Modulation of iron reduction potential by deprotonation at a remote site

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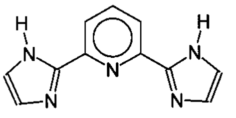
Remote site deprotonation of a coordinated imidazole ligand switches the reduction potential of coordinated iron over a narrow pH range from +0.920 to −0.460 V.

A fundamental concept of coordination chemistry is that ligand type may favour one oxidation state of a metal over another. Thus π-acceptor ligands such as CO and PF_3 stabilise low oxidation states, whereas high oxidation states are favored by π-donor ligands such as fluoride or anionic oxygen donors. Implicit in this concept is the idea that chemical modification of the ligand may change its ligating properties, and thereby modify the reduction potential of the metal to which it is coordinated. Protonation or deprotonation of the ligand at a site remote from the metal–ligand bond is a simple, reversible method of modification, and in this communication we show how the deprotonation of a coordinated imidazole ligand can influence dramatically the redox potential of iron bound to the ligand as well as influencing the spin state.

Ligand **1** in acetonitrile forms the complex $[Fe(\mathbf{1})_2]^{2+}$ expected by analogy with the related benzimidazole ligand **2** whose complexes with iron(II) have been studied previously.[1–3] The dark red complex† showed a strong MLCT band in methanol at 520 nm (ε = 5900 l mol^{-1} cm^{-1}). Upon treatment with Bu^{t}OK in methanol under nitrogen the solution became dark purple and showed the red shift and increase in intensity previously observed[1,2] for $[Fe(\mathbf{2})_2]^{2+}$ upon deprotonation; at the end points corresponding to $[Fe(\mathbf{1}-H)_2]$ the MLCT was at 536 nm (ε = 6220 l mol^{-1} cm^{-1}) and for $[Fe(\mathbf{1}-2H)_2]^{2-}$ 538 nm (ε = 7620 l mol^{-1} cm^{-1}). Admission of air to the basic solution or addition of base in presence of oxygen gave a sky blue solution showing two weaker bands at 588 nm (ε = 870 l mol^{-1} cm^{-1}) and 730 nm (ε = 790 l mol^{-1} cm^{-1}) typical of low spin iron(III) coordinated by a diimine,[4] and no Fe(II) MLCT. The blue complex could be isolated as a sodium salt‡ either from the iron(II) complex after treatment with base or by reaction of $FeCl_3$ with **1** in presence of base. Elemental analysis and ESMS confirmed the presence of iron(III), and X-ray crystallography§ showed the expected pseudo-octahedral structure of the deprotonated complex $[Fe(\mathbf{1}-2H)_2]^-$ (Fig. 1) and showed only slightly shorter Fe–N bond lengths [Fe–N$_{py}$ 1.920(6) Å, Fe–N$_{imid}$ 1.935(7) Å] than those observed for $[Fe(\mathbf{2})_2]^{2+}$.[2]



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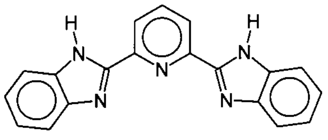

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Since iron(II) coordinated to unsaturated nitrogen heterocyclic ligands is generally very hard to oxidise, the observation of spontaneous oxidation by air was surprising, especially since $[Fe(\mathbf{2})_2]^{2+}$ is not oxidised in base. Cyclic voltammetry studies in acetonitrile (glassy carbon electrode, 0.1 M NEt_4ClO_4 electrolyte , scan rate 200 mV s^{-1}) showed a reversible Fe^{III}–Fe^{II} wave at +0.920 mV *vs.* NHE for $[Fe(\mathbf{1})_2]^{2+}$, typical for an iron(II)–diimine complex. Upon deprotonation however, the Fe^{III}–Fe^{II} wave shifted to −0.460 mV for $[Fe(\mathbf{1}-2H)_2]^-$ confirming the dramatic shift in redox potential, and explaining the observed sensitivity to oxidation by air. Reaction of iron(III) with two equivalents of **1** gave a yellow solution which darkened on standing as a result of reduction to $[Fe(\mathbf{1})_2]^{2+}$. No complex $[Fe(\mathbf{1})_2]^{3+}$ could be isolated, but a complex analysing as $[Fe(\mathbf{1})Cl_3]$ analogous to that formed by **2**[1] could be isolated.

Magnetic moments measured in methanol solution by the Evans method showed $[Fe(\mathbf{1})_2]^{2+}$ to have spin crossover behaviour analogous to $[Fe(\mathbf{2})_2]^{2+}$ [1,3] with a room temperature value of μ_{eff} = 3.6 μ_B, falling close to zero at 200 K. The change in UV–VIS spectrum of $[Fe(\mathbf{1})_2]^{2+}$ upon deprotonation at room temperature is consistent with the transition to a fully low spin state. $[Fe(\mathbf{1}-2H)_2]^-$ in methanol gave μ_{eff} = 1.92 μ_B consistent with low spin Fe(III), while a solution of stoichiometric composition $[Fe(\mathbf{1})_2]^{3+}$ gave μ_{eff} = 6.3 μ_B, indicating high spin Fe(III). It is thus possible to switch the spin states by pH changes.

Deprotonation of coordinated imidazole at the pyrrolic hydrogen has been reported on many occasions[5] and often results in the imidazolate acting as a bridging ligand with formation of binuclear species.[6] For **1** − 2H this is impossible as a result of steric hindrance from the pyridyl moiety, but the basic nature of the deprotonated nitrogens is shown by the strong hydrogen bonds formed between N3 and N5 and the water molecules bound to sodium in $[Fe(\mathbf{1}-2H)_2]$[Na-

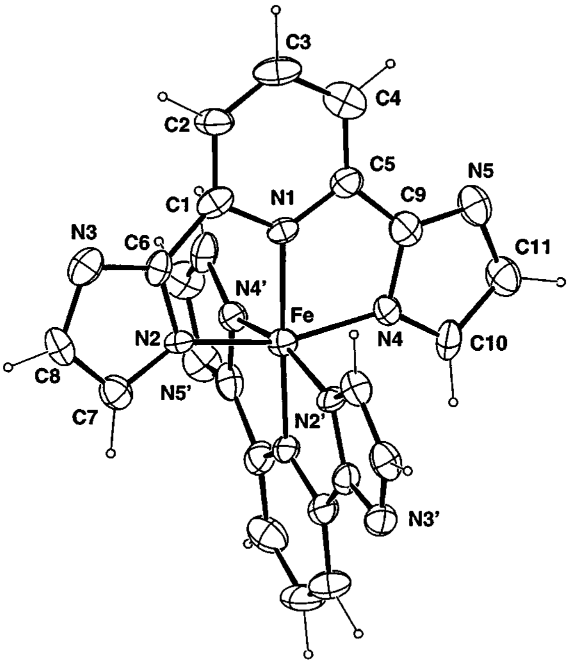

Fig. 1 Structure of the $[Fe(\mathbf{1}-2H)_2]^-$ ion. A crystallographic twofold axis passes through the iron atom perpendicular to the pyridine–pyridine axis. Ellipsoids are shown at the 40% probability level.

$(H_2O)_4]_{0.5}[Na(MeCN)_4(THF)_2]_{0.5}$ [distances N···O 2.78(1) and 2.81(1) Å]. Potentiometric titration of a solution of [Fe(**1**)$_2$]$^{2+}$ [DMF–H_2O (4 : 1), I = 0.1 M KNO_3, in presence of air] with KOH showed the loss of four protons with pK values (estimated by a least squares fitting of the titration curve) of 8.19(5), 8.67(7), 9.86(10) and 9.92(9). These values should be interpreted with some caution since oxidation probably occurs before dissociation of all the protons. After removal of two protons the spectrum of the mixture is very similar to a superposition of the spectra of [Fe(**1**)$_2$]$^{2+}$ and [Fe(**1** − 2H)$_2$]$^-$.The pK_as are close to those previously reported for imidazole bound to Fe(II).[5]

We have found no reference to the effect of imidazole deprotonation upon redox potential in the literature. Although we would intuitively expect that the progressive introduction of negative charge onto the ligand would favour the higher oxidation state, the magnitude of the effect, some 1380 mV, is much greater than we anticipated. Haga *et al.* have studied the effect of deprotonation of coordinated benzimidazole ligands in ruthenium and osmium complexes[7] and has shown a shift of the reduction potential to more negative values upon deprotonation of *ca.* 300 mV per proton. This is broadly consistent with the effect observed here for the removal of four protons. It is of course well known that deprotonated pyrrolic ligands such as porphyrins and phthalocyanines allow stabilisation of iron(III) in a low spin state.

In conclusion, we have shown that it is possible to switch the redox potential of the iron(III)/iron(II) couple from strongly oxidising to strongly reducing over a limited range of pH (between 8 and 10). There is consequently a strong coupling between electron and proton transfer: proton loss from the ligand is followed by electron loss from iron(II), and proton capture by the ligand makes the iron(III) oxidising. We believe that this may be significant for biological oxygen chemistry, where reduction of dioxygen is accompanied by proton transfer to the dioxygen moiety, and oxidation of water requires concomitant deprotonation. It is to be noted that in many oxygen-reducing enzymes, iron is coordinated by imidazole ligands from histidine residues,[8] while in photosystem II the manganese ions are equally thought to have imidazole in the coordination sphere.[9] In such systems deprotonation of the imidazole might allow the attainment of a high oxidation state for manganese; proton transfer from coordinated water to the imidazole would then raise the oxidation potential of the metal to a degree where oxidation of the coordinated oxygen would be possible. Experiments to test this hypothesis are in progress. Finally, we may note that the protonation–deprotonation equilibrium also switches the spin state of the iron, and the affinity of the ligand for the metal, notably in the Fe(III) state.

Notes and references

† A solution of **1**[10] (58 mg, 275 μmol) in a minimum of MeCN was added to a solution of $Fe(ClO_4)_2\cdot 6H_2O$ (50 mg, 138 μmol) in a minimum of MeCN. The red solution was evaporated to dryness, the solid dissolved in 2 ml of MeCN and diethyl ether was slowly diffused into the solution. Orange–red crystals, 85 mg (122 μmol, yield 88%) of [Fe(**1**)$_2$]$(ClO_4)_2\cdot H_2O$. ESMS: *m/z* 576.8 {[Fe(**1**)$_2$]$(ClO_4)^+$} (5%), 259.2 {[Fe(**1**)$_2$](MeCN)$^{2+}$} (70%), 238.7 {Fe(**1**)$_2$]$^{2+}$} (100%). Calc. for $C_{22}H_{20}N_{10}Cl_2O_9Fe$: C, 38.01; N, 20.15; H, 2.90. Found: C, 38.35; N, 20.52; H, 3.08%.

‡ To a solution of [Fe(**1**)$_2$]$(ClO_4)_2\cdot H_2O$ (43 mg, 63 μmol) in 3 ml MeOH were added, slowly and under vigorous stirring, 2.42 ml of a freshly prepared NaOH solution (0.102 M in MeOH, 252 μmol), then the solution was filtered over Celite. The blue solution was evaporated to dryness, the solid dissolved in 6 ml of MeCN and some drops of MeOH and THF slowly diffused into the solution. Blue crystals were separated and dried to give 29 mg (48 μmol, yield 78%) of Na[Fe(**1** − 2H)$_2$]$\cdot(H_2O)_2\cdot$THF ESMS: *m/z* 474.1 {[Fe(**1** − 2H)$_2$]$^{-1}$} (100%). Calc. for $C_{26}H_{26}N_{10}O_3FeNa$: C, 51.58; N, 23.14; H, 4.33. Found: C, 51.74; N, 23.53; H = 4.64%.

§ *Crystal data*: [Fe(**1** − 2H)$_2$][Na$(H_2O)_4]_{0.5}[Na(MeCN)_4(THF)_2]_{0.5}$, M = 343.7, tetragonal, space group $P4\bar{2}_1/c_1$, a = 13.3185(5), c = 19.455(1) Å, V = 3451.0(3) Å^3, T = 200 K, Z = 4, μ(Cu-Kα) = 4.039 mm^{-1}, 1661 observed reflections [$|F_o| > 4\sigma_0(F_o)$], R = 0.051, R_w = 0.046. CCDC 182/1079. See http://rsc.org/suppdata/cc/1998/2681/for crystallographic files in .cif format.

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