

Biomimetic Interaction between Fe^{II} and O₂: Effect of the Second Coordination Sphere on O₂ Binding to Fe^{II} Complexes: Evidence of Coordination at the Metal Centre by a Dissociative Mechanism in the Formation of μ -Oxo Diferric Complexes

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Abstract: We report that the formation of μ -oxo diferric compounds from O₂ and FeCl₂ complexes within the tris(2-pyridylmethyl)amine series (N. K. Thallaj et al. *Chem. Eur. J.*, **2008**, *14*, 6742–6753) involves coordination of O₂ to the metal centre and that this reaction occurs following initial dissociation of the bound equatorial chloride anion. We also report evidence of the formation of a reduced form of dioxygen by an inner-sphere mechanism, thus leading to modification of the ligand. The solid-state structures of [FeCl₂L] complexes (L¹ = mono(α -pivalamidopyridylmethyl)bis(2-pyridylmethyl)amine,

L² = mono(α -pivalesteropyridylmethyl)-bis(2-pyridylmethyl)amine, L³ = bis(α -pivalamidopyridylmethyl)mono(2-pyridylmethyl)amine are described, and spectroscopic data support the structural retention in solution. In [FeCl₂L³], the two amide hydrogen atoms stabilise the equatorial chloride anion in such a way that its exchange by a weak ligand is impossible: [FeCl₂L³] is perfectly oxygen-stable. In [FeCl₂L²], the equa-

torial chloride anion is completely free to move and coordination of O₂ can take place. The reaction product with [FeCl₂L²] is a μ -oxo diferric complex in which the ester function has been transformed into a phenol group. This conversion can be seen as a hydrolysis reaction in basic medium, hence supporting the initial formation of a reduced form of dioxygen in the medium. Complex [FeCl₂L¹] exhibits a very weak reactivity with O₂, in line with a semistabilised equatorial chloride counteranion.

Keywords: iron complexes • ligand effects • N ligands • O–O activation • reaction mechanisms

Introduction

The coordination of dioxygen by non-heme iron centres, a well-known process encountered in biological systems, promoted extensive studies in the area of biomimetic activation of molecular oxygen by synthetic iron complexes over the last ten years.^[1–14] Unlike in the chemistry of iron porphyrin

complexes, in which such a process is well known, the coordination of dioxygen to a single mononuclear non-heme Fe^{II} centre has been considerably less investigated by synthetic chemists. Early studies, however, evidenced that a mononuclear Fe^{II} centre would react to form a μ -peroxo diiron complex.^[15] Over recent years, the formation of μ -oxo diferric complexes from molecular dioxygen and mononuclear Fe^{II} complexes has emerged as a possible general process in synthetic chemistry.^[16–22] Kinetic and electrochemical studies strongly supported the presence of a dioxygen–metal adduct, although the structure of such a species at a single metal site has never been reported in non-porphyrinic chemistry.

We recently reported that Fe^{II} complexes with simple tripodal ligands within the tris(2-pyridylmethyl)amine series react with O₂ to form μ -oxodiiron complexes in a clean way.^[23,24] For a given geometry, increasing the Lewis acidity at the metal centre resulted in an increase in the reaction kinetics. A mechanism with two kinetically observable steps was deduced from single-wavelength UV monitoring of the

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formation of the final μ -oxo complex. The coordination of O_2 to the metal centre as an initial step was believed to be crucial. We report herein that “freezing” the ancillary ligands at the metal site completely inhibits the reaction. We have extended our studies to complexes in which the tripod is substituted at the α position with amide or ester functional groups. Together with structural analyses of the corresponding $FeCl_2$ complexes, we report two key observations: 1) the oxygen sensitivity strongly depends on the lability of the ancillary ligands around the metal centre, thus demonstrating that the coordination of O_2 is a real fact that occurs by a dissociative mechanism as the initial step of the reaction and 2) upon coordination of O_2 , the medium becomes very basic, hence supporting the initial formation of a reduced form of dioxygen, as often observed in biological systems.

Results

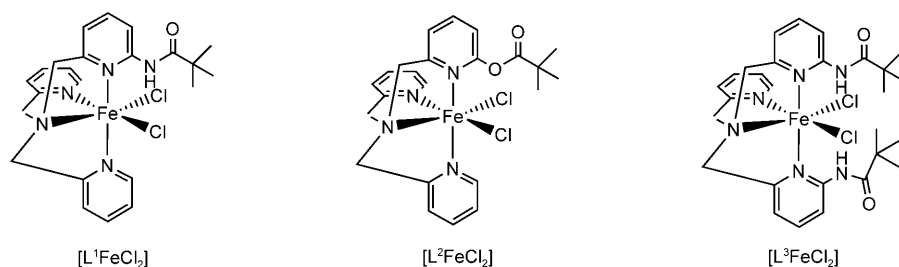
Syntheses of ligands and complexes: Ligands L^1 and L^3 were synthesised according to previously reported procedures.^[25] Ligand L^2 was obtained by the treatment of 6-(bromomethyl)pyridin-2-yl pivalate with bis(2-pyridylmethyl)amine in a yield of 51%. The final compound was obtained as yellowish oil and characterised by 1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. Ligands L^1 – L^3 display irreversible electrochemical oxidation at $E_a = 1.14$, 1.21, and 1.14 V (versus SCE), respectively. Complexes $[FeCl_2L^n]$ ($L^n = L^1$ – L^3) were prepared by the treatment of one equivalent of $FeCl_2$ with a 10% excess of free ligand in THF in an inert atmosphere, following a well-known procedure.^[26] All the obtained complexes are thermally stable and were obtained as yellow–orange solids in excellent yields.

Characterization of the complexes in solution: In the UV/Vis spectra, all the complexes display well-defined metal-to-ligand charge-transfer (MLCT) absorptions with intensities that support the coordination of all three coordinated pyridyl units: $\lambda_1 = 419$ nm ($\epsilon_1 = 0.88 \times 10^3$ mmol $^{-1}$ cm 2), $\lambda_2 = 400$ nm ($\epsilon_2 = 0.74 \times 10^3$ mmol $^{-1}$ cm 2), $\lambda_3 = 379$ nm ($\epsilon_3 = 0.96 \times 10^3$ mmol $^{-1}$ cm 2). All three compounds are paramagnetic in solution at room temperature: their 1H NMR spectra display paramagnetically shifted signals over the range $\delta = -40 \rightleftharpoons +140$ ppm (see the Supporting Information). The well-defined and narrow (on the paramagnetic scale) signals ($45 < \Delta\nu_{1/2} < 135$ Hz) support a pseudo-octahedral geometry around the metal centre in these complexes.^[26] We thus believe that these compounds display the same geometry in solution as that shown in Scheme 1.

The cyclic voltammograms of complexes $[FeCl_2L^n]$ were recorded at room temperature in

a 0.1 M solution of tetrabutylammonium (TBA) hexafluorophosphate in CH_3CN . Whereas $[FeCl_2L^1]$ and $[FeCl_2L^2]$ exhibit waves with $E_{1/2} = 371$ mV (versus SCE; pseudoreversible, $\Delta E = 71$ mV, $I_{pc}/I_{pa} = 0.80$) and 265 mV (versus SCE; reversible, $\Delta E = 67$ mV, $I_{pc}/I_{pa} = 1$), respectively, the data obtained from $[FeCl_2L^3]$ definitively indicate that the redox process is irreversible with $E_a = 573$ mV (versus SCE; see the Supporting Information for the data). It is noteworthy that the 1H NMR spectrum of $[FeCl_2L^1]$, recorded in the presence of KPF_6 and in CD_3CN , did not exhibit a drastic modification. The main changes in the spectra consisted of broadening of the resonances and minor shifts (see the Supporting Information for the spectrum). The molecular conductivities were recorded for each complex at 24°C under similar conditions, and significantly different values were obtained with $\Lambda = 11$, 20, and 6 Scm 2 mol $^{-1}$ for $[FeCl_2L^1]$, $[FeCl_2L^2]$, and $[FeCl_2L^3]$ (at concentrations of 4.0, 3.6, and 3.1 mM), respectively; therefore, suggesting a significantly different electrolytic behaviour for these complexes in solution.

Solid-state structures: All three complexes $[FeCl_2L^n]$ could be obtained as single crystals, thus allowing structural determination by X-ray diffraction studies. As expected from the solution studies, the metal centre lies in a pseudo-octahedral environment in these complexes, with all the metal-to-nitrogen distances above 2.19 Å, in line with a high-spin state for the iron centre. In general, in complexes with single-substituted ligands, the substituted pyridine lies in lateral position (i.e., the unsubstituted pyridines lie in the *cis* position to each other) to minimise the steric intramolecular repulsions.^[24,26,27] Complexes $[FeCl_2L^1]$ and $[FeCl_2L^2]$ are not exceptions to this fact. As expected, the longer metal-to-nitrogen distance corresponds to coordination of the substituted pyridine, and the corresponding $d(Fe-N)$ values range from 2.253(6) to 2.386(3) Å in $[FeCl_2L^2]$ and $[FeCl_2L^3]$, respectively. In complexes with α -substituted ligands, the axial deformation is quantified by the α angle between the plane defined by the Cl1-Fe-Cl2 atoms and the mean plane of the axial pyridine.^[27] In the present case, the deformation is moderate with $\alpha = 4.4$, 5.1, and 4.4° within the $[FeCl_2L^n]$ series. Correlatively, the *trans* equatorial distortion ρ , previously defined,^[24,27] indicates significant – yet not extreme – deviation towards octahedral geometry with values of $\rho = 113$, 114 and 137°.²



Scheme 1. The $[FeCl_2L^n]$ ($L^n = L^1$ – L^3) complexes discussed herein.

All three structures share the common patterns described above. Noticeable differences, however, originate from changes in the orientation of the functional group of the substituted pyridines, depending on the nature of the ligand. In [FeCl₂L¹], the amide hydrogen H1N atom points towards the equatorial chloride Cl2 ion, with $d(\text{H1N}-\text{Cl2})=2.48 \text{ \AA}$, thus indicating hydrogen bonding (Figure 1). Consequently,

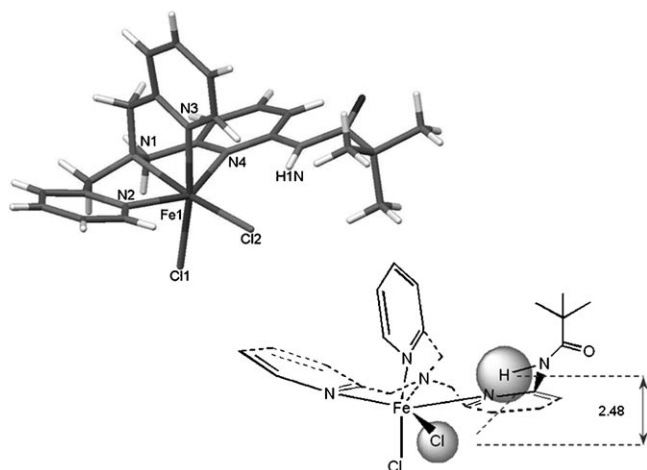


Figure 1. Mercury diagram of [FeCl₂L¹] and schematic drawing featuring the H1N...Cl2 interaction. Selected bond lengths [Å] and angles [°]: N1–Fe1 2.2239(16), N2–Fe1 2.2292(17), N3–Fe1 2.2181(17), N4–Fe1 2.2840(15), Cl1–Fe1 2.4308(6), Cl2–Fe1 2.3679(5); N3–Fe1–N1 77.28(6), N3–Fe1–N2 80.33(6), N1–Fe1–N2 75.53(6), N3–Fe1–N4 82.98(6), N1–Fe1–N4 74.07(6), N2–Fe1–N4 147.83(6), Cl2–Fe1–Cl1 93.56(2).

the carbonyl oxygen atom lies close to the β-H atom of the pyridine onto which the substituent is grafted.

It appears obvious in Figure 2 that the conformation of the pivaloyl ester is more relaxed, that is, less rigid. Because

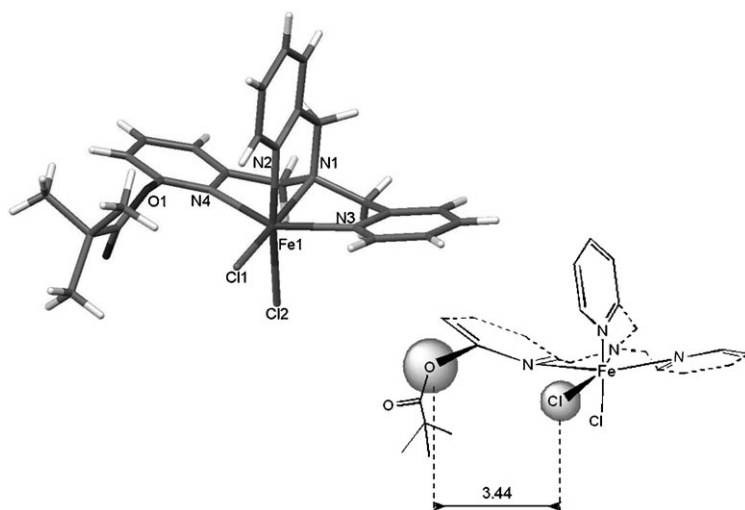


Figure 2. Mercury diagram of [FeCl₂L²] and schematic drawing featuring the O1...Cl1 repulsion. Selected bond lengths [Å] and angles [°]: Fe1–N3 2.219(5), Fe1–N2 2.226(5), Fe1–N4 2.253(6), Fe1–N1 2.258(5), Cl1–Fe1 2.353(2), Cl2–Fe1 2.4497(19); N3–Fe1–N2 82.54(19), N3–Fe1–N4 148.3(2), N2–Fe1–N4 83.08(19), N3–Fe1–N1 75.4(2), N2–Fe1–N1 76.26(19), N4–Fe1–N1 73.8(2), Cl1–Fe1–Cl2 96.26(7).

the NH group has been “replaced” by an oxygen atom, no more hydrogen bonding is seen. As a consequence, a repulsion occurs between O1 and Cl1 with a relatively close contact $d(\text{Cl1}-\text{O1})=3.44 \text{ \AA}$, thus forcing the carbonyl oxygen atom to point downwards by mechanical effect. Figure 3 displays the most rigid structure among the three complexes. The equatorial Cl1 ligand is stabilised by two hydrogen bonds with $d(\text{H6A}-\text{Cl1})=2.45 \text{ \AA}$ and $d(\text{H4A}-\text{Cl1})=2.44 \text{ \AA}$. As in [FeCl₂L¹], the two carbonyl oxygen atoms lie close to the adjacent β-H atoms at the pyridine side.

Reactivity versus dioxygen: The behaviour of the complexes upon addition of dioxygen was monitored by UV/Vis spectroscopic analysis. The three complexes exhibited different reactivity. Bubbling O₂ into a solution of [FeCl₂L¹] over 24 h resulted in a slight increase in absorption between $\lambda=400$ and 300 nm, without the appearance of any well-defined bands, thus indicating a slow and partial transformation.^[28] When [FeCl₂L²] was exposed to O₂, a new species formed within 14 h (by which time the reaction was considered to have gone to completion) with absorption maxima at $\lambda=377 \text{ nm}$ ($\epsilon=1.65 \times 10^3 \text{ mmol}^{-1} \text{ cm}^2$) and 303 nm (shoulder). The treatment of a solution of [FeCl₂L³] resulted in the total absence of spectroscopic modification, even when the medium was kept under oxygen for several days (see the Supporting Information for all the traces). Similar observations can be seen from the ¹H NMR spectroscopic measurements recorded 24 h after the addition of O₂ to the NMR tube. For [FeCl₂L¹], very weak signals, with intensities that just lie above the detection limit, could be seen at $\delta=12$ and 20 ppm, thus suggesting the formation of small amount (less than 5%) of a μ-oxo complex. The case of [FeCl₂L²] is different with complete conversion of the starting material. All the paramagnetically shifted resonances disappeared and a dramatic increase in intensity in the diamagnetic region indicated the release of organic fragments. Finally, the spectrum of [FeCl₂L³] remained completely unaffected over 48 h. Scheme 2 summarises the reactivity of the complexes.

To obtain insight into the structure of the oxygenation product of [FeCl₂L²], the reaction was carried out on a preparative scale. Evaporation of the solvent, followed by washing with diethyl ether afforded a brown compound, which was recrystallised from acetonitrile/diethyl ether. Identification of the reaction product as [((FeL^{2*})₂O)Cl₂] was first realised on the basis of mass-spectrometric analysis. In this complex, L^{2*} originates from the parent L², this latter ligand was

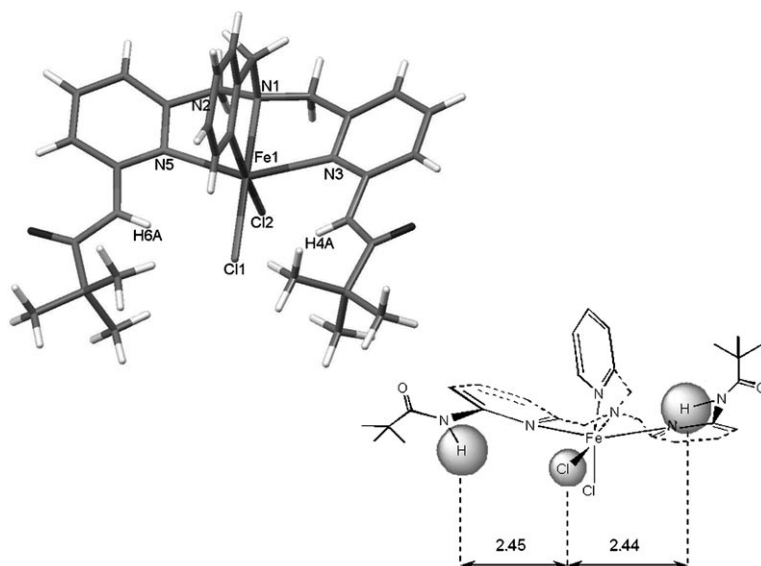


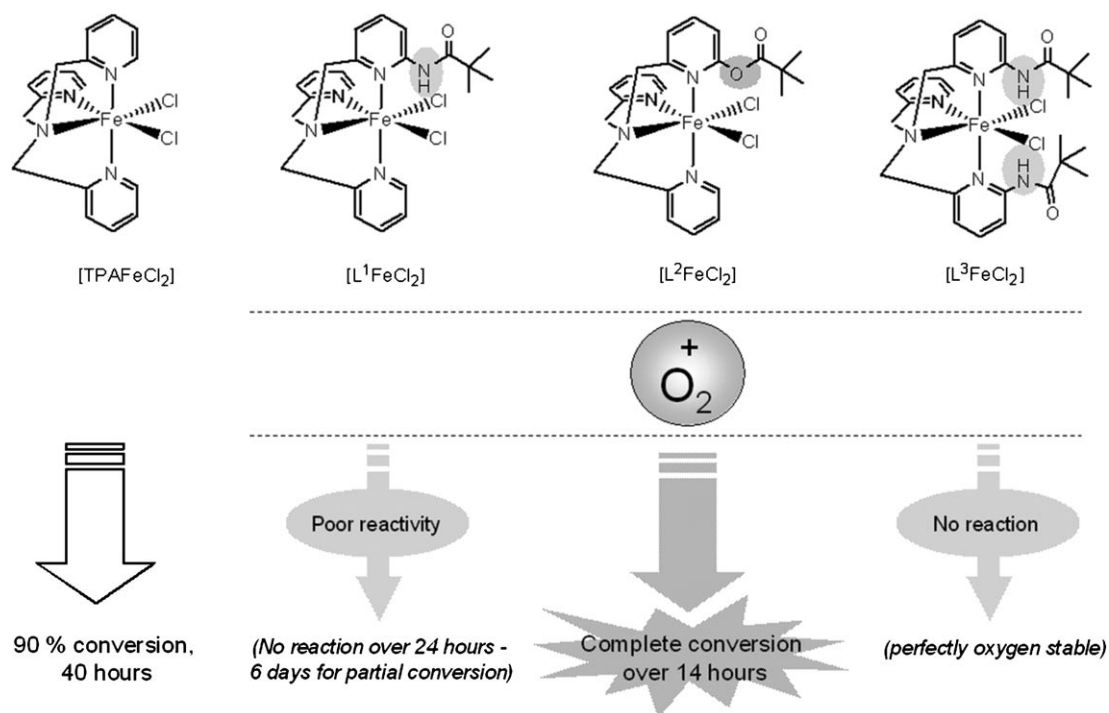
Figure 3. Mercury diagram of $[\text{FeCl}_2\text{L}^3]$ (from the top) and schematic drawing featuring the $\text{H6A}\cdots\text{Cl1}$ and $\text{H4A}\cdots\text{Cl1}$ interactions. Selected bond lengths [\AA] and angles [$^\circ$]: Fe1-N1 2.190(3), Fe1-N2 2.198(3), Fe1-N5 2.303(3), Fe1-N3 2.386(3), Cl1-Fe1 2.3874(10), Cl2-Fe1 2.3672(9); N1-Fe1-N2 78.17(11), N1-Fe1-N5 77.26(11), N2-Fe1-N5 82.57(11), N1-Fe1-N3 74.70(11), N2-Fe1-N3 83.26(10), N5-Fe1-N3 150.61(11), Cl2-Fe1-Cl1 94.16(4).

deacylated by loss of a pivaloyl fragment (see below). In the mass spectrum, two signals were measured at m/z 369.069 (a dicharged species, which corresponds to the dication $[(\text{FeL}^{2*})_2\text{O}]^{++}$) and m/z 773.101 (a monocharged species, which corresponds to $[(\text{FeL}^{2*})_2\text{O}]\text{Cl}^+$). Thus, a μ -oxo difer-

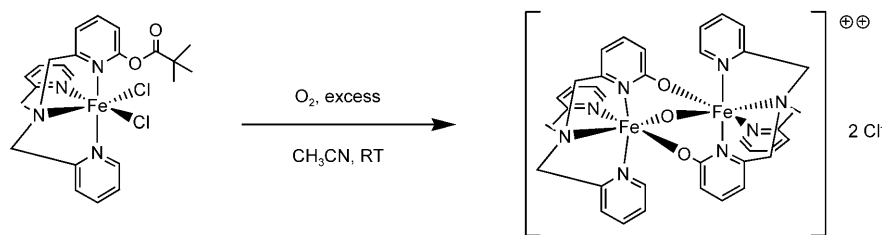
ric compound is formed, in which the ligand has been deacylated upon reaction with O_2 (Scheme 3).

Structure of the $[(\text{FeL}^{2*})_2\text{O}]^{2+}$ ion as the oxygenation product of $[\text{FeCl}_2\text{L}^2]$: Brown-red single crystals could be obtained by slow diffusion of diethyl ether in a freshly oxygenated solution of $[\text{FeCl}_2\text{L}^2]$ in acetonitrile. The crystal structure of this compound confirmed the formulation expected from the mass spectrum as a μ -oxo diferric compound, in which the ligand has been deacylated by loss of a pivaloyl fragment. The ligand L^{2*} thus obtained is the mono(α -hydroxy)-substituted tris(2-pyridylmethyl)amine ligand. In its deprotonated form, this tripod can act as a potentially five-coordinating

ligand, which is the case in the present structure. The oxygen atom from the ligand binds to the neighbouring iron atom, that is, each hydroxy-substituted pyridine acts as a bridging unit. The second bridging group, namely, the oxygen atom, completes the coordination environment of



Scheme 2. Minor modification of the ligand substituent, which leads to spectacular reactivity changes within the corresponding complexes. Left: data of $[\text{FeCl}_2(\text{tpa})]$ obtained from ref. [24].



Scheme 3. Coordinated ligand L² has undergone deacylation upon reaction of [FeCl₂L²] with O₂.

the metal centre. The [(FeL^{2*})₂O] fragment is a dication, and its doubly positive charge is balanced in the studied crystal by the presence of the [FeCl₄]²⁻ dianion. The structure of the dication is displayed in Figure 4.

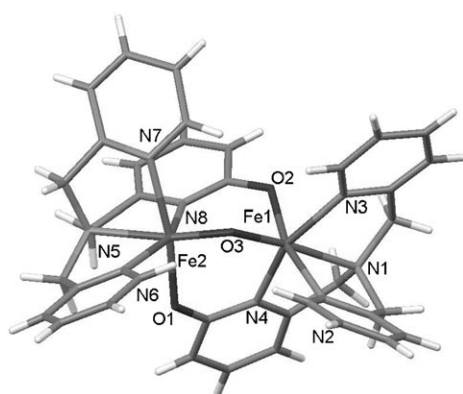


Figure 4. Mercury diagram of the [(FeL^{2*})₂O]²⁺ ion. Selected bond lengths [Å] and angles [°]: Fe1–O3 1.797(7), Fe1–O2 2.027(8), Fe1–N3 2.118(11), Fe1–N4 2.163(12), Fe1–N2 2.181(11), Fe1–N1 2.194(9), Fe2–O3 1.759(9), Fe2–O1 1.953(9), Fe2–N6 2.141(9), Fe2–N7 2.146(10), Fe2–N8 2.185(9), Fe2–N5 2.217(11); O3–Fe1–O2 98.4(3), N3–Fe1–N4 153.9(4), N3–Fe1–N2 80.8(4), N4–Fe1–N2 97.2(4), N3–Fe1–N1 76.5(4), N4–Fe1–N1 77.7(4), N2–Fe1–N1 77.3(4), O3–Fe2–O1 100.9(4), N6–Fe2–N7 95.3(3), N6–Fe2–N8 154.9(4), N7–Fe2–N8 81.2(3), N6–Fe2–N5 76.3(4), N7–Fe2–N5 76.5(4), N8–Fe2–N5 78.8(4), Fe2–O3–Fe1 115.0(5).

The striking feature in this structure is the ∠Fe1–O3–Fe2 angle of 115°, which is sharp in comparison to other structurally characterised μ-oxo complexes.^[24,29,30] This angle is probably due to the assembly effect of the bridging hydroxylate pyridyl unit ($d(\text{Fe1–O2}) = 2.02 \text{ \AA}$ and $d(\text{Fe2–O1}) = 1.95 \text{ \AA}$), which brings the two iron atoms close together, with $d(\text{Fe1–Fe2}) = 3.00 \text{ \AA}$. The metal-to-nitrogen distances lie in the range 2.12–2.21 Å. The presence of the [FeCl₄]²⁻ dianion at the noninteracting distance of

the Fe1–O–Fe2 segment ($d(\text{Cl2–O3}) = 4.03 \text{ \AA}$) does not bring any particular comment.

Single crystals of [(FeL^{2*})₂O]·[FeCl₄] were dissolved in acetonitrile. The UV/Vis spectral data perfectly matched those observed at the end of the oxygenation reaction of [FeCl₂L²] with the characteristic absorptions already mentioned above.

Discussion

Structure of the Fe^{II} complexes in the solid state: All these complexes involve mono- or bis- α -substituted ligands and FeCl₂. As expected, the iron centre lies in a pseudo-octahedral environment with the substituted pyridine in L¹ and L² being located in the lateral position to minimise the steric interactions. Structural parameters indicate moderate – yet noticeable – axial and *trans*-equatorial distortion. As already pointed out, the major differences in these structures arise from the conformation of the α -pyridyl substituents.

The Figure 5 focuses on the main interactions between the bound chloride ions and their environment in complexes [FeCl₂Lⁿ]. The common feature to all these structures is that the axial chloride ion (Cl_{ax}) is stabilised by interaction with two of the vicinal methylene hydrogen atoms H_a and H_b, with Cl_{ax}⋯H_{a,b} distances between 2.77 and 3.01 Å.

Considering the equatorial chloride ion (Cl_{equ}), the situation is more contrasted. Obviously, in the amide-substituted complexes [FeCl₂L¹] and [FeCl₂L³], the equatorial chloride ion interacts with the amide hydrogen atoms and is thus stabilised. The fact that these amido hydrogen atoms point towards the chloride ion induces the peculiar conformation of the pivaloyl amide groups: as salient evidence and when seen from the bottom, [FeCl₂L³] is an almost symmetrical molecule.^[31]

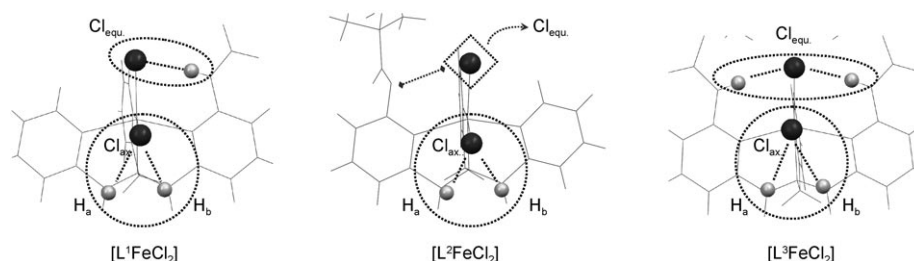


Figure 5. View of the complexes along the Fe–Cl_{ax} axis from the bottom. In all the complexes, the axial chloride ion is stabilised by contact interaction with protons from the methylene groups: the Cl_{ax}⋯H_a and Cl_{ax}⋯H_b distances (dotted circles) lie in the range 3.01–2.77 Å. In [FeCl₂L¹], stabilization of the equatorial chloride ion by hydrogen bonding with one amide proton is observed (see Figure 1). The stabilization is the greatest in [FeCl₂L³], whereas the equatorial chloride ion interacts with two amide protons (see Figure 3). In [FeCl₂L²], not only does stabilization not occur, but a repulsion between the ester oxygen atom and the equatorial chloride ion (dotted square) leads to modification in the conformation (see Figure 2).

The situation looks different in $[\text{FeCl}_2\text{L}^2]$. There is no longer any amido group, instead a repulsive interaction is seen between the oxygen atom of the ester substituent and Cl_{equ} , thus providing complete lability for this ligand. As a consequence, the pivaloyl ester group looks more relaxed, with the ester carbonyl group pointing downwards.

To summarise, in this series of three similar complexes, all the axially bound chloride ions are blocked by hydrogen bonding. This feature is common in all the previously reported structures of pseudo-octahedral dichloroiron(II) complexes, with methylene $\text{C-H}\cdots\text{Cl}_{\text{ax}}$ contacts never greater than 3.01 \AA .^[24,26,27] In the present case, however, major differences are seen within the three complexes. In the equatorial region, the picture is that of an equatorial chloride ion “frozen” by hydrogen bonding with the neighbouring amide groups in $[\text{FeCl}_2\text{L}^3]$; the situation is inverted in $[\text{FeCl}_2\text{L}^2]$ as the equatorial chloride ion is free of any interaction; finally, $[\text{FeCl}_2\text{L}^1]$ offers the intermediate picture of a “semistabilised” equatorial chloride ion.

Structure of the Fe^{II} complexes in solution: The spectroscopic features of distorted pseudo-octahedral dichloroiron(II) complexes in solution are now well established.^[24,26,27] In the present case, all the spectroscopic data converge towards retention of the solid-state structure when the compounds are dissolved, that is, a pronounced MLCT transition in the UV/Vis spectra and characteristic ^1H NMR spectra with relatively narrow β, β' signals.

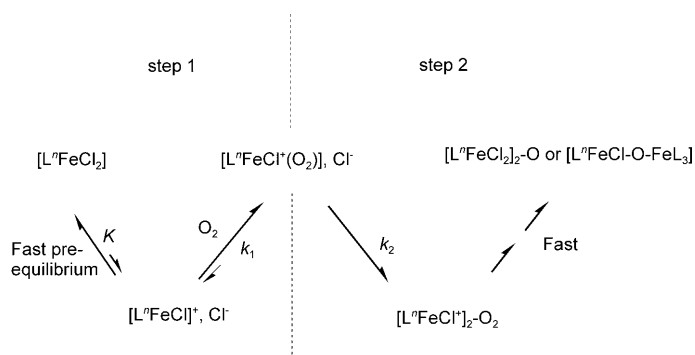
The cyclic voltammetry of the complexes brings additional support to the retention of the geometry in solution. In general, pseudo-octahedral complexes $[\text{FeCl}_2\text{L}]$ (L = monosubstituted tris(pyridylmethyl)amine (TPA) ligand) exhibit reversible waves at potentials close to $E = 200 \text{ mV}$ versus SCE.^[27,32] With a value of $E_{1/2} = 265 \text{ mV}$, complex $[\text{FeCl}_2\text{L}^2]$ lies in the range of stable and moderately distorted complexes with an electron-deficient tripod. In contrast, the value of $E_{1/2} = 371 \text{ mV}$ obtained for $[\text{FeCl}_2\text{L}^1]$ is much higher than expected for an $[\text{FeCl}_2\text{L}^n]$ complex with a monosubstituted tripod. This value lies close to the value obtained from a cationic complex in which the chloride ion has been exchanged with an acetonitrile moiety under the measurement conditions. We previously reported that this exchange could be monitored for methyl-substituted tripods by the addition of KPF_6 to a solution of the complex in CD_3CN for use in ^1H NMR spectroscopic analysis.^[27] In the present case, however, the addition of KPF_6 to a solution of $[\text{FeCl}_2\text{L}^1]$ for ^1H NMR spectroscopic analysis gave no evidence towards important structural modification, with only broadening of the resonances and minor shifts being observed. Thus, the chloride ion in $[\text{FeCl}_2\text{L}^1]$ is—as expected—firmly bound to the metal centre, and the high potential simply reflects hydrogen bonding of the amide group to the chloride ion. As a net effect, the donating ability of the chloride ion is decreased, and the metal centre becomes more electron deficient, that is, more difficult to oxidise. The same situation prevails with $[\text{FeCl}_2\text{L}^3]$, a decrease in the stability of the oxi-

dised species leads to the wave becoming completely irreversible.

Additionally, the conductivity measurements confirm that $[\text{FeCl}_2\text{L}^2]$ behaves in the same way as other TPA-based complexes, that is, the bound chloride ligands can be displaced under polar conditions.^[24,26,27] In contrast, the value found for $[\text{FeCl}_2\text{L}^3]$, by far the lowest value ever measured for this type of compound ($\Lambda = 6 \text{ Scm}^2\text{mol}^{-1}$), strongly suggests that the equatorial chloride ion remains locked in place in solution in this complex. An intermediate case is that of $[\text{FeCl}_2\text{L}^1]$, in which the chloride ion, although not locked, is significantly stabilised.

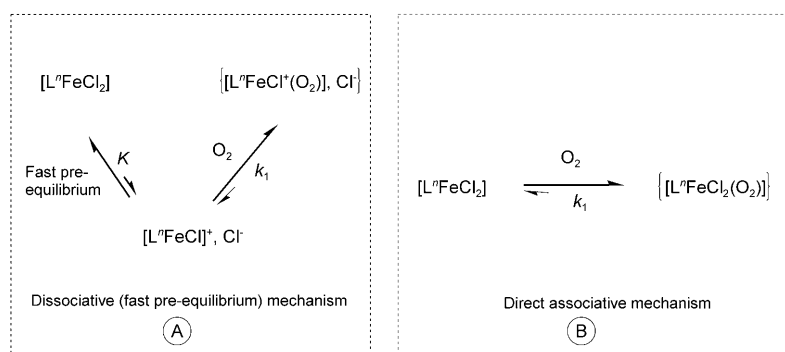
Thus, we have excellent evidence that the structures of $[\text{FeCl}_2\text{L}^n]$ complexes in solution are identical to those observed in the solid state.

Reactivity versus O_2 : general considerations: The formation of μ -oxo diferric derivatives from Fe^{II} complexes and dioxygen has been established for more than three decades in the chemistry of porphyrin compounds.^[33] In general, the situation is far from being as clear with mononuclear non-porphyrinic Fe^{II} complexes. We recently reported that $[\text{FeCl}_2\text{L}^n]$ complexes, in which $\text{L} = \text{TPA}$ or α -halogenated derivatives of this tripod, react cleanly with O_2 to yield diferric complexes with a μ -oxo structure.^[24] Two kinetic steps were evidenced by kinetic analysis of the changes observed upon monitoring the reaction by UV/Vis spectroscopic analysis and interpreted as indicated in Scheme 4.



Scheme 4. The proposed two kinetic steps that lead to the formation of μ -oxo dinuclear complexes by reaction of O_2 with pseudo-octahedral precursors $[\text{FeCl}_2\text{L}^n]$, as previously deduced by monitoring with UV/Vis spectroscopic analysis. In this scheme, adapted from ref. [24], the L^n ligands bear no functional groups. All the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ redox potentials are positive. On the other hand, the O_2/O_2^- reduction occurs at a negative potential; thus, the outer-sphere reduction of O_2 by the metal centre can be ruled out.

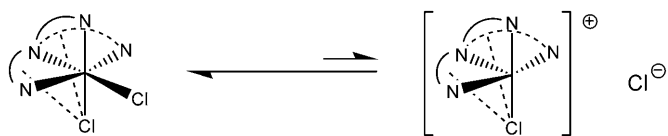
Step 1 of Scheme 4 involves a fast pre-equilibrium that corresponds to the rapid dissociation of a chloride ion from the metal centre, thus yielding $[\text{FeClL}^n]^+\text{Cl}^-$ as the species onto which the dioxygen would coordinate. Thus, this step can be described as a “dissociative” step (depicted as pathway A in Scheme 5). An alternative possibility exists how-



Scheme 5. Reaction of O₂ with the metal centre involves A) dissociative pre-equilibrium or B) direct coordination to the iron centre (focus on the first kinetic step (Step 1 in Scheme 4).

ever in which O₂ would directly coordinate to the metal centre in [FeCl₂Lⁿ] (“direct associative mechanism”, pathway B in Scheme 5).

Originally, we decided to investigate the complexes with amido-substituted tripods to try to stabilise any oxygen adduct of the metal (the judiciousness of this approach will be discussed below). In fact, these complexes turned out to be very poorly reactive (in the case of [FeCl₂L¹]) or even insensitive to dioxygen (with [FeCl₂L³]), whereas this was not the case for [FeCl₂L²], which reacts at a comparable rate to those observed for similar complexes with electron-deficient tripods.^[24] Thus, in light of the structural differences between [FeCl₂L¹] and [FeCl₂L³] on one side and [FeCl₂L²] on the other side and keeping in mind the question of the lability of the bound chloride anions, it became obvious that removal—or at least some flexibility—of one of these ancillary ligands had to take place to allow the reaction to proceed. We thus demonstrated that the mechanism for the oxygenation of [FeCl₂Lⁿ] complexes involves a dissociative pre-equilibrium (pathway A in Scheme 5). Representation at the molecular level of this dissociation is displayed in Scheme 6.



Scheme 6. Molecular representation of the fast-pre-equilibrium as deduced from the present study.

Reactivity of [FeCl₂L²] versus O₂: reaction product and implications: Monitoring of the oxygenation reaction by ¹H NMR spectroscopic analysis indicated complete conversion of the complex over 14 h, with no trace of the starting material seen in the spectrum. Mass-spectrometric and NMR spectroscopic data indicate the formation of [FeL^{2*}]₂O as the main product of the reaction. On a preparative scale, the solid obtained displays the expected μ-oxo core, but the ligand has undergone deacylation. In the

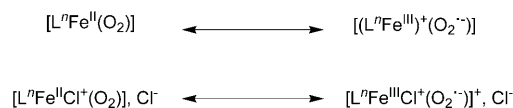
solid state, [FeL^{2*}]₂O is a perfectly stable compound; however, in solution, this complex might partially decompose with time, especially during the crystallization process. This process might explain the presence of [FeCl₄]²⁻ as the counteranion in the crystals.

Deacetylation of L² is not a trivial observation. The cleavage of esters—especially pivaloyl esters—generally occurs in basic media. The present observation strongly suggests the occurrence of a species with a

basic character in the course of the oxygenation of the medium.

If one considers that only dioxygen and Fe^{II} species are present in the reaction medium, the presence of a reduced form of dioxygen is more than likely. Considering the reduction potential of O₂ measured in organic medium at E° = −0.73 V (versus SCE) in dimethyl sulfoxide (DMSO),^[34,35] there is no chance for an outer-sphere reduction of O₂ in our system. Thus, the formation of a reduced form of dioxygen can only proceed after initial coordination to the metal centre.

The description of a “superoxo” [M⁽ⁿ⁺¹⁾⁺(O₂⁻)] species as the mesomeric form of the “oxy” form [Mⁿ⁺(O₂)] is well known in the biological chemistry of iron^[36] (Scheme 7). We,



Scheme 7. The “oxy–Fe^{II}” forms can also be described as “superoxo–Fe^{III}” species.

thus, believe that in the reaction that leads to the formation of [FeL^{2*}]₂O from [FeCl₂L²] and O₂, the first step following the fast pre-equilibrium of dissociation of the equatorial chloride ion is coordination of O₂ to the metal centre. The oxygen adduct thus formed undergoes inner-sphere reduction, thereby leading to a ferric superoxide adduct. Does it mean that the coordinated form {Fe(O₂)} ↔ {Fe–O–O} would be responsible for the cleavage of the ester, which is ideally positioned in the vicinity of the coordinated dioxygen? Or that the free superoxide O₂⁻ ion (a basic and moderately nucleophilic species in organic media) would directly do it? Alternatively, if the superoxide anion is released in the medium, it might be converted into its ultimate product of evolution, which is the OH⁻ ion, and metal-coordinated hydroxides are certainly capable of bringing about hydrolysis of adjacent pivaloyl esters. At present, the answers to these questions remain uncertain.

Concluding Remarks

Iron(II) compounds with tripodal ligands in the tris(2-pyridylmethyl)amine series react cleanly with O₂ provided that access to the metal centre is free. The question of access of dioxygen to five-coordinate metal centres with trigonal-bipyramidal geometry has recently been addressed.^[32] We have now demonstrated herein that for metal centres with pseudo-octahedral symmetry, such a reaction requires dissociation of the ligand as the initial step. Additionally, coordination of dioxygen to the iron centre—instead of any putative outer-sphere reduction mechanism—is strongly supported by the fact that all redox couples of Fe^{II}/Fe^{III} in such compounds are positive.^[24,27,32]

Isolation of a coordinated form of dioxygen at an iron centre in non-porphyrinic chemistry remains a very ambitious challenge. Keeping in mind the stabilization—more than three decades ago—of an “oxy” form of an Fe^{II} centre by using the picket-fence porphyrin,^[37–39] the use of α -amido-substituted tripodal ligands in the TPA family a priori seemed to be an interesting approach and motivated the present study. However, the ancillary chloride ligands of the metal centre in the precursor turned out to be so well stabilised that the oxygenation reaction was hampered. With respect to this point, the use of more weakly coordinating ligands in future studies might be a good approach to enhance the reactivity.

In addition, we realised that another serious potential problem might arise: functional groups supposed to stabilise the coordinated form of O₂ might be not innocent with respect to the presence of any superoxo or peroxidic form. The hydrolysis of an ester, reported herein, but also the *O*-demethylation or oxidative dehydrogenation previously reported^[32,40] are good examples of reactivity observed close to the coordination site of O₂.

Future studies need to solve this paradox by fine-tuning the metal environment with specially designed ligands. Such an approach is currently under investigation in our laboratory.

Experimental Section

General considerations: Chemicals were purchased from Aldrich Chemicals and used as received. All the solvents used during the metalation reactions and workup were distilled and dried according to ref. [41].

Bis(2-aminomethylpyridine) (DPA) was prepared following the procedure described in refs [42, 43]. Ligands L¹ and L² were prepared according to reported procedures from ref. [25]. Analytical anhydrous FeCl₂ was obtained as a white powder by treating iron powder (ACS grade) with hydrochloric acid in the presence of methanol in an argon atmosphere. Preparation and handling of all the compounds were performed in an argon atmosphere by using the Schlenk technique following standard procedures. The purity of the dry dioxygen was 99.99999% (grade 5). Elemental analyses were carried out by the Service d'Analyses de la Fédération de Recherche de Chimie (Université de Strasbourg, France). Mass-spectrometric experiments were carried out by the Service Commun de Spectrométrie de Masse de l'Institut de Chimie de Strasbourg. The struc-

tural determinations were carried out by the Service de Diffraction des Rayons X, Institut de Chimie (Université de Strasbourg).

Physical methods: The ¹H NMR data were recorded in CD₃CN for the complexes and CDCl₃ for the ligands at ambient temperature on a Bruker AC 300 spectrometer at 300.1300 MHz with the residual signal of CD₂HCN (CHCl₃) as a reference for calibration. The UV/Vis spectra were recorded on a Varian Cary 05 E UV/Vis NIR spectrophotometer equipped with an Oxford instrument DN1704 cryostat with optically transparent Schlenk cells. The cyclic voltammetry measurements were obtained from a PAR 173A potentiostat in a 0.1 M solution of TBAPF₆ (supporting electrolyte) in acetonitrile using platinum electrodes and saturated calomel electrode as the reference. For each measurement, the potential was checked by the addition of a small amount of ferrocene (Fc/Fc⁺ = 0.380 V versus SCE) in the cell. The conductivity measurements were carried out under argon at 25 °C with a CDM 210 Radiometer Copenhagen Conductivity Meter using a Tacussel CDC745–9 electrode.

Synthesis of 6-methylpyridin-2-yl pivalate: Pivaloyl chloride (1.86 mL, 12 mmol) was added to a solution of 2-hydroxy-6-methylpyridine (1.20 g, 11 mmol) in acetonitrile (100 mL) and stirred at room temperature for 2 min. Triethylamine (2.3 mL) was added and the reaction mixture was stirred at room temperature for 24 h. The mixture was evaporated to dryness, and the resulting slurry was extracted with dichloromethane (100 mL). The organic phase was washed with water (3 × 100 mL), dried over magnesium sulphate, and the solvent was removed by rotary evaporation. The mixture was purified by chromatography on silica gel with dichloromethane as the eluent, thus yielding a yellowish oil (1.9 g, 75%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.64 (t, 1H), 7.04 (d, 1H), 6.80 (d, 1H), 2.53 (s, 3H), 1.37 ppm (s, 9H).

6-(Bromomethyl)pyridin-2-yl pivalate: 6-Methylpyridin-2-yl pivalate (1 g, 5.2 mmol) was dissolved in carbon tetrachloride (300 mL) and azobisisobutyronitrile (AIBN; 45 mg, approximately 5%) was added. The reaction mixture was heated to reflux and *N*-bromosuccinimide (NBS; 925 mg, 5.2 mmol) was added in ten fractions every 15 min over 150 min. The reaction mixture was maintained under reflux during 7 h and then concentrated to one third of its initial volume and filtered. The solution was collected and evaporated to dryness to yield a yellow solid, and this solid was dissolved in dichloromethane. The desired compound was obtained after chromatography on silica gel as the stationary phase with dichloromethane as eluent, thus yielding a white solid (730 mg, 52%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.77 (t, 1H), 7.37 (d, 1H), 6.95 (d, 1H), 4.51 (s, 2H), 1.38 ppm (s, 9H).

Mono(α -pivalesteropyridylmethyl)bis(2-pyridylmethyl)amine (L²): Bis(2-aminomethylpyridine) (0.424 g, 2.13 mmol) was dissolved in acetonitrile (100 mL) and added to a solution of 6-(bromomethyl)pyridin-2-yl pivalate (0.580 g, 2.13 mmol) in acetonitrile (200 mL). Sodium carbonate (0.500 g) was added to this mixture, which was heated to reflux for 24 h. The medium was filtered and the solution was collected and evaporated to dryness. The slurry was extracted with dichloromethane and washed with water. The solution was dried over magnesium sulphate and the solvent removed by rotary evaporation. Extraction of the residue by pentane afforded L² as an oily solid (0.420 mg, 51%) upon concentration. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 8.51 (m, 2H), 7.71 (m, 1H), 7.61 (m, 2H), 7.55 (m, 2H), 7.50 (m, 1H), 6.85 (d, 1H), 3.87 (s, 4H), 3.84 (s, 2H), 1.36 ppm (s, 9H); MS (ES, positive mode): m/z : 391.2143 [L² + H]⁺, 413.1956 [L² + Na]⁺; elemental analysis (%) calcd for C₂₃H₂₆N₄O₂: C 70.7, H 6.6, N 14.3; found: C 70.2, H 7.0, N 14.2.

Preparation of the [FeCl₂Lⁿ] (Lⁿ = L¹–L³) complexes: Details are given for [FeCl₂L¹], but the following procedure applies to all the complexes: Free L¹ (150 mg, 0.38 mmol) was dissolved in a Schlenk tube containing dry degassed THF (20 mL). Anhydrous FeCl₂ (40 mg, 0.31 mmol) was dissolved in a second Schlenk tube containing dry, degassed THF (10 mL). The solution of FeCl₂ in THF was transferred under argon in the Schlenk tube containing the solution, which was stirred overnight. The reaction mixture was evaporated to dryness, the compound was extracted with dry degassed CH₃CN, filtered under an inert atmosphere, and concentrated. The addition of diethyl ether afforded a yellow solid, which was washed thoroughly with this solvent, prior to drying under

vacuum. [FeCl₂L¹] was obtained (125 mg, 78%) and showed good analytical and spectroscopic data, which are detailed in the text and given the Supporting Information.

Single crystals: These were obtained by slow diffusion of diethyl ether in a sealed tube containing a solution of [FeCl₂Lⁿ] in CH₃CN.

Oxygenation of [FeCl₂L²]: [FeCl₂L²] (approximately 10 mg) was introduced into a small Schlenk tube containing dry degassed CH₃CN (5 mL). Dry O₂ was bubbled into the medium for 5 s. The medium was stirred for 3 days at room temperature. The solvent was removed under vacuum, the residue was washed with diethyl ether, and the solid was recrystallised from acetonitrile/diethyl ether. MS (ES, positive mode): *m/z*: 369.069 [(FeL₂^{2*})₂O]²⁺; 773.101 [(FeL₂^{2*})₂O]Cl⁺.

Single crystals of [(FeL^{2*})₂O][FeCl₄] were obtained several days after layering diethyl ether and a solution of [FeCl₂L²] in CH₃CN, which had been previously oxygenated.

X-ray analysis: Single crystals of [(FeCl₂L¹)₂], [FeCl₂L²], [(FeCl₂L³)₂], and [(FeL^{2*})₂O][FeCl₄] were mounted on a Nonius Kappa-CCD area detector diffractometer (MoKα λ = 0.71073 Å). Quantitative data were obtained at 173 K for all complexes. The complete conditions of the data collection (Denzo software) and structural refinements are given in the Supporting Information. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle) each at 20-s exposure. The structures were solved using direct methods (SIR97) and refined against *F*² using the SHELXL97 software.^[44,45] The absorption was not corrected. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined by using a riding model in SHELXL97.

Crystal data:

[FeCl₂L¹]: Yellow crystals, monoclinic, space group *P*2₁/*c*, *a* = 9.9770(2), *b* = 13.2957(3), *c* = 18.2167(4) Å, β = 101.5850(10)°, *V* = 2367.24(9) Å³, ρ_{calcd} = 1.449 g cm⁻³, *Z* = 4; 5368 unique, observed reflections with *I* > 2σ(*I*) and 293 parameters, the discrepancy indices are *R* = 0.0373 and *R*_w = 0.0873.

[FeCl₂L²]: Yellow crystals, monoclinic, space group *P*2₁/*c*, *a* = 9.5745(5), *b* = 14.7807(13), *c* = 17.4049(14) Å, β = 107.452(4)°, *V* = 2349.7(3) Å³, ρ_{calcd} = 1.462 g cm⁻³, *Z* = 4; 5368 unique, observed reflections with *I* > 2σ(*I*) and 292 parameters, the discrepancy indices are *R* = 0.0954 and *R*_w = 0.2592.

[FeCl₂L³]: Yellow crystals, orthorhombic, space group *P*bca2₁, *a* = 18.7567(5), *b* = 10.1554(2), *c* = 15.9196(3) Å, *V* = 3032.39(12) Å³, ρ_{calcd} = 1.348 g cm⁻³, *Z* = 4; 3608 unique, observed reflections with *I* > 2σ(*I*) and 358 parameters, the discrepancy indices are *R* = 0.0367 and *R*_w = 0.0730.

[(FeL^{2*})₂O][FeCl₄]: Red crystals, orthorhombic, space group *P*na2₁, *a* = 16.5089(6), *b* = 21.9863(10), *c* = 10.6251(5) Å, *V* = 3856.6(3) Å³, ρ_{calcd} = 1.612 g cm⁻³, *Z* = 4; 8342 unique, observed reflections with *I* > 2σ(*I*) and 487 parameters, the discrepancy indices are *R* = 0.1095 and *R*_w = 0.2025.

CCDC-729004, CCDC-729005, CCDC-729006, and CCDC-729007 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.^[46]

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