

# Ferrocene–Metalloacyclam Conjugates: New Redox Systems Whose Two-Electron Activity Can Be Modulated through the Medium

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The two conjugate systems **1** and **2**, in which a ferrocene subunit and a nickel–cyclam fragment are covalently linked, have been prepared and investigated for their redox behavior, using voltammetric techniques. **1** has been synthesized through the reaction of Ni<sup>II</sup> with the free ligand **3**, prepared from the reaction of (ferrocenylmethyl)trimethylammonium iodide with a 5-fold excess of cyclam. **2** has been obtained by a very convenient one-pot template procedure, in which ferrocenesulfonamide acts as a locking fragment in closing an open-chain tetraamine, in the presence of formaldehyde. Both **1** and **2** undergo a two-electron oxidation process through two consecutive reversible one-electron steps, the first one being ascribed to the oxidation of the metallorganic moiety and the second one to the Ni<sup>II</sup> to Ni<sup>III</sup> change. The difference between the two corresponding potentials,  $\Delta E = E_{\text{NiL}} - E_{\text{Fc}}$ , decreases with the increasing donor tendencies of the medium, reflecting the stabilization of the Ni<sup>III</sup> state by the axially bound solvent molecules. Such an effect is not experienced by the coordinatively saturated ferrocene moiety. A ferrocene fragment has also been appended to 1,4,7-triazacyclononane. The ferrocene-functionalized triaza macrocycle **4** complexes Ni<sup>II</sup> according to a 2:1 stoichiometry. The two appended organometallic subunits display independent redox behaviors and release two electrons at the same potential, whereas a further electron is released by the Ni<sup>II</sup> center at a very positive potential, due to the strong repulsive electrostatic effects exerted by the proximate ferrocenium subunits. Ferrocene–metalloacyclam conjugates represent a novel class of versatile multielectron-redox systems, whose activity can be controlled from the outside (solvent, background electrolyte).

## Introduction

Molecular systems capable of exchanging two or more electrons are of interest in the field of redox catalysis and electrocatalysis. Organic systems may display two-electron redox activity, but the corresponding processes are in general poorly reversible or irreversible and are often complicated from a kinetic point of view. On the other hand, the inorganic approach to two-electron-redox agents is rather simple and involves the coupling of two metal-centered fragments, individually displaying a fast and reversible one-electron exchange. For instance, two redox-active fragments X should be covalently linked (by a C–C bond, by an aliphatic chain or other bridges) to give X–R–X. If the –R–bridge does not allow electron communication between the two centers, and if the X-to-X distance is large enough to minimize electrostatic repulsive interactions, the X–R–X system will exchange two electrons *in a single shot*, i.e. through two one-electron processes whose potentials  $E_1$  and  $E_2$  are separated only by the statistical term  $\Delta E = E_2 - E_1 = 36 \text{ mV}$ , at 25 °C. Electronic interactions (through a  $\pi$  system delocalized over the bridge) or electrostatic repulsive effects cause the  $\Delta E$  value to increase: the stronger the interaction, the larger the  $\Delta E$  value. Varying the nature and/or the length of the bridge may allow one to modulate the extent of the separation of the potentials, which can be increased up to several hundred millivolts. Alternatively, redox systems able to exchange two electrons in two distinct steps can be designed by linking two different fragments X and Y. In the absence of interactions between the two redox sites in the conjugate system X–R–Y, the  $\Delta E$  value will approximate the difference of the potentials pertinent to each individual system X and Y.

In this work, design of two-electron-redox systems of the X–R–Y type is considered and some factors affecting the magnitude of the potential separation  $\Delta E$  are envisaged. In particular, the systems under investigation derive from the linking of two well-known one-electron-redox agents deriving from (i) organometallic chemistry (ferrocene) and (ii) coordination chemistry (the [Ni<sup>II</sup>cyclam]<sup>2+</sup> complex). The tendency of

ferrocene, Fc, to undergo a reversible one-electron oxidation process and to form the stable ferrocenium ion, Fc<sup>+</sup>, according to an *outer-sphere* electron-transfer process, has been recognized since its first appearance on the chemical stage.<sup>1</sup> On the other hand, the capability of the cyclam ring to promote the redox activity of the encircled metal center and to favor the access to unusually high oxidation states is well known and documented.<sup>2</sup> In particular, Ni<sup>II</sup> is oxidized to the stable Ni<sup>III</sup> cation at a potential even less positive than that associated with the Fe<sup>II</sup>/Fe<sup>III</sup> process (0.72 V vs NHE, in 1 M HCl).<sup>3</sup> Moreover it has been observed that Ni<sup>II</sup> complexes with cyclam and cyclam-like ligands may undergo electron-transfer processes according to an *inner-sphere* mechanism.<sup>4</sup>

In this work, two distinct ferrocene–[Ni<sup>II</sup>cyclam] conjugate systems, **1** and **2**, have been synthesized and their redox activity in various solvents has been characterized electrochemically. The different natures and intensities of the solute–solvent interactions for the ferrocene and nickel cyclam subunits cause  $\Delta E$  to vary substantially with the donor tendencies of the medium. The present work demonstrates that, for an X–R–Y redox system conjugating a coordinatively saturated fragment X and a coordinatively unsaturated fragment Y, the magnitude of  $\Delta E$  can be modulated over a substantial range of potentials by choosing a solvent displaying more or less pronounced coordinating tendencies.

The ferrocene fragment has been previously appended to or incorporated into macrocyclic frameworks containing (i) ethereal oxygen atoms<sup>5</sup> or (ii) thioetheral sulfur atoms,<sup>6</sup> with the aim of controlling the binding of d<sup>0</sup> or d<sup>10</sup> metal ions, respectively. Two ferrocenylmethyl fragments have been appended at the nitrogen

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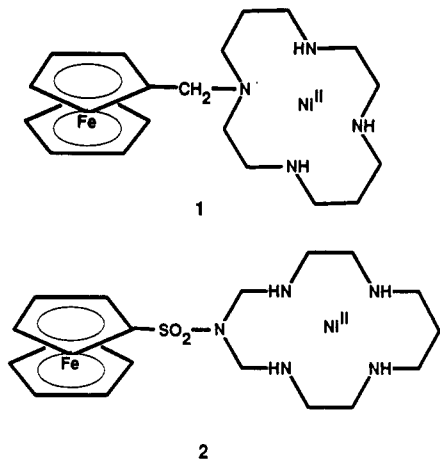
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atoms of an  $N_2S_4$  macrocycle;<sup>7</sup> the cyclic subunit was able to incorporate either a  $Cu^{II}$  or a  $Cu^I$  ion, and the quasi-reversible  $Cu^{II}/Cu^I$  redox process was electrochemically characterized.

### Experimental Section

1,4,8,11-Tetraazacyclotetradecane (cyclam),<sup>8</sup> 1,4,7-triazacyclononane (TACN),<sup>9</sup> and ferrocenesulfonamide<sup>10</sup> were prepared according to the literature.  $N,N'$ -Bis(2-aminoethyl)-1,3-propanediamine (2.3.2-tet) was obtained commercially from Aldrich Chemical Co. and used without further purification.  $^1H$  NMR spectra (solvent  $CDCl_3$ , internal TMS standard) were recorded on a 300-MHz Bruker instrument, IR spectra were obtained on a Perkin-Elmer 1300 infrared spectrophotometer, and UV-Vis spectra were recorded on a Hewlett-Packard 8452 diode-array spectrometer.

**1-(Ferrocenylmethyl)-1,4,8,11-tetraazacyclotetradecane (LCH<sub>2</sub>Fc, 3).** A 2.0-g sample (10.0 mmol) of cyclam was dissolved in 50 mL of water previously flushed with dinitrogen, to which 0.80 g (2.08 mmol) of (ferrocenylmethyl)trimethylammonium iodide<sup>11</sup> (5) was added as a solid. The resulting solution was refluxed under dinitrogen for 3 h, during which trimethylamine was evolved and an orange oil separated. After cooling to room temperature, the mixture was extracted with two 10-mL portions of diethyl ether, and the organic layer was dried over  $Na_2SO_4$  for one night. The ethereal solution was filtered, the filtrate was rotovaporated to dryness, and the resulting orange oil was kept under vacuum (1 Torr) at 40 °C for 36 h. During this time, a waxy orange-yellow product slowly solidified. Yield: 0.53 g (64%, with respect to the starting (ferrocenylmethyl)trimethylammonium iodide). Anal. Calc for  $C_{21}H_{34}N_4Fe$ : C, 63.4; H, 8.5; N, 14.1. Found: C, 63.2; H, 8.5; N, 14.0. IR (Nujol mull): 3280 (N-H str), 3070  $cm^{-1}$  (C-H str of cyclopentadienyl rings).  $^1H$  NMR:  $\delta$  4.10 (9H, m, H of ferrocene), 3.57 (2H, s,  $FcCH_2N<$ ), 2.5 (16H, m,  $>N-CH_2-$ ), 1.75 (4H, m,  $>NCH_2CH_2CH_2N<$ ). UV-vis ( $CH_3CN$ , nm):  $\lambda_{max}$  326 ( $\epsilon = 110$ ), 436 ( $\epsilon = 120$ ).

**1-(Ferrocenylmethyl)-1,4,7-triazacyclononane (TCH<sub>2</sub>Fc, 4).** The synthesis of the ferrocene-triazacyclononane conjugate 4 system followed the same procedure outlined for 3. Reaction of 1.0 g (7.75 mmol) of 1,4,7-triazacyclononane with 1.0 g (2.6 mmol) of (ferrocenylmethyl)trimethylammonium iodide (5) in 30 mL of water yielded 0.49 g (58%, based on the starting ferrocenylmethyl derivative) of 4 as a yellow waxy solid. Anal. Calc for  $C_{17}H_{25}N_3Fe$ : C, 62.4; H, 7.6; N, 12.8. Found: C, 62.2; H, 7.6; N, 12.7. IR (Nujol mull): 3290 (N-H str), 3080  $cm^{-1}$  (C-H str of the cyclopentadienyl rings).  $^1H$  NMR:  $\delta$  4.15 (9H, m, H of ferrocene), 3.55 (2H, s,  $FcCH_2N<$ ), 2.72 (4H, s, H of the methylene groups in positions 5 and 6 of the cyclononane ring), 2.60 (8H, m, H of the methylene groups in positions 2, 3, 8, and 9 of the cyclononane ring). UV-vis ( $CH_3CN$ , nm):  $\lambda_{max}$  324 ( $\epsilon = 140$ ), 434 ( $\epsilon = 135$ ).

**[1-(Ferrocenylmethyl)-1,4,8,11-tetraazacyclotetradecane]nickel(II) Perchlorate Dihydrate ([Ni(LCH<sub>2</sub>Fc)](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O, 1).** A 95-mg sample (0.24 mmol) of LCH<sub>2</sub>Fc (3) was dissolved in 5 mL of methanol, and the

resulting solution was purged with dinitrogen. A solution of 90 mg (0.25 mmol) of  $Ni(ClO_4)_2 \cdot 6H_2O$  dissolved in the minimum amount of water was added to the dinitrogen-purged solution of 3. A jelly precipitate of nickel hydroxide immediately formed. After filtration, the clear orange solution was evaporated to a small volume with continuous bubbling of dinitrogen, to give orange crystals which were filtered out and stored under nitrogen (if exposed to air, the product is slowly oxidized to a deep green ferrocenium derivative). Yield: 50 mg, 32%. Anal. Calc for  $C_{21}H_{38}N_4Cl_2FeNiO_{10}$ : C, 36.4; H, 5.5; N, 8.1. Found: C, 36.0; H, 5.3; N, 7.9. IR (Nujol mull): 3200 (N-H str), 3090 (shoulder, C-H str of the cyclopentadienyl ring), 1100  $cm^{-1}$  (broad, perchlorate anion). UV-vis ( $CH_3CN$ , nm):  $\lambda_{max}$  318 (shoulder), 432 ( $\epsilon = 170$ ). The acquisition of  $^1H$  NMR spectra for complex 1 was prevented by the presence of a significant concentration of a paramagnetic species: the  $Ni^{II}$  aza macrocyclic subunit. Such a paramagnetic species was present even in  $CDCl_3$ , due to the coordination of solvent or water molecules on  $Ni^{II}$  apical positions. On the other hand, solutions of polar solvents (acetonitrile, dimethyl sulfoxide) contain an equilibrium mixture of the square diamagnetic form and of the octahedral paramagnetic form of the  $Ni^{II}$  subunit. Such a behavior is typically observed for  $Ni^{II}$  complexes with cyclam-like macrocycles.<sup>12</sup>

**Bis[1-(ferrocenylmethyl)-1,4,7-triazacyclononane]nickel(II) Perchlorate ([Ni(TCH<sub>2</sub>Fc)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 7).** A 105-mg sample (0.32 mmol) of TCH<sub>2</sub>Fc (4) was dissolved in 10 mL of methanol, and the resulting solution was purged with dinitrogen. A solution of 56 mg (0.15 mmol) of  $Ni(ClO_4)_2 \cdot 6H_2O$  dissolved in 1 mL of methanol was added dropwise to the moderately heated ligand solution, under a dinitrogen flux. After a few minutes, a yellow microcrystalline solid precipitated, which was filtered off, dried under vacuum, and stored under dinitrogen. Yield: 95 mg, 68%. Anal. Calc for  $C_{34}H_{50}N_6Cl_2Fe_2NiO_8$ : C, 44.8; H, 5.7; N, 9.2. Found: C, 44.4; H, 5.5; N, 9.0. IR: 3300 (N-H str), 3080 (C-H str of the cyclopentadienyl ring), 1100  $cm^{-1}$  (broad, perchlorate anion). UV-vis ( $CH_3CN$ , nm):  $\lambda_{max}$  320 (shoulder), 436 ( $\epsilon = 230$ ).  $^1H$  NMR spectra of solutions of complex 7 could not be obtained due to the paramagnetism of the octahedral  $Ni^{II}$  subunit.

**[3-(Ferrocenylsulfonyl)-1,3,5,8,12-pentaazacyclotetradecane]nickel(II) Perchlorate ([Ni<sup>II</sup>(LSO<sub>2</sub>Fc)](ClO<sub>4</sub>)<sub>2</sub>, 2).** A solution of 1.6 g (10 mmol) of 2.3.2-tet in 25 mL of ethanol was slowly added to a stirred solution of 2.38 g (10 mmol) of  $NiCl_2 \cdot 6H_2O$  in 50 mL of ethanol. The resulting blue solution was heated to 60 °C; then 2.65 g (10 mmol) of ferrocenesulfonamide dissolved in 50 mL of ethanol, 1.5 mL of triethylamine, and 10 mL of 40% aqueous formaldehyde (in several portions) were added. Heating and stirring continued for 5 days under a dinitrogen atmosphere; then the resulting yellow solution was filtered under dinitrogen, and the filtrate was treated with 70% aqueous perchloric acid (if this operation is performed in air, the solution turns green, due to the oxidation of the ferrocene moiety). After 3 days, a yellow precipitate was recovered by a fast filtration and washed with cold water. Yield: 27%. Anal. Calc for  $C_{19}H_{31}N_5Cl_2FeNiO_{10}S$ : C, 32.3; H, 4.4; N, 9.9. Found: C, 32.1; H, 4.6; N, 10.0. IR: 3220 (N-H str), 3090 (C-H str of the cyclopentadienyl rings), 1330  $cm^{-1}$  ( $SO_2$  str), 1100  $cm^{-1}$  (broad, perchlorate anion). UV-vis ( $H_2O$ , nm):  $\lambda_{max}$  420 ( $\epsilon = 320$ ).  $^1H$  NMR spectra of 2 could not be obtained in  $CDCl_3$  solution, due to its insolubility; on the other hand, solutions of more coordinating solvents (e.g.  $CH_3CN$ , DMSO) contain the typical equilibrium mixture of the diamagnetic (square) and paramagnetic (octahedral) forms of the  $Ni^{II}$  subunit.<sup>12</sup>

**Electrochemistry.** The solvents used in the electrochemical experiments (MeCN, DMSO, DMF, MeNO<sub>2</sub>, and  $CH_2Cl_2$ ) were purified according to the standard methods prior to use. HMPA (99%, Aldrich) was used as received. Supporting electrolyte  $[Bu_4N]ClO_4$  (Fluka, polarographic grade) was used without further purification. Electrochemical measurements (cyclic voltammetry and differential pulse voltammetry) were performed in a conventional three-electrode cell, using a PAR 273 potentiostat/galvanostat controlled by an IBM AT personal computer and driven by dedicated software. A silver wire was used as a pseudoreference electrode and was calibrated using ferrocene as internal standard. Controlled-potential coulometry experiments were performed on MeCN solutions, employing a platinum gauze as a working electrode.

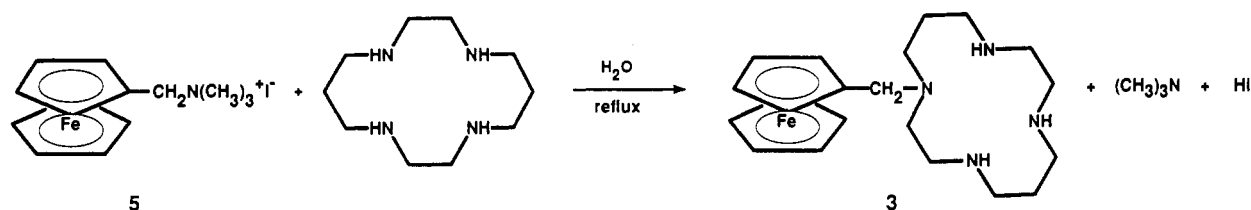
### Results and Discussion

**Design of the Ferrocene-Metalloclam Conjugates.** The ferrocene fragment and the metalloclam subunit have been covalently linked through two different procedures, to give conjugate systems displaying rather different redox activities.

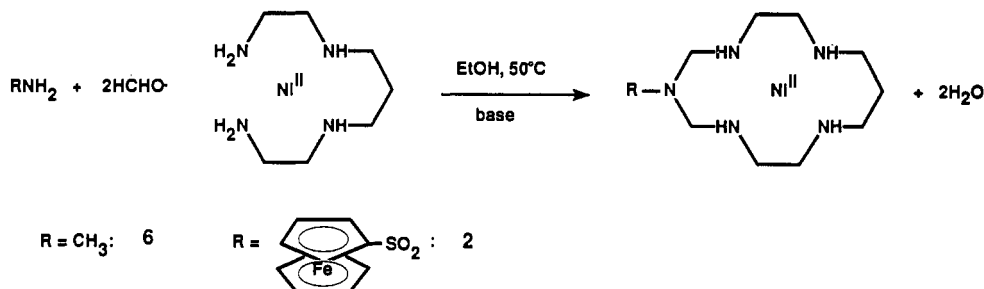
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## Scheme I



## Scheme II

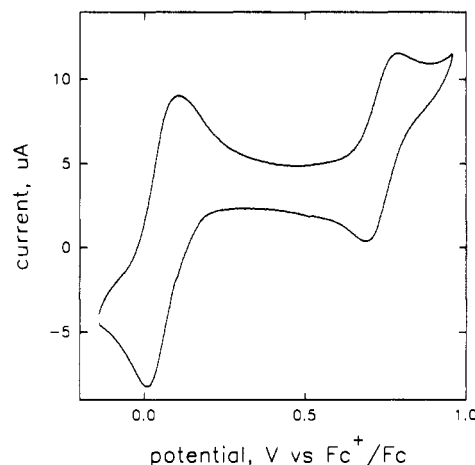


According to the first method, the (ferrocenylmethyl)trimethylammonium cation (**5**) (as the iodide) was reacted with a 5-fold excess of cyclam. (See Scheme I.) Linking takes place by nucleophilic attack of one of the secondary amino nitrogen atoms of the cyclam ring on the methylene moiety of **5**, with evolution of trimethylamine.<sup>7,11</sup> The large excess of cyclam prevents the formation of poly(ferrocenylmethyl)cyclam derivatives. On the other hand, the conjugate system **3** (LCH<sub>2</sub>Fc) can be conveniently separated from unreacted cyclam through extraction in diethyl ether, a medium in which plain cyclam is very poorly soluble. The N-appended ferrocenylmethyl substituent does not modify substantially the coordinating tendencies of the tetraaza macrocyclic subunit, which incorporates the Ni<sup>II</sup> or the Cu<sup>II</sup> ions to give very stable complexes, from both a thermodynamic and a kinetic point of view.

The second ferrocene-metallocyclam conjugate system investigated in this work for its redox activity has been obtained through the reaction between ferrocenesulfonamide, the open-chain tetramine 2.3.2-tet, and 2 equiv of formaldehyde, in presence of the Ni<sup>II</sup> ion acting as a template. (See Scheme II.)

Primary amines, RNH<sub>2</sub>, have been shown to work as convenient locking fragments (or *molecular padlocks*) in the Ni<sup>II</sup> template synthesis of pentaaza macrocycles of type **6** (azacyclams).<sup>13</sup> It has been demonstrated through X-ray investigations and studies in solution on complex **6** that only the four secondary nitrogen atoms are bound to the metal center, according to a coordination mode similar to that of cyclam.<sup>13</sup> The tertiary nitrogen atom in **6** is not involved in coordination but exerts a purely architectural role. We have recently observed that primary sulfonamides can effectively replace primary amines as locking fragments in template syntheses of the type described above and offer the opportunity to append any wished functionality at the cyclam-like ring.<sup>14</sup> In particular, the use of ferrocenesulfonamide affords the rapid and direct preparation of a ferrocene-metallocyclam conjugate, [Ni<sup>II</sup>(LH<sub>2</sub>SO<sub>2</sub>Fc)] (**2**), in which the two redox-active fragments are interfaced by an -SO<sub>2</sub>- group.

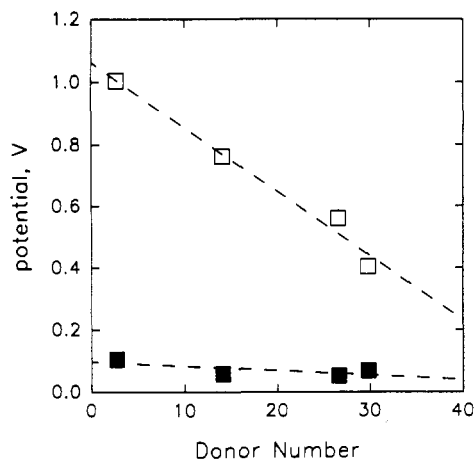
**Two-Electron Redox Activity of the Ferrocene-Nickel Cyclam Conjugates.** Solvent Effects on  $E_{\text{Fc}}$  and  $E_{\text{NiL}}$ . The [Ni<sup>II</sup>(LCH<sub>2</sub>Fc)](ClO<sub>4</sub>)<sub>2</sub> complex is poorly soluble in water, but it dissolves in most common organic solvents. Both cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies in an acetonitrile (MeCN) solution, made 0.1 M in Bu<sub>4</sub>NClO<sub>4</sub>, disclosed a fully



**Figure 1.** Cyclic voltammetry profile for a MeCN solution, made 10<sup>-1</sup> M in Bu<sub>4</sub>NClO<sub>4</sub> and 10<sup>-3</sup> M in [Ni<sup>II</sup>(LCH<sub>2</sub>Fc)](ClO<sub>4</sub>)<sub>2</sub> (**1**) (working electrode platinum microsphere; potential scan rate 200 mV s<sup>-1</sup>). The less anodic wave refers to the one-electron oxidation of the ferrocene subunit, and the more anodic wave corresponds to the Ni<sup>II</sup>-to-Ni<sup>III</sup> oxidation process inside the adjacent polyazamacrocyclic ring.

reversible two-wave profile. Figure 1 reports the CV curve at a 100 mV s<sup>-1</sup> scan rate. The less anodic reversible wave is to be assigned to the oxidation process involving the ferrocene subunit. In fact, the associated  $E_{1/2}$  value (0.059 V vs Fc<sup>+</sup>/Fc) compares well with that observed for the free ligand LCH<sub>2</sub>Fc (**3**) under the same conditions (0.040 V vs Fc<sup>+</sup>/Fc). Thus, appending the tetraaza ring to ferrocene induces a moderate increase of the oxidation potential, due to an electron-withdrawing effect propagated through the methylene moiety. Dropping a Ni<sup>II</sup> ion into the ring induces a further slight increase of the potential, as a probable consequence of the electrostatic repulsion exerted on the ferrocenium subunit by the proximate Ni<sup>II</sup> cation. The more anodic reversible wave observed in the CV profile corresponds to the Ni<sup>II</sup>-to-Ni<sup>III</sup> oxidation process. It should be noted that the associated  $E_{1/2}$  value (0.762 V vs Fc<sup>+</sup>/Fc) is substantially higher than that observed for the oxidation of the [Ni<sup>II</sup>(cyclam)]<sup>2+</sup> complex under the same conditions (0.590 V vs Fc<sup>+</sup>/Fc). However, the comparison with the [Ni<sup>II</sup>(cyclam)]<sup>2+</sup> complex is not correct, as plain cyclam possesses four secondary nitrogen atoms, whereas the macrocyclic subunit of the conjugate system possesses three secondary nitrogen atoms and a tertiary one. It has been shown that substituents on the nitrogen atoms reduce the intensity of the in-plane metal-ligand interactions and, as a

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**Figure 2.** Dependence of the redox behavior of the  $[\text{Ni}^{\text{II}}(\text{LCH}_2\text{Fc})]^{2+}$  conjugate system, **1**, upon Gutmann's donor number ( $\text{kcal mol}^{-1}$ ): (■) potentials referring to the oxidation process involving the ferrocene moiety; (□) potentials corresponding to the  $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$  redox couple of the metalloclam subunit. Solutions were made 0.1 M in  $\text{Bu}_4\text{NClO}_4$ . Investigated media:  $\text{MeNO}_2$ ,  $\text{MeCN}$ ,  $\text{DMF}$ ,  $\text{DMSO}$  (in order of increasing DN).

consequence, make the access to the  $\text{Ni}^{\text{III}}$  state more difficult.<sup>15</sup> Thus, the correct comparison has to be made with the complex of *N*-methylcyclam ( $E_{1/2} = 0.700 \text{ V vs Fc}^+/\text{Fc}$ ).<sup>15</sup> This value is still less positive than that observed for the oxidation of  $\text{Ni}^{\text{II}}$  in the conjugate system. The 60-mV extrapotential should derive from the electrostatic repulsion between the two oxidized subunits. In any case, apart from the moderate electrostatic effects, the conjugate system reproduces well the redox activities brought by its components, ferrocene and  $[\text{Ni}^{\text{II}}(\text{Mecyclam})]^{2+}$ .

The  $[\text{Ni}^{\text{II}}(\text{LCH}_2\text{Fc})(\text{ClO}_4)_2]$  complex displays a similar behavior in all the other investigated solvents: nitromethane ( $\text{MeNO}_2$ ), *N,N*-dimethylformamide ( $\text{DMF}$ ), and dimethyl sulfoxide ( $\text{DMSO}$ ). A reversible two-wave profile is observed in every case, and the oxidation of the ferrocene subunit takes place first. However, the separation of the potentials for the two waves ( $E_{\text{NiL}} - E_{\text{Fc}}$ ) is not the same but decreases along the series  $\text{MeNO}_2 > \text{MeCN} > \text{DMF} > \text{DMSO}$ . Moreover, it has been observed that  $E_{\text{Fc}}$  and  $E_{\text{NiL}}$  correlate well with the solvent donor number, DN.<sup>16</sup> In particular,  $E_{\text{NiL}}$  shows a steep linear decrease with DN, whereas the  $E_{\text{Fc}}$  vs DN least-squares straight line exhibits a slope only slightly negative (see Figure 2). The pronounced influence of the donating tendencies of the solvent (expressed by its DN value) on the potential corresponding to the oxidation of the metalloclam subunit seems to depend upon the axial binding of solvent molecules to the  $\text{Ni}^{\text{II}}$  and  $\text{Ni}^{\text{III}}$  metal centers.  $\text{Ni}^{\text{II}}$  ( $d^8$ ) complexes with cyclam-like macrocycles exist in solution of polar media as an equilibrium mixture of a planar, low-spin form and a trans-octahedral, high-spin form: in absence of strongly coordinating anions, the axial positions of the trans-octahedral complex are occupied by solvent molecules. On the other hand,  $\text{Ni}^{\text{III}}$  complexes ( $d^7$ , low-spin) exhibit a trans-octahedral stereochemistry.<sup>17</sup> In particular, the  $\text{Ni}^{\text{III}}$  cation, due to the greater electrical charge, profits from the axial interactions with solvent molecules, to a larger extent than the  $\text{Ni}^{\text{II}}$  cation. Thus, the stronger the donor tendencies of the solvent, the more stable the  $\text{Ni}^{\text{III}}$  species and the less positive the potential.<sup>18</sup>

On the other hand, the very moderate slope of the  $E_{\text{Fc}}$  vs DN straight line does not necessarily demonstrate that the oxidation process involving the organometallic subunit of the  $[\text{Ni}^{\text{II}}(\text{LCH}_2-$

$\text{Fc})]^{2+}$  conjugate system is insensitive or almost insensitive to the solvent. In fact,  $E_{1/2}$  values are referred to the redox process involving plain ferrocene. It is generally admitted that the  $\text{Fc}/\text{Fc}^+$  redox change is poorly affected by solvational terms.<sup>19</sup> However, whatever their intensity is, the slightly negative slope observed in the diagram of Figure 2 indicates that such solvation effects are more pronounced for the organometallic subunit of conjugate system than for plain ferrocene. Such a behavior may be ascribed to some cooperativity exerted by the proximate positively charged metalloclam subunit.

In any case, the different sensitivity of its components to the solvent makes the  $[\text{Ni}^{\text{II}}(\text{LCH}_2\text{Fc})]^{2+}$  conjugate an interesting two-electron-redox agent, in which the  $E_2 - E_1$  separation can be modulated from the outside, by choosing the appropriate solvent. It should be also noticed that the slope of the  $E_{\text{NiL}}$  vs DN straight line is not so negative to allow a crossing of the two straight lines and to cause an inversion of the  $E_{\text{Fc}}$  and  $E_{\text{NiL}}$  sequence, within accessible values of DN. On the other hand, such a crossing could be anticipated by "raising" the straight line pertinent to the ferrocene subunit. This effect could be reached, as an example, by appending an electron-withdrawing substituent to one of the cyclopentadienyl rings. This is the case of the ferrocene-metalloclam conjugate system  $[\text{Ni}^{\text{II}}(\text{LSO}_2\text{Fc})]^{2+}$ , in which an  $-\text{SO}_2-$  group, the linking segment, is directly bound to ferrocene. The electron-withdrawing tendency of the sulfonamide group has been demonstrated through the voltammetric investigation of *N,N*-diethylferrocenesulfonamide, in a  $\text{MeCN}$  solution 0.1 M in  $\text{Bu}_4\text{NClO}_4$ : the measured  $E_{1/2}$  value is substantially more positive than that observed for plain ferrocene ( $0.208 \text{ V vs Fc}^+/\text{Fc}$ ).

In a  $\text{MeCN}$  solution, 0.1 M in  $\text{Bu}_4\text{NClO}_4$ , the  $[\text{Ni}^{\text{II}}(\text{LSO}_2\text{Fc})]^{2+}$  system undergoes a two-electron oxidation process through two distinct consecutive one-electron steps, as shown by the reversible CV profile. In particular, the  $E_{\text{Fc}}$  value ( $0.375 \text{ V vs Fc}^+/\text{Fc}$ ) is 315 mV more positive than that observed for the  $[\text{Ni}^{\text{II}}(\text{LCH}_2\text{Fc})]^{2+}$  conjugate, due to the expected electron-withdrawing effect exerted by the  $-\text{SO}_2-$  linking segment. Such an effect is also observed to some extent for the oxidation of the metalloclam subunit, which displays a full set of secondary amine nitrogen atoms but exhibits an  $E_{\text{NiL}}$  value ( $0.796 \text{ V vs Fc}^+/\text{Fc}$ ) slightly more positive (by 34 mV) than that observed for the  $[\text{Ni}^{\text{II}}(\text{LCH}_2\text{Fc})]^{2+}$  system, displaying a set of three secondary nitrogen atoms and a tertiary nitrogen atoms. Thus, the electron-withdrawing effect of the  $-\text{SO}_2-$  segment is exerted even on the proximate secondary amine donor atoms of the macrocyclic ring, through the  $-\text{CH}_2-$  groups. Figure 3 reports the  $E_{1/2}$  vs DN plots for the two redox-active subunits of the  $[\text{Ni}^{\text{II}}(\text{LSO}_2\text{Fc})]^{2+}$  system. The diagram is very similar to the one relative to the  $[\text{Ni}^{\text{II}}(\text{LCH}_2\text{Fc})]^{2+}$  system and displayed in Figure 2. In particular, the  $E_{\text{Fc}}$  vs DN least-squares straight line presents a more positive intercept but the same slope as the corresponding one for the  $[\text{Ni}^{\text{II}}(\text{LCH}_2\text{Fc})]^{2+}$  system. The  $E_{\text{NiL}}$  vs DN least-squares straight line coincides, within the standard deviation, with that of the  $\text{CH}_2$ -linked conjugate system.

It should be noted that, also in this case, the two potential vs donor number straight lines cross beyond the DN value of the most donating medium investigated in this work, e.g.  $\text{DMSO}$ . To achieve the inversion of the potential pattern, one has to look at solvents presenting a DN value higher than 34, the value at which the two least-squares straight lines cross. In particular, we chose hexamethylphosphoramide (HMPA), which presents a DN value<sup>16</sup> of  $38.8 \text{ kcal mol}^{-1}$ . However, poorly reversible CV profiles were obtained in this medium, made 0.1 M in  $\text{Bu}_4\text{NClO}_4$ , for both the  $[\text{Ni}^{\text{II}}(\text{LSO}_2\text{Fc})]^{2+}$  system and its individual components. The investigation was complicated by the fact that HMPA has a rather narrow electrochemical window and that the anodic

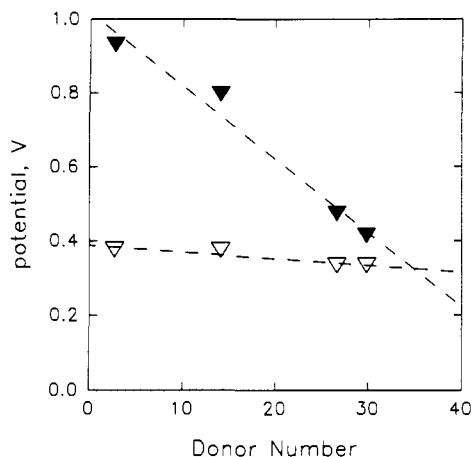
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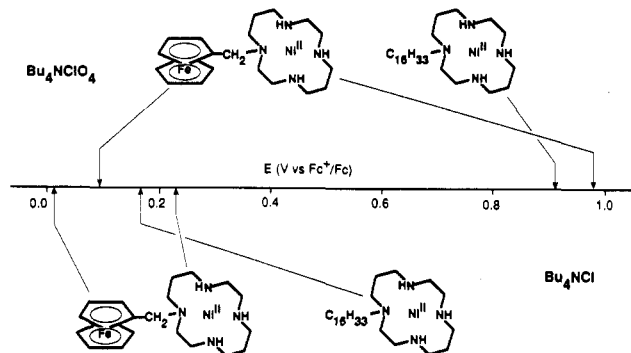


**Figure 3.** Dependence of the redox behavior of the  $[\text{Ni}^{\text{II}}(\text{LSO}_2\text{Fc})]^{2+}$  conjugate system, **2**, upon Gutmann's donor number ( $\text{kcal mol}^{-1}$ ): ( $\nabla$ ) potentials referring to the oxidation process involving the ferrocene moiety; ( $\blacktriangledown$ ) potentials corresponding to the  $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$  redox couple of the metalocyclam subunit. Solutions were made 0.1 M in  $\text{Bu}_4\text{NClO}_4$ . Investigated media:  $\text{MeNO}_2$ ,  $\text{MeCN}$ ,  $\text{DMF}$ ,  $\text{DMSO}$  (in order of increasing DN).

discharge takes place quite early. This behavior is in agreement with the general statement that strong Lewis bases, as generous electron donors, are also good reducing agents.

Crossing of the potential vs DN straight lines before the DMSO value would involve raising the intercept of the  $E_{\text{Fc}}$  vs DN curve and lowering the intercept of the  $E_{\text{NiL}}$  vs DN curve. To achieve that, the design of the conjugate should be appropriately modified. As an example, the chosen substituent, e.g.  $-\text{R}_2\text{NSO}_2-$ , should exert its electron-withdrawing effect on the ferrocene subunit but not on the proximate metalocyclam fragment; in particular, it should not be used as a bridge. Moreover, the bridging segment has to be appended at a carbon atom of the macrocyclic framework and not at a coordinating nitrogen of the cyclam-like ring, which should present a full donor set of secondary amine nitrogen atoms.

**Two-Electron Redox Activity of the Ferrocene–Nickel Cyclam Conjugates. Anion Effect on  $E_{\text{Fc}}$  and  $E_{\text{NiL}}$ .** Besides solvent molecules, anions can occupy the axial positions of the metalocyclam subunit of the investigated conjugate systems. In the experiments described in the previous section, solvents of varying coordinating tendencies had been considered. The anion of the salt used as a background electrolyte,  $\text{ClO}_4^-$ , is a poorly coordinating one, and it is believed not to compete for the axial positions with the solvent molecules, which are present in overwhelming concentration. To explore and evaluate any selectivity effect due to the anion coordination, we carried out electrochemical studies on  $[\text{Ni}^{\text{II}}(\text{LCH}_2\text{Fc})]\text{X}_2$  salts in a  $\text{CH}_2\text{Cl}_2$  solution, made 0.1 M in  $\text{Bu}_4\text{NX}$  ( $\text{X} = \text{ClO}_4, \text{Cl}$ ). We chose dichloromethane, as it is a noncoordinating medium but is polar enough to be used in voltammetry experiments. In the  $\text{CH}_2\text{Cl}_2$  solution, the axial positions of the macrocyclic subunit, in both its reduced and oxidized forms, are occupied by  $\text{X}^-$  anions. Such a situation has been verified in the case of the  $\text{Ni}^{\text{II}}$  complexes of a lipophilic version of cyclam: 1-hexadecyl-1,4,8,11-tetraazacyclotetradecane (*N*-cetyl cyclam).<sup>20</sup> Voltammetric studies on a  $\text{CH}_2\text{Cl}_2$  solution  $10^{-3}$  M in  $[\text{Ni}^{\text{II}}(\text{LCH}_2\text{Fc})](\text{ClO}_4)_2$  and  $10^{-1}$  M in  $\text{Bu}_4\text{NClO}_4$  gave a reversible two-wave profile. The first wave (0.098 V vs  $\text{Fc}^+/\text{Fc}$ ) is ascribed to the oxidation process involving the organometallic moiety of the conjugate; the second wave, which is ascribed to the  $\text{Ni}^{\text{II}}$ -to- $\text{Ni}^{\text{III}}$  oxidation process in the tetraazamacrocyclic subunit, exhibits an  $E_{1/2}$  value (0.972 V vs  $\text{Fc}^+/\text{Fc}$ ) about 50 mV more positive than that observed for the oxidation of  $[\text{Ni}^{\text{II}}(\text{N-cetyl cyclam})](\text{ClO}_4)_2$ . Again, the extrapo-



**Figure 4.** Anion effect on the redox behavior of the  $[\text{Ni}^{\text{III}}(\text{LCH}_2\text{Fc})]^{2+}$  conjugate system, **2**, in a  $\text{MeCN}$  solution made 0.1 M in  $\text{Bu}_4\text{NX}$  ( $\text{X} = \text{ClO}_4, \text{Cl}$ ). Potentials in the upper part of the diagram refer to the perchlorate solution, and potentials in the lower part of the diagram refer to the chloride solution.

tential should be ascribed to the electrostatic repulsion exerted by the proximate ferrocenium fragment, which makes the increase of the electrical charge on the nickel center more difficult.  $E_{1/2}$  values pertinent to the  $[\text{Ni}^{\text{III}}(\text{LCH}_2\text{Fc})](\text{ClO}_4)_2$  system, in a  $\text{CH}_2\text{Cl}_2$  solution 0.1 M in  $\text{Bu}_4\text{NClO}_4$ , are pictorially reported in the upper part of the potential diagram of Figure 4. A two-wave profile has also been observed for a  $\text{CH}_2\text{Cl}_2$  solution  $10^{-3}$  M in  $[\text{Ni}^{\text{II}}(\text{LCH}_2\text{Fc})]\text{Cl}_2$  and  $10^{-1}$  M in  $\text{Bu}_4\text{NCl}$ . However, the separation of the two waves is much smaller than for the perchlorate-containing solution (see Figure 4). Also in this case, the first wave (0.012 V vs  $\text{Fc}^+/\text{Fc}$ ) is ascribed to the oxidation of the ferrocene subunit and the second wave (0.223 V vs  $\text{Fc}^+/\text{Fc}$ ) to the oxidation of the  $\text{Ni}^{\text{II}}$  center. Notice that, again, the  $E_{\text{NiL}}$  value is more positive than that observed for the oxidation of  $[\text{Ni}^{\text{II}}(\text{N-cetyl cyclam})]\text{Cl}_2$  under the same conditions,<sup>20</sup> probably due to the already mentioned electrostatic repulsive effects. The anion effect mimics that of the solvent and reflects the fact that  $\text{Ni}^{\text{III}}$  profits from a strong axial coordination to a much greater extent than  $\text{Ni}^{\text{II}}$ . Thus, replacing the weak donor  $\text{ClO}_4^-$  with the strong donor  $\text{Cl}^-$  makes the  $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$  potential of both the macrocyclic subunit of the conjugate system and the *N*-cetyl cyclam complex substantially decrease (by ca. 750 mV). Such a strong stabilizing effect cannot be experienced by the coordinatively saturated iron center of ferrocene. Thus, the appropriate choice of the supporting electrolyte is a further way to control the two-electron redox activity of the ferrocene–metalocyclam conjugate.

However, anions seem to affect indirectly the  $E_{\text{Fc}}$  value of the conjugate system (although to a lesser extent), through electrostatic effects. Such effects make the  $E_{\text{Fc}}$  potential distinctly more positive for  $[\text{Ni}^{\text{II}}(\text{LCH}_2\text{Fc})](\text{ClO}_4)_2$  than for  $[\text{Ni}^{\text{II}}(\text{LCH}_2\text{Fc})]\text{Cl}_2$ . It appears that the axially bound  $\text{Cl}^-$  ions quench almost completely the electrical charge of the  $\text{Ni}^{\text{II}}$  center, so that  $E_{\text{Fc}}$  in the chloride solution is only slightly more positive than that of plain ferrocene under the same conditions. On the other hand, such a quenching effect is exerted only partially by the weakly axially coordinated perchlorate ions, which causes the oxidation of the organometallic subunit to take place at a potential higher (by 100 mV) than that of the individually taken component ferrocene. In this regard, it is important to note that the free  $\text{LCH}_2\text{Fc}$  ligand does not experience a similar effect,  $E_{\text{Fc}}$  in the perchlorate solution being in this case only 20 mV more positive than that in the chloride solution.

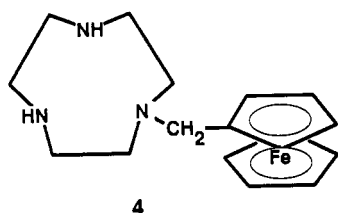
The anion effect could not be investigated for the  $[\text{Ni}^{\text{II}}(\text{LSO}_2\text{Fc})]\text{X}_2$  system, as only the chloride derivative is soluble in  $\text{CH}_2\text{Cl}_2$ .

**Appending the Ferrocenyl Subunit to a Triaza Ring.** The sensitivity to the medium of the redox behavior of ferrocene–metalocyclam conjugate systems of the type described above depends upon the different coordinative situations experienced

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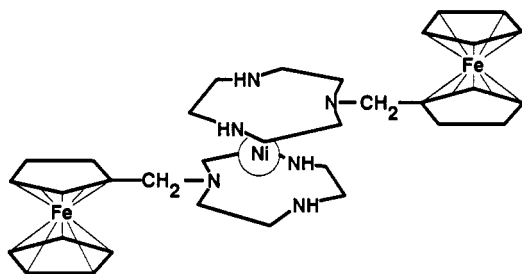
by the two metal centers, saturated (Fe) and unsaturated (Ni). Such a consideration prompted us to envisage a new system in which also the nickel center was coordinately saturated. In this connection, we looked at the 1:2 complex of Ni<sup>II</sup> with 1,4,7-triazacyclononane (TACN). The [Ni<sup>II</sup>(TACN)<sub>2</sub>]<sup>2+</sup> complex presents distinctive *macrocyclic properties*: (i) it is thermodynamically more stable than the corresponding complex with analogous open-chain triamines, (ii) it is rather resistant to demetalation in a strongly acidic solution, and, in particular, (iii) it undergoes a reversible one-electron oxidation process to give a stable Ni<sup>III</sup> species.<sup>9,21</sup> The [Ni<sup>III</sup>(TACN)<sub>2</sub>]<sup>3+</sup> complex presents an axially elongated octahedral stereochemistry, as expected for a low-spin d<sup>7</sup> cation, due to the Jahn-Teller effect.<sup>22</sup> The potential for the [Ni<sup>II</sup>(TACN)<sub>2</sub>]<sup>2+</sup>/[Ni<sup>III</sup>(TACN)<sub>2</sub>]<sup>3+</sup> redox couple is slightly less positive than that observed for the corresponding cyclam complex (0.560 and 0.590 V vs Fc<sup>+</sup>/Fc, respectively, in MeCN, 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>). The slightly greater relative stability of the [Ni<sup>III</sup>(TACN)<sub>2</sub>]<sup>3+</sup> complex compared to [Ni<sup>III</sup>(cyclam)]<sup>3+</sup> reflects the affinity of trivalent nickel for six-coordination.<sup>9</sup> Moreover, temperature-dependent electrochemical studies in aqueous solution have pointed out that also the entropy term favors the formation of the [Ni<sup>III</sup>(TACN)<sub>2</sub>]<sup>3+</sup> complex, compared to [Ni<sup>III</sup>(cyclam)]<sup>3+</sup>.<sup>23</sup>

A ferrocene-TACN conjugate system was prepared by the same procedure used for the synthesis of LCH<sub>2</sub>Fc. In particular, 1-(ferrocenylmethyl)-1,4,7-triazacyclonane (**4**, TCH<sub>2</sub>Fc) was



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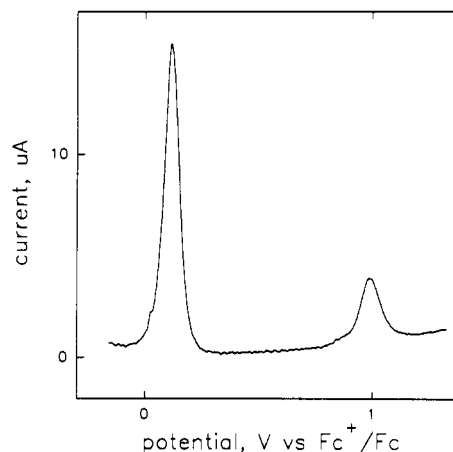
obtained through reaction of the (ferrocenylmethyl)trimethylammonium cation (as the iodide) with a 3-fold excess of TACN. Reaction of **4** with Ni<sup>II</sup>, according to a 2:1 ratio, gave the [Ni<sup>II</sup>(TCH<sub>2</sub>Fc)<sub>2</sub>]<sup>2+</sup> system, whose hypothesized stereochemical arrangement is sketched in **7**.



7

Due to the presence of *two* appended ferrocene fragments, [Ni<sup>II</sup>(TCH<sub>2</sub>Fc)<sub>2</sub>]<sup>2+</sup> is expected to behave as a *three-electron* system. Such a behavior has been documented through electrochemical investigations of an MeCN solution of [Ni<sup>II</sup>(TCH<sub>2</sub>Fc)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, made 0.1 M in Bu<sub>4</sub>NClO<sub>4</sub>. CV and DPV measurements revealed a two-wave profile. In particular, Figure 5 shows the differential pulse voltammetry curve.

The controlled-potential electrolysis experiment, carried out at a potential 150 mV more positive than the  $E_{1/2}$  value (116 mV vs Fc<sup>+</sup>/Fc) associated with the more intense, less anodic wave, indicated the consumption of 1.98 electrons. Thus, this wave can



**Figure 5.** Differential pulse voltammetry profile for an MeCN solution, made 10<sup>-1</sup> M in Bu<sub>4</sub>NClO<sub>4</sub> and 10<sup>-3</sup> M in [Ni<sup>II</sup>(TCH<sub>2</sub>Fc)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**7**) (working electrode platinum microsphere; potential scan rate 5 mV s<sup>-1</sup>; pulse amplitude 10 mV). The less anodic peak refers to the simultaneous oxidation of the two ferrocene subunits, and the more anodic peak corresponds to the Ni<sup>II</sup>/Ni<sup>III</sup> process inside the bis(triaza) macrocyclic environment.

be ascribed to the oxidation of the two appended organometallic moieties. The fact that the DPV peak displays the same features typically observed for a one-electron reversible process (in particular, half-wave width,  $\delta_{1/2} = 90$  mV) indicates that the two redox sites exhibit independent behavior and, in the absence of electrostatic or other exotic effects, the two-electron release is statistically controlled.<sup>24</sup> Thus, the potentials corresponding to the two consecutive steps are  $E_1 = E_{1/2} - 0.018$  V = 0.098 V vs Fc<sup>+</sup>/Fc and  $E_2 = E_{1/2} + 0.018$  V = 0.134 V vs Fc<sup>+</sup>/Fc (at 25 °C). The less intense wave of the DPV profile displayed in Figure 5 ( $E_{1/2} = 0.990$  V vs Fc<sup>+</sup>/Fc) is thus ascribed to the Ni<sup>II</sup>/Ni<sup>III</sup> oxidation process, taking place inside the central bis(triaza) fragment. On the other hand, the controlled-potential coulometry experiment at a potential of 1.10 V vs Fc/Fc<sup>+</sup> did not produce the typical *plateau* but generated a constant increase of the integrated current signal, indicating that the [Ni<sup>III</sup>(TCH<sub>2</sub>Fc)<sub>2</sub>]<sup>5+</sup> system is not stable on the time scale of the constant-potential electrolysis experiment and decomposes. It should be noticed that the  $E_{1/2}$  value measured from the reversible DPV profile is 430 mV more positive than that observed for the formation of the separated component [Ni<sup>III</sup>(TACN)<sub>2</sub>]<sup>3+</sup>. In particular, this difference is more than twice that calculated in the same way, i.e. ( $E_{\text{conjugate}} - E_{\text{Ni(cyclam)}}$ ) for the [Ni<sup>III</sup>(LCH<sub>2</sub>Fc<sup>+</sup>)]<sup>4+</sup> system, in which the Ni<sup>III</sup> cation experiences the repulsion by only *one* ferrocenium fragment. Such a large destabilizing effect should be ascribed to the fact that (i) the central Ni<sup>III</sup> cation feels the repulsions of *two* ferrocenium subunits, (ii) its positive charge may be less shielded by the surrounding ligands, compared to the ferrocene-cyclam conjugate system in which the nickel center is merged in a tetraaza ring, and (iii) the donor set in [Ni<sup>III</sup>(TCH<sub>2</sub>Fc<sup>+</sup>)]<sup>5+</sup> consists of four secondary and two tertiary amino groups instead of the six secondary amino groups of [Ni<sup>III</sup>(TACN)<sub>2</sub>]<sup>3+</sup>.

Voltammetric studies (CV and DPV) on MeNO<sub>2</sub> and DMF solutions of [Ni<sup>II</sup>(TCH<sub>2</sub>Fc)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, which were made 0.1 M in Bu<sub>4</sub>NClO<sub>4</sub>, presented a two-wave profile, with a 2+1 mode of the electron release. In DMSO, only the two-electron wave, pertinent to the consecutive oxidation of the two equivalent organometallic moieties, was observed, the wave expected for the Ni<sup>II</sup>/Ni<sup>III</sup> oxidation process being anticipated by the medium anodic discharge. Again, available potential values were plotted vs the solvent donor number (see Figure 6). In the case of ferrocene subunits, the average value ( $=E_{1/2}$ ) was plotted.

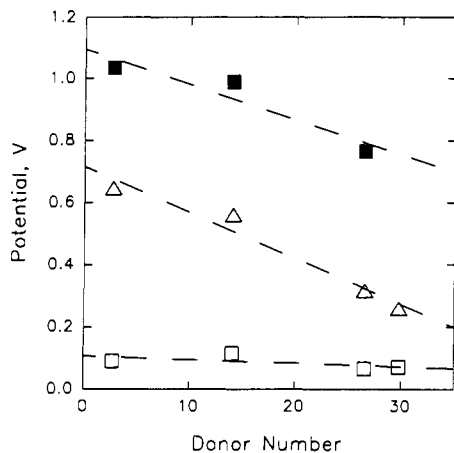
It may be surprising to note that  $E_{1/2}$  values pertinent to the oxidation process involving the coordinatively saturated bis(triaza)

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**Figure 6.** Dependence of the redox behavior of the  $[\text{Ni}^{\text{II}}(\text{TCH}_2\text{Fc})_2]^{2+}$  conjugate system, **7**, upon Gutmann's donor number ( $\text{kcal mol}^{-1}$ ): (□) potentials referring to the two-electron oxidation process involving the two appended ferrocene subunits; (■) potentials corresponding to the  $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$  redox couple of the bis(triaza) macrocyclic central fragment; (Δ) data referring to the reference system  $[\text{Ni}^{\text{II}}(\text{TACN})_2]^{2+}$ . Solutions were made 0.1 M in  $\text{Bu}_4\text{NClO}_4$ . Investigated media:  $\text{MeNO}_2$ ,  $\text{MeCN}$ ,  $\text{DMF}$ ,  $\text{DMSO}$  (in order of increasing DN).

fragment are not constant but decrease with the increasing solvent donicity, even if the slope of the  $E_{\text{NiL}}$  vs DN best fitting straight line is less negative than that observed for the  $[\text{Ni}^{\text{II}}(\text{LCH}_2\text{Fc})]^{2+}$  analogue ( $-0.0114$  and  $-0.0207$   $\text{V kcal}^{-1} \text{ mol}$ , respectively). However, the sensitivity to the medium of the redox potential of nickel bis(triaza) subunit in the conjugate system is not singular, as the same behavior has been observed for the separated component  $[\text{Ni}^{\text{II}}(\text{TACN})]^{2+}$  (see Figure 6). In particular, its  $E_{1/2}(\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}})$  value linearly decreases with a similar slope ( $-0.015$   $\text{V kcal}^{-1} \text{ mol}$ ) with the increasing donor dependencies of the solvent. This indicates that solvent molecules interact, at a solvation sphere level, with the bis(triaza)azamacrocyclic complex,

probably through hydrogen bonds with the hydrogen atoms of the coordinated secondary amino groups. The intensity of such interactions should increase on increasing the charge of the coordinated metal center, accounting for the stabilizing effect on the  $\text{Ni}^{\text{III}}$  state exerted by strongly donating solvents. On the other hand, solute-solvent interactions through hydrogen bonding are not expected to form with the hydrogen atoms of the cyclopentadienyl rings of both reduced and oxidized forms of the appended organometallic subunits.

Thus, also in the case of the three-electron redox agent  $[\text{Ni}^{\text{II}}(\text{TCH}_2\text{Fc})_2]^{2+}$ , the separation of the potential of the two redox events can be controlled through the medium. The ( $E_{\text{Fc}} - E_{\text{NiT}}$ ) difference is especially large, due to the presence of strong electrostatic repulsions, and even if the second redox-active metal center is coordinatively saturated, its magnitude decreases to some extent with the increasing solvent donicity.

### Conclusions

Covalently linked ferrocene-metallocyclam conjugates represent a novel class of multicenter coordination compounds, displaying intriguing redox activity. In particular, the different sensitivities to the solvent molecules and to the anions of the supporting electrolyte make it possible to control *from the outside* the redox behavior of each component and to modulate the potential difference separating the two one-electron steps. An additional fine control of such a redox activity could be achieved through structural modifications of the ferrocene and/or the metallocyclam fragment, a well-developed area of synthetic coordination chemistry. Moreover, more drastic variations of the redox behavior could be obtained by replacing the nickel center with a further 3d cation that displays its redox activity in a distinctly more cathodic (e.g.  $\text{Co}^{\text{III,II}}$ ) or more anodic (e.g.  $\text{Cu}^{\text{III,II}}$ ) part of the electrochemical scale.

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