

Coordination Chemistry of 2,5,8-Trithia[9]-(2,9)-1,10-phenanthrolinephane (L) toward Rhodium(III) at the Polarised Water/1,2-Dichloroethane Interface – A Possible New Approach to the Problem of Separating Rh^{III} from Chloride Media

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Keywords: Rhodium / Macrocyclic ligands / Interfaces / Cyclic voltammetry

The coordination chemistry involved in the assisted transfer of Rh^{III} by interfacial coordination with 2,5,8-trithia[9]-(2,9)-1,10-phenanthrolinephane (L) has been studied at the water/1,2-dichloroethane interface by cyclic voltammetry. The dependence of the half-wave transfer potential on the ligand and metal concentrations suggests the [Rh(L)Cl₂]⁺ formulation for the complex cation involved in the assisted transfer. In contrast, from the reaction of L in refluxing MeCN/water

solution the [Rh(L)Cl][BF₄]₂·2MeCN compound has been isolated and structurally characterised. In the [Rh(L)Cl]²⁺ complex cation L acts as an N₂S₃ donor encapsulating the metal centre within a cavity having a square-based pyramidal geometry. A chloride ligand completes the distorted octahedral coordination sphere around the Rh^{III} ion. (© Wiley-VCH Verlag GmbH, 69451 Weinheim, Germany, 2002)

Introduction

The quest for new macrocyclic ligands capable of specific and effective molecular recognition of metal ions in carrier-assisted membranes or solid-state ion-selective electrodes is a topic of current interest.^[1,2] Attention has mainly been focussed on the assisted transfer of group I and group II ions between two immiscible electrolyte solutions; different crown ether derivatives have been used as neutral carriers for the construction of ion-selective electrodes and for performing selective separations.^[1–4] A smaller number of studies have been performed with transition and heavy metal ions, particularly precious metal ions, probably because of their greater inertness.^[5,6] However, the recovery and removal of precious metals from aqueous solutions is of considerable economic and environmental concern. In particular, the separation and purification of rhodium from other platinum group metals in aqueous chloride solutions is made difficult by the complex chemistry that Rh^{III} exhibits in these media, which are largely employed because platinum group metals are usefully soluble in them. Mixed

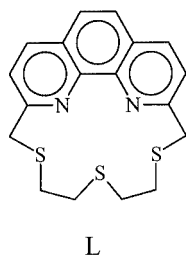
aquachloro complexes of the type [RhCl_{6–n}(H₂O)_n]^{n–3} (0 < n < 6) are formed in different proportions depending primarily on the chloride concentration.^[7] These species are highly hydrophilic and not easily isolated by direct solvent extraction. Some reagents such as SnBr₂, SnCl₂,^[8,9] or SCN[–]^[10] can be used to enhance the extractability of the metal by forming Rh^{III} complexes with better solvent extraction properties, but once the metal is in the organic phase, the stripping process is not that easy. Despite these difficulties, the separation of Rh^{III} has been carried out by using different techniques such as solvent extraction,^[11] ion exchange^[9,12] and liquid membrane separation,^[13–16] and particular attention is paid to research in this area is very guarded. Recently we have reported the synthesis of new mixed aza-thioether crowns containing the 1,10-phenanthroline (phen) unit as an integral part of the macrocyclic structure.^[17–19] These ligands have shown a great affinity for heavier transition metal ions such as Pd^{II}, Pt^{II} and Rh^{III}, with coordination properties strictly dependent upon the conformational constraints imposed by the heteroaromatic moiety on the S-donor thioether linker of the ring. Herein we report a study by cyclic voltammetry of the assisted transfer of Rh^{III} by interfacial complexation with 2,5,8-trithia[9]-(2,9)-1,10-phenanthrolinephane (L) at the polarised water/1,2-dichloroethane interface. The principal target of this work has been to study the coordination chemistry of L towards Rh^{III} at the water/1,2-dichloroethane junction; however, the results obtained could represent a useful start-

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ing point for a novel way of approaching the problem of Rh^{III} separation and purification from aqueous solutions.



Results and Discussion

We reported previously^[18] the reaction of L with RhCl₃ in refluxing MeCN/water to afford a yellow microcrystalline powder after addition of an excess of NH₄PF₆. The resulting complex was formulated as [Rh(L)Cl][PF₆]₂·MeCN on the basis of elemental analysis data and IR and FAB mass spectrometry. ¹³C NMR spectroscopic measurements in CD₃CN confirmed this formulation and indicated an octahedral stereochemistry at the Rh^{III} centre similar to that observed around Ni^{II} in [Ni(L)Cl]⁺,^[19] with all the five donor atoms of the macrocyclic ligand strongly coordinated and with a chloride completing the octahedral environment. After many attempts we have been able to grow crystals of [Rh(L)Cl][BF₄]₂·2MeCN suitable for X-ray diffraction studies by diffusion of Et₂O vapour into a MeCN solution of the complex. The structure determination confirms the rhodium(III) ion to be bound to the pentadentate macrocycle through two N-donors of the phen unit [Rh(1)–N: 2.001(3) and 1.996(3) Å] and three thioether S-donors of the thioether linker of the ligand [Rh(1)–S: 2.3361(9), 2.3219(9) (*trans* to phen) and 2.3033(9) Å (*trans* to Cl)] (Figure 1,

Table 1. Selected bond lengths (Å) and angles (°) for [Rh(L)Cl][BF₄]₂·2MeCN

Rh(1)–Cl(1) 2.3456(8)	Rh(1)–S(1) 2.3361(9)
Rh(1)–S(2) 2.3219(9)	Rh(1)–S(3) 2.3033(9)
Rh(1)–N(1) 2.001(3)	Rh(1)–N(2) 1.996(3)
N(1)–Rh(1)–N(2) 82.35(11)	N(1)–Rh(1)–S(1) 82.62(8)
N(1)–Rh(1)–S(2) 166.43(8)	N(1)–Rh(1)–S(3) 92.74(8)
N(1)–Rh(1)–Cl(1) 89.16(8)	N(2)–Rh(1)–S(1) 164.88(8)
N(2)–Rh(1)–S(2) 84.36(8)	N(2)–Rh(1)–S(3) 89.80(3)
N(2)–Rh(1)–Cl(1) 90.31(8)	S(1)–Rh(1)–S(2) 110.72(3)
S(1)–Rh(1)–S(3) 89.27(3)	S(1)–Rh(1)–Cl(1) 91.12(3)
S(2)–Rh(1)–S(3) 89.94(3)	S(2)–Rh(1)–Cl(1) 88.18(3)
S(3)–Rh(1)–Cl(1) 178.10(3)	

Table 1). The octahedral coordination sphere is completed by a Cl[–] ion [Rh(1)–Cl(1): 2.3456(8) Å]. The phenanthroline moiety and the two adjacent sulfur atoms S(1) and S(2) of the thioether linker lie approximately in an equatorial plane of the octahedron, with the third sulfur atom S(3) and the Cl[–] ligand occupying the two apical positions [S(3)–Rh(1)–Cl(1): 178.10(3)°]. This structure demonstrates the ability of L to host the Rh^{III} ion within its ring cavity without any particular constraint of the organic framework; therefore, L is a possible candidate as a sequestering agent for the recovery of this precious metal ion from aqueous solutions.

In order to test the ability of L to assist the electrochemical extraction of Rh^{III} at the water/1,2-dichloroethane (1,2-DCE) polarised interface, we have made preliminary studies by cyclic voltammetry (CV) with an electrochemical cell as shown schematically below (Cell 1).

Cell 1

Ag	AgCl	NaCl (10 mM)	L (0.025 mM)	RhCl ₃ (2.8 mM)	AgCl	Ag
		NaTPB (10 mM)	TOATPB (10 mM)	LiCl (10 mM)		
		(H ₂ O)	(1,2-DCE)	(H ₂ O)		

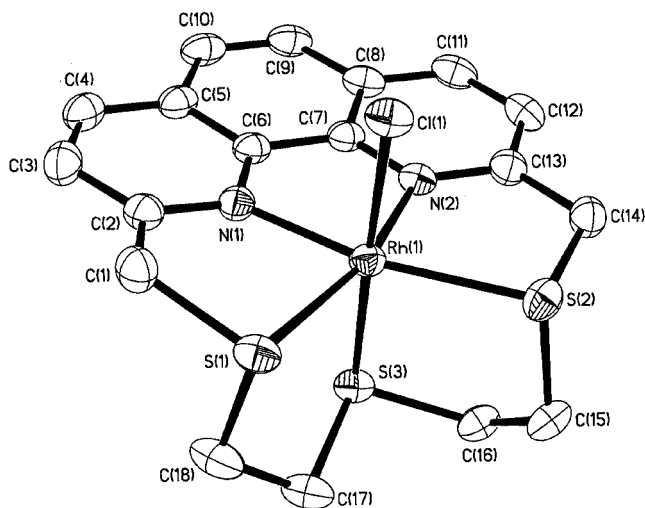


Figure 1. View of the [Rh(L)Cl]²⁺ cation with the numbering scheme adopted; displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms have been omitted for clarity

This type of cell has already been successfully employed to study the transfer of Cu^{II} assisted by 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline (DMDPQ),^[20] and the transfer of Zn^{II}, Cd^{II} and Pb^{II} assisted by cyclic thioether ligands.^[21] Previous work by Homolka,^[22] Matsuda,^[23] Kakiuchi and Senda,^[24] and Reymond et al.^[25,26] has provided a theoretical framework for the determination of parameters such as the complex stoichiometry involved in the transfer process. In the absence of L, there is no visible wave in the cyclic voltammogram within the potential window available, demonstrating the absence of any transfer process of Rh^{III} across the organic phase under these conditions (Figure 2a, dashed line). When the ligand L is present in the organic phase, the CV responses exhibit a well-defined single reversible wave (Figure 2a, full line) related to the transfer of an ionic species with Δ_o^wφ_{1/2} = 30 mV and a peak-to-peak separation of 60 mV; this is consistent with the assisted transfer of Rh^{III} by L across the water/1,2-dichloroethane interface. Measurement of the pH of the aqueous solution containing RhCl₃ (electrode compartment on the right in cell 1) showed that the medium was acidic due to the hydrolysis of

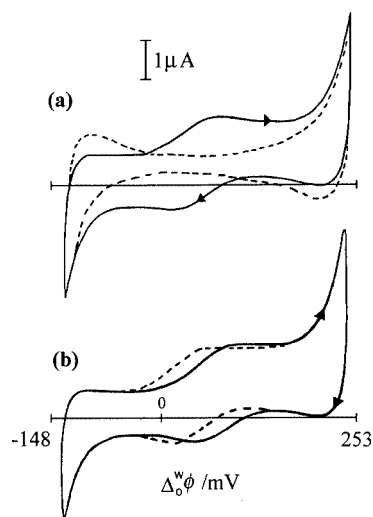


Figure 2. (a) Voltammetric responses in the absence (dashed line) and in the presence (full line) of L in the organic phase for the cell 1 system; (b) voltammetric responses for the cell 1 system in the case of acidic aqueous phase (dashed line) and neutralised aqueous phase by addition of LiOH (full line)

Rh^{III} aquo/chloro complexes^[7] and therefore the assisted transfer of H^+ by the ligand could also occur under these experimental conditions. The peak observed could then indicate either the facilitated transfer of the proton or the Rh^{III} ion by the ligand. In order to identify clearly the transfer of Rh^{III} assisted by L, LiOH was then added to the acidic aqueous phase containing Rh^{III} in order to neutralise it. The cyclic voltammogram recorded under neutral conditions resembles that obtained when the aqueous phase is acidic, with a single reversible wave observed at a slightly more positive $\Delta\phi_{1/2}^{\text{w}}$ (65 mV) with a peak-to-peak separation of 60 mV (Figure 2b).

We also decided to study the protonated ligand transfer across the water/1,2-DCE interface upon changing the pH of the aqueous phase. Figure 3 includes the voltammograms observed when the pH of the aqueous solution (electrode compartment on the right in cell 2) changes from 2 to 12.

While a single well-defined peak appears in the voltammogram at pH 2, no transfer processes are observed at pH 7 and 12, indicating that the proton transfer facilitated by L across the water/1,2-DCE interface occurs only when acidic solutions are used. From the transfer potential at different pH of the aqueous phase, obtained by cyclic voltammetry using cell 2, an ionic partition diagram of the ligand was constructed as described by Reymond et al.^[27] (Figure 4a). This diagram can be used to predict qualitatively the influence of the variation of the Galvani potential difference ($\Delta\phi_{1/2}^{\text{w}}$) and/or aqueous pH on the nature of the transferring species present at the water/1,2-DCE interface. Furthermore, the behaviour of the peak current on changing the pH of the aqueous phase in cell 2 (Figure 4b) allowed the assessment of the acidic constant ($\text{p}K_{\text{a}}$) in water for the ligand L, the value of which was estimated to be 4.3. This value is lower than those reported for 1,10-phenanthroline ($\text{p}K_{\text{a}} = 4.97$)^[28] and 2,9-dimethyl-1,10-phenanthroline

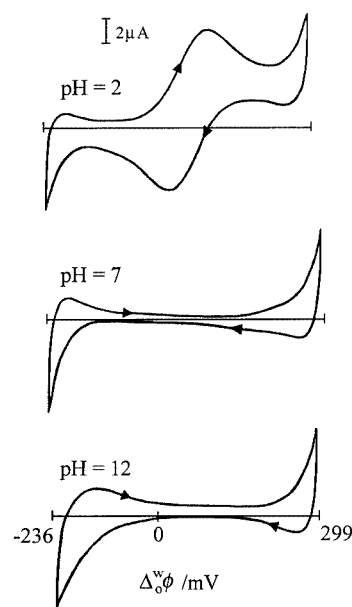


Figure 3. Voltammetric responses for the cell 2 system showing the effect of pH on the assisted transfer of H^+ by L across the water/1,2-DCE interface

Cell 2

X = HCl 10 mM (pH = 2); X = LiCl 10 mM (pH = 7); X = LiOH 10 mM + LiCl 10 mM (pH = 12)

Ag	AgCl	NaCl (10 mM)	L (0.3 mM)	X	AgCl	Ag
		NaTPB (10 mM)	TOATPB (10 mM)	(H ₂ O)		
		(H ₂ O)	(1,2-DCE)			

($\text{p}K_{\text{a}} = 5.85$)^[29] as determined potentiometrically in water solution. A direct pH-potentiometric determination of the $\text{p}K_{\text{a}}$ of L was not possible because of the very low solubility of the ligand in water.

From these results it can be concluded that the rhodium(III)-assisted transfer by L at a polarised water/1,2-DCE interface is possible and that pH control of the aqueous phase is necessary to study the process.

The evaluation of the charge and stoichiometry of the complex involved in the transfer was carried out by studying the voltammetric behaviour of the transfer under neutral pH conditions for the aqueous phase, in the presence of excess metal with respect to the ligand in the organic phase. Cell 3 was used to carry out these studies: bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl)borate (BTTPATPBCl) was used as the organic electrolyte salt because it allows a larger potential window (and it has no effect on the voltammetric signal).

Figure 5a shows the change in mid-peak potential ($\Delta\phi_{1/2}^{\text{w}}$) when the concentration of excess metal is varied. From the slope of the line (-58 ± 6 mV) a charge of +1 for the complex is deduced.^[20] The peak current (i_{pc}) is independent of the concentration of the metal. The effect on $\Delta\phi_{1/2}^{\text{w}}$ of the change of the concentration of the ligand (in the organic phase) in the presence of excess metal (in the aqueous phase) has also been monitored in order to

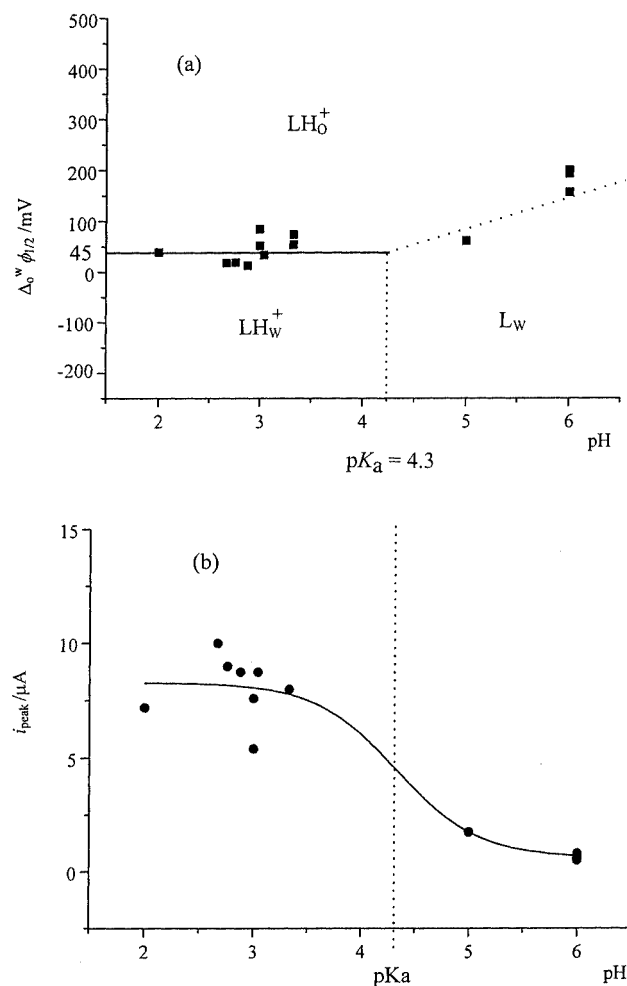


Figure 4. (a) Ionic partition diagram of L at room temperature; (b) change of the peak current upon variation of the pH of the aqueous phase in cell 2

Cell 3					
Ag	AgCl	10 mM LiCl 1 mM BTTPACl (H ₂ O)	L 10 mM BTTPATPBCl (1,2-DCE)	RhCl ₃ LiOH 10 mM LiCl (H ₂ O)	AgCl Ag

evaluate the stoichiometry of the complex.^[20] Since there is no dependence of the half-wave transfer potential on $\log C_L$ (Figure 5b), according to Raymond et al.,^[25,26] the stoichiometry of the complex must be 1:1. From the variation of the peak current intensity on changing the concentration of L on excess metal ion concentration (Figure 5c), and using the modified Randles–Sevcik expression,^[26] it was possible to estimate the diffusion coefficient of the ligand in the organic phase (in fact, due to the metal excess, the current is limited by the diffusion of the ligand): $D_o = 5.1 \times 10^{-6} \text{ cm}^2/\text{s}$. This value is in good agreement with those reported in the literature for 1,10-phenanthroline (phen) and its bulky derivatives in 1,2-dichloroethane ($D_o[\text{phen}] = 9.6 \times 10^{-6}$, $D_o[4,7\text{-diphenyl-phen}] = 4.8 \times 10^{-6} \text{ cm}^2/\text{s}$).^[30]

As already pointed out, the studies reported so far have been conducted by cyclic voltammetry in cell 3, varying

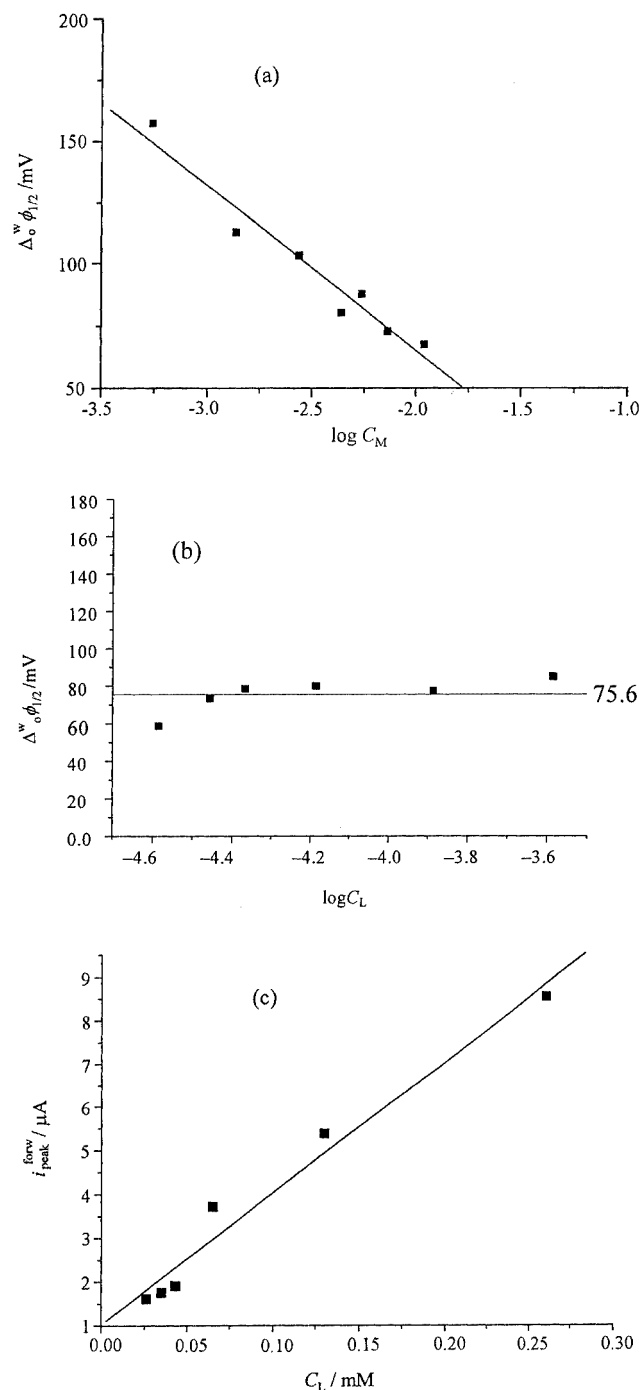


Figure 5. (a) Change in mid-peak transfer potential ($\Delta_o^w \phi_{1/2}$) when the concentration of excess metal in the aqueous phase is varied ($\log C_L = -4$); (b) effect on $\Delta_o^w \phi_{1/2}$ of the change of the concentration of L in the organic phase in the presence of excess metal in the aqueous phase ($\log C_M = -2.3$); (c) current forward peak intensity vs. the log of ligand concentration (C_L) ($\log C_M = -2.3$, slope = $30 \mu\text{A}/\text{mM}$); the system cell considered is cell 3

either the metal or the ligand concentration but keeping the metal-ion concentration in excess. If excess ligand is used and the metal concentration is varied, another voltammetric signal appears when $C_L > C_M$ (Figure 6), which can be assigned to the assisted transfer of a 1:2 Rh/L complex.

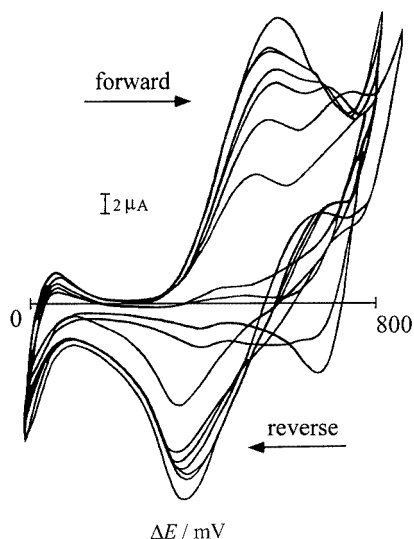


Figure 6. Cyclic voltammograms obtained for the Rh^{III} transfer assisted by L ($C_L = 1.30 \text{ mM}$) for different metal concentrations (C_M ranging from 0.05 to 9.70 mM)

The plot of forward peak current (i_{pc}) vs. C_M for the voltammograms in Figure 6 clearly demonstrates the presence of a transition point between two limiting diffusion regimes (Figure 7). However, a study similar to that performed for the transfer of the 1:1 complex was not possible due to the poor definition of the two voltammetric signals.

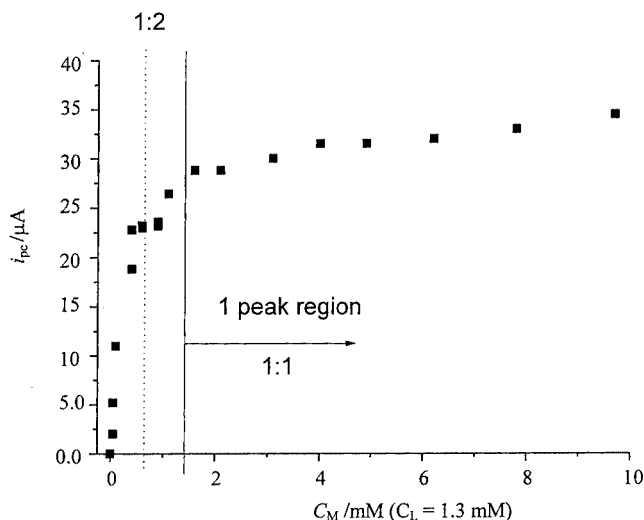


Figure 7. Plot of the forward peak current vs. C_M for the results in Figure 6

The 1:1 complex involved in the assisted transfer seems to have the formulation $[\text{Rh}(\text{L})\text{Cl}_2]^+$. An analogous stoichiometry has been observed for the Rh^{III} complex with a structural analogue of L where S(3) (Figure 1) has been replaced by an oxygen atom. In this case, it has been shown by NMR spectroscopy that the O-donor of the ligand is not

able to coordinate the octahedral metal centre and that the two chloride ligands are mutually *trans*.^[31]

The unassisted transfer of Rh^{III} as RhCl_2^+ occurs at $\Delta_o^w \phi^{0'} [\text{RhCl}_2]^+ = 514 \text{ mV}$ and was determined by applying the methodology proposed by Shao et al.^[32] for determining the half-wave potential of the species limiting the potential window. The value of K_f^0 , corresponding to the complexation of one $[\text{RhCl}_2]^+$ ion with one molecule of L, can therefore be estimated from the dependence of $\Delta_o^w \phi_{1/2}$ on the metal concentration (Figure 5a) using the methodology proposed by Reymond et al.,^[26] which in the case of a metal ion excess is:

$$\Delta_o^w \phi_{1/2, \text{ML}_j^{z+}} = \Delta_o^w \phi_{\text{M}^{z+}}^{0'} - \frac{2.303RT}{zF} \log \left(\sum_{j=0}^m j \beta_j^0 C_{\text{M}_{\text{init}}} \left(\frac{C_{\text{L}_{\text{init}}}}{2} \right)^{j-1} \right)$$

For the case of a 1:1 complex between the $[\text{RhCl}_2]^+$ ion and L this expression can be rewritten as:

$$\Delta_o^w \phi_{1/2, \text{ML}^{z+}} = \Delta_o^w \phi_{\text{M}^{z+}}^{0'} - \frac{2.303RT}{zF} \log (\beta^0 C_{\text{M}_{\text{init}}})$$

where j is the number of ligands in the complex, z the charge of the complex species involved in the assisted transfer, $\Delta_o^w \phi_{1/2, \text{ML}_j^{z+}}$ the half-wave Galvani potential for the transfer of the complex ML_j^{z+} , $\Delta_o^w \phi_{\text{M}^{z+}}^{0'}$ the formal Galvani transfer potential for the metal ion, β_j^0 the stability constant for the complex ML_j^{z+} , and $C_{\text{M}_{\text{init}}}$ and $C_{\text{L}_{\text{init}}}$ the initial concentrations of metal ion and ligand, respectively. Taking $\Delta_o^w \phi^{0'} [\text{RhCl}_2]^+$ to be 514 mV and using the intercept of Figure 5a (−69.7 mV), the value calculated for the formation constant of $[\text{Rh}(\text{L})\text{Cl}_2]^+$ is $\log K_f^0 = 9.7$. This value, when compared with those obtained by cyclic voltammetry at the water/1,2-DCE interface for some 1:3 metal-phenanthroline complexes $\{\log \beta_3^0 [\text{Ca}(\text{phen})_3]^{2+} = 15.8, \log \beta_3^0 [\text{Sr}(\text{phen})_3]^{2+} = 14.0\}$,^[33] clearly shows that, despite its steric hindrance, the thiacycrown ring in L has an overall stabilising effect (in comparison with complexes having higher stoichiometries). This should be due to the donor properties of the S-donors in the ring.

Conclusions

The assisted transfer of Rh^{III} ion with 2,5,8-trithia[9],(2,9)-1,10-phenanthroline (L) at the water/1,2-DCE interface has been demonstrated, thus pointing towards a new approach to the problem of separating Rh^{III} from chloride media. The nature of the Rh^{III} complex involved in the assisted transfer has been elucidated by cyclic voltammetry and it corresponds to the formulation $[\text{Rh}(\text{L})\text{Cl}_2]^+$. This complex cation is different from that obtained by refluxing L with RhCl_3 in MeCN/water solution, which has the formulation $[\text{Rh}(\text{L})\text{Cl}]^{2+}$, and has the same stoichiometry as the Rh^{III} complex obtained with a structural analogue of L having an O-donor instead of the S(3) atom.

Experimental Section

General Procedures and Chemicals: Cyclic voltammetry was performed using a four-electrode potentiostat (Solartron 1287) with ohmic drop compensation. The electrochemical cell was made from borosilicate glass and was of the same design as used previously;^[21] with two Luggin reference probes and a geometrical area for the water/1,2-DCE interface of 0.22 cm². All the measurements were carried out at laboratory temperature (20 ± 3 °C), with scan rates ranging from 10 to 100 mV/s. For each experiment the addition of a fixed amount of ClO₄[−] (LiClO₄ > 99.99% purity from Aldrich) provided a reference for all half-wave potential measurements. The values measured were easily transposed to the Galvani potential scale taking into account the following relationship $E_{1/2} - \Delta_\phi^0 = E_{1/2}(\text{ClO}_4^-) - \Delta_\phi^0(\text{ClO}_4^-)$ and the value of the transfer potential of perchlorate ion [$\Delta_\phi^0(\text{ClO}_4^-) = -176 \text{ mV}$].^[34]

The organic electrolyte salts used in this study were tetraoctylammonium tetrakis(phenyl)borate (TOATPB), prepared as reported previously,^[35] and bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBCl), which was prepared by the metathesis of BTPPACl (Aldrich) and KTPBCl (Fluka). Rhodium(III) unassisted transfer in the absence of L was studied using 10 mM BTPPATPBCl as the supporting electrolyte in the organic phase. 2,5,8-Trithia[9],(2,9)-1,10-phenanthrolineophane (L) was synthesised according to the literature.^[17] LiCl (>99% purity) and RhCl₃·3H₂O (38% Rh) were obtained from Merck. Aqueous solutions were prepared with purified water from Milli Q 185 system (Millipore). 1,2-Dichloroethane (1,2-DCE) (>99.5% purity, Merck) was used without further purification and was handled with all necessary precautions.

Crystal Structure Determination: Crystal data for C₂₂H₂₄B₂ClF₈N₄RhS₃, $M = 752.61$, orthorhombic, $Pccn$, $a = 14.2317(13)$, $b = 31.974(3)$, $c = 12.4458(11) \text{ \AA}$, $V = 5663.4(9) \text{ \AA}^3$, Mo- K_α radiation $\lambda = 0.71073 \text{ \AA}$, $Z = 8$, $D_{\text{calcd.}} = 1.765 \text{ g cm}^{-3}$, $F(000) = 3008$, $T = 150(2) \text{ K}$, $\mu(\text{Mo-}K_\alpha) = 0.994 \text{ mm}^{-1}$. Yellow plate, $0.21 \times 0.16 \times 0.12 \text{ mm}^3$. Bruker SMART1000 CCD area detector diffractometer with Oxford Cryosystems open-flow cryostat.^[36] ω scans, 6808 absorption-corrected reflections (SADABS,^[37] $T = 0.80\text{--}1.00$), 5132 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods using SHELXS-97^[38] and full-matrix least-squares refinement on F^2 was performed using SHELXL-97.^[39] All non-H atoms were refined anisotropically and H atoms were placed geometrically and thereafter allowed to ride on their parent atoms. One of the two BF₄[−] anions exhibited disorder and the refinement was accomplished with restraints to the B–F distances and F–B–F angles, and to the total occupancy of the F atoms.

CCDC-175177 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors wish to thank Dr. Pietro A. Vigato (Istituto di Chimica e Tecnologie Inorganiche e dei Materiali Avanzati, CNR, Padova, Italy) since without his contribution the realisation of this work would not have been possible. M. H. M. Caçote is grateful

to Fundação para a Ciência e Tecnologia for a PRAXIS XXI Ph.D. grant. Work was carried out under INOVELREC – EU contract no. BRPR-CT95–010. L. Tei is grateful to the University of Cagliari for financial support.

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Received November 30, 2001
[I01491]