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Electrochemical Signature of the Coordination Mode in Metal Complexes With a tris-Ferrocenyl Derivative of the Taci Ligand

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A new electroactive ligand L built on the Taci (1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol) platform and bearing three chemically equivalent ferrocene units was prepared and characterized. Electrochemical investigations indicate that electrostatic communication occurs between the three ferrocene groups in L, this electrochemical communication being disrupted in the presence of protons or nucleophilic reagents. Upon addition of metal cations, the electroactivity of L is strongly modified and a remarkable electrochemical signature of the coordination mode adopted by the corresponding complexes is obtained.

Keywords: Ferrocene-derivative; Electrochemical recognition; Metal complexes; Electroactive ligand

INTRODUCTION

The study of molecular systems containing metallocene subunits is a subject of great interest in the field of supramolecular chemistry and electrochemistry [1,2]. For example, the design and synthesis of host molecules containing metallocene units which could accommodate metal cations, anions or neutral molecules at their coordination sites and undergo a specific redox change find attractive applications in host–guest chemistry [3–5]. The increase in the number of redox active centers borne by these systems endows them with intriguing electrical and redox properties [1,6,7], which can be exploited in supramolecular electrochemistry. Structures such as linked metallocenes [7–12], metallodendrimers [13–15], or polymers containing metallocene [6,16–18] may present remarkable intramolecular electrochemical communication between their redox centers and the extent of the electrochemical communication in these multi-redox systems can be controlled and modulated in several ways, including protonation or alkylation of the compounds [8,9,13,19], changes in solvent polarity or addition of guest species [20–22].

We describe here the preparation and characteristics of a new polyferrocenyl-substituted ligand derived from 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (Taci) [23] namely 1,3,5-trideoxy-1,3,5-tris(ferrocenemethylamino)-*cis*-inositol (**L**, Scheme 1).

Taci is a remarkable rigid and versatile ligand and its coordinating properties have been investigated thoroughly by Hegetschweiler *et al.* [24]. Indeed, due to its ability to bind metal cations by oxygen or nitrogen donors, this preorganized ligand offers multiple chelating modes for metal binding and is able to form complexes with almost every metal cation.

The coordination modes and the stoichiometry adopted by the complexes of Taci mainly depend on the individual affinity of the metal cation for oxygen or nitrogen donors and also on the charge and size of the cation [24–26]. On Scheme 2 are shown different encountered coordination modes according to the nature of the complexed metal ion. Three general different situations can be met: (i) coordination with the oxygen atoms (as hydroxyl or more preferably as alkoxo group), (ii) coordination with the amino groups and (iii) coordination with both amino and alkoxo groups (mixed (i) and (ii) coordination).

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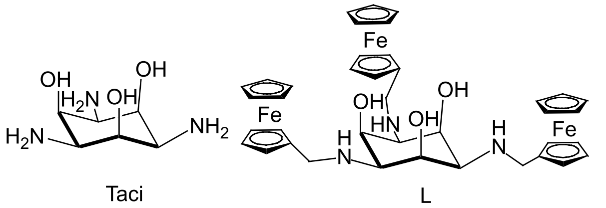


SCHEME 1 Structure of Taci (1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol) and **L** (1,3,5-trideoxy-1,3,5-tris(ferrocenemethylamino)-*cis*-inositol).

Moreover, the ligand in the complex can exist under a zwitterionic (through intramolecular proton transfer from the hydroxyl group to the amino group) or non-zwitterionic form according as the amino group is involved in the first coordination sphere of the bound metal cation.

In the present study, we have introduced redox properties to this ligand by incorporation of ferrocenyl subunits in **L**. It is shown that the presence of these redox active fragments gives an electrochemical signature of the coordination mode of the Taci complexing unit. This is based on the modulation of the intramolecular electrochemical communication between the three equivalent redox centers in the presence of the selected metal cations: the electrochemical features of **L** are deeply modified upon complexation, the type of modification being strongly dependent on the nature of the guest cation.

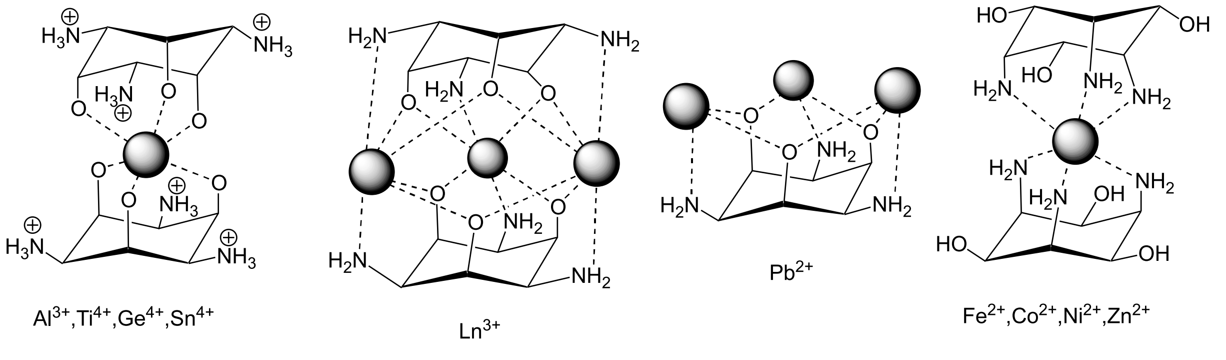
EXPERIMENTAL SECTION

General Information

All solvents and reagents were obtained from commercial suppliers and used without further purification. The precursor Taci used as the sulfate salt was prepared according to literature procedure [23]. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 spectrometer. Chemical shifts are reported in ppm with solvent as internal reference. Mass spectra were acquired on a LCQ-ion trap (Finnigan-Thermoquest, San Jose, USA) equipped with an electrospray source. Electrospray full scan spectra in the range $m/z = 100-2000$ or 2000–3000 amu were obtained by infusion through a fused silica tubing at 2–10 μL/min. The solutions were analysed in the positive mode. The LCQ calibration ($m/z = 50-2000$) was achieved according to the standard calibration procedure from the manufacturer (mixture of caffeine, MRFA and U1-tramark 1621). An ES-Tuning Mix solution (Agilent) was used to calibrate the spectrometer between 2000 and 3000 amu. The temperature of the heated capillary for the LCQ was set to 130°C, the ion-spray voltage was in the range 4–6 kV and the injection time was 5–200 m s. Samples for ES–MS were prepared by dissolving the ligand (10^{-3} M) and the metallic salt in methanol. Elemental analyses were performed by the Service Central d'Analyses (CNRS-France).

Synthesis of L: (1,3,5-Trideoxy-1,3,5-tris(Ferrocenemethylamino)-*cis*-Inositol)

To a suspension of the sulfate salt of Taci [23,27] (0.3 g, 0.925 mmol) in methanol (25 mL), 3.9 equivalents of KOH (0.202 g, 3.608 mmol) were added and the mixture was stirred at room temperature for 30 min. 3.3 equivalents of ferrocenecarboxaldehyde (0.653 g, 3.052 mmol) were then added and the solution was stirred overnight at room temperature. After cooling to 0°C, 13 equivalents of sodium borohydride (0.455 g, 12.02 mmol) were added in small portions and the mixture was stirred for 4 h at room temperature. The solution was then concentrated under vacuum. The residue was taken up in water (50 mL) and the solution was extracted with CH_2Cl_2 (8 × 50 mL). Organic layers were collected, dried over sodium sulfate and evaporated. The yellow residue was purified by precipitation upon dissolution in a minimum of CH_2Cl_2 and slow addition of CH_3CN to give **L**.0.41 Na_2SO_4 (0.469 g) in 61% yield. The microanalysis of C, H and N reveals the presence of an inorganic salt that is 7% of the total mass. This percentage is consistent with the potentiometric titrations as well as with the ^{1}H NMR



SCHEME 2 Different coordination modes observed in the solid state for the metal complexes of Taci.

titration using an internal reference. The inorganic salt was identified by capillary electrophoresis as Na_2SO_4 (Na: 2.24%). ^1H NMR (400 MHz, CD_3OD): δ_H 4.33 (6H, s, Fc); 4,27 (3H, s, $HC_{cycle}{-}OH$); 4,19 (15H, s, Fc); 4,15 (6H, s, Fc); 3,72 (6H, s, $Fc{-}CH_2$); 2,43 (3H, s, $HC_{cycle}{-}NH$). ^{13}C NMR (100 MHz, CD_3OD): δ_C 44.53 (CH_2); 56.36 (CHNH); 68.08 (C_5H_4); 68.47 (C_5H_5); 68.94 (C_5H_4); 69.95 (CHOH). Found: C, 56.44; H, 5.43; N, 5.16; Na, 2.24%. Calc. for $C_{39}H_{45}Fe_3N_3O_3$. 0.41 Na_2SO_4 C, 56.47; H, 5.47; N, 5.07; Na, 2.27%. ES–MS: m/z 771.9 $[M + H]^+$.

Potentiometric Measurements

Solutions of supporting electrolyte, KCl or tetra-*n*-butylammonium trifluoromethanesulfonate (TBAOTf), ligand, base and acid were prepared in methanol or in methanol/water 75/25 v/v (water was obtained by Millipore/milliQ system and methanol was of analytical grade). Carbonate-free solutions of KOH were prepared by dissolution of KOH pellets in methanol or from standardized solutions. HCl solutions were prepared from standardized solutions and triflic acid (HOTf) solutions by diluting pure HOTf in water/methanol or methanol. All potentiometric titrations were carried out at 25.0 ± 0.1°C. Potential values were measured with a Metrohm combined glass electrode. Atmospheric CO_2 was excluded from the cell during the titration by passing Ar across the top of the experimental solution in the reaction cell. The titrant solutions were dispensed from a Metrohm 751 piston burette. The $[H^+]$ of the solutions was determined by measurement of the electromotive force of the cell, $E = E'^0 + Q\log[H^+] + E_j$. E'^0 and Q were obtained from previous calibrations. The liquid-junction potential, E_j, was negligible under the experimental conditions used. K_w was determined from the alkaline region of the titration curve. The value of $K_w = [H^+][OH^-]$ was found to be equal to $10^{-13.85}$ in methanol/water (3:1, v/v) and $10^{-15.70}$ in methanol. The potentiometric equilibrium measurements were made on 20 mL solutions containing 10–20 μmol of the ligand and at an ionic strength of 0.10 M. Protonation constants $K_i^H = [H_iL]/[H_{i-1}L][H]$ were calculated by fitting the potentiometric data obtained for the ligand using the program HYPERQUAD [28,29].

Electrochemical Studies

Experiments were conducted at room temperature in a 1 mL three-electrode cell using a CH Instrument potentiostat (CHI 660B). The Ag/10 mM $AgNO_3$ + 0.1 M tetra-*n*-butylammonium trifluoromethanesulfonate (TBAOTf) in CH_3OH was used as a reference electrode. All the data are referred to the regular Fc/Fc^+ redox (the potential of the regular Fc/Fc^+ redox couple used as an internal standard was −0.150 V vs Ag/10 mM $AgNO_3$ under our experimental conditions). The working electrode consisted of a platinum disk (2 mm diameter) polished with 2 μm diamond paste. DPV curves were recorded at a 10 mV s^{-1} scan rate with pulse height of 25 mV and a step time of 0.2 s. CV curves were recorded at a sweep rate of 0.1 V s^{-1}.

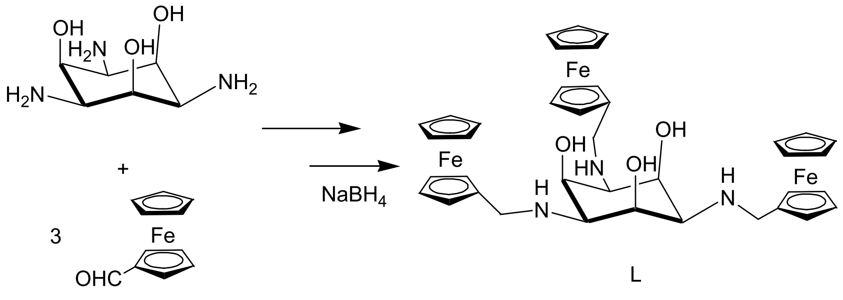
RESULTS AND DISCUSSION

Synthesis

As previously described for alkylation of Taci with carbonated chains [29], the one-pot preparation of 1,3,5-trideoxy-1,3,5-tris(ferrocenemethylamino)-*cis*-inositol, **L** has been performed in methanolic solution by treatment of the sulfate salt of Taci with a slight excess of ferrocenemonocarboxaldehyde, followed by the *in situ* reduction of the formed imines, carried out by using sodium borohydride (Scheme 3). **L** was obtained as **L**.0.41 Na_2SO_4 (this percentage of inorganic salt is in accordance with ^1H NMR titration using an internal reference). Unfortunately, further recrystallization attempts to remove the additional inorganic salt were unsuccessful, due to the partial degradation of the ligand by heating.

Protonation Constants of L

The protonation constants of **L** have been determined in different media from potentiometric



SCHEME 3 Preparation of **L**.

TABLE I Protonation constants ($\log K_i^{\mathrm{H}}$) for **L** determined in different solutions (25°C; 0.10 M ionic strength)

Supporting electrolyte MeOH/H_2O ratios (v/v)	[H**L**]/[**L**][H]	[H_2**L**]/[H**L**][H]	[H_3**L**]/[H_2**L**][H]	[H_3**L**]/$[H]^3$[**L**]	[**L**H_{-1}][H]/[**L**]
KCl 75/25	8.2(1)	7.1(1)	5.8(1)	21.1	-9.9(1)
TBAOTf 75/25	8.1(2)	7.1(1)	5.9(2)	21.1	-9.6(3)
TBAOTf 100/0	10.3(1)	9.3(1)	7.8(2)	27.4	Ignored

titration experiments. Results are given in Table I. In each case, three constants corresponding to the protonation of amino groups have been calculated. These values are close to those obtained with other *N*-alkylated-Taci derivatives in the same experimental conditions: the protonation constants of **L** are higher than the corresponding ones found for 1,3,5-trideoxy-1,3,5-tris(benzylamino)-*cis*-inositol and lower than for 1,3,5-trideoxy-1,3,5-tris(hexylamino)-*cis*-inositol [30]. The separation of the pK^{H} values is in the range 1–1.5, and is higher than the statistical separation ($\log 3 = 0.48$). The protonation of an amino group is thus influenced by other amino groups that are already protonated, in agreement with the short chain, 3 carbon atoms, separating each amino group. In methanol/water (75/25 v/v) a higher pK_a is also found probably corresponding to the deprotonation of an alcohol group of the ligand. The high acidity of this alcohol function is unusual, and has already been reported for an another derivative of Taci, 1,3,5-trideoxy-1,3,5-tris(trimethylamonio)-*cis*-inositol in water [22].

Unfortunately, precipitation of metal complexes during the titration with a strong base (KOH) either in water methanol mixtures or in pure methanol prevented the determination of the affinity constants of metallic species of this ligand.

Electrochemical Results

The electrochemical study was carried out by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in methanol containing 0.1 M tetra-*n*-butylammonium trifluoromethanesulfonate (TBAOTf) as the supporting electrolyte. With tetra-*n*-butylammonium perchlorate as supporting electrolyte or when other solvents (CH_2Cl_2, aqueous methanol...) are used, the poor solubility of electrogenerated compounds was responsible for adsorption phenomena and led to the observation of complex voltammograms. The potentials are referred to the regular ferrocene/ferrocenium redox couple, used as an internal reference.

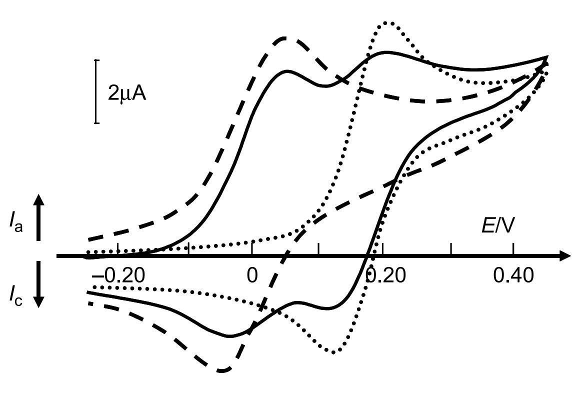


FIGURE 1 CV curves of 1 mM **L** in CH_3OH +0.1 M TBAOTf. Solid line free **L**, dashed line: **L** + NEt_3 (5 eq.), dotted line: **L** + H^+(3 equiv.). *E* vs Fc/Fc^+.

Electrochemical Behavior of L

The curve CV for free **L** in MeOH + 0.1 M TBAOTf revealed the presence of two partially overlapped waves at $E_{1/2} = -10$ mV and $E_{1/2} = +161$ mV respectively, with ΔE_p close to 75 mV for both processes (Fig. 1). Better-resolved voltammetric curves were obtained from DPV experiments (Fig. 2): two well-behaved peaks were seen at -8 and $+164$ mV respectively.

The three ferrocene groups in **L** being chemically equivalent, the observation of two distinguishable signals was attributed to electrostatic interactions through space occurring between the three redox centers, i.e. the oxidation of the initial ferrocene perturbes the two other metallocene groups in the molecule which then oxidize at higher potentials,

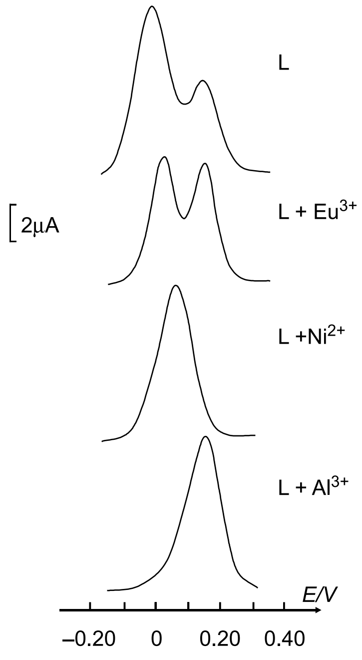


FIGURE 2 DPV curves for **L** (1 mM in CH_3OH +0.1 M TBAOTf) and **L** in the presence of Eu^{3+}(0.75 equiv.), Ni^{2+}(1 equiv.), and Al^{3+}(1 equiv.) cations (these curves correspond to the maximum perturbation of the signal).

TABLE II DPV and CV data for free **L**, protonated **L**, **L** in the presence of Et_3N and **L**–metal complexes[a,b]

	L	**L**+H^+	**L**+Et_3N	**L**+Ni^{2+}	**L**+Eu^{3+}	**L**+Pb^{2+}	**L**+Al^{3+}
E_p (DPV)/mV	−8, +164	+164	−13	+66	+27	+28	+177
$E_{1/2}$ (CV)/mV	−10, +161	+164	−10	+64	+33	+29	+175

[a] Data referred to the regular Fc/Fc$^+$ couple. [b] Data measured after stabilization of the signal.

leading to several oxidation signals by CV or DPV. Indeed, in a molecule with three fully noninteracting equivalent redox centers, a separation ΔE^0 of $(RT/F)\ln 3^2$, i.e. 57 mV, between the first and third electron transfer is expected, leading to the observation of a unique voltammetric curve having the shape of a single electron transfer reaction (one voltammetric wave by CV with $\Delta E_p \sim 60$ mV, and a single peak by DPV). In contrast, significant electronic or electrostatic communication between these three redox centers lead to larger ΔE^0 values and, therefore, to the observation of several CV waves [31,32].

Such electrostatic interactions through space have been encountered in several close compounds containing multiple chemically equivalents ferrocenyl groups connected through calixarene [21,22], oxazolo [10], silicon [14], or amino groups [8,9,13,20]. In these systems, the degree of electrochemical communication between the redox groups is strongly dependent on the polarity of the solvent: the intramolecular communication is maximal in very low polar solvents and can be fully disrupted upon addition of polar solvent. This decrease in the interactions was attributed to the interposition of polar species between the ferrocenium moities [21,22]. In the same way, protonation can be responsible for disruption of electrochemical communication in nitrogen bridged polyferrocene derivatives [8,9,13,20].

The electrochemical behavior of **L** (CV and DPV) was thus examined in the presence of triflic acid (Table II and Fig. 1). Progressive addition of this acid produced the extinction of the first signal and the increase of the second one. The maximal perturbation, i.e full disappearance of the first CV-wave at $E_{1/2} = -10$ mV and full development of the second one at $E_{1/2} = +161$ mV is reached in the presence of 3 molar-equivalents in acid corresponding to the protonation of the three amino groups in **L**. All these variations are linear against the quantity of protons added. This shift to more positive potential upon protonation is due to the electron-withdrawing effect induced by the introduction of positive charges on the nitrogen atoms. Moreover, the observation of a unique electrochemical signal for $\mathbf{L}H_3^{3+}$ indicates that the initial electrochemical communication in **L** is cancelled upon protonation.

In the same manner, the interactions through space in **L**, responsible for the splitting of the CV and DPV curves appear strongly affected by the addition of polar species. In particular, in the presence of increasing amounts of OH^- or triethylamine in a methanolic solution of **L**, the second DPV peak at +164 mV gradually disappears and the first peak at ca. 0 V increases in intensity. In the presence of an excess in added OH^- or triethylamine (4 molar equiv), one peak solely remains at −4 or −13 mV respectively (Fig. 1). As it is unambiguously shown by considering the values of protonation constants of **L** obtained in methanol (see Table I), this behavior cannot be due to the deprotonation of the hydroxyl groups of **L** under these conditions and was attributed to the interposition of the added nucleophilic species between the ferrocene moities, causing a decrease in the interaction between these metallocene groups. Such effect, also observed with tris-ferrocene substituted calixarene derivative, has been previously exploited for the electrochemical sensing of neutral species [20]. It should be outlined that the presence of an inorganic salt (Na_2SO_4) in the starting product has no observable influence on the electrochemical behavior of **L**. Indeed, addition of Na^+ or K^+ cations did not change the CV or DPV curves.

In summary, the electrochemical behavior of **L** indicates that intramolecular communication takes place between the three metallocene groups, leading to the observation of two signals. Upon protonation or in the presence of an exogenous nucleophile, this electrochemical communication between the three ferrocene units is cancelled since one electrochemical signal only is obtained. This result, previously reported for close amino-ferrocenyl-substituted compounds [8,9,13,20,33], in the presence of added protons, indicates that the lone pairs of the amine functions are involved in the communication between the ferrocene groups in **L**. Indeed, the lone pair on the amino group is no longer available to ensure the communication upon protonation or can no more effectively interact with the electrogenerated ferrocenium in the presence of a competitive nucleophilic agent.

Electrochemical Behavior of L in the Presence of Metal Cations

As mentioned above, the stoichiometry and the coordination mode of complexes formed with the Taci ligand strongly depend on the nature of the metal center: hard metal cations are coordinated at the oxygen groups whereas soft metal cations bind the amine groups. Since the electrochemical behaviour of **L** depends on the status of its nucleophilic group, it can be anticipated that the change of the electroactivity of **L** in the presence of a given metal ion will be indicative of the coordination mode and of the nature of the metal ion.

As expected, the progressive addition of Eu^{3+}, Pb^{2+}, Al^{3+} and Ni^{2+} in a methanol solution of **L** caused strong modifications in its electroactivity depending on the added metal cation. The DPV curves recorded in the presence of these metal cations upon stabilization of the signal are represented in Fig. 2.

TABLE III Electrospray mass spectrometry data (m/z) for **L** complexes with metallic cations in methanol[a]

Salt	Complex	m/z
$\mathrm{Ni(OAc)_2}$	$[\mathrm{Ni}\mathbf{L}\mathrm{OAc}]^+$	888
$\mathrm{Zn(OAc)_2}$	$[\mathrm{Zn}\mathbf{L}\mathrm{OAc}]^+$	894
$\mathrm{Pr(OTf)_3}$	$[\mathrm{Pr_3}(\mathbf{L}-3\mathrm{H})_2(\mathrm{OTf})_2]^+$	2257
	$[\mathrm{Pr_3}(\mathbf{L}-3\mathrm{H})_2(\mathrm{OTf})]^{2+}$	1054
$\mathrm{Eu(OTf)_3}$	$[\mathrm{Eu_3}(\mathbf{L}-3\mathrm{H})_2(\mathrm{OTf})_2]^+$	2291
	$[\mathrm{Eu_3}(\mathbf{L}-3\mathrm{H})_2(\mathrm{OTf})]^{2+}$	1071
$\mathrm{Lu(OTf)_3}$	$[\mathrm{Lu_3}(\mathbf{L}-3\mathrm{H})_2(\mathrm{OTf})_2]^+$	2359
	$[\mathrm{Lu_3}(\mathbf{L}-3\mathrm{H})_2(\mathrm{OTf})]^{2+}$	1105
$\mathrm{Pb(NO_3)_2}$	$[\mathrm{Pb_3}(\mathbf{L}-3\mathrm{H})(\mathrm{NO_3})_2]^+$	1514
	$[\mathrm{Pb_3}(\mathbf{L}-3\mathrm{H})(\mathrm{NO_3})(\mathrm{OCH_3})]^+$	1483

[a] Only the m/z peaks corresponding to the most abundant isotopic mass are reported.

Electrochemical Behavior of L in the Presence of Ni^{2+} Cations

Addition of Ni^{2+} cations in a methanolic solution of **L** results in a $\mathrm{Fc/Fc^+}$ two-wave behaviour, i.e. the growth of a new $\mathrm{Fc/Fc^+}$ redox signal ($E_{1/2} = +64\,\mathrm{mV}$ by CV and $E_\mathrm{p} = +66\,\mathrm{mV}$ by DPV), at the expense of both original signals for free **L** (Figs. 2 and 3). The new signal reaches full development after the addition of one molar equivalent of nickel salt suggesting the formation of a 1:1 complex, according to $\mathbf{L} + \mathrm{Ni}^{2+} \rightarrow \mathbf{L}\mathrm{Ni}^{2+}$.

Since Ni^{2+} is a transition metal cation and by comparision with previous results obtained with the parent Taci [26], it can be anticipated that the coordination mode involves the amino groups, the hydroxyl groups remaining uncoordinated. The observation of a unique wave in the presence of Ni^{2+} cation indicates that the formation of the Nickel complex disrupts the electrochemical communication between the three ferrocene subunits in **L**, as it was previously observed with a tren-ferrocene derivative [20]: metallation at the amino groups parallels protonation, both phenomena making the lone pairs unavailable. The 1:1 (Ni^{2+}:**L**) complexation has been further confirmed by ES mass spectrometry (Table III). The ES–MS spectra of methanolic solution of **L** and Ni^{2+} (as its acetate salt) at several molar ratio displayed a signal at $m/z = 888$, corresponding to the $[\mathrm{Ni}\mathbf{L}(\mathrm{OAc})]^+$ monocation, whereas ions coming from the complex NiL_2^{2+} are not detected. In the case of Taci, the formation of a NiL_2^{2+} complex was observed in the solid state, whereas the two stoechiometries NiL and $\mathrm{NiL_2}$ were evidenced in water solution [26]. Our electrochemical results are consistent with the ES–MS data and a final 1/1 stoichiometry. Indeed, it is likely that the steric effects due to the three metallocene units in **L** disfavour the formation of the 1:2 complex, as the ion is coordinated by the nitrogen atoms of the ligand. In addition, Zn^{2+} cation was used for the ES–MS study and the formation of a 1:1 (M:**L**) complex was also observed (Table III).

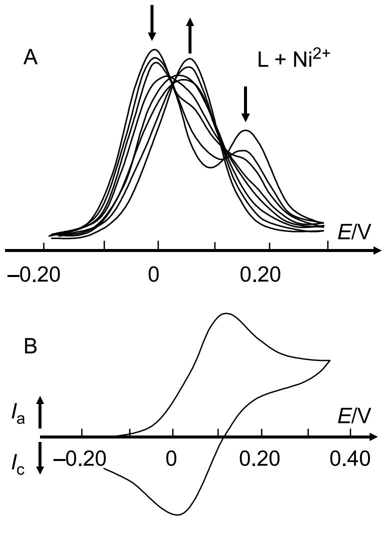


FIGURE 3 (A) DPV curves for **L** (1 mM in $\mathrm{CH_3OH}$ +0.1 M TBAOTf) in the presence of increasing amount of Ni^{2+} cations (0–1 molar equiv.), and (B) CV curve of $\mathbf{L}$ + 1 equiv. Ni^{2+}.

Electrochemical Behavior of L in the Presence of Eu^{3+} And Pb^{2+} Cations

The electrochemical behavior of **L** in the presence of increasing amounts of Eu^{3+} is characterized by the progressive appearance of two CV-waves at $E_{1/2}$ +33 and +166 mV with $\Delta E_\mathrm{p} = 65\,\mathrm{mV}$ for both signals and of two DPV-peaks having similar intensities at +27 and + 164 mV. This evolution is stabilized when 0.75 molar equiv. in Eu^{3+} has been added (Figs. 3 and 4). This result suggests the formation of a 3:2 (Eu^{3+}:**L**) complex which can be formulated as $[(\mathbf{L}-3\mathrm{H})_2\mathrm{Eu}_3]^{3+}$. During the electrochemical titration, the free **L** plays two roles: it acts as a ligand for Eu^{3+} and also as a base. The overall process can be summarized by the following mass balance:

$$1\mathbf{L} + 0.75\mathrm{Eu}^{3+} \rightarrow 0.25[(\mathbf{L}-3\mathrm{H})_2\mathrm{Eu}_3]^{3+} + 0.5\mathbf{L}\mathrm{H}_3^{3+}$$

In this reaction, the formation of one mole of the 3:2 (M:L) sandwich complex is accompanied by the protonation of two moles of ligand that are no longer

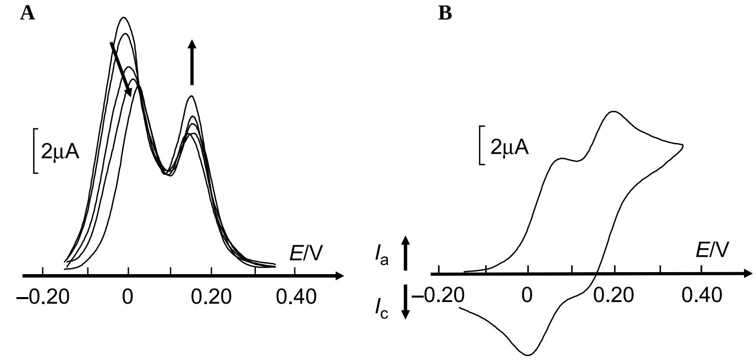


FIGURE 4 (A) DPV curves for **L** (1 mM in CH_3OH +0.1 M TBAOTf) in the presence of increasing amount of Eu^{3+} cation (0–0.75 molar equiv.) and (B) CV curve of **L** + 0.75 Eu^{3+}.

available for the complexation of Eu^{3+}. Accordingly, the final electrochemical response displays the superimposition of the signal due to $[(\mathbf{L}-3H)_2Eu_3]^{3+}$ at +27 mV and that due to the protonated ligand at +164 mV. The formation of $[(\mathbf{L}-3H)_2Eu_3]^{3+}$ which can be described as a sandwich complex in which each Eu^{3+} cation is coordinated by three alcohol and three amine groups (See Scheme 2) is in full agreement with the previous results established for the Taci ligand [25,34,35] and other *N*-substituted derivatives [24,30].

On the other hand, when an excess of base is added in the solution containing $(\mathbf{L}-3H)_2Eu_3^{3+}$ and $\mathbf{L}H_3^{3+}$, the second peak due to the protonated ligand at +164 mV disappears and a new peak, partially overlapped with the first signal at +27 mV, is obtained at −8 mV: it corresponds to the oxidation of free **L**. At this stage, an additional amount of Eu^{3+}(0.75 equiv.) can be complexed by the *in situ* deprotonated $\mathbf{L}H_3^{3+}$ and a solution containing only the $(\mathbf{L}-3H)_2Eu_3^{3+}$ complex and Et_3NH^+ is obtained.

A simpler DPV titration profile can be obtained by performing the titration in the presence of three molar equivalents of base (Et_3N). Under this experimental conditions, a two-wave behavior has been obtained: the initial peak at −8 mV for the electrochemical response of **L** in basic medium vanishes progressively at the expense of a single peak at +27 mV due to the response of the $[(\mathbf{L}-3H)_2Eu_3]^{3+}$ complex (Fig. 5). In agreement with the following mass balance,

$$1\mathbf{L} + 1.5Eu^{3+} + 3B \rightarrow 0.5[(\mathbf{L}-3H)_2Eu_3]^{3+} + 3BH^+$$

$$(B = \text{triethylamine})$$

the maximal perturbation is reached when 1.5 molar equivalent in Eu^{3+} has been added.

The 3:2 coordination mode for the complex formed between (**L**–3H) and Eu^{3+} has been further confirmed by ES mass spectrometry (Table III and Fig. 6). The ES–MS spectra of a methanolic solution of **L** and Eu^{3+} (as its triflate salt) at different molar ratio displayed characteristic signals of a 3:2 (M:L) complex: the dication $[(\mathbf{L}-3H)_2Eu_3(OTf)]^{2+}$ at $m/z = 1071$ and the monocation $[(\mathbf{L}-3H)_2Eu_3(OTf)_2]^+$ at $m/z = 2291$. It should be outlined that similar results, i.e. signals corresponding to 3:2 (M:L) complexes, have been also obtained with other lanthanide cations as Pr^{3+} and Lu^{3+} cations (Table III).

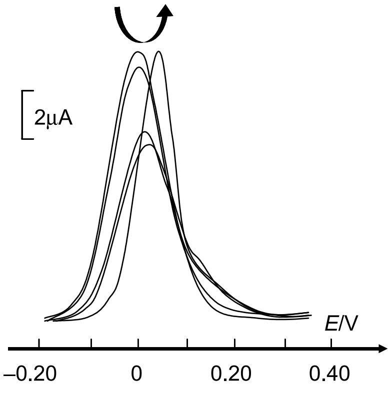


FIGURE 5 DPV curves of 1 mM **L** + 3 equiv. Et_3N in CH_3OH + 0.1 M TBAOTf in the presence of increasing amounts of *Eu* $^{3+}$ cation.

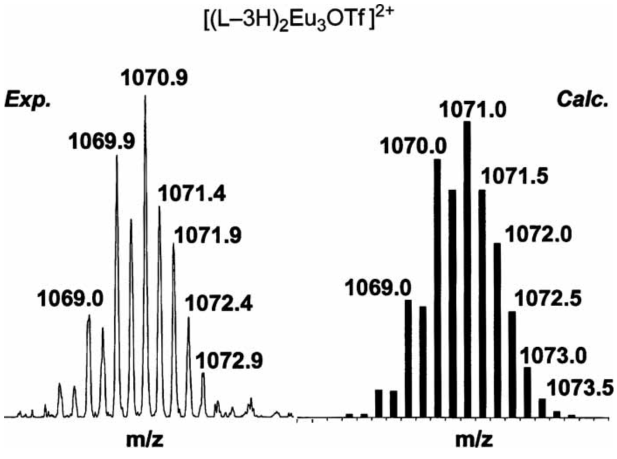


FIGURE 6 Experimental and calculated ES–MS spectra of $[(\mathbf{L}-3H)_2Eu_3(OTf)]^{2+}$.

A similar result has been found with Pb^{2+}. In the absence of base added, from 0 to 1.5 molar equiv. in Pb^{2+}, the initial electrochemical signals of the free ligand are gradually replaced by the one attributed to the complex characterized by a DPV peak at +28 mV and a second peak at higher potential attributed to the formation of $\mathbf{L}H_3^{3+}$. No further modifications in the DPV behaviour of the solution have been observed above 1.5 molar equiv. of Pb^{2+}. The overall process can be summarized by the following mass balance, suggesting, as with the ligand Taci [34], a 3:1 (M:**L**) stoichiometry:

$$\mathbf{L} + 1.5Pb^{2+} \rightarrow 0.5[(\mathbf{L}{-}3H)Pb_3]^{3+} + 0.5\mathbf{L}H_3^{3+}$$

The 3:1 stoichiometry has been further suggested from the ES–MS spectra of methanolic solutions of $\mathbf{L} + Pb^{2+}$ which showed signals at $m/z = 1514$ and 1483 (isotopic peak separation = 1) corresponding to $[Pb_3(\mathbf{L}{-}3H)(NO_3)_2]^+$ and $[Pb_3(\mathbf{L}{-}3H)(NO_3)(CH_3O)]^+$ respectively.

As with Eu^{3+}, the DPV titration profile is simpler in the presence of a base added, the initial single peak corresponding to the free ligand in basic medium at −8 mV being progressively replaced by the one of the complexed ligand at +28 mV, according to the following reaction:

$$\mathbf{L} + 3Pb^{2+} + 3B \rightarrow [(\mathbf{L}{-}3H)Pb_3]^{3+} + 3BH^+$$

$$(B = \text{triethylamine})$$

Thus, for the metal complexes with **L** involving alcoholic and amine donor groups, the free ligand acts as a base during the titration and the final DPV curve displays the overlapping of both protonated and complexed ligand responses. In the presence of an exogeneous base, a more classical modification in the electrochemical response of the solution upon addition of the guest metal cation can be obtained, characterized by the appearance of the signal of the complex and the full disappearance of the signal of the free ligand.

The oxidation potentials of the Pb^{2+} or Eu^{3+} complexes are close since the coordination mode for both complexes involves the same donor atoms, amine and alcohol, and they are slighly lower than the one corresponding to the oxidation of the nickel complex involving only the amine donor groups. It should be also outlined that, in all these complexes, the initial electrochemical communication is disrupted leading to the observation of a single three-electron wave.

Electrochemical Behavior of L in the Presence of Al^{3+} Cations

In order to prevent the hydrolysis of Al^{3+}cation, the study was performed in a dry glovebox, under an inert atmosphere (argon). When Al^{3+} was added to a solution of **L**, the evolution of the electrochemical signal (Fig. 7A) was completely different from that previously obtained with Ni^{2+}, Eu^{3+} or Pb^{2+}. Indeed, the addition of increasing amounts of Al^{3+} in an electrolytic solution of **L** causes an increase in the intensity of the DPV peak at +0.16 V which undergoes a small positive shift, along with the progressive desappearence of the peak at 0 V. This evolution was stabilized when one-molar equivalent of Al^{3+} was added. At this stage, a single DPV-peak at +177 mV and one reversible CV-wave at +175 mV ($\Delta E_p = 81$ mV) is observed. This behavior is attributed to the formation of a 1:1 $\mathbf{L}{-}Al^{3+}$ complex according to the mass balance: $\mathbf{L} + Al^{3+} \rightarrow \mathbf{L}Al^{3+}$. Unfortunately, ES–MS data allowing the confirmation of this 1:1 binding mode between **L** and Al^{3+} ions could not be obtained from solution containing **L** and Al^{3+}. Similarly to the corresponding complex formed with Taci and other derivatives [36–38], the formation of a unique electrochemical signal around +175 mV indicates that the hard metal cation is coordinated by the alkoxo groups of **L**, the protons of the hydroxyl groups in **L** being transferred to the amino groups with formation of ammonium subunits.

The coordination mode of the hard metal cation by a zwitterionic form of the ligand which involves ammonium-substituted ferrocenyl moieties is corroborated by the oxidation potential of the complex ($E_p = +177$ mV) close to the one of protonated **L** ($E_p = +164$ mV). It can be underlined that these potentials are far from that found with Ni^{2+}, Eu^{3+} and Pb^{2+}. In addition, the electrochemical response of the complex was shown to be highly sensitive to the presence of an exogenous base: upon addition of

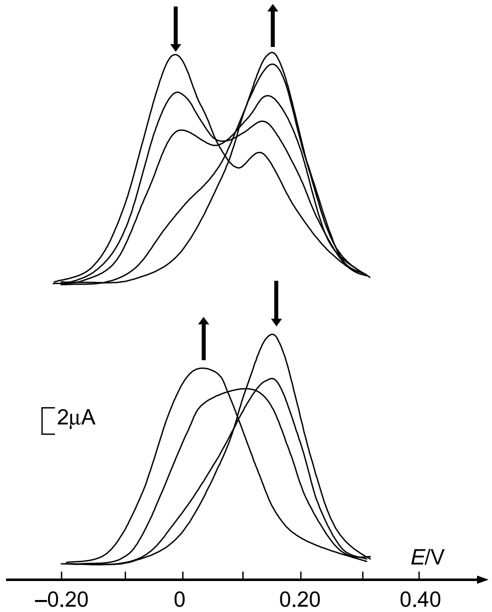


FIGURE 7 (A) DPV curves for **L** (1 mM in CH_3OH +0.1 M TBAOTf) in the presence of increasing amount of Al^{3+} cation (0–1 molar equiv.) and (B) DPV curves for $\mathbf{L}Al^{3+}$ in the presence of increasing amount of Et_3N.

NEt_3 in the solution of the previously formed complex, a pH-induced two-wave behavior is observed with the growth of a large peak at +37 mV at the expense of the original one at +177 mV (Fig. 7B). This behavior is logically attributed to the deprotonation of the ammonium-substituted ferrocenyl moieties in the Al^{3+}-complex, leading to the formation of the corresponding Al^{3+}-complex with amino-substituted ferrocenyl groups which are oxidized at +37 mV.

Moreover, it should be underlined that the presence of sodium salt in the starting material has no influence on the recognition properties of **L** towards the metal cations used in this work. Indeed, if the formation of a Na^+-complex can be reasonably envisaged (by analogy with the Taci results), its stability would be very low compared to the other studied complexes of **L** (this Taci derivative is logically a very poor ligand for group 1 metal cations). Moreover, in this Na^+-complex, **L** would act as a simple polyalcohol ligand and the formation of Na^+-alcohol bonds would have no significant effects on the redox properties of **L**, i.e. the ferrocene moities would not be perturbed by the formation of this sodium-complex.

CONCLUSION

In conclusion, the three equivalent ferrocene subunits in **L** show a significant degree of intramolecular electrochemical communication that can be disrupted by protonation or in the presence of exogenous nucleophilic species. In the presence of metal cations, the electroactivity of **L** is strongly modified and a remarkable electrochemical signature of the coordination mode adopted by the corresponding complexes is obtained. The metal–ligand ratio in the complexes is determined from the molar ratio corresponding to the stabilization of the CV or DPV signal evolution observed upon addition of the selected metal cation in a solution of **L**. In the case of transition metal cations where the ligand behaves as a simple tripodal amine, a unique electrochemical signal corresponding to the electroactivity of the complex is obtained. On the contrary, in the presence of Ln^{3+} or Pb^{2+} cations, the formation of the complex through the formation of metal–alkoxo bonds is accompanied by the formation of $\mathbf{L}H_3^{3+}$, **L** acting as an internal base: two signals due to the electroactivities of both the complex and $\mathbf{L}H_3^{3+}$ are thus observed. In the presence of Al^{3+}, the ligand adopts a zwitterionic form and a unique electrochemical signal is obtained, attributed to the oxidation of the ferrocene–ammonium fragment in the Al^{3+}-complex. Moreover, the observation of a unique electrochemical signal in the complexes indicates that the electrochemical communication in **L** is disrupted upon formation of the complexes.

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