74.71(7), N(31)–Fe(1)–O(17) 84.92(8), N(21)–Fe(1)–O(17) 92.72(8), N(1)–Fe(1)–O(16) 154.74(8), O(7)–Fe(1)–O(16) 81.54(7), O(8)–Fe(1)–O(16) 132.74(7), N(31)–Fe(1)–O(16) 88.50(8), N(21)–Fe(1)–O(16) 88.12(8), O(17)–Fe(1)–O(16) 58.11(7)

Compound **1** is stable for prolonged periods in the solid state under an inert atmosphere. The pyridine solvate molecules are lost upon removal of crystals from the mother liquor, thermogravimetric analysis shows that at 118 °C a sample of the freshly crystallised complex loses 27.8 % of its mass, c.f. for $1·C_5H_5N$ the solvent of crystallisation constitutes 27.5 % by mass. The FAB^+ mass spectrum contains a peak at *m/z* = 388 corresponding to $[Fe(dipic)]^+$, peaks at higher *m/z* ratios could not be assigned.

Following dissolution of **1** in wet pyridine under aerobic conditions, $[C_5H_5NH]_2[dipic]$ (^1H NMR and infra-red spectroscopic evidence) is precipitated. Upon filtration and standing in air overnight, deep red crystals deposit from the filtrate. X-ray crystallography reveals the product to be the diiron(III) complex $[Fe_2(\mu\text{-}O)(dipic)_2(C_5H_5N)_4]$ (**2**) (Figure 2) in which $dipic^{2–}$ is tridentate at Fe(1) via the N(7), O(11) and O(11B) atoms with N(7) *trans* to the μ-oxo atom O(1); the complex co-crystallises with molecules of pyridine and water. The octahedral coordination at Fe(1) is completed by pyridine ligands bound axially through N(1) and N(1B). The oxo atom O(1) lies on an crystallographic inversion centre, hence the Fe(1)–O(1)–Fe(1A) axis is 180°. The acute bite angle of $dipic^{2–}$ distorts the geometry at Fe(1), thus O(11)–Fe(1)–O(11B) and O(1)–Fe(1)–O(11) are 150.67(18)° and 104.67(9)°, respectively. The shortness of Fe(1)–O(1) [1.7808(8) Å] compared to Fe(1)–O(11) [2.048(3) Å] suggests significant π-bonding within the Fe(1)–O(1) linkage. The *trans* influence of O(1) lengthens Fe(1)–N(7) [2.106(6) Å] compared with $[Fe(dipic)_2]^–$ species [2.037(3)–2.076(3) Å],[8,9,22] Fe(1)–O(11) [2.048(3) Å] being marginally longer than in the homoleptic complexes [2.001(2)–2.035(2) Å]. The Fe(1)–N(1) bonds [2.218(5) Å] are identical in length to **1** [2.218(2), 2.234(2) Å]. The solv-

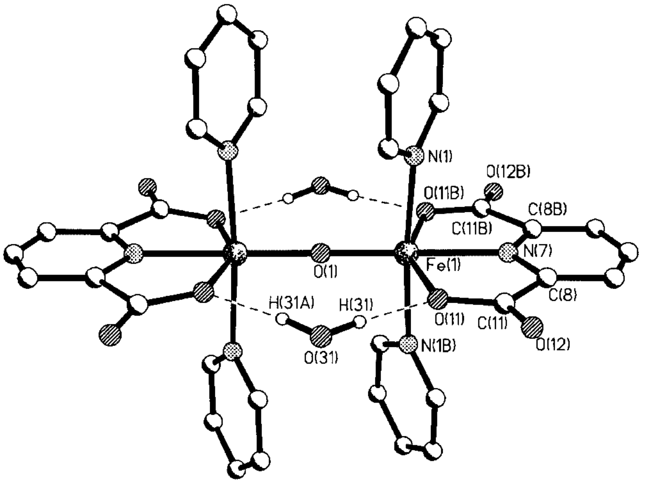

Figure 2. Molecular structure of $2·2C_5H_5N·2H_2O$ (C–H bonds and pyridine solvate molecules omitted for clarity); selected bond lengths (Å) and angles (°): Fe(1)–O(1) 1.7808(8), Fe(1)–O(11) 2.048(3), Fe(1)–N(7) 2.106(6), Fe(1)–N(1) 2.218(5), O(10)–Fe(1)–O(11) 104.67(9), O(11)–Fe(1)–O(11B) 150.67(18), O(1)–Fe(1)–N(7) 180.0, O(11)–Fe(1)–N(7) 75.33(9), O(11)–Fe(1)–N(1) 87.72(12), N(7)–Fe(1)–N(1) 87.45(10), O(1)–Fe(1)–N(1) 92.55(10), O(11B)–Fe(1)–N(1) 90.99(12), N(7)–Fe(1)–N(1) 87.45(10), N(1B)–Fe(1)–N(1) 174.9(2), Fe(1)–O(1)–Fe(1A) 180.0

ate water molecule hydrogen bonds to the dipicolinate [H(31)···O(11) 1.895(11) Å, O(31)···O(11) 2.868(5) Å, O(31)–H(31)···O(11) 172(5)°], O(31) being essentially coplanar with this ligand. There are no other significant intermolecular contacts. In its infra-red spectrum, the band for the asymmetric ν_{FeOFe} stretch appears at 862 cm^{-1}.

Upon storage in a sample vial for several days the deep red crystals of **2** transform into a pale brown solid with the release of pyridine vapour (olfactory evidence). Microanalysis suggested the stoichiometry $[Fe_2O(dipic)_2(H_2O)_4]$ i. e. the pyridine ligands and solvate molecules are lost upon removal from contact with the mother liquor. We propose that the μ-oxo bridge is retained during this process and that the new aqua complex is isostructural with $[Fe_2(\mu\text{-}O)(4\text{-}Cl\text{-}dipic)_2(H_2O)_4]$ (4-Cl-dipic = 4-chlorodipicolinate, Figure 3), which is accessible from iron(III) chloride hexahydrate, the diethyl ester of 4-Cl-dipicH_2 and urea.[5] Pyridine loss is suppressed when **2** is stored in a sample vial housed within a larger one containing a small volume of this solvent. The lability of the pyridine ligands in **2** suggests that this compound may be a useful synthon for new complexes with the $Fe_2(\mu\text{-}O)(dipic)_2$ subunit.

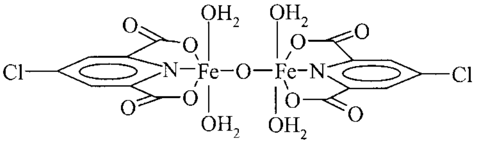

Figure 3. The structure of $[Fe_2(\mu\text{-}O)(4\text{-}Cl\text{-}dipic)_2(H_2O)_4]$;[5] complex $[Fe_2(\mu\text{-}O)(dipic)_2(H_2O)_4]$ is proposed to be isostructural

Quinaldinate Complexes

The reaction of Hquin with elemental iron has not been reported elsewhere. We have found that Hquin reacts with iron powder (molar ratio 2:1) under identical conditions to those used to synthesise **1** to give $[Fe(quin)_2(C_5H_5N)_2]$ (**3**). The ν_{COO} bands in **3** (1652, 1361 cm^{-1}) are comparable to $[Fe(pic)_2(C_5H_5N)_2]$ (1645, 1348 cm^{-1}),[2] microanalytical data confirms the proposed stoichiometry although the FAB$^+$ mass spectrum contains no peaks which are assignable to a molecular ion or daughter fragments. Compound **3** is air- and moisture-stable in the solid state under ambient conditions. We have been unable to obtain crystals suitable for X-ray crystallographic analysis in order to establish its geometry. As with **1**, there is paramagnetic shifting of the signals in the ^{1}H NMR spectrum.

Complex **3** is more stable towards methanol under aerobic conditions than its picolinate counterpart. Whereas $[Fe(pic)_2(C_5H_5N)_2]$ reacts with methanol at room temperature to give a diiron(III) complex $[Fe_2(\mu\text{-}OMe)_2(pic)_4]$,[23] refluxing a methanolic suspension of **3** for four days is sufficient only to displace the coordinated pyridine ligands and generate the iron(II) species $[Fe(quin)_2(MeOH)_2]$ (**4**). The sluggishness of this reaction reflects the greater steric bulk of quinaldinate compared with picolinate and, possibly, that **3** is polymeric. The directing influence of the pyridine ligands on the course of the picolinate reactions is crucial, as under anaerobic conditions $[Fe(pic)_2]_n$ reacts at room temperature with methanol to give $[Fe(pic)_2(MeOH)_2]$.[2]

Crystals of **4** suitable for X-ray analysis were deposited from the reaction mixture. The molecular structure (Figure 4) reveals a centrosymmetric geometry at the iron centre, with an FeN_2O_4 core comprising methanol ligands in axial positions and *N,O*-chelating quinaldinate anions with a *trans*-arrangement in the equatorial plane. The geometric parameters of **4** and the formation of one-dimensional hydrogen-bonded chains between carbonyl oxygen atoms and methanol ligands in adjacent molecules [H(21O)···O(11′) 1.650(6) Å, O(21)···O(11′) 2.621(1) Å, O(21)-H(21O)···O(11′) 170(3)°] correspond with the diaqua, diethanol and di(*n*-propanol) analogues, as well as $[Fe(pic)_2(MeOH)_2]$.[2,17,18,21] Additionally, there are only very modest dimensional differences between **1, 2** and **4**. In the infra-red spectrum ν_{OH} appears at 3180 cm^{-1} and ν_{COO} at 1635 and 1387 cm^{-1}. Complex **4** is stable towards moisture and oxidation over several months in the solid state.

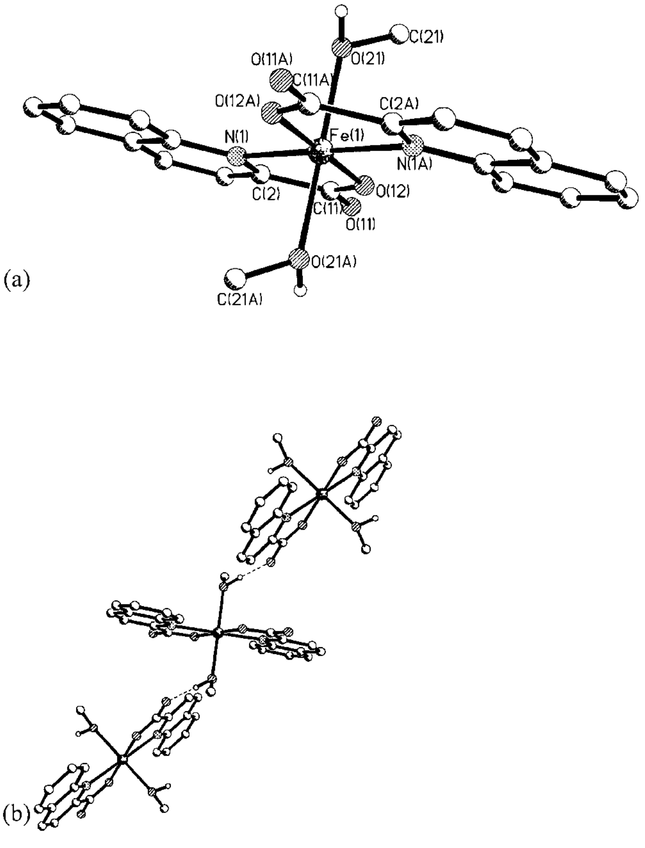

Figure 4. (a) Molecular structure of **4** (C–H bonds omitted for clarity); selected bond lengths (Å) and angles (°): Fe(1)–O(12) 2.0534(14), Fe(1)–O(21) 2.1624(14), Fe(1)–N(1) 2.2571(17), O(21)–C(21) 1.439(2), O(12)–Fe(1)–N(1) 76.39(6), N(1A)–Fe(1)–N(1) 180.0, O(21A)–Fe(1)–N(1) 88.98(6), O(21)–Fe(1)–N(1) 91.02(6), O(21A)–Fe(1)–O(21) 180.0, O(12A)–Fe(1)–O(12) 180.00(3), O(12)–Fe(1)–O(21) 91.48(5), O(12)–Fe(1)–N(1A) 103.61(6), O(12)–Fe(1)–O(21A) 88.52(5); (b) hydrogen-bonding networks in **4**

Following dissolution of **3** in DMF, vapour diffusion with diethyl ether gives golden-brown needles of $[Fe_2(\mu\text{-}$

O)(quin)$_4$(dmf)$_2$] (**5**). This conversion mirrors the behaviour of [Fe(pic)$_2$(C$_5$H$_5$N)$_2$] towards dmf, which affords [Fe$_2$(μ-O)(pic)$_4$(dmf)$_2$].[2] The asymmetric ν_{FeOFe} and ν_{COO} vibrations in **5** (882, 1676, 1315 cm^{-1}) differ by 15–30 cm^{-1} from the picolinate complex (867, 1653, 1344 cm^{-1}). The insolubility of this complex in organic solvents prevented acquisition of ^{1}H NMR and mass spectra.

Although Hquin and Hpic behave in a similar fashion towards iron powder, there is a significant difference towards iron(III) salts. Whereas Hpic gives [Fe(pic)$_3$],[2] the corresponding reaction with Hquin in methanol at room temperature gives the binuclear complex [Fe$_2$(μ-OH)$_2$(quin)$_4$] (**6**).[15,20] Presumably steric constraints preclude tris(chelation) of quin$^-$ at an iron(III) centre, since [M(quin)$_3$] complexes exist for bismuth(III) and lanthanide(III) ions.[24,25]

Summary

The reaction of H$_2$dipic with iron powder in pyridine affords [C$_5$H$_5$NH][Fe(dipic)(Hdipic)(C$_5$H$_5$N)$_2$], in which the deprotonated acid exhibits two different coordination modes. In wet pyridine this complex converts into the oxo-bridged diiron(III) species [Fe$_2$(μ-O)(dipic)$_2$(C$_5$H$_5$N)$_4$] whose coordinated solvent molecules are susceptible to displacement by atmospheric water in the solid state. Hquin reacts with iron powder to give [Fe(quin)$_2$(C$_5$H$_5$N)$_2$], whose pyridine ligands are displaced under forcing conditions by methanol or at room temperature by dmf, affording *trans*-[Fe(quin)$_2$(MeOH)$_2$] and [Fe$_2$(μ-O)(quin)$_4$(dmf)$_2$] respectively.

The detailed investigation of (dipicolinato)iron complexes in aqueous media by Gourdon et al. demonstrates that several structural motifs can be readily derived.[4,7,10,11] The chemistry of (Hdipic)$^-$ and dipic^{2-} is enriched by the capacity of the carbonyl oxygens of the carboxylate groups to bind to adjacent metal centres, generating polynuclear structures.[27–30] A recent example illustrates that the carboxylate oxygen atom can also engage in hydrogen-bonding interactions with coordinated water molecules to form supramolecular networks.[31] That (Hdipic)$^-$ binds to iron(II) in **1** without the formation of a polymeric structure via the pendant carboxylate group is unusual, instances of this *O*,*O*′ mode at europium(III) and silver(I) generate infinite chains wherein both of the acid groups link metal ions.[32,33] 2,6-H$_2$dipic is the sole positional isomer of this ligand for whom geometric constraints do not preclude *N*,*O*,*O*′ chelation to a single metal centre. Studies using other isomers where such tridentate chelation is prohibited by the disposition of the acid groups lead to coordination polymers.[34–37] Investigations into how these other diacids react with elemental iron are currently underway in our laboratory.

The lability of the coordinated solvent molecules in **1**–**3** suggests that these complexes could be valuable precursors to new mono- and polyiron dipic/quin species, which will benefit investigations into Gif chemistry. The facility of the reactions of H$_2$dipic and Hquin with elemental iron also indicates that reactions of these acids with other electropositive metals will undoubtedly deliver complexes with new structural motifs.

Experimental Section

Materials and Instrumentation: Syntheses and work-up procedures were conducted under argon or oxygen-free dinitrogen using Schlenk line techniques, unless stated otherwise. Pyridine was distilled from calcium hydride, all other solvents and reagents were used as supplied. Infra-red spectra were recorded as pressed KBr discs with Perkin–Elmer System 2000 and Nicolet Nexus FTIR/Raman spectrometers, microanalyses were carried out by the University of St. Andrews and UMIST Microanalytical Services. FAB mass spectra (positive ionisation mode, 3-nitrobenzyl alcohol matrix) were recorded by the EPSRC National Mass Spectrometry Service (Swansea), ^{1}H NMR spectra (200.0 MHz) were recorded with a Bruker DPX 200 spectrometer.

Synthesis of Complexes 1–6

[C$_5$H$_5$NH][Fe(dipic)(Hdipic)(C$_5$H$_5$N)$_2$] (1): Iron powder (320 mg, 5.7 mmol) and H$_2$dipic (1.80 g, 10.8 mmol) were heated in pyridine (50 cm^3) at 110 °C under argon for 5 h. The red solution was filtered anaerobically while hot to remove unreacted iron, and the filtrate was cooled to –20 °C overnight. Red crystals of **1** ·3C$_5$H$_5$N suitable for X-ray analysis were collected by filtration under argon, concentration of the filtrate in vacuo gave a second crop of complex. Yield 2.29 g (74 %). C$_{24}$H$_{17}$FeN$_4$O$_8$ (545.2): calcd. C 52.87, H 3.14, N 10.28; found C 52.24, H 3.19, N 9.85. Selected IR bands (cm^{-1}): $\tilde{\nu}$ = 3435 s (ν_{OH}), 1673 s, 1648 s, 1368 s, 1350 s (ν_{COO}). MS: *m*/*z* = 388 [Fe(dipic)]$^+$. ^{1}H NMR ([D$_5$]pyridine): δ = 75.5 (br), 52.7 (br), 4.7 (br) ppm.

[Fe$_2$(μ -O)(dipic)$_2$(C$_5$H$_5$N)$_4$] (2): Under aerobic conditions **1** (200 mg) was dissolved in pyridine (10 cm^3) with sonication, giving a red solution with a colourless precipitate of [C$_5$H$_5$NH]$_2$[dipic]. The solution was filtered and the filtrate left open to air for 12 h, after which time deep red crystals of **2**.2C$_5$H$_5$N·2H$_2$O (118 mg) suitable for X-ray analysis had deposited. C$_{34}$H$_{26}$Fe$_2$N$_6$O$_9$ (774.2): calcd. C 52.7, H 3.4, N 10.9; found C 52.1, H 2.9, N 10.4. Selected IR bands (cm^{-1}): $\tilde{\nu}$ = 1674 s, 1367 m (ν_{COO}), 862 m ($\nu_{FeOFe(asym)}$). Crystalline **2** changed colour from dark red to beige with the release of pyridine over four days at room temperature upon storage in a sample vial. Microanalysis suggested conversion to [Fe$_2$(μ-O)(dipic)$_2$(H$_2$O)$_4$]. C$_{14}$H$_{14}$Fe$_2$N$_2$O$_{13}$ (529.9): calcd. C 31.73, H 2.66, N 5.28; found C 31.91, H 2.43, N 5.24. Selected IR bands (cm^{-1}): $\tilde{\nu}$ = 3462 s, 2923 s (ν_{OH}), 1656 s, 1626 s, 1379 s, 1366 s (ν_{COO}), 924 m ($\nu_{FeOFe(asym)}$).

[Fe(quin)$_2$(C$_5$H$_5$N)$_2$] (3): Iron powder (75 mg, 1.35 mmol) and Hquin (352 mg, 2.03 mmol) were heated in pyridine (40 cm^3) at 110 °C for 3.5 h under argon. Unreacted iron powder was filtered off anaerobically whilst hot, **3** precipitated as a purple solid from the filtrate upon cooling to room temperature and was collected by filtration under argon. Yield 370 mg (49 %). C$_{30}$H$_{22}$FeN$_4$O$_4$ (558.3): calcd. C 64.53, H 3.97, N 10.03; found C 63.92, H 3.99, N 9.80. Selected IR bands (cm^{-1}): $\tilde{\nu}$ = 1652 s, 1361 m (ν_{COO}). ^{1}H NMR (CDCl$_3$): δ = 42.0 (br), 37.9 (br), 32.6 (br), 30.8 (br), 29.5 (br), 28.6 (br), 26.3 (br), 25.4 (br), 13.0 (br), 10.4 (br) ppm.

***trans*-[Fe(quin)$_2$(MeOH)$_2$] (4):** Under aerobic conditions a suspension of **3** (140 mg, 0.25 mmol) in methanol (20 cm^3) was heated at reflux for four days. The resulting brown microcrystalline solid was filtered off and washed with diethyl ether. Yield 89 mg (76 %).

Crystals amenable to X-ray crystallographic analysis were obtained directly from the reaction. $C_{22}H_{20}FeN_2O_6$ (464.2): calcd. C 56.9, H 4.0, N 6.0; found C 56.0, H 4.4, N 6.1. Selected IR bands (cm^{-1}): $\tilde{\nu}$ = 3180 s (ν_{OH}), 1635 s, 1387 s (ν_{COO}). ^{1}H NMR ([D$_7$]DMF): δ = 34.1 (br), 32.1 (br), 12.0 (br), 4.4 (br), 2.3 (br) ppm.

[Fe$_2$(μ -O)(quin)$_4$(dmf)$_2$] (5): Under aerobic conditions a solution of **3** (84 mg, 0.15 mmol) in DMF (5 cm^3) was vapour-diffused with diethyl ether. After three days golden-brown needles of **5** were deposited. Yield 51 mg (67 %). $C_{50}H_{38}Fe_2N_6O_{11}$ (1010.5): calcd. C 59.4, H 3.8, N 8.3; found C 59.2, H 3.6, N 8.4. Selected IR bands (cm^{-1}): $\tilde{\nu}$ = 1676 s, 1315 m (ν_{COO}), 882 m ($\nu_{FeOFe(asym)}$).

[Fe$_2$(μ -OH)$_2$(quin)$_4$] (6): Under aerobic conditions, Hquin (256 mg, 1.45 mmol) was added to iron(III) nitrate nonahydrate (194 mg, 0.48 mmol) in methanol (10 cm^3), giving a yellow solution. Addition of diethyl ether precipitated **6** as a yellow solid. Yield 295 mg (80 %). $C_{40}H_{26}Fe_2N_4O_{10}\cdot 2H_2O$ (870.3): calcd. C 55.20, H 3.47, N 6.44; found C 55.71, H 3.03, N 6.37. Selected IR bands (cm^{-1}): $\tilde{\nu}$ = 3456 m (ν_{OH}), 1663 s, 1372 s (ν_{COO}). MS: m/z = 802 [Fe$_2$(quin)$_4$]$^+$.

X-ray Crystallography: Diffraction studies on **1**$\cdot 3C_5H_5N$ and **2**$\cdot 2C_5H_5N\cdot 2H_2O$ were performed using a Bruker SMART-CCD diffractometer, for **4** a Rigaku MM007/Saturn was used, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) in each case. All data were corrected for Lorentz polarisation and long-term intensity fluctuations. The structures were solved by direct methods, non-hydrogen atoms were refined with anisotropic displacement parameters, all hydrogen atom positions were idealised. In **2** $\cdot 2C_5H_5N\cdot 2H_2O$ the disordered pyridine solvate molecules were refined with all of the ring atoms as carbons and the hydrogen atoms distributed over all of the possible sites. Structural refinements were by the full-matrix least-squares method on F^2 using the program SHELXTL-PC.[26] CCDC-225950 (for **2**), -225951 (for **1**) and -248948 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1$\cdot$3C$_5$H$_5$N: $C_{44}H_{38}FeN_8O_8$, T = 125(2) K, M = 862.67, monoclinic, space group $P21/n$, a = 9.5494(11) Å, b = 20.107(2) Å, c = 21.744(3) Å, β = 98.873(2)°, V = 4124.0 Å^3, Z = 4, D_c = 1.389 Mg$\cdot$m^{-3}, μ = 0.430 mm^{-1}, F_{000} = 1792. Of 17970 measured data, 5899 were unique (R_{int} = 0.0508) to give $R1[I > 2\sigma(I)]$ = 0.0387, $wR2$ = 0.0777.

2$\cdot$2C$_5$H$_5$N$\cdot$2H$_2$O: $C_{44}H_{40}Fe_2N_8O_{11}$, T = 293(2)K, M = 968.54, orthorhombic, space group $Ccca$, a = 14.0035(5) Å, b = 25.4518(10) Å, c = 12.2416(5) Å, V = 4363.1(3) Å^3, Z = 4, D_c = 1.474 Mg$\cdot$m^{-3}, μ = 0.736 mm^{-1}, F_{000} = 2000. Of 10044 measured data, 1473 were unique (R_{int} = 0.0280) to give $R1[I > 2\sigma(I)]$ = 0.0573, $wR2$ = 0.1589.

4: $C_{22}H_{20}FeN_2O_6$, T = 93(2)K, M = 464.25, monoclinic, space group $P21/n$, a = 10.493(4) Å, b = 7.227(2) Å, c = 13.506(5) Å, β = 107.095(7)°, V = 978.9(6) Å^3, Z = 2, D_c = 1.575 Mg$\cdot$m^{-3}, μ = 0.815 mm^{-1}, F_{000} = 480. Of 7718 measured data, 1731 were unique (R_{int} = 0.0379) to give $R1[I > 2\sigma(I)]$ = 0.0347, $wR2$ = 0.0768.

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