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Redox processes in supramolecular coordination compounds

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CONTENTS

A. INTRODUCTION

Most of the reactions of coordination compounds are redox processes and, in most cases, the electron transfer process is centred on the metal. Moreover, due to the essential d nature of the anti-bonding or non-bonding orbitals involved, redox activity is displayed according to one or more one-electron steps. An intriguing point associated with this chemistry is that the energy of the redox orbitals can be varied by varying donor strength of the ligand and the stereochemistry of the metal complex. Thus, the access to a given oxidation state of the metal centre can be controlled by modifying the coordinating tendencies of the ligating system; in particular, changing the nature and/or the number of the donor atoms induces the largest variations in the redox reactivity, whereas subtle changes are usually achieved through structural modifications of the ligand framework. The relative stability of two consecutive oxidation states of a metal, i.e. M^{n+} and $M^{(n+1)+}$, is exactly expressed by the corresponding electrode potential $E^\circ\{(n+1)+/n+\}$ and thousands of E° values for one-electron redox changes involving metal complexes have been determined through electrochemical investigations in aqueous and non-aqueous solutions. The correlation between the electrode potential and various parameters expressing ligand's donor tendencies has been considered and elucidated for many classes of coordination compounds during the last three decades.

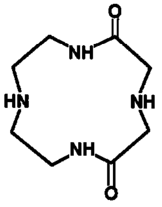
The above considerations demonstrate that metal complexes represent convenient and versatile fragments to build up (i) multicentre systems of sophisticated redox activity and (ii) assemblies able to display useful functions related to the electron transfer. According to Lehn's definition, association of two or more chemical entities gives a *supramolecular system* [1]. In this connection, the interest of many researchers is now being focused on the redox properties of supramolecular, rather than simple molecular systems. Moreover, assembling a redox active fragment with one or more different subunits may generate a system in which the individual properties of each subunit are concerted to produce a function, to give what is defined a *supramolecular device* [2]. Some examples of redox active supramolecular systems, taken from our recent work, will be discussed in the following sections. In particular, the design of multi-centre systems able to display multi-electron redox activity will be considered in detail. We will then describe some metal-containing supramolecular devices (i) for the activation of anions in aqueous solution and (ii) for the transport of electrons and ions across liquid membranes.

B. DESIGN OF TWO-ELECTRON REDOX SYSTEMS

Redox processes involving non-metal-centred substrates of the organic chemistry and biochemistry typically take place through two-electron steps. On the other hand, metal-centred systems undergo two-electron redox changes only if the metal belongs to the p block, e.g. Tl(III,I), Sn(IV,II). It has been mentioned in the previous section that the versatile d block metal ions typically display their redox activity through one-electron steps. Moreover, if the d metal, in a given coordinative environment, is prone to two or more one-electron redox changes, the corresponding E values are usually separated by a substantial difference of potential (several hundreds of mV). However, the problem of making available metal-based redox systems able to exchange two electrons at the same potential (or in a single shot) can be simply overcome by assembling two equivalent metal-centred redox active fragments [3]. Two general strategies to two-electron systems of this type are possible: (i) the two redox centres are held together through a covalent bond: this goal can be achieved, for instance, through the design of a dinucleating ligand offering exactly equivalent coordination sites; (ii) the two metal-containing redox active fragments are held together through coordinative interactions: this situation can be realized if the two redox active equivalent subunits present coordinating tendencies and bind an appropriate metal ion; this metal ion should not display any redox activity, but should play a purely architectural role.

(i) Covalently linked redox sites: biscyclam homodimetallic complexes

Poly-aza macrocycles represent convenient coordinating environments to promote and control the redox activity of a metal ion [4]. Basically, due to their closed nature, these chelating agents exert strong coordinative interactions towards the encircled metal ion, which makes the energy of the antibonding orbitals, essentially metallic in character, especially high, so favouring electron abstraction and attainment of unusually high and otherwise unstable oxidation states [5].



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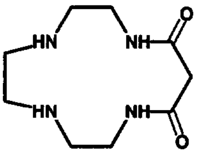

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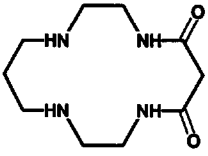

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As an example, macrocycles **1–3** (current names 12-, 13-, and 14-dioxocyclam, respectively), which contain two secondary amine groups and two deprotonable amido groups, favour the access to the Cu(III) oxidation state [6,7]. Fairly stable $[Cu^{III}(L^{2-})]^+$ complexes, of a typical yellow colour, can be obtained in aqueous solution through oxidation by peroxydisulphate of the corresponding divalent complexes, $[Cu^{II}(L^{2-})]$. Noticeably, the oxidation process is fast, in contrast to what is usually observed for redox reactions involving $S_2O_8^{2-}$. The potentials associated with the electrochemically reversible $[Cu^{III}(L^{2-})]^+ [Cu^{II}(L^{2-})]$ redox change, determined through cyclic voltammetry experiments, are strongly dependent upon the ligand's structural features, as shown in the unidimensional potential diagram in Fig. 1. The diagram shows that a decrease of the macrocyclic ring size, from the 14-membered ring to the 12-membered ring, makes the Cu^{III}/Cu^{II} redox couple potential less and less positive, i.e. makes access to the trivalent state of copper easier and easier. The above trend can be qualitatively accounted for by considering the substan-

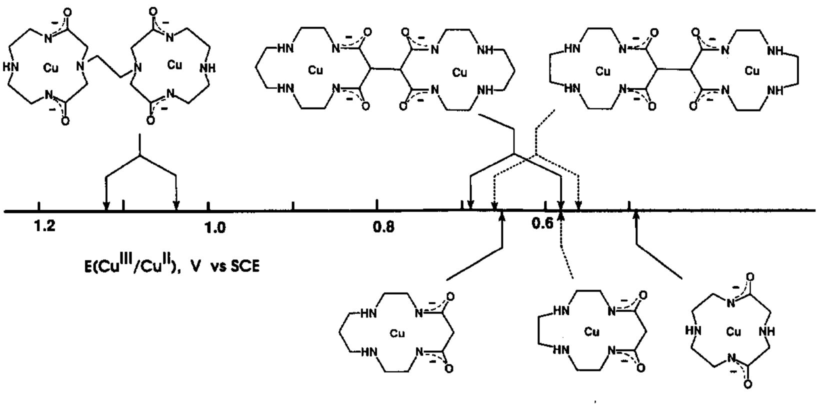


Fig. 1. Half-wave potentials determined by voltammetric investigations in aqueous solutions, for the Cu^{III}/Cu^{II} redox change in single-ring and double-ring dioxocyclamato complexes (E(V) vs. SCE).

tially different sizes of the two copper ions: the larger Cu(II) ion fits well the 14-membered ring, but is too large to allow the favourable coplanar coordination by the 12-membered ligand. On the other hand, the much smaller Cu(III) ion (d^8, low spin) perfectly fits the 12-membered cavity, allowing a regular square coordination.

Dinucleating ligands containing dioxocyclam subunits can be prepared by extremely simple synthetic routes [8,9]. Synthesis does not involve coupling of two preformed dioxocyclam rings, but proceeds through the one-step condensation of a tetraester with the appropriate polyamine, in a 1:2 molar ratio, as illustrated in Fig. 2.

In one case (synthesis of **4**, [13-13]-bisdioxocyclam, and **5**, [14-14]-bisdioxocyclam) the tetraester tetraethyl-1,1,2,2-ethanetetracarboxylate is reacted with an open-chain tetramine. In the other (synthesis of **6**, [12-12]-bisdioxocyclam), the tetramethyl ester of EDTA is condensed with diethylenetriamine. Synthetic procedures are, in any case, especially convenient, as they are of the one-pot type and involve non-sophisticated reagents. Moreover, after 2–3 days of reflux, the product separates as a crystalline or microcrystalline solid in satisfactory yield from the ethanolic solution. Each subunit of the dinucleating ligand incorporates a copper(II) ion with simultaneous deprotonation of the two amido groups at a value of pH > 5. The $[\mathrm{Cu}^{\mathrm{II}}_2(\mathrm{L}^{2-}\text{—}\mathrm{L}^{2-})]$ complex undergoes in aqueous solution a two-electron oxidation process to the $[\mathrm{Cu}^{\mathrm{III}}_2(\mathrm{L}^{2-}\text{—}\mathrm{L}^{2-})]^{2+}$ species, according to two one-electron consecutive steps. For the three investigated complexes of the dinucleating ligands **4**–**6**, the first oxidation step, eqn. (1), takes place at a potential E_1 which is about 100 mV less positive than the E_2 potential associated with the second oxidation step, eqn. (2).

$$[\mathrm{Cu}^{\mathrm{II}}_2(\mathrm{L}^{2-}\text{—}\mathrm{L}^{2-})] = [\mathrm{Cu}^{\mathrm{II}}\mathrm{Cu}^{\mathrm{III}}(\mathrm{L}^{2-}\text{—}\mathrm{L}^{2-})]^{+} + \mathrm{e}^{-} \quad E_1 \qquad (1)$$

$$[\mathrm{Cu}^{\mathrm{II}}\mathrm{Cu}^{\mathrm{III}}(\mathrm{L}^{2-}\text{—}\mathrm{L}^{2-})]^{+} = [\mathrm{Cu}^{\mathrm{III}}_2(\mathrm{L}^{2-}\text{—}\mathrm{L}^{2-})]^{2+} + \mathrm{e}^{-} \quad E_2 \qquad (2)$$

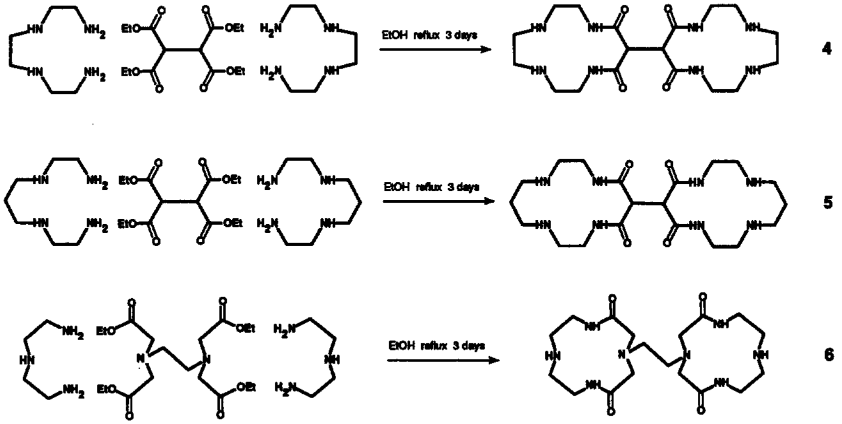


Fig. 2. Synthesis of bisdioxocyclam ligands with 12-, 13-, and 14-diamino-diamido rings.

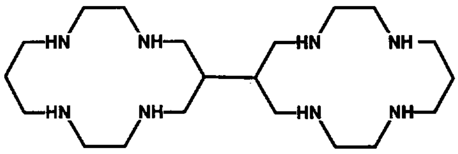
Simple statistical considerations account for the fact that step (1) is favoured with respect to step (2) [10]. As a matter of fact, a statistical factor of 2 is associated with half-reaction (1) as the electron can be abstracted from two sites and can be dropped back just on one. On the other hand, the statistical factor for half-reaction (2) is 1/2: the electron is abstracted from one ring and, in the reverse process, it can choose among two equivalent oxidizing sites. Thus, if E is the potential associated with the redox change in absence of any exotic effect, one should have:

$$E_1 = E - \frac{RT}{F} \ln 2 = E - 18\ \text{mV} \qquad (\text{at } 25^\circ\text{C})$$

$$E_2 = E + \frac{RT}{F} \ln 2 = E + 18\ \text{mV} \qquad (\text{at } 25^\circ\text{C})$$

Therefore, the difference $\Delta E = (E_2 - E_1)$ for a statistically controlled process should be 36 mV. The larger ΔE value observed indicates that other factors influence the two-electron oxidation of the dicopper(II) complexes of the dinucleating systems **4–6**. As any electron communication between the two rings can be excluded, due to the saturated nature of the bridging segment, these effects should be essentially electrostatic. In particular, the fact that the E_2 value is larger than the statistically predicted value (E_1 + 36 mV) reflects the extra energy spent to increase the charge of a copper centre from 2+ to 3+ in presence of a Cu^{3+} cation at a finite distance. Noticeably, for bisdioxocyclamato(4-) complexes of **4** and **5**, the E_1 and E_2 values lie slightly below and slightly above, respectively, the E value observed for the single-ring complex (see the potential diagram in Fig. 1). However, such a situation is not observed with the complexes of the 12-membered ring ligands **1** and **6**. In this case, the E_1 value for the dinuclear complex is more than 500 mV more positive than the E value observed for the mononuclear 12-dioxocyclamato(2-) complex. This paradoxical behaviour can be accounted for by considering that the reference ligand **1** contains two secondary amine nitrogen atoms, whereas each coordinating subunit of bismacrocycle **6** contains one secondary amine nitrogen atom and one tertiary amine nitrogen atom. A tertiary amine nitrogen atom, due to steric repulsive effects, exerts substantially less intense coordinative interactions than a secondary one, which destabilizes the higher oxidation state of the bound metal centre and makes the potential considerably more positive. The destabilizing effect of the higher oxidation state of d metal centres due to the progressive alkylation of the secondary nitrogen atoms of tetra-aza macrocycles has been clearly documented [11,12].

In spite of the closed nature of the ligand, metal dioxocyclamato(2-) complexes rapidly demetallate in acidic solution. This behaviour is related to the very fast protonation of the oxygen atom of the deprotonated amido group, which retains a partial negative charge: the poorly coordinating amido group is formed and the metal ion is extruded from the ring [13]. Hydrogenation of a dioxocyclam subunit, e.g. that of 14-dioxocyclam, gives a tetramine ring, e.g. cyclam. Decorporation of a d metal centre from the cyclam ring is an extremely slow process [14]. For instance, [Cu^{II}(cyclam)]$^{2+}$ and [Ni^{II}(cyclam)]$^{2+}$ do not decompose, but indefinitely last in a concentrated acid solution (e.g. 1 M $HClO_4$). Moreover, cyclic polyamines of the cyclam type retain the typical macrocyclic property of promoting the redox activity of the encircled metal ions [15]. This makes saturated poly-aza macrocycles very useful building blocks for supramolecular systems in which the presence of a redox active metal centre is required. By hydrogenating 14-14-bisdioxocyclam (using diborane in refluxing diglyme), molecule **7**, 14-14-biscyclam, is obtained [16].



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Due to the above-mentioned features, **7** is an ideal ditopic receptor for transition metal ions. Reaction with two equivalents of a given metal ion gives the homodimetallic complex, e.g. [Cu$^{II}_2$(L—L)]$^{4+}$ or [Ni$^{II}_2$(L—L)]$^{4+}$ [17]. Both complexes undergo a metal-centred two-electron oxidation process. In the case of nickel, formation of stable [Ni$^{III}_2$(L—L)]$^{6+}$ complexes takes place in any polar solvent (water, MeCN, DMSO, etc.). However, in the case of copper, a fairly stable [Cu$^{III}_2$(L—L)]$^{6+}$ is obtained only in the very special solvent: concentrated perchloric acid (70%, 11.56 M). This reflects the typical tendency of Cu^{III} tetra-aza-macrocyclic complexes to give rise to a base-catalyzed decomposition [18]. Figure 3 illustrates the results of a voltammetric investigation on the oxidation behaviour of Ni(II) and Cu(II) complexes of cyclam and biscyclam in a 70% $HClO_4$ solution. The diagram indicates that the two-electron oxidation of the two homodimetallic complexes investigated proceeds in a similar way as that observed for the previously discussed bisdioxocyclamato-(4-) complexes. Firstly, the E value for each mononuclear system lies between the E_1

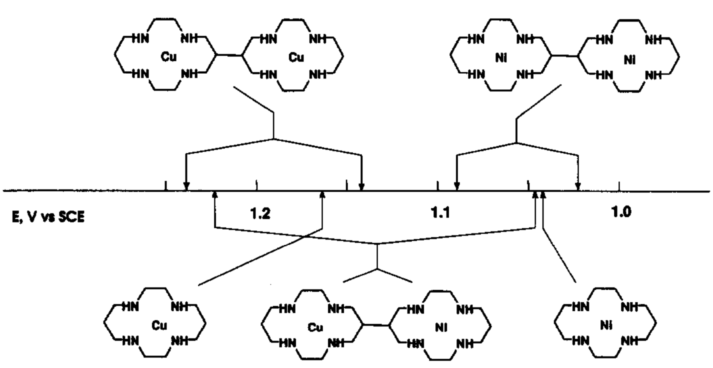
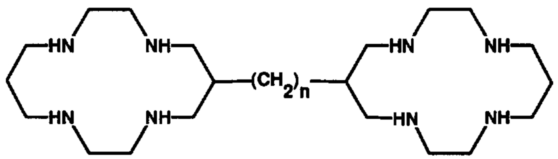


Fig. 3. Half-wave potentials, determined by voltammetric investigations in a 70% $HClO_4$ solution, for the M^{III}/M^{II} redox change in cyclam and biscyclam complexes (M = Ni, Cu). Strongly acidic conditions are required to prevent decomposition of the Cu^{III} cyclic tetramine fragment. (E(V) vs. SHE).

and E_2 values of the corresponding dimetallic complex. Secondly, the ΔE value observed with each dinuclear system is slightly larger than expected on purely statistical bases, indicating the existence of a moderate electrostatic effect associated to the release of the second electron.

The inertness of the metallocyclam subunit allows the preparation of a heterodimetallic complex using biscyclam in which, for instance, one of the rings contains Cu(II) and the other contains Ni(II). As a matter of fact, reaction of biscyclam with one equivalent of $Cu^{II}(ClO_4)_2$ and one equivalent of $Ni^{II}(ClO_4)_2$ in refluxing ethanol, followed by separation through a G-25 Sephadex column, gave 1/4 of $[Cu^{II}(L{-}L)](ClO_4)_4$, 1/2 of $[Ni^{II}Cu^{II}(L{-}L)](ClO_4)_4$ and 1/4 of $[Ni^{II}(L{-}L)](ClO_4)_4$ (in order of elution) [16]. The relative amount of the homo- and hetero-dimetallic species formed is statistically controlled, indicating that incorporation of each metal centre is not specifically influenced by the presence of a proximate divalent cation. As far as the redox chemistry is concerned, voltammetry investigations in 70% $HClO_4$ solution indicated two consecutive one-electron oxidation steps separated by a ΔE of 180 mV. The first process should be associated to the oxidation of the Ni(II) centre, whereas the second should correspond to the oxidation of Cu(II). Noticeably, the ΔE value is larger than that calculated from the difference of the potentials associated with the oxidation of the corresponding cyclam complexes: $E([Cu^{III,II}L]^{3+/2+}) - E([Ni^{III,II}L]^{3+/2+}) = 130$ mV. Again, this effect should reflect the greater difficulty of increasing the charge of the second metal centre (Cu(II)) under the electrostatic repulsive interaction of an adjacent tripositive cation (Ni(III)).

Electrostatic effects in the two-electron changes involving two-site systems should be removed by making the distance between the redox centre higher. This has been verified through the synthesis of a new class of biscyclam dinucleating ligands. In this class, the two cyclam rings are bridged by an aliphatic chain, $-(CH_2)_n-$, which joins two nitrogen atoms and n was varied from 2 to 4 [19].



n = 2 : **8**
n = 3 : **9**
n = 4 : **10**

Synthesis of **8–10** 14-n-14-biscyclam molecules is based on a different approach than that used for the C–C biscyclam analogue and involves the bridging by the appropriate segment $X-(CH_2)_n-X$ of two cyclam molecules. In each ring, all but one amine nitrogen atoms has been protected by tosyl groups.

The oxidation behaviour of the $[Ni^{II}_2(14\text{-}n\text{-}14\text{-biscyclam})](ClO_4)_4$ complexes was investigated in MeCN solution by voltammetric techniques. Figure 4 illustrates

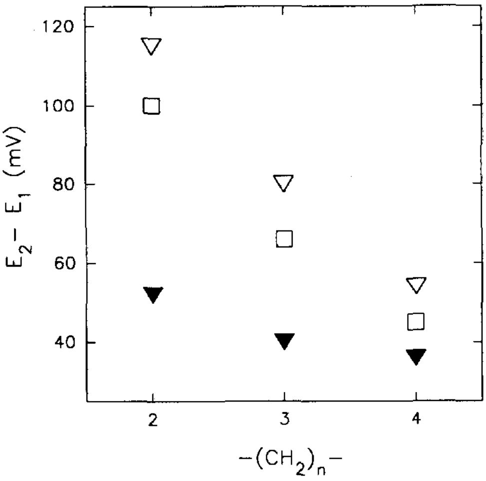


Fig. 4. Effect of the length of the connecting $-(CH_2)_n-$ chain on the potential difference, ΔE, for the second and first oxidation step of the homo-dimetallic complexes Ni^{II}_2(14-*n*-14-biscyclam)]$(ClO_4)_4$ and [Cu^{II}_2(14-*n*-14-biscyclam)]$(ClO_4)_4$. □, Ni in MeCN; ▼, Ni in 70% $HClO_4$; ▽, Cu in 70% $HClO_4$.

the variation of ΔE with the increasing number of the methylene groups in the bridge. ΔE progressively decreases, indicating a corresponding decrease of the electrostatic repulsive effects. For $n = 4$, repulsive effects vanish and ΔE has a purely statistical nature.

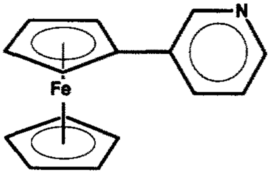
Figure 4 also reports the ΔE values obtained for [Ni^{II}_2(14-*n*-14-biscyclam)]$(ClO_4)_4$ and [Cu^{II}_2(14-*n*-14-biscyclam)]$(ClO_4)_4$ complexes in the common solvent 70% $HClO_4$. The roughly straight-line dependence of ΔE upon *n* again indicates progressive vanishing of the repulsive electrostatic interactions with the increasing bridge length. However, the substantially larger negative slope suggests that the copper complexes are more sensitive to the electrostatic effect than the corresponding nickel complexes: this has been explained on the basis of the different stereochemical features of the biscyclam complexes in the various oxidation states and on the different shielding exerted by the axially bound perchlorate ions (in the Cu(II) and Ni(III) species, in 70% $HClO_4$) [19]. In any case, at $n = 4$, repulsive effects completely disappear, independently of the nature of the metal centre ($\Delta E = 36$ mV).

(ii) Redox sites which are held together through coordinative interactions

In the previous examples, two redox active fragments A, i.e. the metallocyclam subunits, have been fixedly bound together through a covalent bond or by a covalently bonded segment, to give the multi-electron system A—A. Alternatively, coordinative interactions can be used to link the two equivalent redox centres. This strategy should involve: (i) assembling of the redox active fragment A with a frament L, which possesses coordinating tendencies, to give the conjugate system A—Li; (ii) binding of two (or even more) A—L molecules to a given metal centre, M, to give the multi-site redox system [A—L···M···L—A].

This second approach has been tested quite recently in our laboratory by using ferrocene as a redox active fragment. Ferrocene (Fc) is one of the most classical redox agents of organometallic chemistry and its tendency to undergo a one-electron oxidation process to form the solution stable ferricenenium ion (Fc^+) has been documented since its first appearance on the chemical stage [20]. The Fc^+/Fc change is so clean and reversible that it is now widely used as a reference couple (in the form of an internal standard) for electrochemical investigations in poorly polar solvents [21]. In this sense, the Fc^+/Fc couple can be considered as the non-aqueous counterpart of SCE.

As a ligating subunit, we chose another classical and versatile system of coordination chemistry, pyridine, which forms stable complexes with most metal ions.



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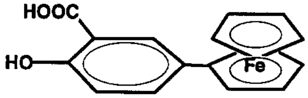
The conjugate system 3-ferrocenyl-pyridine (pyFc, **11**) was obtained by the reaction of ferrocene with the diazo-derivative of 3-amino-pyridine. Two equivalents of pyFc react with the square $[Pt^{II}Cl_4]^{2-}$ complex to give $[Pt^{II}(pyFc)_2Cl_2]$ [22]. Trans effects are expected to direct the substitution of the two chloride ions by the two pyridine molecules towards the formation of the cis derivative. The single crystal X-ray investigation confirmed the formation of the *cis*-$[Pt^{II}(pyFc)_2Cl_2]$ square complex [22]. Voltammetry investigations and controlled potential coulometry experiments in non-aqueous solutions (MeCN, DMSO), showed that the *cis*-$[Pt^{II}(pyFc)_2Cl_2]$ system undergoes a two-electron oxidation process to give the stable $[Pt^{II}(pyFc^+)_2Cl_2]^{2+}$ cation, through two consecutive one-electron steps, whose ΔE is that expected on a purely statistical basis: 36 mV. The results of the electrochemical investigation indicate that repulsive electrostatic effects between the two ferrocene subunits do not operate in the system, which can therefore be used as a convenient two-electron redox agent able to exchange two electrons at the same potential, or in a single shot. Ferrocene-based two-electron systems have previously been obtained by linking two ferrocene molecules with a C—C bond or through a carbon chain [23]. The use of a d block metal ion as a bridging fragment offers a novel opportunity to orient the redox active subunits, ferrocene molecules in the present case, at 90° each other. Bridging segments available from organic chemistry typically favour orientations of 109°, 120° and 180°, i.e. the angles associated with the carbon atom hybridization.

The ferrocene fragment can be linked to any molecule possessing coordinative tendencies to give ligands which bring redox activity. An example is given by ferrocenyl-hydroxy-benzoic acid (**12**, $FcsalH_2$), i.e. a system in which the ferrocene subunit has been appended on the back of salycylic acid [24].



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The salicylate ion is known to form stable complexes in solution with the Fe(III) ion. Titration by standard base of a 50/50 water/dioxan solution containing 1 equivalent of Fe(III) and 3 equivalents of $FcsalH_2$ indicated that, at pH = 7, 100% of the $[Fe^{III}(Fcsal^{2-})_3]^{3-}$ is formed. In analogy with the corresponding salicylate complex, $[Fe^{III}(Fcsal^{2-})_3]^{3-}$ should exhibit an octahedral stereochemistry, as illustrated in Fig. 5.

Controlled potential coulometry of the 50/50 water/dioxan solution containing $[Fe^{III}(Fcsal^{2-})]^{3-}$ disclosed a three-electron oxidation process. As the oxidation process involves the three ferrocene subunits appended on the back of each salicylate moiety, the neutral species $[Fe^{III}(Fc^{+}sal^{2-})_3]$ should form. Differential pulse voltammetry investigations on the same solution gave a single symmetric peak whose half-height width was 90 mV. Such a profile corresponds to a three-electron process controlled by the sole statistical effect. Thus, the $[Fe^{III}(Fcsal^{2-})_3]^{3-}$ complex releases three electrons, one from each ferrocene subunit, according to three one-electron steps whose potentials are separated by 28 mV ($=(RT/F)\ln 3$, at 25°C).

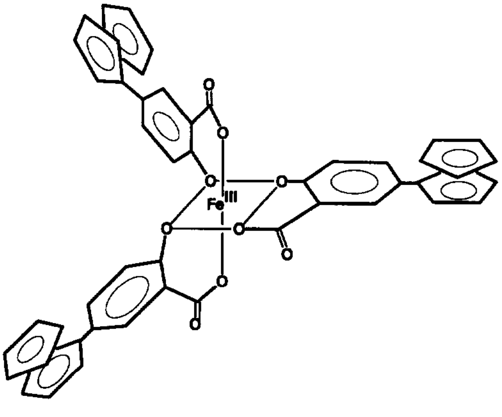
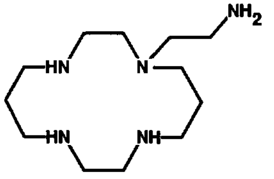


Fig. 5. Supposed structure of the $[Fe^{III}(Fcsal^{2-})_3]^{3-}$ complex. The complex, in a 50/50 water/dioxan solution, releases three electrons to the platinum electrode according to three consecutive one-electron steps whose potentials are separated by 28 mV: the process is statistically controlled.

The above examples demonstrate that metal centres can be used to link redox active fragments in order to generate multi-electron redox systems. If a stable system is desired, a metal ion prone to the formation of inert complexes should be chosen. This is the case of the *cis*-$[Pt^{II}(pyFc)_2Cl_2]$ system. On the other hand, the $[Fe^{III}(Fcsal^{2-})_3]^{3-}$ species possesses a labile centre and the redox active ligand can be lost, for instance through the addition of acid. The two metal centres previously discussed (Pt(II),Fe(III)) do not exhibit individual redox activity in the coordinative environments considered and play a merely architectural role. Metal ions displaying independent redox activity can also be used as a building block to link two or more redox active fragments. This would generate more complex systems in which the multi-electron redox process occurs in several steps placed at distinctly different potentials.

C. SUPRAMOLECULAR DEVICES FOR ANION ACTIVATION: REDUCTION OF THE PERCHLORATE ION

The extreme kinetic inertness towards demetallation of d metal complexes has been emphasized in the previous sections. In particular, the M(II)/M(III) redox chemistry of cyclam and biscyclam complexes in a 70% $HClO_4$ solution is based on the kinetic stability induced by this ligand. However, special behaviour is displayed by the nickel(II) complex with the functionalized macrocycle *N*-aminoethylcyclam (**13**):



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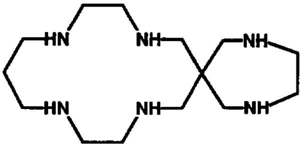
Molecule **13** (L) belongs to the class of the *scorpiands*, i.e. ligands which couple the rigidity of the in-plane coordinating tetra-aza ring to the flexibility of the alkylamino side chain: this chain can interact with the already chelated metal centre, through one of the axial positions, just as the tail of a scorpion [25]. However, in acidic solution, the proton successfully competes with the metal centre and the tripositive cation $[M^{II}(LH^+)]^{3+}$ containing a pendant alkylammonium group is formed. In particular, if the high-spin violet $Ni^{II}L(ClO_4)_2$ complex salt is dissolved in perchloric acid solution, in the concentration range 10^{-3} to 2 M, the solution is yellow, corresponding to the low-spin square $[Ni^{II}LH^+)]^{3+}$ complex. However, if the same complex is dissolved in a more concentrated $HClO_4$ solution ($\geqslant$3 M), an intense green-yellow colour immediately forms and chlorine develops. The absorption spectrum of the solution exhibits an intense band centred at 290 nm, which is typical of Ni(III) tetra-aza-macrocyclic complexes. Moreover, the ESR spectrum of the frozen solution displays axial symmetry, with $g_{\perp}$ considerably greater than $g_{\parallel}$, unequivocally demonstrating the formation of an authentic low-spin d^7 cation in an octahedrally elongated coordinative environment. The above evidence indicates that ClO_4^- is reduced by the Ni(II) macrocyclic complex. Whereas this reaction is thermodynamically justified (E° value for the $ClO_4^- + 7e^- + 8H^+ = 1/2Cl_2 + 4H_2O$ half-reaction, 1.39 V vs. SHE, is larger than that associated with the $[Ni^{III}(LH^+)]^{4+} + e^- = [Ni^{II}(LH^+)]^{3+}$ half-reaction, $E = 1.20$ vs. SHE in 1 M $HClO_4$), its occurrence is rather unexpected in view of the well-known inertness of the perchlorate ion towards redox reactivity in solution. To explain this unusual behaviour, it was suggested that the ammonium ion of the side chain interacts through hydrogen bonding with the ClO_4^- ion, making possible the redox reaction with the Ni(II) metal centre. In any case, combination of a reducing ion (Ni(II)) and of a proximate positively charged group seems essential for the ClO_4^- reduction. As a matter of fact, no reaction takes place in the absence of one of the two properties: the plain $[Ni^{II}(cyclam)]^{2+}$ complex does not react with concentrated $HClO_4$, and no reaction is observed with the scorpiate complex of Cu(II), a cation displaying much less pronounced reducing tendencies than Ni(II).



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Quite interestingly, it has recently been observed that reduction of ClO_4^- in concentrated perchloric acid solution also takes place in the presence of the Ni(II) complex with the functionalized macrocycle **14** [26]. On the basis of a detailed kinetic investigation, a different mechanism has been proposed for the ClO_4^- decomposition process: in particular, ClO_2 was detected as a product. However, the perchlorate reducing agent presents the same distinctive features of the previously mentioned scorpiate complex: (i) a reducing metallocyclam fragment and (ii) proximate ammonium group(s). It should be noticed that the Ni(II) complex of macrocycle **14** possesses two ammonium groups at a moderate distance and should activate ClO_4^- quite efficiently: rather curiously, its reaction with ClO_4^- is much slower than that observed with the one ammonium-containing Ni(II) complex of ligand **13**, which takes place instantaneously.

Thus, Ni(II) complexes of the functionalized macrocycles **13** and **14** represent a sharp example of a supramolecular device in that they combine two distinct properties: (i) binding and anion activation; (ii) release of electrons to produce an interesting and unprecedented function: the fast and specific reduction of the perchlorate ion.

Notice that the above reactions should not be confused with the slow oxidation of $[\mathrm{Ni^{II}(cyclam)}]^{2+}$ which takes place in hydrochloric acid solution in an open beaker. In this case, Ni(II) is oxidized to Ni(III) by aerial oxygen. The process is spontaneous due to the strong stabilizing effect on Ni(III) exerted by the chloride ions, which makes the Ni(III)/Ni(II) potential substantially lower than that of the O_2/H_2O half-reaction (in 1 M HCl: 0.73 and 1.23 V vs. SHE, respectively).

D. DESIGN OF LIPOPHILIC REDOX SYSTEMS TO BE USED AS CARRIERS FOR THE COUPLED TRANSPORT OF ELECTRONS AND IONS ACROSS LIQUID MEMBRANES

One of the most promising areas in which the concepts of supramolecular chemistry can be applied is the design of carrier systems for membrane transport experiments. Generally speaking, a membrane is a permeable barrier which separates two phases. A water immiscible liquid interfacing two aqueous layers may act as a liquid membrane if it contains a molecular system C, the carrier, that makes the two aqueous phases communicate. For instance, C can take a species A from one of the aqueous layers (the source phase) and transport it to the other aqueous layer (the receiving phase), profiting from a gradient of the concentration of A. The nature of the interaction between C and A and the stability of the $C \cdot A$ adduct form the basis of the selective transport, making liquid membranes a versatile and promising tool in separation science and technology [27]. The object of the transport, A, can be an ion pair M^+X^-. In this case, the carrier C should be a specific ligand for the M^+ cation and X^- will be transported as the counterion of the metal/carrier complex: $[MC]^+X^-$. The transport experiment will reach its steady state when both source and receiving phases have the same concentration in M^+X^-. Selective transport of cations, in particular alkali metal ions, across liquid membranes has been investigated thoroughly during the last two decades, selectivity being achieved by using carriers of designed coordinating and structural features (in particular, crown ethers and cryptands of the appropriate cavity size) [28]. Fewer experiments have been carried out for the selective transport of X^-, driven by an X^- concentration gradient. This is essentially due to the difficulty in designing effective and selective carriers for anions. However, transport of anions can be achieved through a different approach, in particular by coupling the transport of X^- species with the counter transport of the most simple negative particles of chemistry: electrons [29]. A conventional scheme of such a type of experiment is described in Fig. 6.

The prerequisite for the experiment is that the carrier C is redox active and, in particular, is prone to the one-electron oxidation to the C^+ form. Moreover, a gradient of redox potential should be created between the two aqueous phases. In particular, the anion source phase (ASP) should be put at the more positive potential, whereas the anion receiving phase (ARP) should be put at the less positive potential. The difference of redox potential between the two aqueous phases can be generated chemically by dissolving a conventional oxidizing agent, Ox, in the ASP and a conventional reducing agent, Red, in the ARP. The mechanism of the three-phase process is illustrated in Fig. 6. The carrier C is oxidized by Ox at the membrane/

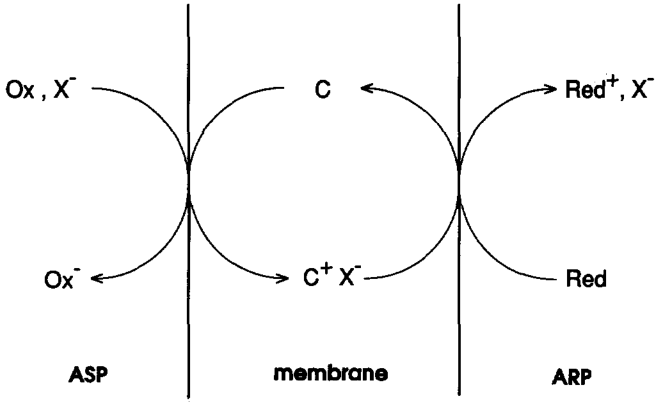


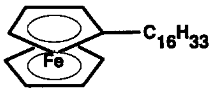
Fig. 6. Scheme of transport of X^- anions across a liquid membrane, mediated by the C^+/C redox change and driven by a chemically generated gradient of redox potential. Anions are transported by the oxidized form of the carrier, C^+, from the anion source phase (ASP), to the anion receiving phase (ARP). Electrons are transported in the opposite direction by the reduced form of the carrier, C. C can be a derivative of ferrocene (see text).

ASP interface and, to maintain electroneutrality, the oxidized form C^+ simultaneously extracts an X^- anion. The $[C^+,X^-]$ ion pair diffuses at the other side of the membrane where C^+ is reduced to C and X^- is released to ARP. Thus, after one cycle, one X^- anion has been transported from its source phase to the receiving phase, and one electron has been transported in the opposite direction. During the experiment, the redox system used as a carrier shuttles between the two edges of the membrane, carrying anions with its oxidized form C^+ and electrons with its reduced form C. The transport will stop when the difference of the redox potential between ASP and ARP is nil. Thus, working with an excess concentration of the aqueous redox agents, X^- can be transferred at 100%.

The requirements a molecular system has to satisfy in order to work properly as a carrier are essentially two: (i) the system, both in its reduced, C, and oxidized, C^+, forms, must be definitively lipophilic in order to be confined in the membrane: (ii) the C^+/C redox change should be fast and uncomplicated from a kinetic point of view [30]. Point (i) can be easily fulfilled by appending on the envisioned molecular system an appropriate lipophilic group, e.g. a long carbon chain; the appended aliphatic group should not interfere with the redox active site of the system. Requirement (ii) suggests that we consider systems whose redox activity is centred on an incorporated metal. Indeed, redox active systems derived from classical coordination chemistry [31] and organometallic chemistry have been proven as efficient carriers for e^-/X^- cross-transport, as described in the following sections.

(i) Carriers based on ferrocene: selective transport of anions and electrons

Ferrocene seems an ideal C system in that it undergoes a fast and reversible one-electron oxidation to the stable Fc^+ form. However, the plain Fc^+/Fc redox system cannot be used as a carrier as it does not fulfil requirement (i). As a matter of fact, Fc^+ is hydrophilic enough to partition between the liquid membrane (e.g. CH_2Cl_2) and water. Appending of an hexadecyl side-chain on one of the cyclopentadienide rings definitively confines the C^+/C redox system to the membrane.



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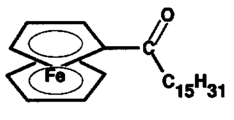

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1-Hexadecylferrocene (**15**, $C_{16}H_{33}Fc$) has been employed to transport ClO_4^- ions, profiting from a chemically generated gradient of potential: Ox = Fe^{3+}, Red = $[Fe^{II}(CN)_6]^{4-}$ [32]. In particular, ASP was 0.5 M in $HClO_4$ and the ClO_4^-/e^- cross-transport was independently followed by monitoring the appearance and the increase of the concentration of the perchlorate ion in ARP and of the $[Fe^{III}(CN)_6]^{3-}$ ion in ASP. It should be noticed that the three-phase transport process can be considered as the sum of the two-phase processes: eqn. (3) occurring at the ASP/membrane interface:

$$Fe^{3+}_{(aq)} + X^-_{(aq)} + C_{16}H_{33}Fc_{(membr)} = Fe^{2+}_{(aq)} + [C_{16}H_{33}Fc^+,X^-]_{(membr)} \tag{3}$$

and eqn. (4) occurring at the membrane/ARP interface ($X = ClO_4$):

$$[Fe^{II}(CN)_6]^{4-}_{(aq)} + [C_{16}H_{33}Fc^+,X^-]_{(membr)}$$
$$= [Fe^{III}(CN)_6]^{3-}_{(aq)} + X^-_{(aq)} + C_{16}H_{33}Fc_{(membr)} \tag{4}$$

If, in ASP, ClO_4^- is replaced by Cl^-, no e^-/Cl^- transport is observed. It is suggested that the two-phase process at the ASP/membrane interface does not proceed due to the much higher energy to be spent in transferring Cl^- ion from water to the CH_2Cl_2 solution compared with the much less hydrated anion ClO_4^- (ΔG° values for the $H_2O \rightarrow CH_2Cl_2$ process are 49.8 and 10.0 kJ mol^{-1} for Cl^- and for ClO_4^-, respectively) [33]. Moreover, if ASP is made 0.5 M in both $HClO_4$ and HCl, only the ClO_4^- ion is transported. The above experiments demonstrate that anions can be selectively separated by using a redox active liquid membrane device and by taking profit from a chemically generated gradient of redox potential. The element of selectivity is essentially the hydration energy of the X^- anion.

Alternatively, in this type of experiment, attention can be focused on the electron transport rather than on the anion transport. In this sense, redox active liquid membranes can be considered as useful devices to control oxidation and reduction reactions in an unusually selective way. For instance, if excess $[Fe^{II}(CN)_6]^{4-}$ were added to an aqueous solution 1 M in $HClO_4$ containing Ce(IV) and Fe(III), both oxidizing agents would be quickly reduced to Ce(III) and Fe(II), respectively. This state of affairs is fully accounted for on the basis of the values of the corresponding redox potentials, as illustrated in the vertical potential diagram displayed on the left of Fig. 7.

Simultaneous reduction also takes place by using the liquid membrane device: in particular, the solution containing Ce(IV) and Fe(III) in 1 M $HClO_4$ should be separated from the solution containing $[Fe^{II}(CN)_6]^{4-}$ by a layer of CH_2Cl_2 containing $C_{16}H_{33}Fc$. Occurrence of the electron transport from the oxidizing aqueous phase to the reducing aqueous phase can be justified on the basis of the juxtaposition of the two electrochemical scales, in water and in CH_2Cl_2, as illustrated in Fig. 7. Such a juxtaposition cannot be made a priori, but is merely empirical. Thus, the three-phase reduction of Ce(IV) and Fe(III) by $[Fe^{II}(CN)_6]^{4-}$ takes place as the potential associated with the $C_{16}H_{33}Fc+/C_{16}H_{33}Fc$ couple is lower than those of the Ce(IV)/Ce(III) and Fe(III)/Fe(II) couples, but is higher than that associated to the $[Fe^{III}(CN)_6]^{3-}/[Fe^{II}(CN)_6]^{4-}$ redox change.

Using Fig. 7, it is evident that choosing a lipophilic redox system C^+/C characterized by a potential that is intermediate between those of the Ce(IV)/Ce(III) and Fe(III)/Fe(II) couples should allow one to perform selective reduction of Ce(IV) in the presence of Fe(III). Such a redox system could be designed by appending at the ferrocene moiety an electron-withdrawing group, which makes the oxidation to ferrocenium more difficult and the potential more positive. This can be done, for instance, by attaching the 1-hexadecanoyl group $-COC_{15}H_{31}$, rather than the 1-hexadecyl group $-C_{16}H_{33}$, to one of the cyclopentadienide rings (by the way, $C_{15}H_{31}COFc$, **16**, is an intermediate in the synthesis of $C_{16}H_{33}Fc$, **15**). As a matter

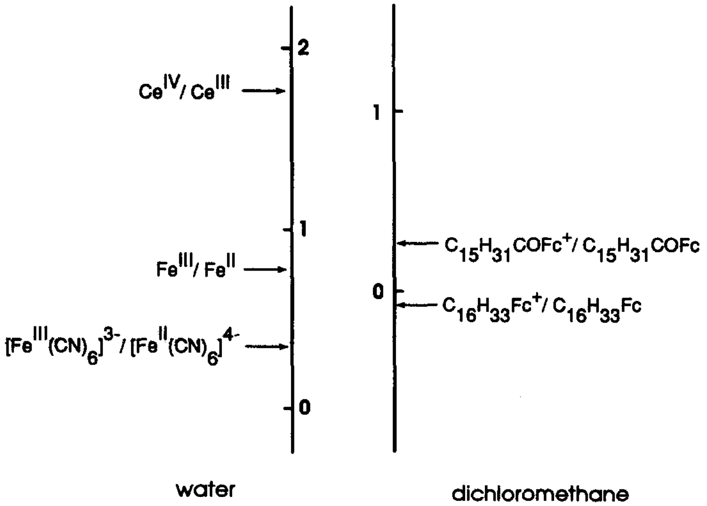


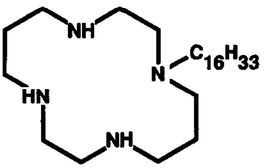
Fig. 7. Using ferrocene derivatives as selective electron carriers. Juxtaposition of the electrochemical scale in water (potentials vs. SHE) and of the electrochemical scale in the solvent used as liquid membrane, e.g. CH_2Cl_2 (potentials vs. the Fc^+/Fc internal reference). Juxtaposition is empirical and is obtained on the basis of preliminary two-phase oxidation and reduction experiments.

of fact, cyclic voltammetry experiments have shown that the $E_{1/2}(C_{15}H_{31}COFc^+/C_{15}H_{31}COFc)$ value is about 300 mV more positive than the $E_{1/2}(C_{16}H_{33}Fc^+/C_{16}H_{33}Fc)$ value. According to the juxtaposed electrochemical scales shown in Fig. 7, the $C_{15}H_{31}COFc$ redox system should be able to reduce Ce(IV) but not Fe(III). Indeed, in a three-phase experiment in which the oxidizing phase contained both Ce(IV) and Fe(III) and $C_{15}H_{31}COFc$ was used as a carrier, only Ce(IV) was reduced, whereas Fe(III) remained intact [34].

One could consider that the redox active liquid membrane device discussed above is in some way reminiscent of the voltaic cell (which was invented at the University of Pavia about a couple of centuries ago) [35]. As a matter of fact, Volta's battery is also a multi-phase device in which the solutions of the oxidizing agent and of the reducing agent are separated. If, in a voltaic cell, a half-cell contains $[Fe^{II}(CN)_6]^{4-}$ whereas the other half-cell contains both Ce(IV) and Fe(III), electrons flow through electrodes and metal wire from the reducing half-cell to the oxidizing half-cell. Ce(IV) and Fe(III) ions are reduced in sequence and, in contrast to observations in the liquid membrane experiment described earlier, there is no way to discriminate between the two oxidizing agents (unless one is able to open the circuit immediately after the reduction of Ce(IV) is complete). In this sense, compared with the electrical cell, the liquid membrane device introduces selectivity. In particular, any oxidation and reduction process can be controlled by a redox active membrane by moving the C^+/C system up and down along the electrochemical scale in CH_2Cl_2. This consideration may stimulate the design of further lipophilic metal centred redox systems, whose potentials span the entire electrochemical scale in the solvent used as a liquid membrane.

(ii) Electron carriers based on the metallocyclam subunit

The rich and versatile redox behaviour as well as extreme kinetic stability make cyclam complexes sound candidates for the role of electron carriers for redox active liquid membranes. The lipophilicity prerequisite can be fulfilled by appending the usual $-C_{16}H_{33}$ side chain at one of the amine nitrogen atoms of cyclam. *N*-Cetylcyclam, **17**, L, forms complexes with 3d metal ions which are soluble in apolar or poorly polar solvents (benzene, chloroform, dichloromethane) and insoluble in water [36].



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Electron transport experiments have been performed by using a $[M^{III}LX_2]^+,X^-/[M^{II}LX_2]$ carrier system (M = Co [37], Ni [38]). The redox system used as a carrier presents, in both oxidized and reduced forms, an octahedrally distorted stereochemistry, with the two X^- anions occupying the axial positions. The scheme of the e^-/X^- cross-transport mediated by the $[M^{III}LX_2]^+,X^-/[M^{II}LX_2]$ redox system is illustrated in Fig. 8. Notice that the $[M^{III}LX_2]X/[M^{II}LX_2]$ couple can be associated with the $[C^+,X^-]/C$ redox change, as in the case of ferrocene-based systems. However, the analogy is not complete as the axially bound X^- anions are labile (with the exception of the Co(III) complex) and exchange with other anions present in the aqueous layers interfacing the liquid membrane. Thus, metallocyclam carriers, unlike carriers based on the Fc^+/Fc couple, cannot be used for the selective separation of anions, driven by a gradient of redox potential, as they are prone to a passive anion transport. However, in this case too, the nature of the anion has a dramatic effect on the transport. For instance, when M = Ni, electrons can be transported from the aqueous reducing phase containing Fe(II) in 1 M HCl to the aqeuous oxidizing phase containing $S_2O_8^{2-}$ in 1 M NaCl. However, if Cl^- is replaced by ClO_4^- in both aqueous phases, the transport is not facilitated (the opposite of that observed with ferrocene based carrier experiments!). This must be ascribed to the fact that X^- anions, which occupy the axial positions of the metal-centred carrier, have a substantial effect on the relative stability of its oxidation states. In particular, strongly ligating anions such as Cl^- stabilize the higher oxidation state, so favouring the access to Ni(III). In particular, in the juxtaposed electrochemical scales (see Fig. 9), the potential associated with the $[Ni^{III}LCl_2]Cl/[Ni^{II}LCl_2]$ lies below that of the aqueous $S_2O_8^{2-}/SO_4^{2-}$ redox couple, whereas the potential for the $[Ni^{III}L(ClO_4)_2]ClO_4/[Ni^{II}L(ClO_4)_2]$ change in CH_2Cl_2 stays above. Thus, the anion

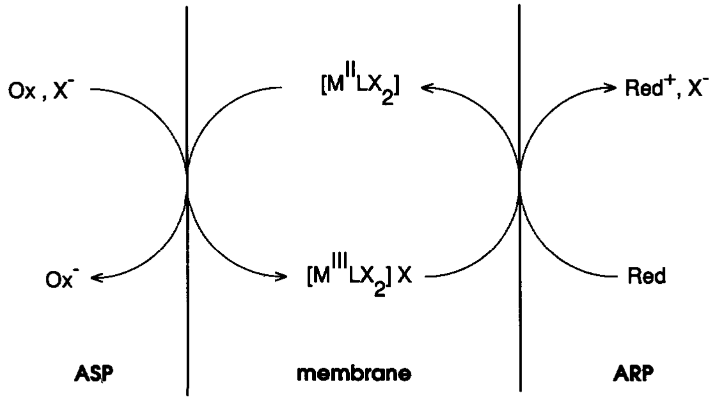

Fig. 8. Scheme of the e^-/X^- cross-transport mediated by the $[M^{II}LX_2]/[M^{III}LX_2]X$ redox system (M = Co, Ni; L is the lipophilic version of cyclam, **17**). The mechanism is analogous to that illustrated in Fig. 6: $[M^{II}LX_2]$ = C. However, due to the labile nature of the M–X axial bonds, anions can also be exchanged at the membrane/water interface in the absence of electron transfer. Thus, this system cannot be used for the selective separation of anions driven by a gradient of redox potential.

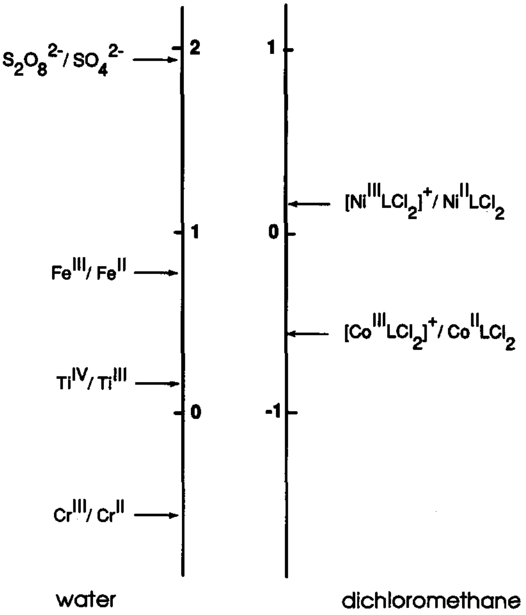

Fig. 9. Using a lipophilic metallocyclam complex to transport electrons across liquid membranes. Juxtaposition of the electrochemical scale in water (potentials vs. SHE) and of the electrochemical scale in the solvent used as liquid membrane, e.g. CH_2Cl_2 (potentials vs. the Fc^+/Fc internal reference; L is the lipophilic version of cyclam, **17**). Changing of the metal (Co or Ni) allows the electron carrier system to be positioned in the cathodic or anodic part of the scale.

hydration term, which should favour the two-phase oxidation of $[Ni^{II}L(ClO_4)_2]$, is more than compensated for by the ligand field term. It is just the latter term which makes the oxidation of $[Ni^{II}LCl_2]$ possible by aqueous $S_2O_8^{2-}$, under two-phase conditions.

Figure 9 shows that the nickel-containing electron carrier, which is situated in the anodic part of the electrochemical scale in CH_2Cl_2, permits the transport of electrons from aqueous reducing agents of moderate to strong reducing power: Fe^{2+}, Ti^{3+} and Cr^{2+}. Noticeably, the transport rate ($Ti^{3+} > Cr^{2+} > Fe^{2+}$) does not parallel the reducing tendencies, as expressed by the $E°$ values [38]. Thus kinetic effects, other than the thermodynamic contributions, introduce a further element of selectivity in liquid membrane mediated oxidation and reduction processes.

Replacing nickel by cobalt brings the potential of the carrier system down in the cathodic part of the electrochemical scale (see Fig. 9) and makes it possible to carry out electron transport experiments involving strongly reducing agents, e.g. Cr^{2+}, and fairly weak oxidizing agents, e.g. Fe^{3+} [37].

In conclusion, the ferrocene derivatives **15** and **16** and the cobalt and nickel complexes of the tetra-aza macrocycle **17** appear as rather naïve examples of supramolecular devices in which the simple coupling of two independent properties (metal-centred redox activity + lipophilicity) generates the e^-/X^- transport function. It has been shown that this function is essentially controlled by the magnitude of the potential of the redox system used as a carrier. More sophisticated carriers can be designed by adding further subunits able to display further useful properties (i.e. a photosensitive fragment or an acid or basic site). They will make the transport experiment more subtly controlled through the variation of different effects or parameters, e.g. illumination, pH.

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