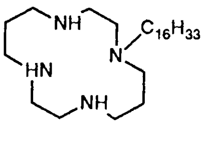
Redox-active Liquid Membranes: Transport of Electrons Across a Dichloromethane Layer mediated by the $[Co^{III}L^1X_2]^+$–$[Co^{II}L^1X_2]$ Redox System (L^1 = 1-hexadecyl-1,4,8,11-tetra-azacyclotetradecane, X = Cl or ClO_4)

Giancarlo De Santis, Luigi Fabbrizzi,* Antonio Poggi, and Barbara Seghi
Dipartimento di Chimica Generale, Università di Pavia, via Taramelli 12, 27100 Pavia, Italy

The lipophilic complex $[Co^{III}L^1Cl_2]Cl$ (L^1 = 1-hexadecyl-1,4,8,11-tetra-azacyclotetradecane) can transport electrons, through the Co^{III}–Co^{II} redox change, from an aqueous phase containing Cr^{II} to an aqueous phase containing the mild oxidizing agents Fe^{III} or $[Ni^{III}L^3]^{3+}$ (L^3 = 1,4,8,11-tetra-azacyclotetradecane), in aqueous HCl, across a bulk CH_2Cl_2 membrane. The transport of electrons, to which a counter transport of Cl^- ions is coupled, implies that the potential associated with the $[Co^{III}L^1Cl_2]Cl + e^- \longrightarrow [Co^{II}L^1Cl_2] + Cl^-$ half-reaction (−0.60 V *vs.* ferrocenium–ferrocene, measured in a CH_2Cl_2 solution, 0.1 mol dm^{-3} in NBu_4Cl) should lie between that associated with the aqueous Cr^{III}–Cr^{II} couple and that associated with the aqueous ox–ox^- couple (ox = Fe^{III} or $[Ni^{III}L^3]^{3+}$). Replacement of Cl^- by ClO_4^- stops the electron transport from Cr^{II} to Fe^{III} or $[Ni^{III}L^3]^{3+}$. This is ascribed to the especially high potential associated with the $[Co^{III}L^1(ClO_4)_2]ClO_4 + e^- \longrightarrow [Co^{II}L^1(ClO_4)_2] + ClO_4^-$ half-reaction. In particular, the $[Co^{II}L^1(ClO_4)_2]$ complex in a CH_2Cl_2 solution, covered by a layer of aqueous $HClO_4$, is not oxidized even by bubbling dioxygen. This complex can transport electrons, across the bulk CH_2Cl_2 membrane, from aqueous Cr^{II} only to the very strong oxidizing agent Ce^{IV} in aqueous $HClO_4$.

Electrons can be transported from an aqueous solution containing a reducing agent (the electron source phase, e.s.p.) to an aqueous solution containing an oxidizing agent (the electron receiving phase, e.r.p.), separated by a water immiscible liquid, provided that the non-aqueous layer (the liquid membrane) contains a hydrophobic redox system capable to act as a carrier of electrical charges. In particular, the redox system in its reduced form should transport electrons from the e.s.p. to the e.r.p. and in its oxidized form should transport anions from the e.r.p. to the e.s.p. As a thermodynamic prerequisite, the potential associated with the redox system acting as an electron carrier should be intermediate between that associated with the oxidant ox–ox^- aqueous system in the e.r.p. and that associated with the reductant red^+–red aqueous system in the e.s.p.: $E_{ox} > E_c > E_{red}$. Comparison of the above potential values is not straightforward, as they belong to two distinct and not correlated electrochemical scales: E_{ox} and E_{red} to the aqueous scale (eventually calibrated *vs.* n.h.e.) and E_c to the electrochemical scale pertinent to the non-aqueous solution which constitutes the liquid membrane.

Transition-metal complexes are efficient and versatile electron carriers.[1–3] In particular, it has been shown in a recent paper from this laboratory[4] that the $[Ni^{III}L^1Cl_2]^+$–$[Ni^{II}L^1Cl_2]$ system (L^1 = *N*-cetylcyclam = 1-hexadecyl-1,4,8,11-tetra-azacyclotetradecane) can transport electrons from an aqueous solution containing a metal-centred reducing agent {*e.g.* Fe^{II}, Ti^{III}, Cr^{II}, $[Co^{II}(H_2L^2)]^{4+}$ (L^2 = 1,8-diamino-3,6,10,13,16,19-hexa-azabicyclo[6.6.6]eicosane), in 1 mol dm^{-3} HCl} to an aqueous solution containing excess of $S_2O_8^{2-}$ in 1 mol dm^{-3} NaCl. The redox system used as an electron carrier was able to discriminate aqueous reducing agents, the rate of the electron-transport process varying according to a sequence which does not correlate at all with the sequence of the red^+–red electrode potentials: $Ti^{III} > Cr^{II} > Fe^{II} > [Co^{II}(cage)]^{4+}$. The redox couple investigated (Ni^{III}–Ni^{II} in the tetra-aza macrocyclic environment of cyclam, made lipophilic through the insertion of a C_{16} aliphatic chain on the ligand framework) is situated in the higher part of the electrochemical scale. Thus, the very strong oxidizing agent $S_2O_8^{2-}$ had to be employed, which, through the redox-active membrane, was able to oxidize, at extremely different rates, a series of metal-centred reducing agents.



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An interest in developing a redox system able to discriminate oxidizing rather than reducing agents prompted us to consider a redox couple situated in the lower part of the electrochemical scale. In particular, the Co^{III}–Co^{II} couple was considered, still in the form of an *N*-cetylcyclam complex. We describe here the use of the $[Co^{III}L^1X_2]^+$–$[Co^{II}L^1X_2]$ redox system as a carrier for the transport of electrons from an aqueous phase containing the strong reducing agent Cr^{II} to an aqueous phase containing oxidizing agents of varying nature and strength. It will be shown how drastically variation of the X^- anion (Cl^- or ClO_4^-) may alter, through ligand-field effects, the course of the transport process.

Experimental

Synthesis of $[Co^{III}L^1Cl_2]Cl$.—A 0.5 mol dm^{-3} aqueous solution (2.8 cm^3) of $CoCl_2$ was added to an ethanolic solution of *N*-cetylcyclam[4] (600 mg in 15 cm^3). A dark brown solution formed, to which 4 mol dm^{-3} HCl (5 cm^3) was added: the bright green solution was evaporated under reduced pressure to give a green precipitate, which was treated with CH_2Cl_2–water (30 cm^3 : 30 cm^3). The green non-aqueous layer was separated from the aqueous layer (pink, due to the presence of unreacted excess of $CoCl_2$) and dried overnight on anhydrous Na_2SO_4. On evaporation a green microcrystalline compound was obtained (yield: 65%) (Found: C, 52.75; H, 9.85; N, 9.30. Calc. for $C_{26}H_{56}Cl_3CoN_4$: C, 52.90; H, 9.55; N, 9.50%).

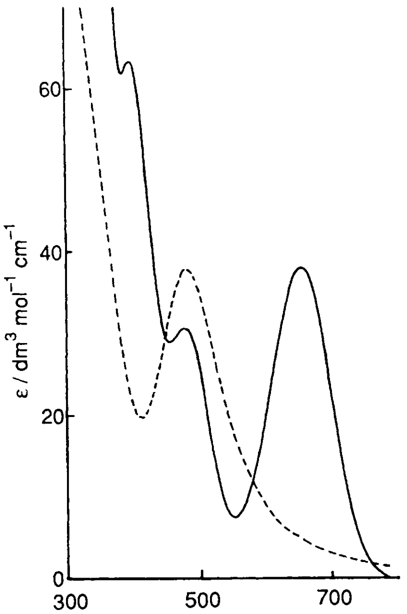

Figure 1. Absorption spectra of (——) a CH_2Cl_2 solution of $[Co^{III}L^1Cl_2]Cl$ and (- - - -) a CH_2Cl_2 solution of $[Co^{II}L^1Cl_2]$, generated through two-phase reduction with aqueous Cr^{II} of the solution of $[Co^{III}L^1Cl_2]Cl$

Electrochemical and Spectrophotometric Investigations.—The $E_{\frac{1}{2}}$ value associated with the $[Co^{III}L^1Cl_2]Cl + e^- \longrightarrow [Co^{II}L^1Cl_2] + Cl^-$ half-reaction (in CH_2Cl_2, 0.1 mol dm^{-3} in NBu_4Cl) at 25 °C) was determined through voltammetry studies, using a conventional three-electrode cell. A silver wire was used as a pseudo-reference electrode, which was calibrated using ferrocene as an internal standard. A P.A.R. model 273 potentiostat/galvanostat, driven by an IBM AT personal computer through a dedicated program, was used. U.v.–visible spectra of aqueous and dichloromethane solutions were measured by using an Hewlett-Packard 8452A diode array spectrophotometer or a Cary 2300 (Varian) apparatus.

Electron-transport Experiments.—For electron-transport experiments a V-shaped glass cell was used.[4] In this vessel the two aqueous layers (e.s.p. and e.r.p., 30 cm^3 each) were separated by a CH_2Cl_2 layer of 30 cm^3 (the bulk liquid membrane) and by a glass wall. The membrane, 5×10^{-4} mol dm^{-3} in $[Co^{III}L^1Cl_2]Cl$, was magnetically stirred at 200 revolutions min^{-1}. The two aqueous layers were mechanically stirred by two glass rods driven by two twin electrical motors, at a constant rate (200 revolutions min^{-1}). During the transport experiments, dinitrogen saturated in CH_2Cl_2 flowed in both arms of the cell. The progress of the three-phase oxidation and reduction reaction was monitored by syringing out, at selected time intervals, portions of the e.r.p. aqueous layer (about 200 μl, to fill a 1-mm quartz cuvette) and measuring the spectrum of the oxidizing agent of interest. After each measurement the aqueous portion was returned to the e.r.p. Three-phase experiments were carried out in a room thermostatted at 25 ± 1 °C.

Results and Discussion

Synthesis and Characterization of the Electron Carrier.—The $[Co^{III}L^1Cl_2]Cl$ complex was prepared according to the classical route to cobalt(III) tetra-aza macrocyclic complexes, *i.e.* through reaction of a solution of $CoCl_2 \cdot 6H_2O$ with a solution of L^1, using aerial dioxygen as an oxidizing agent.[5,6] Due to the hydrophobic nature of the ligand, ethanol, instead of water, was used as a solvent. Some concentrated hydrochloric acid was added to prevent the formation of μ-hydroxo species. A microcrystalline green precipitate was obtained, completely insoluble in water and soluble in poorly polar, water immiscible media such as $CHCl_3$ and CH_2Cl_2. Figure 1 shows the u.v.–visible spectrum of the $[Co^{III}L^1Cl_2]Cl$ complex in CH_2Cl_2. The spectrum is that typically observed for *trans*-dichloro tetramine low-spin cobalt(III) complexes.

The reduction behaviour of the $[Co^{III}L^1Cl_2]Cl$ complex was investigated through cyclic voltammetry experiments on a CH_2Cl_2 solution, made 0.1 mol dm^{-3} in NBu_4Cl, at 25 °C, using a platinum microsphere as a working electrode. A reversible wave was observed ($E_{\frac{1}{2}}$ = 0.602 V *vs.* ferrocenium–ferrocene), which is assigned to the Co^{III}–Co^{II} redox change and is described by half-reaction (1).

$$[Co^{III}L^1Cl_2]Cl + e^- \longrightarrow [Co^{II}L^1Cl_2] + Cl^- \quad (1)$$

Bulk reduction of the cobalt(II) complex can be performed chemically, under two-phase conditions, by equilibrating under dinitrogen a deaerated layer of a CH_2Cl_2 solution of $[Co^{III}L^1Cl_2]Cl$ (10^{-3} mol dm^{-3}) with an equal volume of a deaerated aqueous solution 0.1 mol dm^{-3} in Cr^{II} in 1 mol dm^{-3} HCl. On shaking, the green non-aqueous layer turns pink: Figure 1 displays the spectrum of the reduced dichloromethane solution, corresponding to the $[Co^{II}L^1Cl_2]$ complex.

Reoxidation of the lipophilic cobalt(II) tetra-aza macrocyclic complex can be performed under two-phase conditions, using appropriate aqueous oxidizing agents. In particular, we used an uncommon oxidizing solution: an aqueous solution of the $[Ni^{III}L^3Cl_2]ClO_4$ (L^3 = cyclam = 1,4,8,11-tetra-azacyclotetradecane) complex salt in 1 mol dm^{-3} HCl. It should be noted that this complex, which can be isolated as a stable dark green solid after oxidation by $Na_2S_2O_8$ of a solution of $[Ni^{II}L^3][ClO_4]_2$ in concentrated hydrochloric acid,[7] lasts in aqueous 1 mol dm^{-3} HCl for at least 24 h without any decomposition, as shown by the persistence of the typical nickel(III) band at 312 nm (ε = 11 570 dm^3 mol^{-1} cm^{-1}). It* undergoes a reversible one-electron reduction process to the corresponding $[Ni^{II}L^3]^{2+}$ complex. The potential associated with the Ni^{III}–Ni^{II} redox change in 1 mol dm^{-3} HCl, obtained from the reversible voltammetric profile, is 0.73 V *vs.* n.h.e., indicating that $[Ni^{III}L^3Cl_2]^+$ is a mild oxidizing agent. After equilibration with an aqueous solution 10^{-3} mol dm^{-3} in $[Ni^{III}L^3Cl_2]ClO_4$ and 1 mol dm^{-3} in HCl, the pink CH_2Cl_2 layer reverts to the original green colour; moreover, its spectrum superimposes with that of the solution prior to the two-phase reduction and oxidation treatment.

Electrode potentials of aqueous redox couples cannot be directly compared with the potential associated with the $[Co^{III}L^1Cl_2]Cl$–$[Co^{II}L^1Cl_2]$ couple, measured in a CH_2Cl_2 solution.† However, on the basis of the above two-phase

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* Present in 1 mol dm^{-3} HCl solution as the elongated octahedral *trans*-dichloro complex, as demonstrated by e.s.r. spectroscopy: the spectrum of a frozen solution displays axial symmetry, with $g_\perp$ considerably greater than $g_\parallel$ (2.18 and 2.02, respectively). The $g_\parallel$ feature is split into *seven* lines [$A_\parallel$ = 28.6 G (2.86×10^{-3} T)], due to the presence of two equivalent chlorine atoms along the *z* axis.

† An $E_{\frac{1}{2}}$ value of −0.01 V *vs.* saturated calomel electrode (s.c.e.) has been measured for the one-electron reduction of the $[Co^{III}L^4Cl_2]Cl$ complex in aqueous KCl. *N*-Methylcyclam (L^4),[8] like *N*-cetylcyclam, possesses three secondary nitrogen atoms and one tertiary nitrogen atom. However, the $E_{\frac{1}{2}}$ value obtained in aqueous solution cannot be compared to that measured in CH_2Cl_2 nor can any thermodynamic term for the phase-transfer process of the redox species be evaluated, due to the difference of the reference half-reactions.

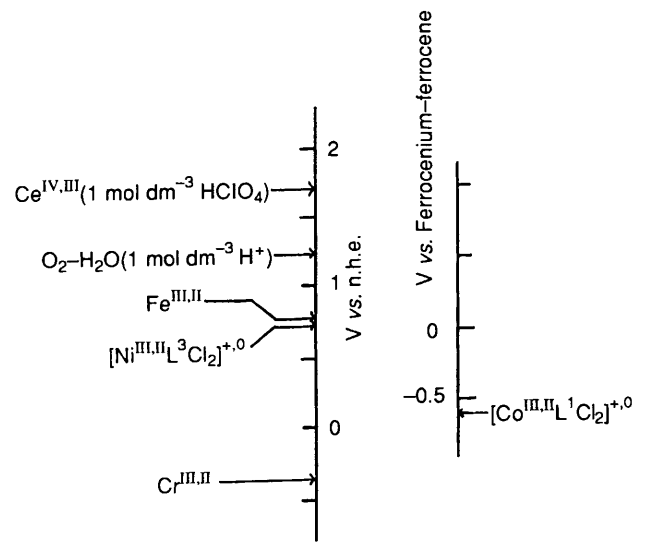

Figure 2. Tentative juxtaposition of the electrochemical scale in water (potentials *vs.* n.h.e.) and of the electrochemical scale in CH_2Cl_2 solution (potentials *vs.* ferrocenium–ferrocene reference couple). Such a juxtaposition can account for the results of two-phase (CH_2Cl_2–water) redox: $[Co^{III}L^1Cl_2]Cl$ in CH_2Cl_2 solution can be reduced by any aqueous reducing agent having a lower potential than that of the non-aqueous $[Co^{III}L^1Cl_2]Cl$–$[Co^{II}L^1Cl_2]$ couple (*e.g.* Cr^{II}), whereas $[Co^{II}L^1Cl_2]$ can be oxidized by any aqueous oxidizing agent having a more positive potential (*e.g.* $[Ni^{III}L^3Cl_2]^+$)

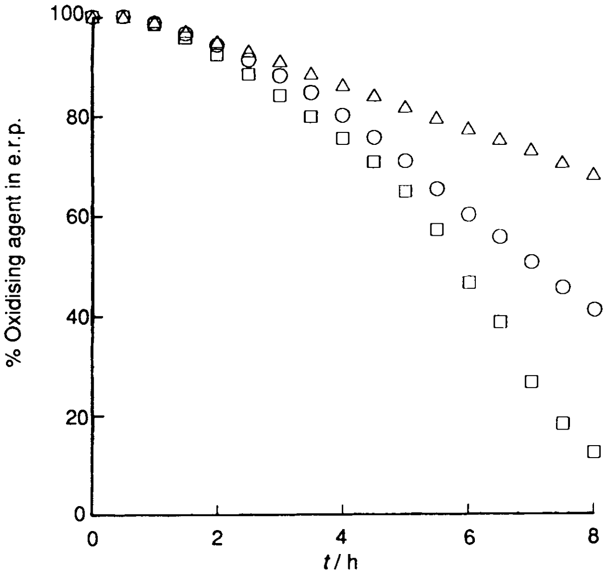

Figure 3. Variation of the percentage concentration of the oxidizing agent ox in the e.r.p. during electron-transport experiments. ox = $[Ni^{III}L^3Cl_2]^+$ (□); Fe^{III} (○), for electron-transport experiments of the type Cr^{II}, HCl–$[Co^{III}L^1Cl_2]Cl$–ox, HCl; Ce^{IV} (△), for the electron-transport experiments Cr^{II}, $HClO_4$–$[Co^{III}L^1(ClO_4)_2]ClO_4$–ox, $HClO_4$

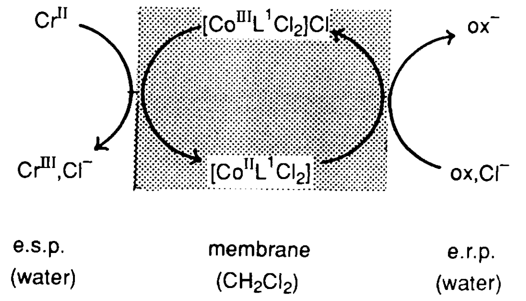

Figure 4. Transport of electrons across the bulk CH_2Cl_2 membrane mediated by the lipophilic $[Co^{III}L^1Cl_2]Cl$–$[Co^{II}L^1Cl_2]$ redox system. The flow of electrons from the e.s.p. to the e.r.p. is balanced by a counterflow of chloride ions

experiments, the two electrochemical scales (*i*) in aqueous solution (*E vs.* n.h.e.) and (*ii*) in dichloromethane solution (*E vs.* ferrocenium–ferrocene) can be tentatively juxtaposed. In particular, in order to explain two-phase reactions, the scales should be juxtaposed in such a way that the $E([Co^{III}L^1Cl_2]Cl$–$[Co^{II}L^1Cl_2])$ value* is higher than that corresponding to the Cr^{III}–Cr^{II} aqueous couple (–0.43 V *vs.* n.h.e.), but lower than that corresponding to the tetra-aza macrocyclic Ni^{III}–Ni^{II} aqueous couple. Such a tentative arrangement of the two potential scales is outlined in Figure 2.

From the above considerations, oxidizing agents whose $E(ox–ox^-)$ is equal or more positive than that associated with the $[Ni^{III}L^3Cl_2]^+$–$[Ni^{II}L^3]^{2+}$ couple should be able to oxidize $[Co^{II}L^1Cl_2]$ to $[Co^{III}L^1Cl_2]Cl$, under two-phase conditions. This has been confirmed by using as an oxidizing solution an aqueous solution of Fe^{III} in 1 mol dm^{-3} HCl ($E^{\ominus}$ = 0.77 V *vs.* n.h.e.). The pink CH_2Cl_2 layer of the $[Co^{II}L^1Cl_2]$ complex turns green, when equilibrated with an aqueous layer of Fe^{III} in HCl.

Electron-transport Experiments mediated by the $[Co^{III}L^1Cl_2]Cl$–$[Co^{II}L^1Cl_2]$ *Redox System*.—The two-phase tests described in the preceding paragraph allowed the design of three-phase experiments in which electrons are transported from the aqueous reducing phase (e.s.p.), containing Cr^{II}, to the aqueous oxidizing phase (e.r.p.), containing Fe^{III} or $[Ni^{III}L^3Cl_2]^+$, across a bulk CH_2Cl_2 membrane in which the lipophilic $[Co^{III}L^1Cl_2]Cl$ complex, the oxidized form of the carrier, is dissolved. Experiments were carried out in a V-shaped glass cell,[4] in which a CH_2Cl_2 solution (30 cm^3), 5 × 10^{-4} mol dm^{-3} in $[Co^{III}LCl_2]Cl$, separated a solution (30 cm^3) 0.10 mol dm^{-3} in Cr^{II} from a solution (30 cm^3) 10^{-3} mol dm^{-3} in one of the tested oxidizing agents: Fe^{III} or $[Ni^{III}L^3Cl_2]^+$. Both aqueous layers were 1 mol dm^{-3} in HCl. Aqueous phases were stirred mechanically at 200 revolutions min^{-1}; the bulk liquid membrane was stirred magnetically at 200 revolutions min^{-1}. The progress of the electron transport was monitored by withdrawing by a syringe 200 µl of the solution in the e.r.p. at selected time intervals and measuring its absorption spectrum. In particular, the reduction of the iron(III) species was followed through the decay of the band at 336 nm and reduction of the $[Ni^{III}L^3Cl_2]^+$ complex was followed through the decay of the band at 312 nm.

Plots of the percentage concentration of the oxidizing agent ox in the e.r.p. *vs.* time are reported in Figure 3. It can be seen that, after the experiments have been started, there exists a sort of induction period (less than 1 h), in which %ox varies very slightly. Afterwards, %ox decreases more quickly, according to a roughly linear pattern. In particular, the slope of the %ox *vs.* time straight line is more negative for the $[Ni^{III}L^3Cl_2]^+$ complex than for Fe^{III}, indicating that the three-phase oxidation and reduction reaction is faster with $[Ni^{III}L^3Cl_2]^+$ than with Fe^{III}. When the experiments were interrupted (after 8 h), 90% of $[Ni^{III}L^3Cl_2]^+$ had been reduced and only 55% of Fe^{III}.

The electron-transport experiment is outlined in Figure 4.

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* The electrochemically determined potential refers to a CH_2Cl_2 solution 0.1 mol dm^{-3} in NBu_4Cl. The concentration of Cl^- in a CH_2Cl_2 layer in equilibrium with an aqueous layer 1 mol dm^{-3} in Cl^- is much lower and can be calculated using partition data reported by Abraham and Liszi.[9] In particular, $[Cl^-]$ = 2 × 10^{-9}. Using this value, a more realistic potential associated with half-reaction (1) under two-phase conditions can be calculated through the Nernst equation, –0.15 V *vs.* ferrocenium–ferrocene.

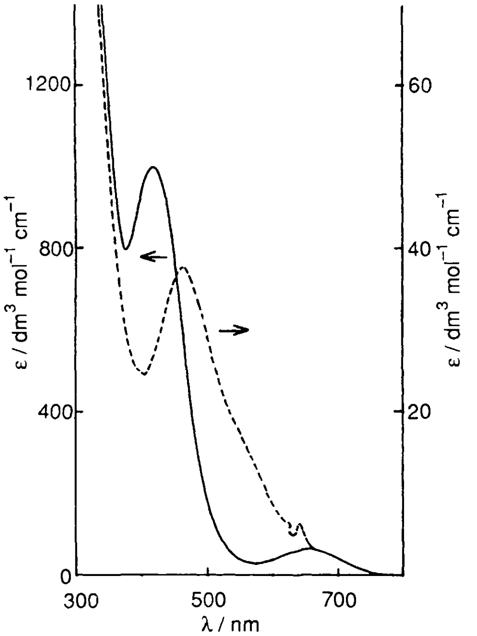

Figure 5. Absorption spectra of a CH_2Cl_2 solution of 5 × 10^{-4} mol dm^{-3} $[Co^{III}L^1Cl_2]Cl$, which had been treated, under two-phase conditions, with an aqueous layer 0.1 mol dm^{-3} in Cr^{II} and 1 mol dm^{-3} in $HClO_4$ (- - - -), assigned to the $[Co^{II}L^1(ClO_4)_2]$ chromophore, and of the reduced solution which had been further treated, under two-phase conditions, by a solution 5 × 10^{-3} mol dm^{-3} in Ce^{IV} and 1 mol dm^{-3} in $HClO_4$ (———), the yellow species which forms is thought to be $[Co^{III}L^1(ClO_4)_2]ClO_4$

According to this scheme, the lipophilic $[Co^{III}L^1Cl_2]Cl$ complex is reduced by Cr^{II} at the membrane/e.s.p. interface to the $[Co^{II}L^1Cl_2]$ form and simultaneously releases a Cl^- anion to the aqueous phase. Then, the $[Co^{II}L^1Cl_2]$ complex diffuses to the other side of the membrane, where it releases an electron to the aqueous oxidizing agent ox and takes up a chloride ion. On the whole, electrons are transported from the e.s.p. to the e.r.p. by the reduced form of the metal-centred carrier; chloride ions are transported from the e.r.p. to the e.s.p. by the oxidized form of the carrier. Notice that the Cl^- transport is only postulated and not experimentally detected. Complete reducton of ox, under the described conditions, is expected to cause a change in Cl^- concentration in the e.r.p. from 1.000 to 0.999 and from 1.000 to 1.001 mol dm^{-3} in the e.s.p. It should also be noted that, after 8 h, in the faster transport experiment, each carrier molecule has performed an average of 1.8 travels back and forth across the membrane.

At time = 0 the carrier in the membrane is all present in its oxidized form $[Co^{III}L^1Cl_2]Cl$. Through two-phase reduction, $[Co^{II}L^1Cl_2]$ is formed, which moves to the other side of the membrane: during this initial period the concentration of ox in the e.r.p. remains constant (see Figure 3). Afterwards, the rate of the process seems to be controlled by the rate of the process at the membrane/e.r.p. interface. In particular, this process goes faster with $[Ni^{III}L^3Cl_2]^+$ than with Fe^{III}. It may be hypothesized that the electron exchange between the reduced carrier $[Co^{II}L^1Cl_2]$ and the aqueous oxidizing agent $[Ni^{III}L^3Cl_2]^+$ or Fe^{III} (which exists in 1 mol dm^{-3} HCl as the chloro- or aquachloro-complex) takes place somewhere in the boundaries of the two phases according to an inner-sphere type mechanism, which involves the formation of a chloride bridge between the metal centres Co^{II} and M^{III}. Apparently, the electron-transfer process involving $[Ni^{III}L^3Cl_2]^+$ is substantially faster than that involving Fe^{II}.

The rate of transport of chemical species in experiments with bulk liquid membranes is typically affected by exotic effects, such as the geometry of the vessel employed and stirring rates. However, as the same cell was used and the stirring rates kept constant, it is assumed that mass-transfer effects are the same for the different experiments, so that differences in transport rate are to be ascribed essentially to chemical, kinetic in nature, effects.

Replacement of HCl *with* $HClO_4$ *as a Background Electrolyte in the e.s.p. and e.r.p.*—It has been shown in the previous paragraph that a counterflow of anions from the e.r.p. to the e.s.p. balances the opposite flow of electrons. To explore possible effects connected to the nature of the anion (hydration energy, co-ordinating tendencies, steric effects, *etc.*), we wished to perform transport experiments of the type described above, in which HCl was replaced by $HClO_4$ as a background electrolyte in both aqueous layers. The following experiment was performed: e.s.p., 0.10 mol dm^{-3} Cr^{II}, 1 mol dm^{-3} $HClO_4$; membrane, 5 × 10^{-4} mol dm^{-3} $[Co^{III}L^1Cl_2]Cl$; e.r.p., 10^{-3} mol dm^{-3} Fe^{III}, 1 mol dm^{-3} $HClO_4$. Also in this case, the progress of the experiment was followed by spectrophotometric monitoring of the concentration of Fe^{III} in the e.r.p. However, no decrease in the concentration of Fe^{III} was observed, even after several hours; the electron transport does not take place.

To assess the side of the membrane responsible for the failure of the electron transport, two-phase experiments were carried out. First, a CH_2Cl_2 layer 5 × 10^{-4} mol dm^{-3} in $[Co^{III}L^1Cl_2]Cl$ was equilibrated with an aqueous layer 0.10 mol dm^{-3} in Cr^{II} and 1 mol dm^{-3} in $HClO_4$: on shaking, the green non-aqueous layer became a pale pink. The spectrum of the reduced CH_2Cl_2 solution is shown in Figure 5 (----). Two-phase reoxidation of the non-aqueous layer was attempted by using an aqueous solution 5 × 10^{-3} mol dm^{-3} in Fe^{III} and 1 mol dm^{-3} in $HClO_4$: however, no colour change of the CH_2Cl_2 layer was detected and spectrum remained unchanged. Thus, a much stronger oxidizing agent was employed: Ce^{IV}, E° (Ce^{IV}–Ce^{III} in 1 mol dm^{-3} $HClO_4$) = 1.70 V *vs.* n.h.e.[10] On equilibration with an aqueous solution 5 × 10^{-3} mol dm^{-3} in Ce^{IV} and 1 mol dm^{-3} in $HClO_4$, the dichloromethane layer became bright yellow and its spectrum is shown in Figure 5 (——). The yellow species, generated in a similar way in $CDCl_3$, displays a well defined n.m.r. spectrum, which suggests the formation of an authentic low-spin cobalt(III) species. Slow evaporation of the yellow CH_2Cl_2 solution produced an oily material which could not be recrystallized and fully characterized. However, the i.r. spectrum of a dispersion in Nujol of the oily material presents an intense band at 1 080 cm^{-1}, attributable to the perchlorate anion. No bands pertinent to bound water molecules were observed. On the basis of the above evidence, we believe that the yellow species formed in the CH_2Cl_2 layer corresponds to the complex $[Co^{III}L^1(ClO_4)_2]ClO_4$.

It should be noted that the axial Co^{III}–Cl bonds in *trans*-dichlorotetramine complexes are very stable from both a *kinetic* and a *thermodynamic* point of view. As a consequence, even after many hours of shaking with aqueous 1 mol dm^{-3} $HClO_4$, co-ordinated chloride ions of the 5 × 10^{-4} mol dm^{-3} $[Co^{III}L^1Cl_2]Cl$ complex in CH_2Cl_2 are not replaced by ClO_4^- ions, as shown by the persistence of the green colour and of the absorption spectrum. However, in the reduced complex, $[Co^{II}L^1Cl_2]$, the Co^{II}–Cl bonds are *labile*. Thus, after reducton by Cr^{II} in aqueous $HClO_4$, the axially bound chloride ions are replaced by perchlorate ions from the aqueous layer. Chloride ions are probably more tightly bound than perchlorate ions to the divalent metal centre, but they are replaced due to a concentration effect (10^{-3} *vs.* 1 mol dm^{-3}) and go into the aqueous phase. Therefore, the dotted-line spectrum in Figure 5 should correspond to the species $[Co^{II}L^1(ClO_4)_2]$. On oxidation by Ce^{IV} in $HClO_4$, the corresponding trivalent complex is formed, $[Co^{III}L^1(ClO_4)_2]ClO_4$, in which a third perchlorate ion has been taken up from the aqueous phase, to form an ion pair. Note that the described sequence of two-phase redox processes is fully reversible. If the yellow dichloromethane solution, which contains $[Co^{III}L^1(ClO_4)_2]ClO_4$, is equilibrated first with an aqueous layer 0.1 mol dm^{-3} in Cr^{II} and 1 mol dm^{-3} in HCl, then with a further aqueous layer 5×10^{-3} mol dm^{-3} in Fe^{III} and 1 mol dm^{-3} in HCl, the pristine green $[Co^{III}L^1Cl_2]Cl$ complex is restored, whose spectrum superimposes with that of the original solution.

The above behaviour can be accounted for by assuming that replacement of Cl^- by ClO_4^- makes the potential associated with the $[Co^{III}L^1X_2]X$–$[Co^{II}L^1X_2]$ couple increase drastically. Modulation of the Co^{III}–Co^{II} redox couple potential through variation of the ligating tendencies of the axially bound anions was observed by Endicott and co-workers[11] in *trans*-diacido cyclam complexes; decreasing the axial ligand field made the Co^{III}–Co^{II} potential increase gradually. In the present case, the potential associated with the $[Co^{III}L^1(ClO_4)_2]ClO_4$–$[Co^{II}L^1(ClO_4)_2]$ redox couple should be very positive. Looking at the two juxtaposed electrochemical scales (see Figure 2), this potential should be situated above that of the Fe^{III}–Fe^{II} couple in 1 mol dm^{-3} $HClO_4$ ($E_{\frac{1}{2}} = 0.77$ *vs.* n.h.e.) and below that associated with the Ce^{IV}–Ce^{III} couple in 1 mol dm^{-3} $HClO_4$ (1.70 *V vs.* n.h.e.). Unfortunately, the $E_{\frac{1}{2}}$ value for the Co^{III}–Co^{II} couple could not be determined: cyclic voltammetry investigation on the dichloromethane yellow solution, 10^{-3} mol dm^{-3} in the cobalt(III) complex and 0.1 mol dm^{-3} in NBu_4ClO_4, did not disclose any wave, even at moderate potential scan rates (to 10 mV s^{-1}), possibly due to an especially low rate of heterogeneous electron transfer.

Of special interest is the reactivity of the cobalt(II) complexes towards dioxygen. When an aqueous layer 1 mol dm^{-3} in HCl is stratified over a CH_2Cl_2 layer containing $[Co^{II}L^1Cl_2]$, and dioxygen is bubbled through the non-aqueous layer, a green colour develops in the dichloromethane phase due to the formation of $[Co^{III}L^1Cl_2]Cl$. This behaviour is quite obvious, if one compares values for the electrode potentials pertinent to the aqueous O_2–H_2O couple ($[H^+] = 1$ mol dm^{-3}, 1.23 V *vs.* n.h.e.) and to the non-aqueous $[Co^{III}L^1Cl_2]Cl$–$[Co^{II}L^1Cl_2]$ couple (see Figure 2). On the other hand, if dioxygen is bubbled through a CH_2Cl_2 layer containing the $[Co^{II}L^1(ClO_4)_2]$ complex, which has been covered by an aqueous layer containing 1 mol dm^{-3} $HClO_4$, no oxidation to the yellow cobalt(III) complex takes place. This suggests that the potential associated with the $[Co^{III}L^1(ClO_4)_2]ClO_4$–$[Co^{II}L^1(ClO_4)_2]$ redox couple, on the non-aqueous electrochemical scale, should be higher than 1.23 V on the aqueous scale, according to the juxtaposition illustrated in Figure 2. Indeed, the stability of the $[Co^{II}L^1(ClO_4)_2]$ species towards dioxygen may be very surprising, when one considers the typical difficulty in preventing aerial oxidation of cobalt(II) tetra-aza macrocyclic complexes in water or other co-ordinating solvents. Thus, combined use (*i*) of non-co-ordinating solvents and (*ii*) of poorly donating anions can be recommended as a novel route to air-stable cobalt(II) tetramine complexes.

On the basis of the above two-phase experiments, the following electron-transport process has been designed: e.s.p., 0.10 mol dm^{-3} Cr^{II}, 1 mol dm^{-3} $HClO_4$; membrane, 5×10^{-4} mol dm^{-3} $[Co^{III}L^1(ClO_4)_2]ClO_4$ ('yellow solution'); e.r.p., 10^{-3} mol dm^{-3} Ce^{IV}, 1.0 mol dm^{-3} $HClO_4$, 0.1 mol dm^{-3} HNO_3. Nitric acid was added to the e.r.p. to stabilize Ce^{IV} which slowly decomposes in pure $HClO_4$ and cannot be used in experiments which last for hours, as do the electron-transport experiments described. In the presence of nitrate, Ce^{IV} is stable on the time-scale of the electron-transport experiments. Nitrate ion should not compete for the transport with the much more concentrated ClO_4^-, nor should the potential associated with the Ce^{IV}–Ce^{III} redox couple be substantially altered [$E(Ce^{IV}$–$Ce^{III})$ in 1 mol dm^{-3} $HNO_3 = 1.61$ V].[9] In any case, the two-phase oxidation to the yellow cobalt(III) species is also accomplished by Ce^{IV} in aqueous 1.0 mol dm^{-3} $HClO_4$, 0.1 mol dm^{-3} HNO_3 solution, as shown by preliminary experiments. The e^-/ClO_4^- cross-transport takes place, as judged from the decrease in concentration of Ce^{IV} in the e.r.p. (see Figure 3). However, the rate of the process is much slower than that observed in the experiments in which HCl was the aqueous background electrolyte. At this stage of the investigation it is difficult to assess whether the low rate is to be ascribed to the nature of the aqueous oxidizing agent or of the counterflowing anion. A direct comparison cannot be made with the previously employed aqueous oxidizing agents. Both $[Ni^{III}L^3(H_2O)_2]^{3+}$ and Fe^{III} cannot oxidize the reduced form of the carrier, in the presence of ClO_4^-, on the other hand, Ce^{IV} cannot be used as an oxidizing agent in aqueous 1 mol dm^{-3} HCl, as it tends to oxidize Cl^- to Cl_2, which dissolves in the membrane performing a single-phase oxidation. Surely, if the inner-sphere mechanism is really operative in the redox process at the membrane/e.r.p. interface, the ClO_4^- ion cannot compete with Cl^- as an efficient bridge for the electron transfer from Co^{II} to the oxidized metal centre.

Conclusion

Oxidation and reduction reactions can take place using separated solutions of the oxidizing agent and of the reducing agent, which are interfaced by an immiscible liquid containing an appropriate redox system (the redox-active membrane). The membrane is a filter, permeable to electrons and anions. Permeability can be controlled by varying the potential of the lipophilic redox system dissolved in the membrane. The potential of the metal-centred redox system investigated in this work, $[Co^{III}L^1X_2]X$–$[Co^{II}L^1X_2]$, can be varied by varying the nature of X. For X = Cl the redox potential of the carrier is low enough to permit reduction (using Cr^{II} as a source of electrons) of a mild oxidizing agent as Fe^{III}. When $X = ClO_4$ this redox potential is drastically raised and the liquid membrane filters electrons only to strong oxidizing agents such as Ce^{IV}.

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