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LETTER

5-Ferrocenyl-salicylate: a convenient ligand to build up multi-electron redox systems

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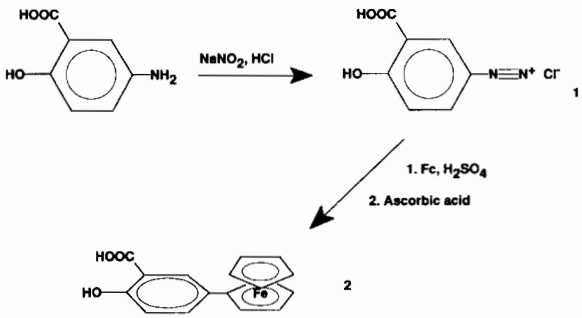
Multi-electron redox systems are usually obtained by linking through a covalent bond two or more redox active fragments [1]. A further route to multisite redox systems we were interested in exploring was to synthesize a ligand L bringing independent redox activity and to assemble some molecules of L around an appropriate metal centre.

In this connection, we considered the possibility of appending a very popular and versatile redox centre, ferrocene (Fc), active through the one-electron Fc/Fc^+ reversible couple, to a classical chelating agent: salicylate. The tendency of salicylate to give an especially stable complex of 1:3 stoichiometry with Fe^{III} in solution is well established [2].

The ferrocene/salicylic acid conjugate system was obtained through the synthetic steps outlined in Scheme 1. First, 5-amino-2-hydroxy-benzoic acid (Fluka, purum) was diazotized in aqueous HCl, at 0 °C, to produce the stable diazonium salt **1**. Then, **1** and ferrocenium were reacted in sulfuric acid solution, at 50 °C. After reduction with ascorbic acid, the crude 5-ferrocenyl-2-hydroxy-benzoic acid (**2**, 5-ferrocenyl-salicylic acid, $Fc\text{-}H_2L$) was obtained and was treated with 0.2 mol dm^{-3} NaOH. The alkaline solution, which contained **2** in its doubly deprotonated form, $Fc\text{-}L^{2-}$, was acidified with HCl. $Fc\text{-}H_2L$ precipitated as a yellow microcrystalline solid and was recrystallized from toluene. ^1H NMR ($CDCl_3$): 4.06 (5H, s); 4.30 (2H, t); 4.60 (2H, t); 6.97 (1H, d) 7.67 (1H, dd); 8.10 (1H, d); 12–13 (1H, s). Mass spectrum: $m/z = 322$.



Scheme 1.

The complexing ability of the ferrocenylsalicylate ion, $Fc\text{-}L^{2-}$, toward Fe^{III} was investigated through pH-titration experiments in a 50/50 water/dioxane solution, 0.1 mol dm^{-3} in $NaClO_4$, at 25 °C. First, a solution containing $Fc\text{-}H_2L$ was titrated with standard NaOH, to determine pK_{A1} and pK_{A2}: corresponding values are reported in Table 1. Then, titration was performed on a solution containing 1 equiv. of Fe^{III} and 3 equiv. of $Fc\text{-}H_2L$. Best fitting [3] of the titration curve was obtained by assuming the stepwise formation of the following three species: $[Fe^{III}(Fc\text{-}L^{2-})]^+$, $[Fe^{III}(Fc\text{-}L^{2-})_2]^-$ and $[Fe^{III}(Fc\text{-}L^{2-})_3]^{3-}$. A similar pattern had been previously observed in the investigation of the Fe^{III}– salicylate system in aqueous solution [4, 5]. Constants of the stepwise complexation equilibria involving $Fc\text{-}H_2L$ and Fe^{III} are reported in Table 1.

Figure 1 displays the pH dependence of the concentration of the $[Fe^{III}(Fc\text{-}L^{2-})]^+$, $[Fe^{III}(Fc\text{-}L^{2-})_2]^-$ and $[Fe^{III}(Fc\text{-}L^{2-})_3]^{3-}$ species, as calculated using the corresponding stability constants. A cyclic voltammetry (CV) investigation, using a platinum microsphere electrode, was performed on this solution over the pH range 2–8. At each pH value, a single peak was observed on the oxidation scan, followed by a peak of the same intensity on the reverse scan. Variation of the $E_{1/2}$ value with pH is shown in Fig. 1. It should be noted that in most of the investigated pH range, at a given pH value, several species coexist. Therefore, the measured $E_{1/2}$ value does not correspond to the redox process involving a single species, but it is associated to the Fc/Fc^+ redox change taking

TABLE 1. 5-Ferrocenyl-salicylic acid (**2**, $Fc\text{-}H_2L$): log K values associated to the stepwise equilibria of acid dissociation and complexation of Fe^{III} in a 50/50 water/dioxane solution, made 0.1 mol dm^{-3} in $NaClO_4$, at 25 °C

$Fc\text{-}H_2L = Fc\text{-}HL^- + H^+$	−4.35
$Fc\text{-}HL^- = Fc\text{-}L^{2-} + H^+$	< −10.7
$Fe^{3+} + Fc\text{-}H_2L = [Fe^{III}(Fc\text{-}L^{2-})]^+ + 2H^+$	11.26
$[Fe^{III}(Fc\text{-}L^{2-})]^+ + Fc\text{-}H_2L = [Fe^{III}(Fc\text{-}L^{2})_2]^- + 2H^+$	9.61
$[Fe^{III}(Fc\text{-}L^{2-})_2]^- + Fc\text{-}H_2L = [Fe^{III}(Fc\text{-}L^{2-})_2]^{3-} + 2H^+$	9.29

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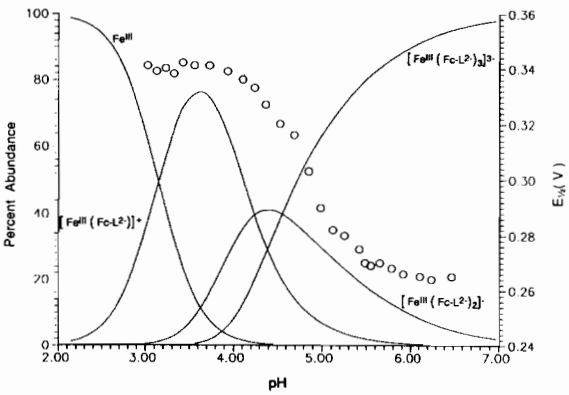

Fig. 1. pH dependence of the relative abundance (%) of Fe^{II} complexes of 5-ferrocenylsalicylate (solid lines, left scale) and of the half-wave potential (○, right scale) measured in a 50/50 water/dioxane solution, at 25 °C. Fe^{III}/Fc-H_2L ratio = 1:3.

place in the different species present at the equilibrium. For instance, at pH = 4.5, the three complexes $[Fe^{III}(Fc\text{-}L^{2-})]^+$, $[Fe^{III}(Fc\text{-}L^{2-})_2]^-$ and $[Fe^{III}(Fc\text{-}L^{2-})_3]^{3-}$ are present in nearly equal concentrations: thus, the $E_{1/2}$ value should be considered as the weighted average of the different values pertinent to the Fc/Fc^+ redox change occurring in the three metal complexes and also in the uncomplexed forms of Fc-H_2L. At pH = 7 and over, only one species is present at 100%: $[Fe^{III}(Fc\text{-}L^{2-})_3]^{3-}$. Thus, the measured $E_{1/2}$ value (0.263 V versus Ag/AgCl) corresponds to a single and well defined redox process. The controlled potential coulometry experiment carried out on the solution at pH = 7, at a potential of 0.4 V versus Ag/AgCl, indicated the release, to the platinum gauze anode, of 3 moles of electrons per mole of complex.

It should be noted that, for a three-electron process involving totally independent redox active centres, at 25 °C, electrons should be released according to three one-electron steps separated by 28 mV, a quantity arising form statistical effects*. For such a process, the separation of the anodic and cathodic peaks in the cyclic voltammetry profile should be the same as observed for a one-electron exchanging system, i.e. 57 mV [6]. The peak separation observed in the cyclic voltammogram of the solution at pH = 7, containing 100% of the $[Fe^{III}(Fc\text{-}L^{2-})_3]^{3-}$ complex, is 75 mV, i.e. only slightly larger than expected for a multi-electron process regulated only by statistical effects. This indicates that extremely weak interactions exist between the three ferrocene redox sites.

*In a statistically regulated three-electron redox system, the three one-electron steps should take place at the potentials: $E_1 = E - (RT/F)\ln 3$; $E_2 = E$; $E_3 = E + (RT/F)\ln 3$. $(RT/F)\ln 3 = 28.1$ mV, at 25 °C [6].

This behaviour is quite reasonable, if one considers that the three ferrocene subunits are external to the coordination polyhedron of the iron(III) tris-salicylate complex and electrostatic repulsive effects between the redox centres are shielded by the Fc-L^{2-} ligand framework. Thus, the three electrons are exchanged by the $[Fe^{III}(Fc\text{-}L^{2-})_3]^{3-}/[Fe^{III}(Fc^+\text{-}L^{2-})_3]$ redox couple, at the platinum electrode, almost in a single shot. The measured $E_{1/2}$ is an average value and exactly corresponds to the release/uptake of the second of the three electrons, a process which is not affected by statistical terms. This value is slightly less positive than that observed with ferrocene in the same conditions: 0.295 V versus Ag/AgCl. However, the correct comparison should be made, rather than with the oxidation of ferrocene, with the redox process involving the uncoordinated Fc-L^{2-} anion. To obtain the corresponding $E_{1/2}$ value, a 50/50 water/dioxane solution of Fc-H_2L was titrated with standard NaOH and, after, each addition of base, the $E_{1/2}$ value was measured by cyclic voltammetry. In slightly acidic solution (pH = 3, 100% of Fc-H_2L) $E_{1/2} = 0.320$ V versus Ag/AgCl. After the addition of 1 equiv. of NaOH (100% of Fc-HL^-) $E_{1/2} = 0.285$ V versus Ag/AgCl. Finally, after the addition of 2 equiv. of NaOH (100% of Fc-L^{2-}) $E_{1/2} = 0.250$ V versus Ag/AgCl. The decrease of the $E_{1/2}$ value with the increasing negative charge on the salicylic moiety is quite reasonable. Moreover, binding to 1/3 of the Fe^{III} cation does not seem to disturb too much the oxidation of the peripheral ferrocene subunits: the average potential obtained with the $[Fe^{III}(Fc\text{-}L^{2-})_3]^{3-}$ complex is only slightly more positive than that observed for the uncoordinated Fc-L^{2-} anion.

The Fe^{III} ion, when complexed by salicylate or by 5-ferrocenyl-salicylate, does not display any reversible redox activity. Thus, in the described system, it simply plays an architectural role, organizing redox active fragments around itself. Ligands bringing independent redox activity of the type described above can be assembled also around a redox active metal centre, to create multi-electron systems, operating at different potentials**.

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**A recent example has been given with the $[Ru^{II}(bipy)_2L]^{2+}$ complex (L = 4-ferrocenylvinyl-4′-methyl-2,2′-bipyridine), in which redox activity is displayed by both the ruthenium metal centre and the ferrocene subunit lying on the back of the conjugate 2,2′-bipyridine framework [7].

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