

# A Redox-switchable Ligand for which the Binding Ability is enhanced by Oxidation of its Ferrocene Unit

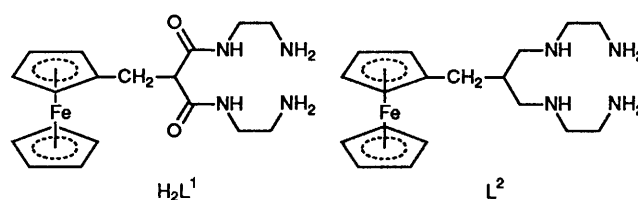
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Electrochemical investigations on a ferrocene-modified tetraamine diketone ligand have demonstrated an unusual enhancement of the binding ability towards  $\text{Ni}^{2+}$  when the redox subunit is switched to the ferrocenium form.

Considerable attention has been paid in the last few years to conjugate systems containing a redox function and a fragment able to bind a metal cation; these systems can behave either as chemical sensors<sup>1</sup> or as redox-switchable ligands.<sup>2</sup> In particular, the redox and binding properties of quinone-modified lariat ethers and podands,<sup>3</sup> of ferrocene-containing polythioethers (polythia ferrocenophanes)<sup>4</sup> and of conjugate molecules containing one or more crown ethers or polythiapolyaza crown ethers and one or more ferrocene units<sup>5</sup> have been investigated. The most interesting quantity pertinent to these systems is  $\Delta E$  ( $\Delta E = E_{\text{Fc}} - E_{\text{Fc}^+}$ ), i.e. the difference between the potentials due to the redox functions in the complexed ( $E_{\text{Fc}}$ ) and uncomplexed ( $E_{\text{Fc}^+}$ ) molecules. All the reported  $\Delta E$  values are positive: quite reasonably, the presence of a positive charge (the complexed metal cation) close to the redox centre makes easier the attainment of a lower oxidation state ( $\Delta E > 0$  in the case of reducible redox functions) and more difficult the attainment of a higher oxidation state ( $\Delta E > 0$  in the case of oxidizable redox functions).

We have now synthesised the new ferrocene-modified, water-soluble, tetradentate ligands  $\text{H}_2\text{L}^1$  and  $\text{L}^2$  by aminolysis of diethyl (ferrocenylmethyl)malonate<sup>6</sup> with ethane-1,2-diamine and through the reduction of  $\text{H}_2\text{L}^1$  with diborane in tetrahydrofuran, respectively. The ligand  $\text{H}_2\text{L}^1$  contains a dioxotetraamino binding framework<sup>7</sup> and is able to complex  $\text{Ni}^{2+}$  in water, with the simultaneous release of the two amido protons, forming the neutral, square-planar complex  $[\text{NiL}^1]$  [equation (1)]. On the other hand,  $\text{L}^2$  bears a tetraamine



**Table 1** Electrochemical and complexation equilibria data for  $\text{H}_2\text{L}^1$  and  $\text{L}^2$  and their nickel(II) complexes

	$\text{H}_2\text{L}^1$	$\text{L}^2$
$\log K_{\text{red}}$	-9.73(5)	15.10(5)
$\log K_{\text{ox}}^a$	-9.0(1)	14.7(1)
$E_{\text{Fc}}/\text{mV}$ (uncomplexed) <sup>b</sup>	402 <sup>c</sup> (10.5)	351 <sup>c</sup> (11.0)
$E_{\text{Fc}}^+$ (nickel complex) <sup>b</sup>	360 <sup>c</sup> (10.5)	376 <sup>c</sup> (7.0)
		1067 <sup>d</sup> (7.0)

<sup>a</sup> Calculated on the basis of the experimentally determined  $\Delta E$  (see text) and  $\log K_{\text{red}}$  values. <sup>b</sup> vs. NHE, in aqueous solution, 0.1 mol dm<sup>-3</sup> in  $\text{NaClO}_4$ ,  $\pm 3$  mV; the pH values at which the experiments were carried out are given in parentheses. Notice that the  $\text{p}K_{\text{a}}$  values for the first protonation are 8.85(1) for  $\text{H}_2\text{L}^1$  and 9.95(1) for  $\text{L}^2$ ; no variation was observed in the voltammograms on increasing the pH to the limiting value of 12. <sup>c</sup> Relative to ferrocene-ferrocenium. <sup>d</sup> Relative to the  $\text{Ni}^{\text{II}}-\text{Ni}^{\text{III}}$  couple.



binding fragment<sup>8</sup> and binds  $\text{Ni}^{2+}$  in aqueous solution to give a square stereochemistry [equation (2)]. The complexation

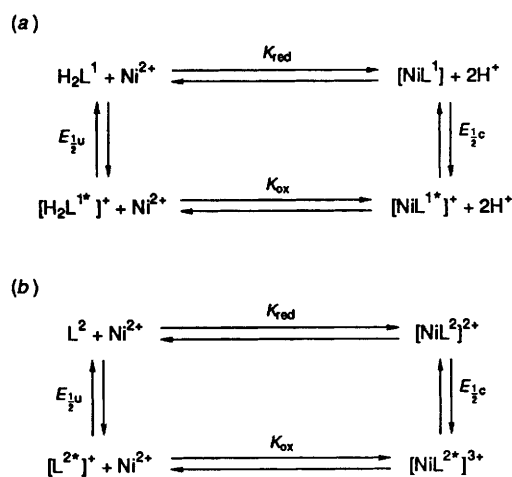


constants pertinent to equations (1) and (2) (i.e.  $K_{\text{red}}$ , see following discussion) have been determined by means of potentiometric titration experiments (Table 1).

Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) of the uncomplexed systems  $\text{H}_2\text{L}^1$  and  $\text{L}^2$  in aqueous solution (0.1 mol dm<sup>-3</sup> in  $\text{NaClO}_4$ ) were carried out at pH values at which the presence of charged (protonated) species is precluded (see Table 1) and disclosed in both cases a one-electron reversible redox process, ascribed to oxidation of the ferrocene moiety to ferrocenium,  $E_{\text{Fc}}$  402 and 351 mV vs. normal

hydrogen electrode (NHE), respectively. In spite of the similarity of the appended binding fragments, the ferrocene subunits display a strikingly different electrochemical behaviour upon co-ordination of the ligands to  $\text{Ni}^{2+}$ . In particular, DPV and CV experiments on aqueous solutions of  $[\text{NiL}^1]$  and  $[\text{NiL}^2]^{2+}$  (0.1 mol dm<sup>-3</sup> in  $\text{NaClO}_4$ , pH adjusted to values at which 100% of the metal in solution was in the desired complexed form, see Table 1) revealed an opposite trend: in the case of  $[\text{NiL}^2]^{2+}$ , the ferrocene-ferrocenium redox change takes place at a more positive potential than in the free ligand ( $\Delta E = +25$  mV); in the case of  $[\text{NiL}^1]$  this oxidation takes place at a more negative value ( $\Delta E = -42$  mV). Thus, paradoxically, the presence of a proximate positively charged centre ( $\text{Ni}^{2+}$ ) makes it distinctly easier, and not more difficult, to form the positively charged ferrocenium subunit. The case of  $[\text{NiL}^1]$  represents, to our knowledge, the first example of a redox-functionalized ligand that features a negative  $\Delta E$ .

The apparent paradox can be explained in terms of electro-



Scheme 1

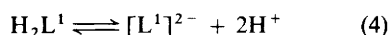
static effects. Placing a dipositive  $\text{Ni}^{2+}$  cation in the tetramine donor set of  $\text{L}^2$  makes the oxidation of the proximate ferrocene subunit more difficult. On the other hand, on complexation  $\text{H}_2\text{L}^1$  becomes deprotonated and a double negative charge forms on the ligand system. This negative charge is not completely offset by the  $\text{Ni}^{2+}$  ion and the oxidation potential of the appended ferrocene is thereby shifted cathodically.

A thorough explanation of the above effect is given, from a different point of view, by Scheme 1,<sup>9</sup> in which the complexation and redox equilibria pertinent to ligand  $\text{H}_2\text{L}^1$  (a) or  $\text{L}^2$  (b) with  $\text{Ni}^{2+}$  are summarized:  $K_{\text{red}}$  represents the complexation constant relative to the neutral, ferrocene-bearing ligands, while  $K_{\text{ox}}$  is relative to the oxidized, ferrocenium-bearing ligands. Equation (3)<sup>9</sup> holds for the situation described by Scheme 1 and

$$\Delta E = (RT/nF)\ln(K_{\text{red}}/K_{\text{ox}}) \quad (3)$$

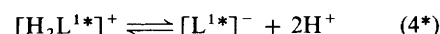
allows one to calculate  $K_{\text{ox}}$  from the experimentally obtained  $\Delta E$  and  $K_{\text{red}}$  values. In particular (see Table 1),  $K_{\text{ox}} > K_{\text{red}}$  in the case of  $\text{H}_2\text{L}^1$  and  $K_{\text{ox}} < K_{\text{red}}$  in the case  $\text{L}^2$ . Ligand  $\text{L}^2$  displays behaviour typical of all reported ferrocene-modified ligands,<sup>1,5,10</sup> in which a decrease in the complexation constant is observed when a metal cation is co-ordinated by a ligand bearing a charged substituent (e.g. ferrocenium) instead of a neutral one (ferrocene).

The case of  $\text{H}_2\text{L}^1$  can be explained by a closer examination of the complexation process [equation (1)]. This can be split into two steps, represented by equations (4) and (5), whose equilib-



rium constants are  $K_4$  and  $K_5$  (notice that individual values of  $K_4$  and  $K_5$  cannot be determined). Thus,  $K_{\text{red}} = K_4K_5$ . Similar

equations (4\*) and (5\*) can be written for the oxidized,



ferrocenium-bearing ligand 1  $[\text{H}_2\text{L}^{1*}]^+$ . In this case,  $K_{\text{ox}} = K_4^*K_5^*$ . The electrostatic repulsive effect, exerted by the positively charged ferrocenium subunit in  $[\text{H}_2\text{L}^{1*}]^+$  on the leaving amido protons, makes the value of  $K_4^*$  higher than that of  $K_4$ . On the other hand,  $K_5$  should be higher than  $K_5^*$ , following the general trend. Thus, it appears that  $K_4^*$  increases with respect to  $K_4$  more significantly than  $K_5^*$  decreases with respect to  $K_5$ , and on balance  $K_{\text{ox}} > K_{\text{red}}$ .

The compound  $\text{H}_2\text{L}^1$  represents the first example of a new class of redox-switchable ligands, capable of binding enhancement towards cations upon oxidation of the appended redox function. It should be noted that  $[\text{NiL}^{2+}]^{2+}$  undergoes a further one-electron reversible oxidation process, which is ascribed to the  $\text{Ni}^{\text{II}}$  to  $\text{Ni}^{\text{III}}$  change. Its  $E_{\frac{1}{2}}$  value (1067 mV vs. NHE) is more positive than that observed for plain  $[\text{NiL}^{3+}]^{2+}$  ( $\text{L}^3 = 3,7$ -diazanonane-1,9-diamine) (1032 mV vs. NHE), as expected,<sup>11</sup> due to the electrostatic repulsive effects exerted by the proximate ferrocenium subunit. The complex  $[\text{NiL}^1]$  displays a further irreversible wave in both CV and DPV profiles.

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