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Redox switchable ligands suitable for transition metal ions: Protonation, complexation and electrochemical properties of a ferrocene-modified tetraamine diketone and its saturated analogue

Giancarlo De Santis[a]; Luigi Fabbrizzi[a]; Maurizio Licchelli[a]; Piersandro Pallavicini[a]; Angelo Perotti[a]; Antonio Poggi[a]
[a] Dipartimento di Chimica Generale, Università di Pavia, Pavia, Italy

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Redox switchable ligands suitable for transition metal ions: protonation, complexation and electrochemical properties of a ferrocene-modified tetraamine diketone and its saturated analogue

GIANCARLO DE SANTIS, LUIGI FABBRIZZI*, MAURIZIO LICCHELLI,
PIERSANDRO PALLAVICINI, ANGELO PEROTTI and ANTONIO POGGI

Dipartimento di Chimica Generale, Università di Pavia, 27100 Pavia, Italy

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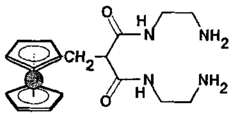
The new ferrocene-containing water-soluble ligands 1 and 2 were synthesized and their protonation and complexation properties toward Ni^{II} and Cu^{II} studied as a function of pH, by means of potentiometric titration experiments. Electrochemical measurements were performed in aqueous solution on pure 1 and 2 and in the presence of Ni^{II} and Cu^{II} cations, in the pH range 2–12, allowing us to determine the redox potential values relative to the ferrocene oxidation in the free ligands and in their Ni^{II} and Cu^{II} complexes. 1 and 2 behave as redox switchable ligands, the former enhancing, the latter decreasing its binding ability upon oxidation of the appended ferrocene function. Besides, the Cu^{II} complex of ligand 1 and the Ni^{II} complex of ligand 2 behave as two-centre two-electron redox systems, the complexed metal cation being subject to further oxidation to M^{III}.

INTRODUCTION

The concept of *redox switchable ligand* is usually associated with two-component systems featuring a coordinating subunit linked to a *reducible* redox-active fragment.[1] The reduction of the latter sets up one or more negative charges, which *enhance* the ligand's binding ability, due to favourable electrostatic interaction with the complexed cations. The most frequently used reducible fragments in redox switchable ligands are nitroarenes,[2] quinones,[3] and the azo group,[4] usually coupled with ligands selective for s block cations, such as open-chain and cyclic polyethers or cryptands.

On the other hand, a huge number of two-component systems, containing both an *oxidizable* redox function and a coordinating unit, has been reported in the literature.[5] Ferrocene is by far the most popular redox function in this kind of systems, because of the wide choice of functionalization pathways which it offers.[6] It has been appended to (or incorporated in) crown ethers,[7] cryptands,[8] polythiaethers,[9] polythiapolyaza crown ethers,[10] calixarenes,[11] open-chain[12] and macrocyclic polyaza ligands,[13] i.e. to coordinating fragments suitable both for non-transition and transition metal cations. Usually, oxidation of ferrocene to the ferrocenium form sets up a monopositive charge which makes the complexation of a metal cation *less favourable*, because of repulsive electrostatic interaction. The use of two-component systems containing ferrocene and a coordinating unit as redox switchable ligands[5b,14] has been recently reviewed.[5c] As a matter of fact, the reversible nature of the oxidation of the ferrocene fragment allows one to switch the system back and forth from a higher to a lower binding state.



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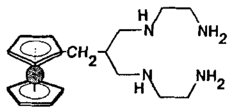

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In a general study of multi-centre multi-electron redox systems,[13c,15] we have considered several two-component systems containing ferrocene and a polyamino binding subunit:[12b,13] the latter fragment promotes a rich redox activity of the complexed transition metal ion.[16] In a recent communication[12b] we have demontrated that ferrocene-containing redox switchable ligands **1** and **2**, although quite similar, can either *increase* (in the case of **1**) or *decrease* (in the case of **2**) their binding ability toward Ni^{II} upon oxidation of the ferrocene subunit. In this work we describe the syntheses and characterization of **1**, **2** and of their Ni^{II} and Cu^{II} complexes.

Moreover, we report their acid-base properties and their complexation behaviour toward Ni^{II} and Cu^{II} ions in aqueous solution. Finally, through electrochemical measurements we have established that (i) in the absence of metal ions the oxidation potential of the ferrocene fragment in **1** and **2** is pH-dependent, its value being a function of the degree of protonation of the amino groups; (ii) on oxidation of the ferrocene subunit, **1** enhances its binding ability toward Ni^{II} and Cu^{II}, while **2** does the reverse; (iii) the Cu^{II} complex of **1** and the Ni^{II} complex of **2** behave as two-centre two-electron redox systems, as the complexed metal cation is prone to reversible oxidation to M^{III}.

RESULTS AND DISCUSSION

Syntheses

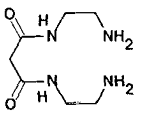
Appending the ferrocene subunit to a diamino-diamido or tetraamino framework is of particular interest for coordination chemistry, as it opens the route to ferrocene-containing two-component systems capable of selectively bind transition metal cations. Moreover, the coupling of a lipophilic unit such as ferrocene to a hydrophilic unit such as 1,4,8,11-tetramino undecane-5,7-dione (**5**) or 1,4,8,11-tetra-azeundecane (**6**) makes these redox switchable ligands and their complexes *amphiphilic*, so that a fair solubility is found in solvents ranging from water to dichloromethane. This allows the extension of the (coordination) chemistry of these two-component systems to such a fundamentally important solvent as water, an opportunity which has been rarely exploited as the ferrocene fragment is a typical lipophilic function, although evidence for the redox switchable properties of a ferrocenyl cryptand in aqueous media has been recently presented.[8e] Moreover, we have demonstrated[13a] that it is possible to exploit the effect of external agents (e.g. solvent, electrolyte) for the modulation of the interactions between the two subunits, as ferrocene is a coordinatively saturated fragment whereas tetraamino or diamino-diimido metal complexes are not.

The synthesis of **1** is based on the aminolysis of diethyl malonate and of its α-substituted derivatives, a facile procedure which has led to the preparation of a number of plain or functionalized open-chain[17] and cyclic[18] tetraamino diketones. Reduction of **1** to **2** with diborane in THF is straightforward, except for the fact that long reaction times (i.e. at least three days) are required for the reaction to be completed.

The preparation of the Ni^{II} and Cu^{II} complexes of **1** leads to the isolation of easy-to-handle and stable crystalline solids, which have been characterized by spectral and elemental analysis. Unfortunately, metal complexes of ligand **2** appear less stable. Attempts to isolate the solid compounds gave good results only using Ni^{II}: in particular, the metal cation and the product had to be stored under a nitrogen atmosphere in order to avoid the oxidation of the ferrocene moiety and the subsequent decomposition of the whole molecule. In the case of Cu^{II}, it was impossible to prepare even solutions of the desired complex as oxidation of the ferrocene molecule, followed by decomposition, occurred even under strictly anaerobic conditions. This suggests a decomposition process in which the complexes Cu^{II} cation plays some role, in agreement with what was found[19] for ferrocene-containing polythiamacrocycles, in which complexation of a Cu^{II} ion resulted in the spontaneous oxidation of the ferrocene moiety and concomitant reduction of Cu^{II} to Cu^{I}.

Solution chemistry in the reduced (switched off) state

(i) Protonation equilibria. By means of potentiometric titrations of solutions containing the ligands plus excess acid, it was possible to determine the protonation constants of the examined systems. Table 1 reports the $\log K_n$ values for the protonation equilibria of **1** and **2**. For comparison, values were determined also for the unsubstituted analogues **5** and **6**, and for the benzyl-substituted analogue **7**.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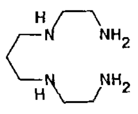
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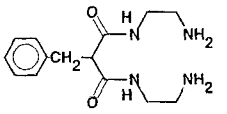
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Compound **1** binds two protons through its two primary amino groups, through two consecutive steps. Ligand **2**, which has two additional secondary amino moieties available for protonation, binds four protons through four consecutive steps. Distribution diagrams for the protonated species for ligands **1** and **2** are shown in Fig 1. The percent concentration of species vs pH profiles show that ligands **1** and **2** exist more than 95% as free (unprotonated) species at pH values higher than 10.1 and 11.1, respectively.

Comparison with the $\log K_n$ data relative to the unsubstituted systems **5** and **6** and to the benzyl-

Table 1 Protonation and complexation constants of ligands **1**, **2** and **5**–**7**

	$\log K_1^{(a)}$	$\log K_2^{(a)}$	$\log K_3^{(a)}$	$\log K_4^{(a)}$	$\log K_{red}^{(b)}$		$\log K_{ox}^{(c)}$	
					Ni	Cu	Ni	Cu
1	8.85	8.35	—	—	−9.73	−4.64	−9.0	−3.9
2	9.95	9.44	6.40	4.26	15.10	—	14.7	—
5	9.01	8.66	—	—	−10.66	−5.13	—	—
6	10.25	9.50	7.28	6.02	16.4	23.9	—	—
7	9.07	8.35	—	—	−10.67	−4.91	—	—

[a] Standard deviation = ±0.01 log units.
[b] Standard deviation = ±0.05 log units.
[c] Calculated through eqn. (1) (see text) on the basis of experimental $\log K_{red}$ and ΔE values; standard deviation = ±0.1 log units.

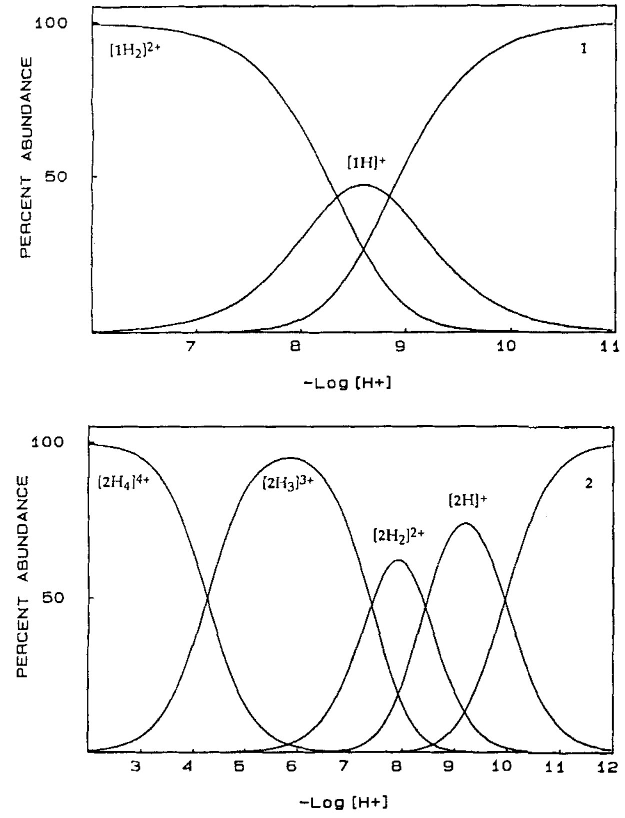
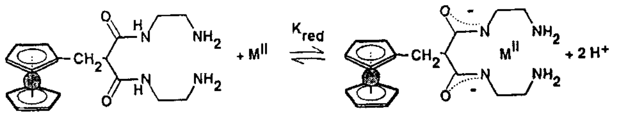


Figure 1 Distribution diagrams for ligand **1** (a) and ligand **2** (b) in water. The species pertinent to each curve are indicated in the diagram.



M = Ni, 4a
M = Cu, 4b

Scheme 1

substituted ligand **7** does not evidence any particular effect of the (ferrocenyl)methyl moiety on the first and second protonation steps. On the other hand, a small but significant difference is found in the constants relative to the third and fourth protonation, when **2** and **6** are compared. The proton affinity is smaller in the case of **2** by 0.9 (third protonation) and 1.8 (fourth protonation) log units. As it is known[20] that **6** binds the third and fourth proton with its two secondary nitrogens (i.e. N-4 and N-8), it can be supposed that the same is valid for **2** and that the bulky (ferrocenyl)methyl group limits to some extent the flexibility of the tetraamine chain, thus preventing the attainment of the maximum distance between the protonated N atoms. In particular, the proximate protonated N-4 and N-8 atoms should be forced into a closer arrangement than in **6**, consistent with the noticeable lowering of 1.8 log units for the fourth protonation in **2**.

(ii) Complexation equilibria. The coordinating tendencies of **1** and **2** toward aqueous Ni^{II} and Cu^{II} ions have been investigated by means of potentiometric titrations with standard base of solutions containing the appropriate ligand and $M(ClO_4)_2$ [M = Ni, Cu] in equivalent amounts, plus excess acid. The two ligands have been found to behave at their unsubstituted analogues **5** and **6**. In particular, **1** loses the two amido protons to form the bis-amino, bis-amido neutral complexes $[M^{II}(H_{-2}\mathbf{1})]$ (M = Ni, **4a**; M = Cu, **4b**), according to scheme 1, as expected for a plain or substituted linear[17,21] or cyclic[22] tetramino diketone.

Figure 2 reports the titration profile (pH vs B/L; B/L = added base/ligand molar ratio, see caption to the figure) for both the nickel and copper complexes. A *plateau* is observed between B/L = −2 and B/L = 2, which corresponds to the complexation process and whose position in the pH scale is inversely proportional to the corresponding complexation constant (K_{red}). Computer elaboration of the data obtained from potentiometric titrations allowed us to determine the $\log K_{red}$ values relative to the process described in scheme 1: these values are reported in Table 1 together with those of the reference compounds **5** and **7**. Notice that $\log K_{red}$ values for ligands **1**, **5**, and **7** are negative as they refer to an equilibrium of the type depicted in scheme 1. In particular, the positive free energy change

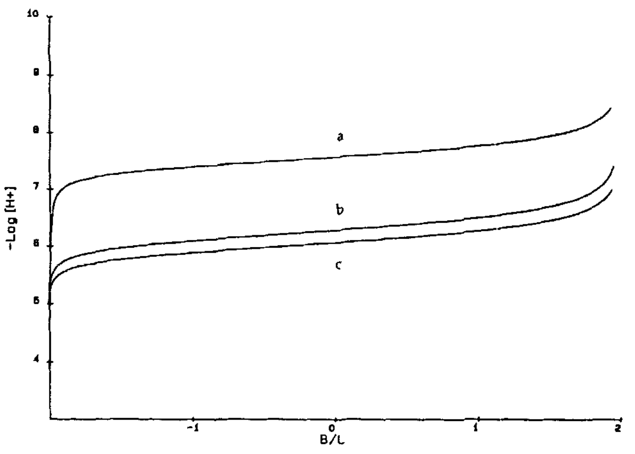


Figure 2 Titration curves relative to (a) ligand **1** and Ni^{II} (1/1 molar ratio) plus excess acid; (b) ligand **1** and Cu^{II} (1/1 molar ratio) plus excess acid; (c) ligand $[1^*]^+$ and Cu^{II} (1/1 molar ratio) plus excess acid. B/L is the ratio of the moles of standard base added (B) over the moles of ligand (L). Negative values indicate the excess of acid (e.g. $-1 = 1$ equivalent of standard acid).

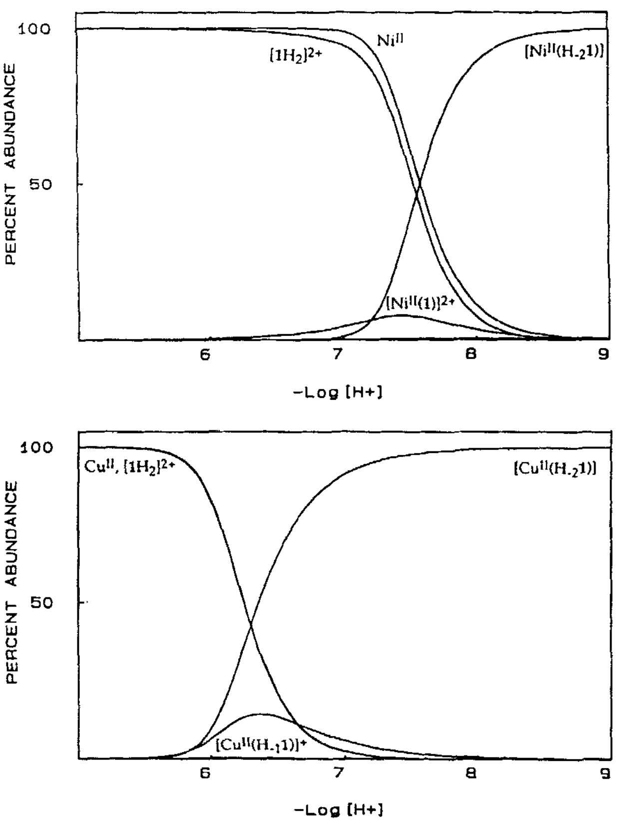


Figure 3 Distribution curves of the species present at the equilibrium in the system Ni^{II}/ligand **1** (a) and Cu^{II}/ligand **1** (b) with a 1:1 molar ratio. The species pertinent to each curve are indicated in the diagram.

results from the balance of the endoergonic term due to the deprotonation of the two amido groups and the exoergonic term due to the complexation process.

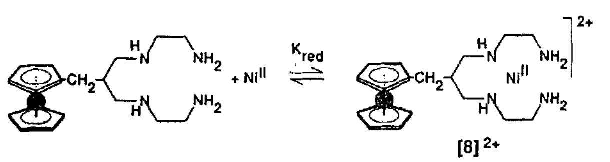
By combination of protonation and complexation constants, distribution diagrams were calculated for solutions containing ligand **1** and $M(ClO_4)_2$ ($M = Ni^{II}$ and Cu^{II}) in 1:1 molar ratio. The % of species vs pH curves are shown in Fig 3. It can be seen that **4a** and **4b** represent the only species present in solution at pH values higher than 8.9 and 8.1, respectively.

Comparison of the log K_{red} values for the ferrocene-substituted ligand **1** with those of the corresponding plain ligand **5** evidences a slightly, but significantly, greater affinity of the former toward both Ni^{II} and Cu^{II}. The hypothesis of an increased coordinating ability of the two primary amino groups is to be discarded on the basis of the log K_1 and log K_2 values, which are slightly *lower* for ligand **1**. On the other hand, the deprotonation of the two amido groups to form the bis-amino bis-imido neutral complexes $[M^{II}(H_{-2}1)$ plays an important role on the complex formation process and the proximate (ferrocenyl)methyl group could exert some effect on it. In particular, for related cyclic systems it has been suggested[23] that the hydrophobicity of the groups appended to a poly-amino poly-amido binding unit may help increase the acidity of the amide protons, thus rendering their dissociation (and consequently complexation) easier. This hypothesis may be invoked also in the case of **1**, as it is further supported by the log K_{red} value for the benzyl-substituted ligand **7** with Cu^{II}, which is greater than that of **5**.

As far as ligand **2** is concerned, potentiometric titration experiments (performed on solutions containing the ligand and $Ni(ClO_4)_2$ in equivalent amounts, plus excess acid) showed a complexation behaviour similar to that of the corresponding unsubstituted tetraamino ligand **6**, which is known to bind a Ni^{II} cation according to a square planar geometry,[24] as described in scheme 2.

Figure 4 reports the distribution diagram for a solution containing **2** and Ni^{II} perchlorate in a 1:1 molar ration. The complexed species $[8]^{2+}$ is the only present in solutions at pH > 5.9.

The log K_{red} value is in this case significantly lower for **2**, with respect to **6**. The third and fourth protonation constants are low in the case of **2**, but, as has been pointed out in the previous discussion, this can be explained by the increased repulsion between the protonated groups, caused by the bulky (ferrocene)-methyl moiety. Thus, the donating ability of the unprotonated N-4 and N-8 should not vary on passing from **6** to **2**. The Ni^{II} ion in the complex of the



$[8]^{2+}$

Scheme 2

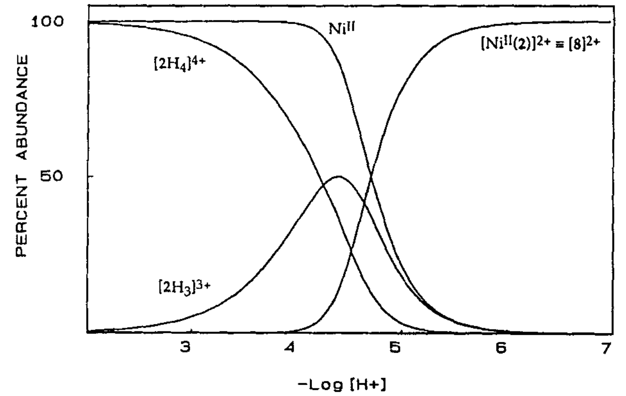


Figure 4 Distribution curves of the species present at the equilibrium in the system Ni^{II}/ligand **2** in a 1:1 molar ratio. The species pertinent to each curve are indicated in the diagram.

unsubstituted ligand **6** is known[24] to be in equilibrium between a tetracoordinated square planar and an hexacoordinated octahedral form, in which two solvent molecules occupy the axial positions of the octahedron. According to this, the decreased log K_{red} value of **2** could be ascribed to the unfavourable steric effect of the (ferrocenyl)methyl moiety on the solvent coordination in the two axial positions of the Ni^{II} complex.

(iii) Visible spectra. Compounds **1** and **2** show a single band spectrum in the visible region, centred at 432 nm ($\varepsilon = 150$) and 428 nm ($\varepsilon = 135$), respectively, typical of the ferrocene chromophore.[25] The spectra of the complexes resemble those of the free ligands, being dominated by the ferrocene absorption (**4a**: $\lambda_{max} = 436$ nm, $\varepsilon = 172$; **4b**, $\lambda_{max} = 446$ nm, $\varepsilon = 159$; $[\mathbf{8}]^{2+}$, $\lambda_{max} = 432$, $\varepsilon = 140$), in agreement with the low extinction coefficient values expected for the Ni^{II} and Cu^{II} complexes with the binding subunit. Complexes of ligand **5**[17] display in fact a single band spectrum in the visible region, centred at 450 nm ($\varepsilon = 69$) and 516 nm ($\varepsilon = 63$), in the case of Ni^{II} and Cu^{II}, respectively, while the Ni^{II} complex of ligand **6**,[24] which exists in solution as an equilibrium of a square (diamagnetic) and an octahedral (paramagnetic) form, presents a more complicated spectrum featuring only low-intensity bands ($\lambda_{max} = 346$, $\varepsilon = 5$ and $\lambda_{max} = 538$, $\varepsilon = 3$ (shoulder), pertinent to the octahedral form; $\lambda_{max} = 448$, $\varepsilon = 8$ pertinent to the square form, in the case of $[Ni(\mathbf{6})](ClO_4)_2$ in water, at 20 °C).

In addition, it has been possible to evaluate the spectra pertinent to the metal-diimido-diamino and metal-tetraamino moiety by using a solution of the appropriate ligand as the blank, to which a stoichiometric amount of $M(ClO_4)_2$ was successively added and whose pH was regulated (by addition of a 0.1 mol dm^{-3} NaOH solution) to values at which the formation of the desired complex was complete. Although the method is too rough to obtain significant ε values, a single band spectrum was observed in the case of **4a** ($\lambda_{max} = 452$ nm) and **4b** ($\lambda_{max} = 518$ nm), which further confirms that these complexes exist in solution in the same square planar form as those with the plain ligand **5**.

By the same method, complex $[\mathbf{8}]^{2+}$ revealed a single band spectrum in the 350–800 nm region, with λ_{max} centred at 444 nm. By comparison with the band positions in the Ni^{II} complex of the plain ligand **6**, it can be argued that in $[\mathbf{8}]^{2+}$ the Ni^{II} ion is mainly in the square planar form, a further confirmation of the hypothesis that the (ferrocenyl)methyl group sterically inhibits the axial coordination of water molecules on the proximate nickel ion.

The oxidized (switched on) state

In redox switchable ligands, bearing either a reducible or an oxidizable redox function, the *switched on* state appears in most cases as quite an elusive species. Its properties are usually inferred by voltammetric sweep experiments performed on the *switched off* ligands and on their complexes. Consequently the *switched on* state lives only for the time pertinent to these experimental techniques, i.e. few seconds or less, and just in the diffusion layer around the electrode. No attempts were usually made to isolate the 'switched on' compounds or at least to generate a bulk solution of them. This is quite reasonable if one considers that in many cases the redox subunit is a purely organic reducible molecule (e.g. quinone or nitroarene derivatives), which, once switched, becomes a reactive radical.

Better results could be obtained in this sense by the use of organometallic or coordination complexes as the redox subunit, due to the particular stability that many of these compounds display in more than one of their possible oxidation states. In particular, the oxidized (i.e. *switched on*) form of ferrocene consists of the monopositive ferrocenium cation, whose stability and ready availability have been recognized since the appearance of ferrocene on the scientific stage.[26] Significantly, solid compounds containing the ferrocenium cation can be easily isolated[26] and have recently become available commercially.[27] Moreover, some elegant examples of ferrocene-bearing redox switchable systems have been described[14,28] in which the ferrocenium form is quantitatively generated and its peculiar properties exploited.

We wished to prepare the oxidized (ferrocenium) forms of ligands **1** and **2** and of their complexes **4a**, **4b** and $[\mathbf{8}]^{2+}$ and to directly measure the enhancement or decrease in the binding ability of the ligands when in their *switched on* form. To this aim, we prepared solutions containing the ferrocenium-bearing ligands $[\mathbf{1^*}]^+$ and $[\mathbf{2^*}]^+$ (the asterisk denotes in the text a molecule which bears a *ferrocenium* instead of a ferrocene fragment) by means of controlled potential electrolysis on **1** and **2**. By using the same method, solutions containing the ferrocenium-bearing complexes $[\mathbf{4a^*}]^+$, $[\mathbf{4b^*}]^+$ and $[\mathbf{8^*}]^{3+}$ have ben prepared starting from solutions of the corresponding **4a**, **4b** and $[\mathbf{8}]^{2+}$ complexes. The integrated current curve indicated in every case the consumption of 1.0 mol of electrons per mol of the considered system, corresponding to the one-electron oxidation of ferrocene, and a blue solution was obtained, whose visible spectrum displayed a band with a maximum centred around 632 nm, typical of the ferrocenium moiety.[28b] The stability of each oxidized system was checked at different pH values by monitoring the absorbance at 632 nm vs time on a portion of the electrolyzed solution, transferred in a quartz cell under a nitrogen atmosphere.

The switched on complexes $[\mathbf{4a^*}]^+$ (examined pH range: 10.5–12), $[\mathbf{4b^*}]^+$ (pH 8–12) and $[\mathbf{8^*}]^{3+}$ (pH 8–12) were found to be stable, as less than 3% decomposition was observed after 4 days.

Unfortunately, the switched on ligands $[\mathbf{1^*}]^+$ and $[\mathbf{2^*}]^+$ proved to be stable only in acidic solution (at pH = 4.0 the absorbance at 632 nm diminished of 6% and 15% in the case of $[\mathbf{1^*}]^+$ and $[\mathbf{2^*}]^+$, respectively, after a 24 h period) while in neutral or basic conditions the oxidized species disappeared at a rate which was faster as the pH value or the ligand concentration were made higher (e.g. at pH = 8 the absorbance at 632 nm of a solution of $[\mathbf{1^*}]^+$ of 10^{-3} mol dm^{-3} concentration diminished of 30% in a 4 hours period). Moreover, it has to be noted that the disappearance of the spectrum of the oxidized species did not correspond to restoration of that pertinent to the reduced species; this indicates a decomposition process of the ferrocenium moiety, probably due to a nucleophilic cyclopentadienyl displacement.

According to this, we were unble to directly measure the complexation constants of the switched on ligands with the wanted precision, as the potentiometric titration method requires the examined solution to be maintained at pH values in the range of 4–12 for prolonged time periods (several hours), depending on how long was required for a stable potential value to be reached after each addition of base.

Thus, the ability of the redox switch to decrease or enhance the binding properties of the two-component systems, depending on its 'off or on' position, has to be evaluated with the usual indirect electrochemical methods, as it is discussed in the next subsection.

However, a qualitative experiment was carried out on the switched on ligand $[\mathbf{1^*}]^+$. A solution of $[\mathbf{1^*}]^+$ in water (concentration and ionic strength as in the potentiometric titration experiments on ligand **1**; pH = 2) was generated by controlled potential electrolysis. An equivalent amount of $Cu(ClO_4)_2$ was added and a titration started after having imposed to the computer-controlled system to collect data at reduced time intervals. The resulting titration curve is reported in Fig 2. Comparison with that of the corresponding switched off ligand **1** shows complexation of Cu^{II} to take place at a lower pH for ligand $[\mathbf{1^*}]^+$ than for ligand **1**, indicating an enhanced complexing ability upon oxidation of the appended ferrocene. Data elaboration led to the determination of a complexation constant ($\log K_{ox} = -4.0 \pm 0.1$) that, although affected by a large uncertainty, supports this trend. This unexpected result is fully confirmed by electrochemical studies with cyclic voltammetry methods.

Electrochemistry

(i) Ferrocene—centred processes: 1 and 2 as redox switchable ligands. Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) experiments on the uncomplexed ligands **1** and **2** were carried out in aqueous solution (made 0.1 mol dm^{-3} in $NaClO_4$) in the pH range 2–12. A one-electron reversible redox process was observed in both cases and it was ascribed to the oxidation of ferrocene to ferrocenium. The $E_{1/2}$ value at which this takes place depends on the pH of the solution, as the protonation of the amino groups influences the oxidation of the appended ferrocene moiety by means of electrostatic interactions. The potentials relative to the free (unprotonated) species and those relative to the fully protonated ones (i.e. $[\mathbf{1}H_2]^{2+}$ and $[\mathbf{2}H_4]^{4+}$) can be determined by observing the distribution diagrams reported in Fig 1 and setting the pH of the solution at values at which only the desired species exist. The results are reported in Table 2 and indicate a moderate pH effect in the case of **1**, where the two charges on the distant protonated primary amino groups make the oxidation of the ferrocene fragment more difficult by only 14 mV. In the case of **2**, the four unit charge increase and, in particular, the presence of two protonated amino groups in the proximity of ferrocene make the oxidation of the latter occur at a potential 75 mV more positive in the fully protonated species with respect to the neutral one.

Table 2 Redox potentials relative to the ferrocene fragment

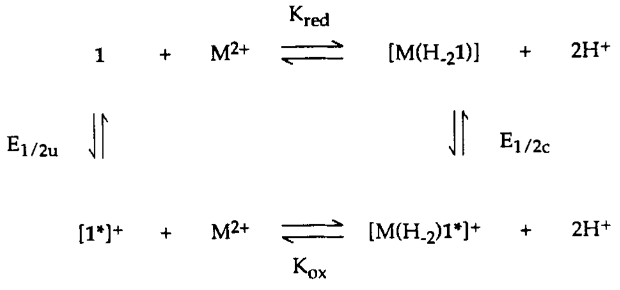
	ligand **1**[(a)]	*ligand* **2**[(a)]
free ligand	402	351
fully protonated ligand	416[b]	426[c]
Ni^{II} complex	360	376
Cu^{II} complex	361	—

[(a)] Potentials expressed in mV vs NHE (normal hydrogen electrode), ±3 mV.
[(b)] Ferrocene oxidation potential in $[\mathbf{1}H_2]^{2+}$.
[(c)] Ferrocene oxidation potential in $[\mathbf{2}H_4]^{4+}$.

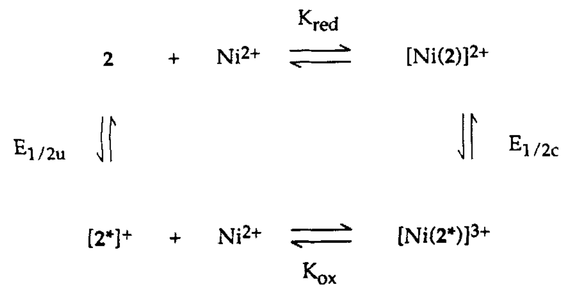
Determination of the ferrocene oxidation potential in the species of intermediate protonation degree is made impossible by the coexistence of more than one species at intermediate pH values. The observed potential is a ratio[29] of those pertinent to the each of the species in equilibrium and it is closer to that of the most abundant one. As a consequence, the ferrocene oxidation signal, in both DPV and CV profiles, *shifts* between the limiting potential values on progressive pH variation.

In solutions containing the complexes **4a**, **4b** and $[\mathbf{8}]^{2+}$ (0.1 mol dm^{-3} in $NaClO_4$, pH adjusted at values at which the complex is the only species present) DPV and CV measurements demonstrated that the oxidation of the ferrocene fragment takes place at a different value than in the free ligands. The results are reported in Table 2 and evidence an opposite trend for the complexes of ligand **1** with respect to the Ni^{II} complex of ligand **2**. In **4a** and **4b** the ferrocene redox potential is in fact *less positive* than in ligand **1**, while in $[\mathbf{8}]^{2+}$ it is *more positive* than in **2**. It must be emphasized that the 'normal' behaviour is that of ligand **2** and of its complex, as the literature has thus far reported only examples of redox switchable ligands in which the oxidation (or reduction) process centred on the redox subunit takes place at a *more positive* potential when a cation is complexed by the binding subunit.

In addition, this means that when the ferrocene subunit is switched on (i.e. oxidized), **1** *enhances* its binding ability toward Ni^{II} and Cu^{II}, while **2** *decreases* it.



Scheme 3a



Scheme 3b

The well known 'square scheme',[7c] which summarizes the complexation and redox equilibria for a redox switchable ligand, has been adopted for both ligand **1** and **2**, as shown in scheme 3a and 3b, respectively. Equation 1 holds in both cases.

$$\Delta E = (RT/nF)\ln(K_{red}/K_{ox}) \qquad (1)$$

ΔE represents the difference between the ferrocene oxidation potential in the complexed species and that in the uncomplexed one. K_{red} is the complexation constant pertinent to **1** and **2** bearing the netural ferrocene subunit while K_{ox} is that of the ferrocenium-bearing ligands $[\mathbf{1}^*]^+$ and $[\mathbf{2}^*]^+$.

As ΔE is negative in the case of **1**, the unprecedented result of $K_{ox} > K_{red}$ is obtained, which paradoxically means that the complexation process between Ni^{II} or Cu^{II} cations and the binding subunit is easier when the latter carries a positively charged instead of a neutral appended fragment! This can be explained by considering that the complexation process for a tetraamino-diketone ligand and for **1** in particular (see scheme 1) can be formally split into two steps, as indicated by eqns (2) and (3) (M = Ni, $[MH_{-2}\mathbf{1}] = \mathbf{4a}$; M = Cu, $[MH_{-2}\mathbf{1}] = \mathbf{4b}$).

$$\mathbf{1} \rightleftharpoons [H_{-2}\mathbf{1}]^{2-} + 2H^+ \qquad (2)$$

$$[H_{-2}\mathbf{1}]^{2-} + M^{2+} \rightleftharpoons [MH_{-2}\mathbf{1}] \qquad (3)$$

Each of these two formal equilibria is regulated by its constant, i.e. K_2 and K_3, and it is $K_{red} = K_2K_3$.

The same can be written in the case of $[\mathbf{1}^*]^+$, obtaining eqns (2*) and (3*),

$$[\mathbf{1}^*]^+ \rightleftharpoons [H_{-2}\mathbf{1}^*]^- + 2H^+ \qquad (2^*)$$

$$[H_{-2}\mathbf{1}^*]^- + M^{2+} \rightleftharpoons [MH_{-2}\mathbf{1}^*]^+ \qquad (3^*)$$

and $K_{ox} = K_2^*K_3^*$. Due to electrostatic interactions it must be both $K_2^* > K_2$ and $K_3^* < K_3$, but the effect of the positive ferrocenium fragment on the very unfavourable deprotonation process of the proximate amido groups appears to be so striking that $K_{ox} > K_{red}$.

Log K_{ox} values may be calculated with eqn. (1) on the basis of experimental log K_{red} and ΔE values: the results are listed in Table 1. Noticeably, the log K_{ox} value calculated for the complexation of Cu^{II} ions by ligand **1** *is* 3.9, in fair accord with the 4.0 value found by means of potentiometric titration on the preoxidized ligand $[\mathbf{1}^*]^+$ (see previous subsection).

*(ii) Redox processes centred on the complexed metal: **4b** and $[\mathbf{8}]^{2+}$ as two-centre two-electron redox systems.* The Cu^{II} complex of ligand **1** (**4b**) and the Ni^{II} complex of ligand **2** ($[\mathbf{8}]^{2+}$) display a second, more positive, reversible wave on both CV and DPV experiments, with $E_{1/2} = 951$ mV and 1067 mV vs NHE, respectively. This is assigned to the oxidation of M^{II} to M^{III} on the basis of the comparison with

the behaviour of the corresponding complexes with plain ligands **5** and **6**. $[Cu^{II}[H_{-2}\mathbf{5})]$ is in fact known[30] to undergo a reversible oxidation to a Cu^{III} species in aqueous solution (literature[30] reports $E_{1/2} = 940$ mV vs NHE in 0.5 mol dm^{-3} Na_2SO_4; we found $E_{1/2} = 941$ mV vs NHE in 0.1 mol dm^{-3} $NaClO_4$), while the Ni^{II} complex of ligand **6** undergoes a reversible oxidation to Ni^{III} (we measured $E_{1/2} =$ 1032 mV vs NHE, in 0.1 M $NaClO_4$). Moreover, the more positive wave is absent in the pure ligand and grows in intensity when substoichiometric amounts of metal perchlorate are added to the examined solution, reaching a maximum at a 1:1 molar ratio (pH set at values in which complexation is complete; no variations were observed on addition of further amounts of M^{II}).

Thus complexes **4b** and $[\mathbf{8}]^{2+}$ behave as *two-centre two-electron redox systems*, i.e. are capable of exchanging two electrons at two distinct potentials, being made up of two components each one endowed of independent redox activity. Assembling the two components in a supramolecular system usually results in a not too large variation in their redox potentials with respect to the condition of separation, provided that a 'non-communicating' spacer (e.g. an alkyl chain) is used to connect them and no special interaction is set on between the two components.[13a,15a] This is quite the case or **4b** and $[\mathbf{8}]^{2+}$, as a variation of 10 mV and 35 mV is respectively observed in the complexed metal oxidation potentials with respect to $[Cu^{II}(H_{-2}\mathbf{5})]$ and $[Ni^{II}(\mathbf{6})]^{2+}$. This shift is to be ascribed to the presence of a ferrocenium cation in proximity to the complexed metal, as ferrocene, at the potentials at which the second redox event takes place, is already oxidized.

Finally, also the ferrocene unit must be sensitive to the presence of a proximate charge (i.e. the complexed metal cation). The correct comparison with the separate component is impossible in this case, as one should use ferrocene as reference or, better, an alkyl substituted ferrocene molecule, which are insoluble in aqueous solution. Thus, the ferrocene fragment in the free ligands **1** and **2** must be taken in consideration as the closest available 'separate component' and, as has been exhaustively discussed in the previous subsection, the assembling with a metal complex causes a small but appreciable variation in its potential. Noticeably, **4b** is the first example of two-centre two-electron redox system in which one of the two components undergoes a redox event at a lower potential in the assembled system than as a separate unit.

CONCLUSIONS

The new ferrocene-bearing redox switchable ligands **1** and **2**, featuring good solubility in water and selective binding tendencies toward transition metal cations, have been prepared through a facile synthetic procedure. It has been evidenced that ligand **1** enhances its binding ability toward Ni^{II} and Cu^{II} when its ferrocene subunit is switched to the ferrocenium form, thanks to the favourable electrostatic interactions between the positively charged redox subunit and the leaving amido protons. This suggests that it is possible to create a new class of redox switchable ligands which enhance their binding ability upon oxidation of the redox subunit, provided that the binding subunit loses protons in the complexation process. Thus, ligating fragments such as salicyclic acid, catecol, amides or even amines[31] can be envisaged as possible candidates for the preparation of other systems of this kind.

Moreover, aqueous solutions of the *switched on* ligands and of their complexes can be generated, through controlled potential electrolysis: these solutions are fairly stable, at least under controlled pH conditions. This could allow the use of **1** (and **2**) as a real redox switchable ligand, as it is available in bulk quantities in both of its possible binding states.

EXPERIMENTAL

(Ferrocenyl)methyl-diethyl malonate[32] (**3**), and 1,4,8,11-tetramino undecane-5,7-dione[17] (**5**) were prepared as described in the literature. 1,4,8,11-tetraaza undecane (**6**) was prepared as described for the analogous 1,5,8,12-tetraaza dodecane[33] and distilled at reduced pressure (125 °C, 10^{-2} torr). 1,2-diaminoethane and benzyl diethylmalonate were obtained from Fluka and used without further purification.

UV-visible spectra were recorded on a Hewlett-Packard 8452A diode-array spectrometer, ^1H NMR spectra on a 300-MHz Bruker instrument, IR spectra were obtained on a Perkin-Elmer 1300 infrared spectrophotometer.

6-(ferrocenyl)methyl-1,4,8,11-tetraaza undecane-5,7-dione (1)

8.0 g (22.2 mmol) of freshly prepared (ferrocenyl)methyl-diethyl malonate (**3**) was added in portions to 50 cm^3 of ice-cooled anhydrous 1,2-diamino ethane, under a nitrogen atmosphere. The resulting solution was allowed to slowly return to room temperature and magnetic stirring was maintained for 6 days, after which an orange-brown solution with some suspended orange solid was obtained. Avoiding prolonged contact with atmospheric moisture, the mixture was rotavaporated to 5 cm^3 and the resulting slurry filtered under nitrogen. The obtained solid was repeatedly washed with diethyl ether and 6.5 g of microcrystalline orange-brown product was recovered (76% yield).

Anal. Calcd. for $C_{18}H_{26}FeN_4O_2$: C, 56.00; H, 6.73; N, 14.41. Found: C, 55.84; H, 6.71; N, 14.42. IR (KBr): ν max (cm^{-1}) 3280 (N-H of amido groups), 3080 (C-H of cyclopentadienyl rings), 1650 (C=O)- ^1H NMR (in $CDCl_3$): δ 6.84 (broad t, -NH-CO); 4.12 (m, H of ferrocene); 3.75 (t, $-CH_2-CH-(CONHR)_2$); 3.28 (m, $CONH-CH_2-CH_2$); 3.00 (d, $Fc-CH_2-$); 2.78 (t, $-CH_2-NH_2$); 1.55 (broad, $-NH_2$).

6-(ferrocenyl)methyl-1,4,8,11-tetraaza undecane (2)

1.5 g (3.89 mmol) of **1** were partially dissolved in $100\,cm^3$ of anhydrous THF, under a nitrogen atmosphere. $100\,cm^3$ of a 1 M solution of BH_3 in THF was added and the resulting mixture was kept at reflux for 3 days. A clear orange solution was obtained which was cooled to room temperature, treated with $50\,cm^3$ of CH_3OH and rotavaporated to $10\,cm^3$. The resulting deep orange oily solution was purged with nitrogen and added to a purged mixture of $50\,cm^3$ CH_3OH, $20\,cm^3$ H_2O and $15\,cm^3$ of 12 M HCl, under a nitrogen atmosphere (exclusion of atmospheric oxygen is necessary at this stage, as amino-substituted ferrocenes undergo fast oxidation in acidic solution). The resulting solution was refluxed for 1 h, then cooled to room temperature, made basic with 5 M NaOH and extracted with $3 \times 50\,cm^3$ CH_2Cl_2. The organic extracts were gathered and dried over Na_2SO_4, then rotavaporated to minimum volume. The resulting oily substance contained some buthanol (as an impurity of the BH_3 solution in THF or maybe formed during the prolonged reflux period by cleavage of the THF ring) which was eliminated by heating it at 40 °C, 0.1 torr, for 24 h. 0.8 g of crude product were recovered as a dense oil (57% yield). A 0.30 g portion was further purified by dissolution in diethyl ether and by treatment with gaseous HCl, which caused the formation of a flocky precipitate of **2**·4HCl (0.35 g, 83% yield. Anal. Calcd. for $C_{18}H_{34}Cl_4N_4Fe$: C, 42.91; H, 6.75; N, 11.11. Found: C, 43.05; H, 6.80; N, 10.98). The isolated salt was dissolved in water, treated with excess 5 M NaOH and extracted with $3 \times 20\,cm^3$ CH_2Cl_2. After drying the organic part on Na_2SO_4, 0.21 g of **2** were recovered as a dense oil after evaporation. IR (film, on NaCl pellets): ν max (cm^{-1}) *3190 (>N-H and N-H_2); 3090 (C-H* of the cyclopentadienyl ring). ^1H NMR (in $CDCl_3$): δ 4.09 (m, H of ferrocene); 3.58 (d, $FcCH_2-$); 2.5 (m, $-CH_2-NH$, $-CH_2-NH_2$ and $HN-CH_2-CH(R)-CH_2-NH-$); 1.5 (broad, $-NH_2$).

[6-(ferrocenyl)methyl-4,8-diimido-1,11-diaza undecane-5,7-dione]-copper(II) ($[Cu(H_{-2}1)]$, 4b)

0.2 g (0.52 mmol) of **1** were dissolved in $20\,cm^3$ of a degassed 10:1 water/ethanol mixture, under a nitrogen atmosphere. $5.2\,cm^3$ (0.52 mmol) of a 0.10 M aqueous solution of copper sulphate and $2.1\,cm^3$ of a 0.50 M water solution of sodium hydroxide were added dropwise. The resulting brown-violet suspension was filtered, rotavapored to dryness and the obtained solid treated with $10\,cm^3$ of hot a 6:4 CH_2Cl_2/CH_3OH mixture. Na_2SO_4 was separated by filtration and the solution was allowed to slowly evaporate to give 0.18 g (70% yield) of **4b**, in the form of brown-violet crystalline needles, which include $\frac{1}{2}$ CH_2Cl_2 molecules per molecule of complex (exposition to reduced pressure—5 torr—for 12 h did not change the analysis of the compound). Anal. Calcd. for $C_{18}H_{24}CuFeN_4O_2 \cdot \frac{1}{2}\,CH_2Cl_2$: C, 45.34; H, 5.10; N, 11.43. Found: C, 45.22; H, 5.12; N, 11.28. IR (nujol mull in NaCl pellets): ν max (cm^{-1}) 3250 (N-H_2); 3080 (C-H of the cyclopentadienyl rings); 1580 (C=O).

[6-(ferrocenyl)methyl-4,8-diimido-1,11-diaza undecane-5,7-dione]-nickel(II) ($[Ni(H_{-2}1)]$ 4a)

The synthesis was performed as in the case of **4b**. Yield 52%. The product is in the form of microcrystalline aggregates which include one CH_2Cl_2 molecule per molecule of complex. Anal. Calcd. for $C_{18}H_{24}FeN_4NiO_2$: C, 43.25; H, 4.93; N, 10.61. Found: C, 43.30; H, 5.01; N, 10.63. IR (nujol mull in NaCl pellets): ν max (cm^{-1}) 3250 (N-H_2), 3090 (C-H of the cyclopentadienyl rings), 1580 (C=O).

6-benzyl-1,4,8,11-tetraaza undecane-5,7-dione (7)

1.5 g (5.99 mmol) of benzyl diethyl malonate was added in three portions to $30\,cm^3$ of ice-cooled anhydrous 1,2-diaminoethane, under a nitrogen atmosphere. The resulting solution was stirred at room temperature for 6 days, after which it was rotavapored to $5\,cm^3$ and the resulting slurry filtered under nitrogen. The obtained white solid was washed with diethyl ether and recrystallized from acetonitrile to give 1.3 g of product (78% yield). Anal. Calcd. for $C_{14}H_{22}N_4O_2$: C, 60.45; H, 7.91; N, 20.13. Found: C, 60.38; H, 7.90; N, 20.10. IR (nujol mull in NaCl pellets): ν max (cm^{-1}) 3290 (N-H of amido groups), 1650 (C=O). ^1H NMR (in $CDCl_3$): δ 7.2 (m, 5H, aromatic); 6.7 (broad, 2H, CO-NH-); 3.72 (t, 1H, CO-CH(R)-CO); 3.2 (m, 6H, $C_6H_5-CH_2-$ and $CONH-CH_2-$); 2.68 (t, 4H, $-CH_2-NH_2$); 1.5 (broad s, $-NH_2$).

Diaquo-[(6-(ferrocenyl)methyl-1,4,8,11-tetraaza undecane]-nickel(II) perchlorate ($[8](ClO_4)_2.2H_2O$)

0.150 g (0.42 mmol) of **2** was dissolved in $30\,cm^3$ of nitrogen purged ethanol. Under continuous nitrogen bubbling, 0.14 g (0.38 mmol) of $Ni(ClO_4)_2.6H_2O$ dissolved in $5\,cm^3$ of ethanol was added with a dropping funnel. Immediate precipitation of a yellow solid was observed, which was filtered, washed with diethyl ether, dried under vacuum and stored under nitrogen (0.14 g, 56% yield, based on added metal). Anal. Calcd. for $C_{18}H_{34}Cl_2FeN_4NiO_{10}$: C, 33.16; H, 5.26; N, 8.59. Found: C, 33.11; H, 5.27; N, 8.56. IR (nujol mull in NaCl pellets): ν max (cm^{-1}) 3280 (>NH and -N-H_2), 3080 (C-H of the cyclopentadienyl rings), 1100 (ClO_4^-).

Electrochemistry

Cyclic voltammetry (CV) and Differential Pulse Voltammetry (DPV) were performed in a conventional three-electrode cell with 0.1 mol dm^{-3} $NaClO_4$ as supporting electrolyte, using a PAR 273 potentiostat/galvanostat controlled by an IBM AT personal computer and driven by dedicated software. A saturated calomel electrode, connected to the cell through a salt bridge filled with NaCl solution, was used as the reference electrode. Controlled potential electrolysis experiments were performed employing a platinum gauze as the working electrode.

Potentiometric titrations

Potentiometric titrations in the absence and in the presence of metal ions (as perchlorate salts) were carried out through an automatic system controlled by an Apple IIe computer and consisting of: (i) a Radiometer PHM84 research pH-meter, using a G202B radiometer glass electrode and an Ingold saturated sodium chloride calomel reference electrode, filled in an Ingold cell system; (ii) a Radiometer ABU80 Autoburette; (iii) a Metrom thermostatted cell and (iv) a HETO thermostat. The temperature was maintained at 25 (+/−0.1) °C and each titration was performed on a solution of 50 ml adjusted to a 0.1 mol dm^{-3} ionic strength with $Na(ClO_4)$. Typical concentrations of the ligands and of the metal ions (1/1 molar ratio) were in the $0.5\text{–}1.0 \times 10^{-3}$ mol dm^{-3} range. Details of the experimental procedure have been described elsewhere.[34] The data were processed on a VAX11/870 computer, using SUPERQUAD program.[35]

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