Modulation of the Communication between Redox Centers in a Tris(ferrocene)-tren Ligand by Complexation of Lanthanide Ions

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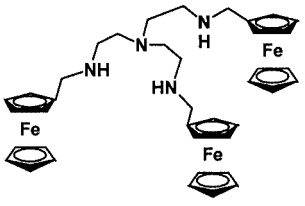
The tripodal ligand L built on the tren platform and bearing three chemically equivalent ferrocene units was prepared and characterized. Electrochemical investigations indicate that electrostatic communication occurs between the three ferrocene groups in L, which leads to the observation of two distinct voltammetric waves. The electrochemical communication between the three ferrocene moieties is disrupted in 1:1 ($L:M^{3+}$) type complexes formed between L and Y^{3+} or Eu^{3+} metal cations and their electrochemical response tends towards that of a single three-independent-electrons oxidation wave. Modulation of the electrochemical properties of L in the presence of lanthanide ions might be exploited with a view to their electrochemical sensing in organic and aqueous media.

Introduction

Macromolecular systems containing multiple redox active centers have been the subject of numerous studies due to their intriguing electrical and redox properties, and their potential use as functional nanostructured materials.[1−3] In particular, structures such as linked metallocenes,[3−7] metallodendrimers,[6,8,9] or polymers containing metallocenes[2,10,11] may present remarkable intramolecular electrostatic communication throughout the redox active sites due to their spatial proximity. An interesting feature of the multi-redox systems is that the extent of communication between the redox centers can be controlled and modulated in several ways, including protonation or alkylation of the compounds,[4−7,12] or changes in solvent polarity[5,13] and supporting electrolyte composition.[14] Here, we report how the degree of electrostatic communication between three chemically equivalent redox centers in the tren-based tris(ferrocene) ligand L is deeply changed upon complexation of the secondary nitrogen bridging atoms by Eu^{3+} and Y^{3+} ions.

Moreover, important applications in sensors are envisaged for multi-redox molecules and macromolecular systems, with the opportunity of coupling the interactions of analyte-redox material into transducible responses.[15−17] We demonstrate that the very simple redox receptor L might be used for the electrochemical detection and titration of lanthanide ions (Eu^{3+} and Y^{3+} which is considered as a pseudo lanthanide), through the modification of the interactions between the redox active groups that occurs in the presence of these guests metal cations.



L

Results and Discussion

The homotrimetallic ligand L used in this study is based on the tripodal tetramine tren, namely the tris(2-aminoethyl)amine, which is a well-known ligand for metal cations[18] and an excellent platform on which to build sensing devices. For example, a redox-responsive receptor[19] for

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halide anions and fluorescent sensors[20−22] for the recognition of anions, transition metals or protons have been developed by linking cobaltocenium[19] and photoactive fragments[20−22] to the tren unit.

Synthesis and Characterization of L

The tripodal receptor L was readily synthesized in a two-step procedure. Reaction of the tris(2-aminoethyl)amine with three equivalents of ferrocenecarboxaldehyde in biphasic media (water/diethyl ether) allows the precipitation of the trisimine intermediate, which is further reduced with sodium borohydride to produce L as an oily solid. Crystals of the protonated form of L could be obtained from a solution containing L along with ten equivalents of HCl_{aq}. It has to be noted that the solid state of the hydrochloride form of L is highly unstable and fuses rapidly when manipulated at room temperature. This results in a poor quality crystal. However, the data collection (Table 3) undoubtedly reveals a triply-protonated molecular structure, LH_3^{3+}, $3Cl^-$, depicted in Figure 1.

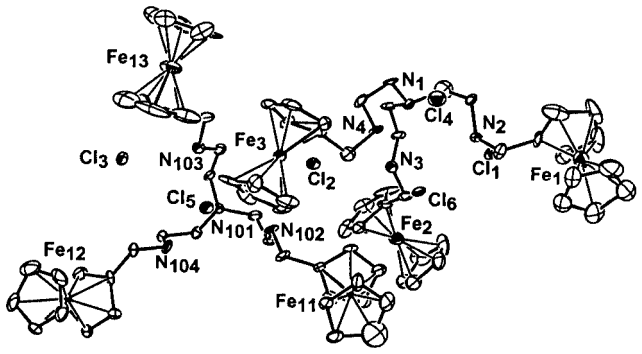


Figure 1. X-ray structure of the two entities of LH_3^{3+}, $3Cl^-$. Hydrogen atoms and solvent molecules are omitted for clarity. Hydrogen bonds lengths [Å]: Cl(1)···H−N(2), 2.31; Cl(6)···H−N(2), 2.26; Cl(2)···H−N(3), 2.27; Cl(6)···H−N(3), 2.27; Cl(4)···H−N(4), 2.20; Cl(6)···H−N(4), 2.27; Cl(2)···H−N(102), 2.20; Cl(5)···H−N(102), 2.24; Cl(3)···H−N(103), 2.21; Cl(5)···H−N(103), 2.22; Cl(1)#···H−N(104), 2.24; Cl(5)···H−N(104), 2.23 [symmetry transformation: # $-x+1$, $y-1/2$, $-z+3/2$; d(N−H) = 0.92 Å]

The X-ray structure determination shows that LH_3^{3+}, $3Cl^-$ crystallizes in the $P2_12_12_1$ space group of the orthorhombic system, revealing two independent molecular entities. These two entities display very close crystallographic data. The molecular structure, formulated as $[C_{39}H_{51}Fe_3N_4]Cl_3{\cdot}2CH_3CN{\cdot}C_2H_5CO_2CH_3{\cdot}H_2O$, consists of a tricationic LH_3^{3+}, three Cl^- counterions and four disordered solvent molecules (two acetonitrile molecules, one ethyl acetate, and one water molecule). The three metallocene units are located on the same side of the bridging nitrogen atom; the three iron centers in L are separated by ca. 11 Å and the distance between the iron center of a metallocene unit and its bridging secondary nitrogen is ca. 4.4 Å. The three chloride anions are closer to the secondary nitrogen atoms [N(2−4)···Cl distances of ca. 3.1 Å) than to the tertiary nitrogen, N(1)···Cl ranging between 3.73 and 4.43 Å. Cl(5) and Cl(6) are located inside the tren cavities, defined by N(101−104) and N(1−4), respectively, suggesting that these chloride anions are complexed by L via three convergent N−H···Cl hydrogen bonds (the distances between Cl(6) and N(2−4) are close to 3.1 Å). On the contrary, Cl(3) and Cl(4) interact only with HN(103) and HN(4), respectively. Finally, when referring to the two entities, Cl(1) bridges HN(2) and HN(104) (from an entity in a symmetrical position) and Cl(2) bridges HN(3) and HN(102).

Complexation Studies

Potentiometric titration studies and electrospray-mass spectra (ES-MS) experiments were first used to investigate the complexation of L by lanthanide ions.

Potentiometric Titration

The protonation constants of L and the stability constants of the corresponding Eu^{3+} and Y^{3+} complexes were calculated using the HYPERQUAD program,[23,24] from potentiometric titration curves obtained in a CH_3OH/H_2O solution (3:1, v:v) containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). Three pK_a values (9.37, 8.13, and 6.47 at 25 °C) were measured for L. The species LH_4^{4+} could not be reached, its pK_a being too low to be observed. In agreement with the results of Fabbrizzi et al.,[21] based on other tren derivatives, the three protons in LH_3^{3+} are bound to the secondary amino groups. Protonation of the sole secondary amino groups is corroborated by the crystallographic data of the hydrochloride form of L showing that *(i)* LH_3^{3+}, $3Cl^-$ was obtained in the presence of a large excess of HCl and *(ii)* the Cl^- ions are closer to the secondary amino groups than to the apical nitrogen atom. As already observed for alkylated-tren derivatives, the pK_a's are lower than those of the tren parent.[25,26] Stability constants of the complexes formed between L and the Y^{3+} or Eu^{3+} cations were then determined at a molar ratio of 1:1 (L/M^{3+}). Measurements were made in the 2.5 to 7 pH range, the precipitation of hydroxylated species being observed above pH 7−8. The best fit of the data was obtained by considering only the 1:1 species (LM) and $[LM(OH)_2]$ and yielded log$K$(LM) = 9.17(0.05) and 9.48(0.05) with $K(LM) = [LM]/[M][L]$, log$K$(LM{OH}$_2$) = 13.50(0.05) and 13.00(0.05) with $K(LM\{OH\}_2) = [LM]/[LM(OH)_2][H^+]^2$, for the LEu and LY complexes, respectively. Coordination numbers for lanthanide or yttrium (which is often treated as a "pseudo-lanthanide") trivalent cations are typically between seven and ten,[27] and only four coordination sites can be afforded by the amino groups in L. It can thus be assumed that counterions and/or solvent molecules are also coordinated to the metal center in LEu and LY complexes.

ES-MS Qualitative Speciation

The binding of the Eu^{3+}, Y^{3+}, La^{3+}, and Sm^{3+} cations by L was studied by electrospray-mass spectrometry. Solutions of complexes were prepared by mixing equimolar solutions (1 mg·mL^{-1}) of L and the nitrate salt of a given metal cation in acetonitrile:water (1:1, v:v). In all cases, only one kind of complex was detected (Figure 2 and Table 1).

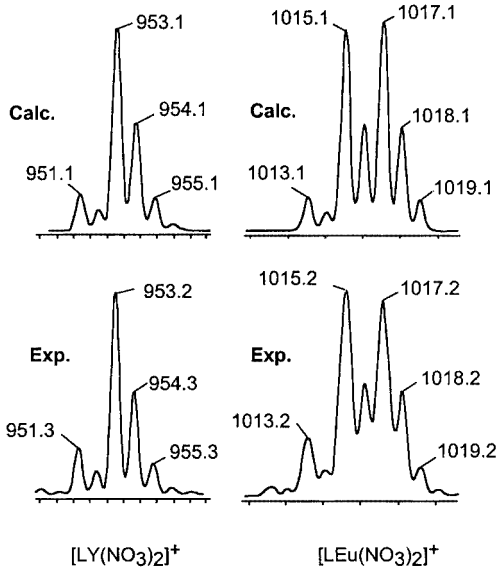


Figure 2. Calculated and experimental ES-MS spectra of $[LY(NO_3)_2]^+$ and $[LEu(NO_3)_2]^+$

Table 1. Electrospray-mass spectroscopic data (*m*/*z*) for L + M^{3+} 1:1 complexes (M = Eu, Y, Sm, La)

Species	Eu^{3+}	Y^{3+}	Sm^{3+}	La^{3+}
$[LM(NO_3)_2]^+$	1017.2	953.2	1016.2	1003.3
$[LM(NO_3)_3]^+$	1079.2	1015.2	1078.3	1065.3

All the isotopic peaks are separated by 1.0 *m*/*z* unit, revealing a charge state of +1 for the corresponding ions. Calculated spectra (Figure 2) show unambiguously that these signals correspond to the $[LM(NO_3)_2]^+$complexes, i.e. a 1:1 (L/M^{3+}) stoichiometry is observed, two nitrate anions being coordinated to the metal center. Interestingly, a second and smaller signal {10% in intensity compared with the signal of $[LM(NO_3)_2]^+$} corresponding to the complex $[LM(NO_3)_3]^+$ was also observed from the mass spectra. It can be assumed that the positive charge of this last species is provided by oxidation of one ferrocene unit of the complex under our experimental conditions. Spectra showing the same features were also obtained starting from isolated LY and LEu complexes.

Electrochemical Results

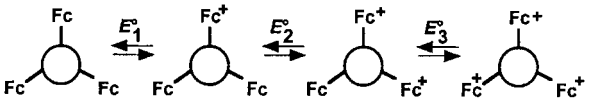
Electrochemical Behavior of Free L

The electrochemical behavior of the free receptor L was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in methanol containing 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. In weakly polar solvents such as CH_2Cl_2, the poor solubility of the electrogenerated compounds was responsible for adsorption phenomena and led to the observation of complex voltammograms. CV experiments revealed the presence of two partially overlapping waves at $E_{1/2}$ = +25 mV and +135 mV, with ΔE_p = 90 mV in both cases. Two peaks at +30 mV and +140 mV were observed by DPV (Table 2). The three ferrocene groups in L being chemically equivalent, this behavior (observation of two distinguishable signals) can be attributed to interactions occurring between the three redox centers. Indeed, a separation $\Delta E°$ of $(RT/F)\ln 2^3$, i.e. 57 mV, between the first and third electron transfer is expected in a molecule with three completely non-interacting equivalent redox centers,[28,29] leading to the observation of a voltammetric curve with the shape of a single-electron transfer reaction (one CV wave with $\Delta E_p \approx 60$ mV, and a single peak by differential pulse voltammetry). In contrast, significant electronic or electrostatic communication between these three redox centers should lead to larger $\Delta E°$ values and, therefore, to the observation of multiple CV waves.[29,30] The degree of communication between the three ferrocene groups in L was evaluated via the determination of the three formal potentials $E°^1$, $E°^2$, and $E°^3$, corresponding to the successive oxidations of the three ferrocene subunits (Scheme 1).

Table 2. Electrochemical data for free L, LH_3^{3+}, LEu, and LY complexes

	Experimental CV data[a]				Formal potentials[b]		DPV data
	E_{pa}, V[c]	E_{pc}, V[c]	ΔE_p, mV[c]	$E_{1/2}$, V[d]	$E°$, V	$\Delta E°$, mV[e]	Ep, V[f]
Free L	0.070	−0.020	90	0.025	0.001 ($E°^1$)	67 ($\Delta E°^{2-1}$)	0.030
	0.180	0.090	90	0.135	0.068 ($E°^2$)	71 ($\Delta E°^{3-2}$)	0.140
					0.139 ($E°^3$)	138 ($\Delta E°^{3-1}$)	
LEu	0.190	0.098	92	0.144	0.112 ($E°^1$)	33 ($\Delta E°^{2-1}$)	0.140
					0.145 ($E°^2$)	26 ($\Delta E°^{3-2}$)	
					0.171 ($E°^3$)	59 ($\Delta E°^{3-1}$)	
LY	0.199	0.097	102	0.148	0.122 ($E°^1$)	33 ($\Delta E°^{2-1}$)	0.150
					0.155 ($E°^2$)	26 ($\Delta E°^{3-2}$)	
					0.181 ($E°^3$)	59 ($\Delta E°^{3-1}$)	
LH_3^{3+} [g]	0.270	0.130	140	0.180	[h]	[h]	0.175

[a] All potentials are referred to the regular Fc/Fc^+ couple. [b] Calculated by fitting simulated voltammograms to experimental data. [c] E_{pa} and E_{pc} are the anodic and cathodic peak potentials. ΔE_p states for the peak-to-peak potential splitting ($E_{pa}-E_{pc}$). [d] $E_{1/2}$ is the apparent half-wave potential [(E_{pa} + E_{pc})/2]. [e] $\Delta E°$ represents the difference between the calculated redox potentials. [f] DPV peak potential. [g] L in the presence of five equivalents of H^+. [h] Not determined (see the text).



Scheme 1. Schematic representation of the three oxidation steps of L

The experimental voltammograms were fitted to digitally simulated voltammograms using the ESP software.[31] Results are depicted in Figure 3(A) and the three formal potentials evaluated from the optimization of the fitting analysis are given in Table 2. ΔE° values of ca. 70 mV between two consecutive redox systems (i.e. $E^{\circ 2} - E^{\circ 1}$ and $E^{\circ 3} - E^{\circ 2}$) were found. These results are in accordance with those already reported for bis[5] and tris[13] ferrocenyl compounds that showed significant communication between the redox centers and were characterized by two distinguishable voltammetric waves.

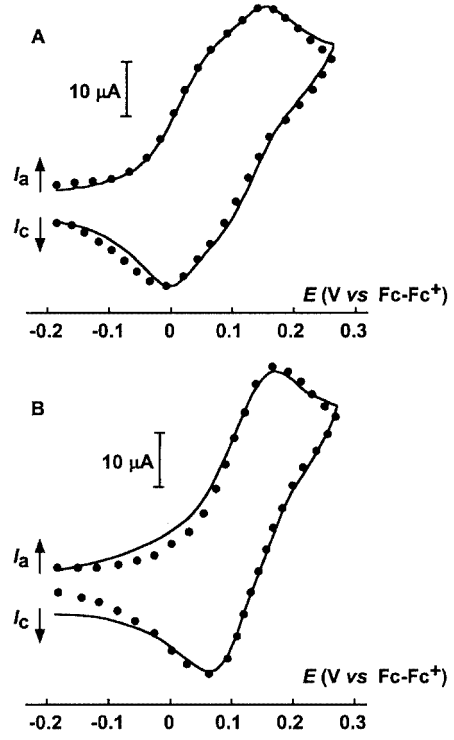


Figure 3. Experimental (continuous line) and best-fit simulated (dotted line) cyclic voltammograms of (A) 1 mM free L and (B) 1 mM LEu complex in CH_3OH containing 0.1 M TBAP; sweep rate 0.1 $V \cdot s^{-1}$

Since the three ferrocene groups in L are relatively far one from one another and separated by simple bonds, electronic communication through the bonds could not be invoked. Thus, it is reasonable to deduce that there are electrostatic interactions occurring between the electrogenerated positive charge of the first ferricinium group and the lone pair of a nitrogen atom connected to a second ferrocene group, the latter being more difficult to oxidize. In the same way, the third ferrocene group is oxidized at a higher potential than the second one. This hypothesis will be further discussed in the following paragraph.

Electrochemical Behavior of the Eu^{3+} and Y^{3+} Complexes of L

The same electrochemical experiments were conducted starting from chloride or nitrate salts of the isolated LEu and LY complexes. Results are summarized in Table 2. Both complexes exhibit one quasi-reversible CV wave [see for example Figure 3(B), for LEu] at $E_{1/2}$ = 144 (ΔE_p = 92 mV) and 148 mV (ΔE_p = 102 mV), and one DPV peak at E_p = 140 and 150 mV for LEu and LY complexes, respectively. These observations reveal a strong decrease in the communication between the three redox active units. The metallocene moieties of the complexed L therefore exhibit a more independent electrochemical behavior and the shape of the resulting voltammograms tends towards that of a single three-independent-electrons oxidation wave.

As mentioned previously, the determination of the three formal potentials E° corresponding to the three successive oxidations of the ferrocene groups in the complexes was performed by fitting simulated voltammograms to experimental CV curves. The data are summarized in Table 2. Firstly, due to electrostatic repulsion effects arising between the bound metal cation and the positive charge on the electrooxidized ferrocenyl unit, these potentials are logically shifted to more positive values as compared to those measured for the free receptor. Moreover, the three successive oxidations in both complexes are separated by ca. 30 mV and the separation between the first and the third redox events ($E^{\circ 3} - E^{\circ 1}$) is 59 mV, showing that the communication between the three ferrocene units is almost fully cancelled upon metallation of the receptor. The strong decrease in the interactions is thus a direct consequence of the complexation of L by metal ions through the secondary nitrogen atoms, and this result confirms that the lone pairs of the secondary amines are involved in the communication between the ferrocene groups in L.

In order to further confirm the above hypothesis, CV and DPV experiments were conducted on L in acidic media. Addition of $HClO_4$ in a solution of L led to the emergence of a single DPV peak at E_p = 175 mV and of a unique CV wave at $E_{1/2}$ = 180 mV (ΔE_p = 140 mV). These observations clearly indicate a strong decrease in the interactions between the three iron centers upon protonation of L, in accordance with that already observed with others nitrogen-bridged polyferrocenes.[4−7,12] Moreover, as in the metallic complexes, the average apparent potential for the first oxidation of the ferrocene centers is shifted to more positive values upon protonation of L. The potential shift is due to the electron-withdrawing effect induced by the introduction of positive charges on the bridging nitrogen atoms. Unfortunately, owing to complex voltammograms due to adsorption phenomena the potentials for the three electron transfers in LH_3^{3+} could not be accurately evaluated using electrochemical simulation. However, the potential shift for the first oxidation of L ($E^{\circ 1}$) induced by its protonation can be roughly evaluated to ca. +160 mV. This value is in agree-

ment with the results of Plenio et al.[32] who studied a number of ferrocene-nitrogen compounds and their protonated forms. They found a linear relationship between the inverse Fe−N distance (provided by X-ray data) and the shift of the potential of the ferrocene-ferricinium couple observed upon protonation of the neutral compounds. In particular, a shift of +190 mV was found for an iron-ammonium distance equal to 4.56 Å,[32] that is similar to the 4.4 Å Fe−N distance in LH_3^{3+} (Figure 1).

Electrochemical Behavior of L_1 after Addition of Increasing Amounts of Eu^{3+} or Y^{3+} Cations

We took advantage of the disruption of the communication in L upon complexation to investigate the sensing properties of this redox receptor towards lanthanide cations. Electrochemical experiments were carried out by DPV in CH_3OH solution containing 0.1 M TBAP. Results are illustrated in Figure 4. The addition of increasing amounts of Eu^{3+} or Y^{3+} cations (as nitrate or chloride salts) in a solution of L causes the linear growth of the intensity of the second DPV peak, along with the decrease of that for the first one. It must be pointed out that such evolution is observed because the electrochemical signal due to the lanthanide complex (140 and 150 mV for LEu and LY respectively) is very close to the second redox event in free L (E_{p2} = 140 mV). The first peak disappears and the second one reaches full development when one molar equivalent of metal salt has been added. This result is in keeping with ES-MS and potentiometric titration experiments and confirms the 1:1 binding mode between L and Eu^{3+} or Y^{3+} ions. Moreover, it has to be noted that a very slight precipitate was observed in the solution following the addition of a small amount of metal cation (ca. 0.1 molar equivalent), accompanied by a slight decrease in the intensity of the electrochemical signals. This precipitate disappeared when more metal cation was added. The intermediate formation of an insoluble complex, most likely an oligomeric assembly, at a low M^{3+}-to-L ratio could explained these observations.

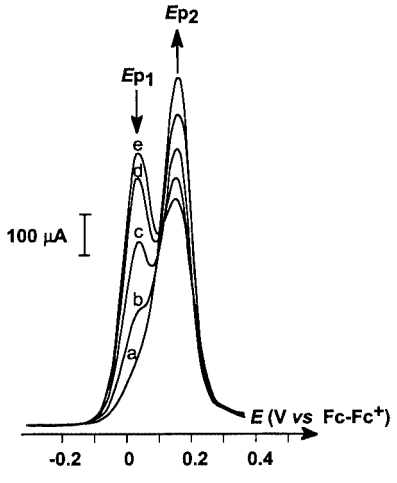


Figure 4. DPV curves for L (1 mM in CH_3OH +0.1 M TBAP) in the presence of increasing amounts of Eu^{3+} cations: Eu^{3+}/L = 0.1 (a), 0.25 (b), 0.5 (c), 0.75 (d) and 1 (e); sweep rate 0.01 $V{\cdot}s^{-1}$; pulse height 25 mV; step time 0.2 s

Analysis of the intensities of the two DPV peaks allowed us to draw amperometric titration curves (Figure 5), which clearly show the linear growth above 0.2 equivalent of the second DPV peak and the linear decrease of the first one upon addition of increasing amounts of trivalent cation. The same experiments were conducted in a CH_3OH/H_2O mixture (3:1, v:v) containing 0.1 M TBAP or $LiClO_4$. No major changes were observed, i.e. the same amperometric calibration curves were obtained, indicating that the electrochemical response of L towards lanthanide ions is not affected by the presence of water.

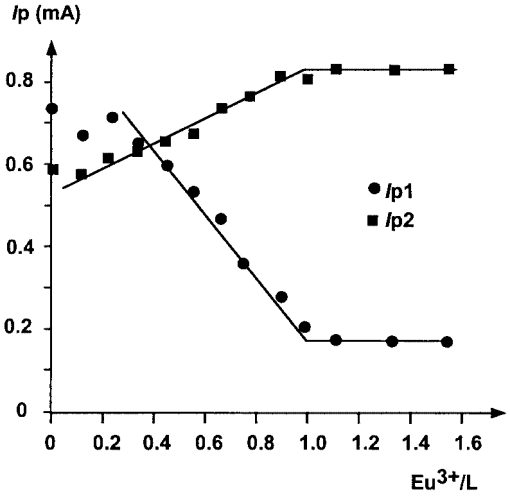


Figure 5. Amperometric titration curves: evolution of the DPV peak currents as a function of the Eu^{3+}-to-L ratio (see Figure 4)

Conclusion

The three chemically equivalent ferrocene subunits in L show a significant degree of electrostatic communication, which is responsible for the observation of two distinct electrochemical signals. These interactions are severely disrupted upon complexation of this tren-based ligand by lanthanide ions to form 1:1 (L:M) complexes. This leads to the observation of a unique voltammetric wave. Changes in the redox features of L in the presence of lanthanide ions can thus be exploited to detect and sense these guest species. Although a number of redox-active receptors able to electrochemically sense metal cations have been described previously,[33−35] to the best of our knowledge, L is the first example of a multi-redox ligand allowing an amperometric titration of metal cations in organic and aqueous media, via a large decrease in the communication between the redox active sites upon complexation.

Experimental Section

General Remarks: Hydrated metal ions (chloride or nitrate salts) were obtained from Aldrich. All compounds were of reagent grade and were used without further purification. Methanol (SDS, 99%,

purex analytical grade) was used as received. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka and dried under vacuum at 80 °C for 3 days. ^{1}H and ^{13}C NMR spectroscopic experiments were conducted at 22 °C on a Bruker AC250 spectrometer using the solvent deuterium signal as internal reference. FAB (positive mode) mass spectra were recorded with an AEI Kratos MS 50 spectrometer fitted with an Ion Tech Ltd. gun and using *m*-nitrobenzyl alcohol as a matrix. ES-MS spectra were recorded on a Micromass Quattro mass spectrometer, equipped with an electrospray source. The temperature was set at 80 °C. The electrospray probe (capillary) voltage was optimized in the range 3.5−5 kV for positive ion electrospray. The sample cone voltage was set within the range 40−200 V. Complexes in solution [1 mg·mL^{-1} in CH_3CN/H_2O (3:1, v:v)] were infused in CH_3CN containing 0.01% HCOOH, through a fused silica tubing, using a syringe pump at a flow rate in the range 5−10 μL·min^{-1}. Potentiometric titrations were performed at 25 °C and the solutions were prepared in CH_3OH/H_2O (3:1, v:v). The ionic strength was fixed at I = 0.1 M with TBAP. An automatic titrator system (DMS, 716 Titrino Metrohm) equipped with a combined glass electrode and connected to an IBM Aptiva microcomputer was used. The electrodes were calibrated to read pH according to the classical method.[36] The ligand and its metal(III) complex of ca. 0.001 M were titrated with standardized 0.025 M NaOH at 25 °C. Argon was bubbled through the solutions to exclude CO_2 and O_2. A NaOH solution was standardized against potassium hydrogenphtalate. Carbonate content was checked by Gran's method. The titration data were refined by the non-linear least-squares refinement program HYPERQUAD[23,24] to determine the stability constants. The values of the stability constants are the mean values calculated from three titrations.

Electrochemical Studies: Experiments were conducted in a conventional three-electrode cell using an EGG PAR model 273 potentiostat, at 20 °C under an argon atmosphere. The Ag|10 mM $AgNO_3$ + 0.1 M TBAP in CH_3CN was used as a reference electrode. The potential of the regular Fc/Fc^+ redox couple used as an internal standard was 0.130 V under our experimental conditions. The working electrode consisted of a platinum disk (5 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. Electrochemical simulations and best fitting of experimental data were performed by the Electrochemical Simulations Package [ESP software, version 2.4, by Dr. Carlo Nervi (nervi@lem.ch.unito.it)]. The common approximation, which considers that formal potentials and half-wave potentials are identical, was applied.[30] The electrochemical parameters used for the digital simulation are: α = 0.5, k^0 = 0.02 cm·s^{-1}, and D = 10^{-5} cm^2·s^{-1}, α and k^0 being respectively the transfer coefficients and the heterogeneous transfer constant of the corresponding electrochemical reactions and D being the diffusion coefficient of the species. These values were assumed to be constant for all the systems studied since a slight modification of these parameters does not significantly affect the results.

Synthesis of L: Tris(2-aminoethyl)amine (0.5 g, 3.42 mmol) were dissolved in water (15 mL). A solution of ferrocenecarboxaldehyde (2.2 g; 3 × 3.42 mmol) in diethyl ether (15 mL) was then added and the biphasic solution was stirred vigorously in a sealed vessel for 12 hours. The orange precipitate was then filtered off, washed with diethyl ether (5 × 10 mL), and dried under vacuum. The trisimine intermediate was obtained in 95% yield (2.44 g). ^{1}H NMR (250 MHz, CD_3OD): δ = 2.73 (t, 6 H, N-CH_2CH$_2$-), 3.18 (t, 6 H, N-CH$_2$CH_2-), 4.07 (s, 15 H, Fc), 4.32 (m, 6 H, Fc), 4.51 (m, 6 H, Fc), 8.01 (s, 3 H, *H*C=N) ppm. ^{13}C NMR (250 MHz, CD_3OD): δ = 57.98, 61.58, 71.51, 71.90, 73.56, 82.16, 167.44 ppm. FAB-MS, *m/z*: 735 [M + H]$^+$. UV/vis, λ_{max} (ε/M^{-1}·cm^{-1}): 326 (6700), 455 nm (1300). $C_{39}H_{42}Fe_3N_4$, H_2O (752.32): calcd. C 62.26, H 5.89, N 7.45; found C 62.37, H 5.87, N 7.71.

Trisimine (500 mg) was dissolved in CH_3OH (50 mL) after which $NaBH_4$ (100 mg) was slowly added. The solution was then stirred for 4 hours. CH_3OH was removed by distillation, the residue was dissolved in H_2O (100 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic phases were washed with water (2 × 10 mL), dried with $MgSO_4$, and the solvents evaporated to give the expected compound as a brown oil. Yield 93%. (470 mg). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.90 (br. s, 3H N*H*), 2.50 (t, 6 H, N-CH_2CH$_2$-), 2.61 (t, 6 H, N-CH$_2$CH_2-), 3.45 (s, 6 H, Fc-CH_2) 4.08−4.16 (m, 27 H, Fc) ppm. ^{13}C NMR (250 MHz, $CDCl_3$): δ = 47.17, 49.05, 54.32, 67.79, 68.40, 68.62, 86.42 ppm. FAB-MS, *m/z*: 741 [M + H]$^+$. UV/Vis λ_{max} (ε/M^{-1}·cm^{-1}): 323 (440), 436 nm (370). $C_{39}H_{48}Fe_3N_4$ (740.36): calcd. C 63.27, H 6.53, N 7.57; found C 62.55, H 6.64, N 7.53.

LEu and LY Complexes: The LEu and LY complexes were isolated by mixing L and one equivalent of metal cation (as chloride or nitrate salts) in CH_3OH. The solution was stirred for one hour and the complexes were precipitated as a yellow powder upon addition of diethyl ether. Complexes were characterized by ES-MS measurements (see the text). No reproducible elemental analysis could be obtained and crystals suitable for X-ray studies could not be grown, due to hygroscopic properties

X-ray Crystallographic Study: Crystals of the hydrochloride form of L (LH_3^{3+}, 3Cl$^-$) were obtained by slow diffusion of diethyl ether into a solution of L with ten equivalents of HCl_{aq} in ethyl acetate/acetonitrile. Due to its instability, the crystal was mounted on the X-ray diffractometer and its structure determined at low temperature (143 K). Diffraction data (Table 3) were collected with a SMART CCD diffractometer (Mo-K_α radiation, graphite-monochromator, λ = 0.71073 Å). Intensity data were corrected for Lorentz polarization effects and absorption. Structure solution and refinement were performed with the SHELXTL package. Hydrogen

Table 3. Summary of crystallographic data for LH_3^{3+}, 3Cl$^-$

Formula	$C_{39}H_{51}Cl_3Fe_3N_4$ ·2CH_3CN·$C_2H_5CO_2CH_3$·H_2O
M	1037.97
Cryst. Syst.	orthorhombic
Space Group	$P2_12_12_1$
a [Å]	19.274(4)
b [Å]	22.753(5)
c [Å]	23.361(5)
V [Å^3] / Z	10245(4) / 8
D_x [g cm^{-3}]	1.346
λ [Å]	0.71073
T, K	143(2)
Size [mm]	0.2 × 0.2 × 0.2
Color	brown
μ [mm^{-1}]	1.039
F(000)	4352
No. of reflns. collected	18436
θ range [°]	1.64−28.97
Data/restraints/parameters	16889/0/996
Goodness on fit S	1.242
$\Delta\rho_{min}$/ $\Delta\rho_{max}$ [e·Å^{-3}]	1.956/-1.029
R {$I>2\sigma(I)$}[a]	0.1008

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

atoms were included in calculated positions with isotropic thermal coefficients. CCDC-194179 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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