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Reversible (De)protonation-Induced Valence Inversion in Mixed-Valent Diiron(II,III) Complexes

Eric Gouré,[†] Grégory Thiabaud,[†] Michaël Carboni,[†] Nathalie Gon,[†] Patrick Dubourdeaux,[†] Ricardo Garcia-Serres,[†] Martin Clémancey,[†] Jean-Louis Oddou,[†] Adeline Y. Robin,[‡] Lilian Jacquamet,[‡,§] Lionel Dubois,[⊥] Geneviève Blondin,[†] and Jean-Marc Latour*[,†]

[†]Laboratoire de Chimie et Biologie des Métaux-pmb UMR 5249, UJF-Grenoble 1/CEA-DSV-iRTSV/CNRS, Grenoble F-38054, France

[‡]Institut de Biologie Structurale J.-P. Ebel, Commissariat à l'Énergie Atomique/Centre National de la Recherche Scientifique/Université Joseph Fourier, Groupe Synchrotron, Grenoble, France

[⊥]Laboratoire de Reconnaissance Ionique et Chimie de Coordination, CEA, INAC, SCIB, CEA-Grenoble, 38054 Grenoble Cedex 09, France

S *Supporting Information*

ABSTRACT: The coupling of electron and proton transfers is currently under intense scrutiny. This Communication reports a new kind of proton-coupled electron transfer within a homodinuclear first-row transition-metal complex. The triply-bridged complex $[Fe^{III}(\mu\text{-OPh})(\mu_2\text{-mpdp})Fe^{II}(NH_2Bn)]$ (**1**; $mpdp^{2-}$ = *m*-phenylenedipropionate) bearing a terminal aminobenzyl ligand can be reversibly deprotonated to the anilinate complex **2** whose core $[Fe^{II}(\mu\text{-OPh})(\mu_2\text{-mpdp})Fe^{III}(NHBn)]$ features an inversion of the iron valences. This observation is supported by a combination of UV−visible, ^{1}H NMR, and Mössbauer spectroscopic studies.

The coupling of electron and proton transfers is currently attracting much interest owing to the recognition that it can avoid high-energy intermediates and the fact that electrostatic charge builds up in biological or chemical processes.[1,2] Moreover, it has been demonstrated that pH changes strongly influence electron transfer and, reciprocally, that electron transfers can tune proton exchanges. Many examples of proton-coupled electron transfers have thus been studied in the recent past that include both organic molecules (i.e., phenol oxidation)[3] and metal complexes (i.e., ruthenium complexes).[1,4] In the inorganic domain, a great deal of work has been devoted to mononuclear complexes with oxygen ligands and, in particular, those of ruthenium and osmium. Conversely, first-row transition-metal complexes of nitrogen ligands have received far less attention.[5] In the case of dinuclear complexes, most of the studies have focused on ruthenium/osmium or dimanganese complexes involving (de)protonable bridging ligands with the metal pair accepting/releasing electrons. In this respect, it is worth noting that a single example of a reversible pH-induced intramolecular electron transfer in a dinuclear system has been described by Neyhart and Meyer.[6] Indeed, upon a pH jump from 1.1 to 8.9, a valence inversion occurs in the heterodinuclear complex $[(tpy)(bpy)Os^{III}(\mu\text{-}4,4'\text{-bpy})Ru^{II}(H_2O)(bpy)_2]^{5+}$ (tpy = terpyridine; bpy = bipyridine), which transforms into $[(tpy)(bpy)Os^{II}(\mu\text{-}4,4'\text{-bpy})Ru^{III}(OH)(bpy)_2]^{4+}$ with the release of a proton.

In the course of our studies of diiron complexes, we found that complex $[Fe_2(L\text{-}BnNH_2)(mpdp)](H_2O)(ClO_4)_2$ (**1**) having a triply-bridged core $[Fe^{III}(\mu\text{-OPh})(\mu_2\text{-mpdp})Fe^{II}(NH_2Bn)]$ ($mpdp^{2-}$ = *m*-phenylenedipropionate) and bearing a terminal aminobenzyl ligand (Scheme 1) can be reversibly deprotonated to the anilinate complex **2**, whose core $[Fe^{II}(\mu\text{-OPh})(\mu_2\text{-mpdp})Fe^{III}(NH\text{-}Bn)]$ features an inversion of the iron valences. This is the first example of a proton-coupled valence inversion for both a homodinuclear complex and first-row transition metals.

The synthesis of the aniline ligand ($HL\text{-}BnNH_2$) was realized according to an adaptation of the published procedure[7] (see the Supporting Information, SI), and the mixed-valent diiron complex **1** was obtained by the reaction of the ligand with ferrous perchlorate and subsequent air oxidation.[8] Crystals were grown from an acetonitrile solution by slow evaporation, and the X-ray structure[9] of **1** is depicted in Figure 1 (see the SI for crystallographic data). The bond distances of Fe1 are significantly shorter (average = 2.054 Å) than those of Fe2 (average = 2.144 Å), which indicates that **1** is a mixed-valent $Fe^{III}Fe^{II}$ complex and that Fe1 is in the ferric state and Fe2 in the ferrous one. It is worth noting that the aminobenzyl group is bound to Fe2 in a trans position to the phenoxo oxygen O1 with an Fe2−N20 distance of 2.162(11) Å, which is close to the Fe−O_{water} distance (2.156 Å) of the aqua complex $[Fe_2(L\text{-}Bn)(mpdp)(OH_2)](BPh_4)_2$,[10] which presents the same valence localization. Only a few aniline iron(II) complexes have been structurally characterized in the literature.[11] This is due to the low donating ability of the anilino amine group, and its coordination in **1** is probably favored by chelation. This view is supported by the fact that the Fe−$N_{aniline}$ distances in hexacoordinate high-spin Fe^{II} complexes average 2.26 Å when the aniline is unsupported and 2.19 Å when it is chelating. The possibility that, in an acetonitrile solution of **1**, a solvent molecule replaces the aniline ligand is not supported by the spectroscopic studies detailed below.

The Mössbauer spectrum of an acetonitrile solution of ^{57}Fe-enriched **1** (Figure 2a) was recorded at 77 K in an acetonitrile solution. Its deconvolution reveals two equally intense quadrupole

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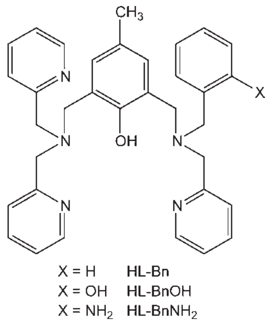
Scheme 1. Binucleating Ligand Used in This Study and Related Ones



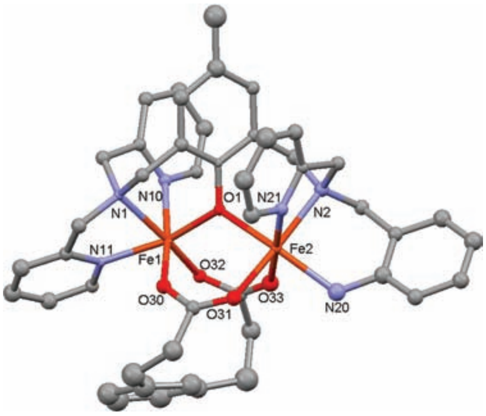


Figure 1. X-ray structure of the dication of **1**.[9] Important bond distances (Å) and angle (deg): Fe1−O32 1.949(8), Fe1−O30 1.949(8), Fe1−O1 1.956(8), Fe1−N11 2.120(9), Fe1−N10 2.162(10), Fe1−N1 2.192(9), Fe2−O1 2.057(8), Fe2−O31 2.073(8), Fe2−N21 2.135(10), Fe2−N20 2.162(11), Fe2−O33 2.208(9), Fe2−N2 2.229(10), Fe1−Fe2 3.473(3); Fe1−O1−Fe2 119.8(4).

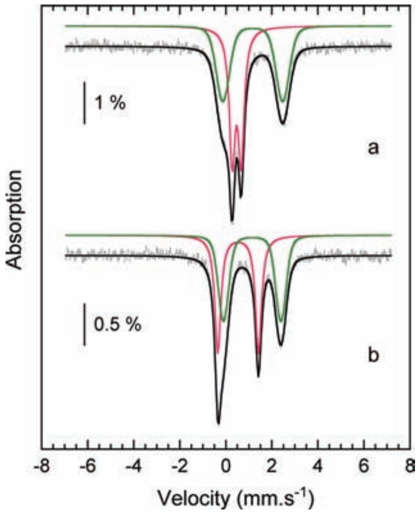


Figure 2. Experimental (hatched marks) and simulated (solid line) Mössbauer spectra of an acetonitrile solution of **1** before (a) and after (b) the addition of 1.5 equiv of NEt$_3$. The ferric and ferrous contributions are indicated above the spectra as pink and green traces, respectively.

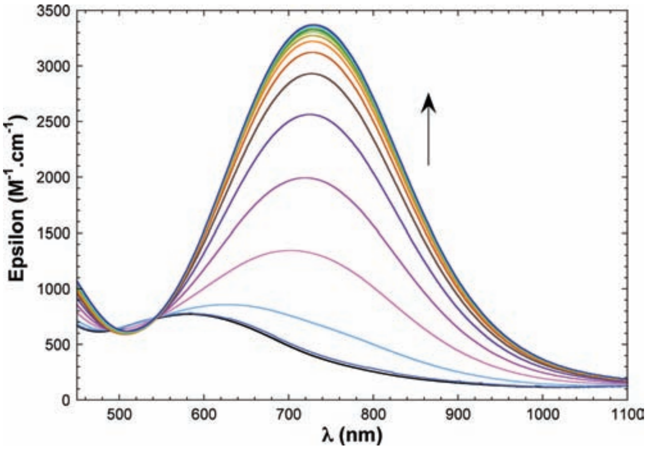


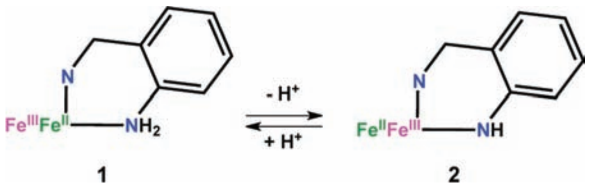
Figure 3. Evolution of the UV−visible spectrum of a 0.3 mM acetonitrile solution of **1** (black) upon the addition of *i*Pr$_2$EtN by 0.2 equiv aliquots up to 3 equiv of base.

doublets with parameters δ = 0.47(1) mm·s^{-1}, ΔE_Q = 0.39(2) mm·s^{-1} and δ = 1.17(1) mm·s^{-1}, ΔE_Q = 2.60(2) mm·s^{-1} corresponding respectively to high-spin Fe^{III} and high-spin Fe^{II} ions. The quadrupole splitting of the ferrous site, which is very sensitive to its coordination, is close to that of the aqua complex (ΔE_Q = 2.66 mm·s^{-1} in the solid state[10] and 2.41 mm·s^{-1} in an acetonitrile solution[8]) and differs significantly from that of the acetonitrile complex (ΔE_Q = 3.14 mm·s^{-1}).[8] The UV−visible spectrum of **1** is shown in Figure 3. Its maximum absorption is located at 586 nm (ε = 1000 M^{-1}·cm^{-1}; vs 575 nm, ε = 1000 M^{-1}·cm^{-1}, for the acetonitrile complex[8]). These spectroscopic data confirm that the aniline group is still bound to the ferrous ion in an acetonitrile solution of **1**.

Titration of an acetonitrile solution of **1** by *N*,*N*-diisopropylethylamine (Figure 3) caused the appearance of a new intense absorption at 729 nm (ε = 3370 M^{-1}·cm^{-1}). The transformation occurred with one isosbestic point at 543 nm, in agreement with a simple transformation between two chromophores. Such an intense transition is reminiscent of that assigned to an anilinate-to-Fe^{III} ligand-to-metal charge transfer in a trianilinetriazacyclononane complex.[12] It is worth noting that this transformation can be reversed by the addition of perchloric acid. To evaluate the pK_a of the bound aniline ligand, **1** was treated by various bases of pK_a in water in the range 4−12 and the reaction monitored at 729 nm. From the plot of the solution absorbance versus the pK_a of the added base (Figure S1 in the SI), the pK_a of the bound aniline was estimated as 8.4(2) in water and ca. 16 in acetonitrile.[13]

A first investigation of the valence locations was undertaken by ^{1}H NMR. The spectra of these types of diiron complexes are characterized by a very large spectral range extending from +600 to −50 ppm for complexes of the benzyl ligand HL-Bn[10] and down to −100 ppm for those of the 2-hydroxybenzyl ligand HL-BnOH.[7] The spectrum of a CD$_3$CN solution of **1** (Figure S2 in the SI) bears a strong similarity to that of the complex of the benzyl ligand,[8] therefore indicating the same valence distribution as that found in the solid state. After the addition of 1.5 equiv of NEt$_3$, the ^{1}H NMR spectrum (Figure S2 in the SI) changed significantly and showed a striking similarity to that of the 2-hydroxybenzyl complex,[7] with a spectral range extending even to −200 ppm. This suggested that the two complexes have the

Scheme 2. Reversible Intervalence Charge Transfer Triggered by (De)protonation of the Terminal Aniline Ligand



same valence distribution, with the ferric site bound to the anilinate nitrogen while in **1** this aniline nitrogen is bound to the ferrous ion.

To probe this valence localization, the Mössbauer spectrum of an acetonitrile solution of ^{57}Fe-enriched **1** after the addition of 1.5 equiv of NEt_3 was recorded at 77 K (Figure 2b). This spectrum can be deconvoluted into two equally intense quadrupole doublets with parameters δ = 0.54(1) mm·s^{-1}, ΔE_Q = 1.77(2) mm·s^{-1} and δ = 1.14(1) mm·s^{-1}, ΔE_Q = 2.49(2) mm·s^{-1} corresponding respectively to high-spin Fe^{III} and high-spin Fe^{II} ions. The quadrupole splitting of the ferric site is extremely large, which indicates that this site is highly distorted. Large ΔE_Q values of the ferric site have been noted also for the hydroxo[8] (1.51 mm·s^{-1}) and 2-hydroxybenzyl[7,13] diferric complexes (0.99 and 1.09 mm·s^{-1}), as well as for the ferric site of mixed-valent Fe_2[7,14] (1.22 and 0.96 mm·s^{-1}) and FeMn[15] (1.04 mm·s^{-1}) 2-hydroxybenzyl complexes. By contrast, when the ferric ion is bound in the dipyridylamine site, small values of ΔE_Q ($\leq$0.5 mm·s^{-1}) are always observed[7,8] as in **1**. Therefore, these high quadrupole splitting values appear to be characteristic of complexes in which the ferric site possesses an anionic ligand trans to the bridging phenolate. This combination of anionic ligands in mutual trans positions generates a strong axial anisotropy of the charge distribution, resulting in very large ΔE_Q values. It is worth noting that binding of an anion in a cis position with respect to the bridging phenolate does not give rise to such high quadrupole splitting values (ΔE_Q = ~0.5−0.6 mm·s^{-1}).[16,17] Therefore, Mössbauer spectroscopy such as ^{1}H NMR indicates that upon deprotonation of the aniline ligand the valences of the two iron atoms have been inverted, as shown in Scheme 2.

In summary, we have described the synthesis and characterization of a new mixed-valent Fe^{II}Fe^{III} complex that possesses an aniline ligand bound to Fe^{II}. Aniline is not a strong ligand, and only a few aniline iron complexes have been described in the literature. Interestingly, the aniline ligand can be deprotonated in solution, forming the anilinate derivative. Replacing the neutral aniline by the anilinate induces the switching of the valences of the two iron atoms because the anion favors the higher oxidation state, Fe^{III}, over Fe^{II}. This behavior is reminiscent of the semimet hemerythrins, which experience a similar reversible valence interchange upon switching the pH from 6 to 8 because of the reversible binding of hydroxide:[18] $[(His)_3Fe^{III}(\mu_3)Fe^{II}(His)_2] \leftrightarrows [(His)_3Fe^{II}(\mu_3)Fe^{III}(OH)(His)_2]$ with $(\mu_3) = (\mu\text{-OH})(\mu\text{-Asp})(\mu\text{-Glu})$.[19] Hence, **1** can be viewed as a new kind of molecular switch responding to its protonation state. Studies are currently in progress to analyze this new kind of proton-coupled electron transfer.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Description of the syntheses of the ligand and complexes, crystallographic data of **1**, and spectroscopic analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jean-marc.latour@cea.fr.

Notes

[§] Deceased.

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