Cyclic Voltammetry and Spectroelectrochemistry of Rhodium Phthalocyanines

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The electrochemistry of Rh^{III}(pc) (pc = phthalocyanine dianion) complexes containing chloride, pyridine, dimethyl sulfoxide (dmso) and cyanide as axial ligands was investigated by cyclic voltammetry and UV/VIS spectroelectrochemistry. The compounds were K[Rh(pc)(CN)$_2$], [Rh(pc)(Cl)(py)] and [Rh(pc)Cl(dmso)]. For all of these the first oxidation occurs at the phthalocyanine ligand with the formation of a π-cation radical species. The addition of one electron to the complexes leads to one of two different reduction products depending on the nature of the axial ligands. The first reduction of [Rh(pc)Cl(py)] and [Rh(pc)Cl(dmso)] occurs at the metal, followed by rapid dimerization of the reduced species. The first and subsequent reductions of K[Rh(pc)(CN)$_2$] occur at the ring.

Metallophthalocyanine, M(pc) where pc = phthalocyanine dianion, redox species have been observed as intermediates in a variety of catalytic processes.[1,2] Such complexes exhibit a rich electrochemical behaviour due to the accessibility of a range of oxidation states centred on the phthalocyanine ligand and, for some transition-metal phthalocyanines, on the central metal.[3–14] Electrochemical studies of phthalocyanines have concentrated mainly on complexes of the first-row transition metals, with only a few reports on those of the second and third row.[14–16]

Rhodium(III) phthalocyanine complexes have been synthesised[17,18] and some photochemical properties reported.[19,20] Except for the cyclic voltammetry data reported for K[Rh^{III}(pc)(CN)$_2$],[15] there has been no detailed study of the nature of the oxidation or reduction products of these complexes. Monomeric rhodium(III) porphyrin complexes, which are structurally similar to the phthalocyanine complexes, undergo electroreduction at either the central metal or at the porphyrin ring.[21–24] The factors that govern the site of reduction in ruthenium(III) porphyrin complexes are not yet fully understood.

Electrochemical properties of K[Rh(pc)(CN)$_2$], [Rh(pc)Cl(py)] (py = pyridine) and [Rh(pc)Cl(dmso)] (dmso = dimethyl sulfoxide) are reported in this work and compared with those of corresponding porphyrin complexes.

Experimental

Materials.—Following the procedure reported before,[25,26] [Rh(pc)Cl] was prepared from RhCl$_3$ and *o*-cyanobenzamide as follows: a mixture of RhCl$_3$ (0.2 g), *o*-cyanobenzamide (1.8 g) and naphthalene (0.6 g) (molar ratio 1 : 12.6 : 5.06) was heated for 1 h and the resulting blue solid was Soxhlet extracted with glacial acetic acid until the washings were colourless, then dried at 100 °C for 12 h to remove traces of acetic acid. Yield *ca.* 60%.

Chloro(phthalocyaninato)(pyridine)rhodium(III) [Rh(pc)Cl(py)] was prepared by refluxing [Rh(pc)Cl] (0.1 g) in pyridine (20 cm^3) for 8 h. The resulting blue solution was chromatographed on an aluminium oxide column and eluted with chloroform to give a purple solid (Found: C, 60.6; H, 2.6; N, 16.0. Calc. for $C_{37}H_{21}ClN_9Rh$: C, 60.8; H, 2.9; N, 17.3%). IR (KBr disc): ν(Rh–Cl) 350 cm^{-1}.

Chloro(dimethyl sulfoxide)(phthalocyaninato)rhodium(III) [Rh(pc)Cl(dmso)] was prepared by refluxing [Rh(pc)Cl] (0.1 g) in dmso (30 cm^3) for 3 h. The solution was then evaporated to dryness and the resulting blue solid was recrystallized twice from acetone (Found: C, 55.0; H, 3.4; N, 14.3. Calc. for $C_{34}H_{22}ClN_8Rh$: C, 56.0; H, 3.0; N, 15.4%). IR (KBr disc): ν(Rh–dmso) 925, ν(Rh–Cl) 345 cm^{-1}.

Potassium dicyano(phthalocyaninato)rhodium(III) K[Rh(pc)(CN)$_2$]·3H$_2$O was prepared by refluxing [Rh(pc)Cl] (0.05 g) with an excess of KCN (0.03 g) in dimethylformamide for 3 h. The resulting blue solution was evaporated to dryness, and the residue then washed with water and recrystallized twice from acetone. Yield *ca.* 70% (Found: C, 53.9; H, 2.3; N, 17.0. Calc. for $C_{34}H_{16}KN_{10}Rh\cdot 3H_2O$: C, 53.9; H, 2.9; N, 18.5%). IR (KBr disc): ν(Rh–CN) 2145 cm^{-1}.

The solvents CH$_2$Cl$_2$ and MeCN were dried over calcium hydride and phosphorus pentaoxide, respectively, and then distilled. Dimethylformamide (dmf) and dmso were stirred in alumina and then distilled. Acetone was freshly distilled. Tetrabutylammonium perchlorate and tetraethylammonium perchlorate were recrystallized and used as electrolytes for electrochemical studies. Ferrocene was recrystallized from ethanol before use as an internal standard. All other materials were reagent grade used without further purification.

Methods.—Electrochemical data were collected with a BAS CV 27 voltammograph connected to an HP 7047A X-Y recorder. All measurements were carried out under an atmosphere of nitrogen. For cyclic voltammetry, a platinum disc (diameter 1.6 mm) was used as a working electrode and a platinum wire as an auxiliary electrode. A silver wire coated with silver chloride was used as a quasi-reference electrode. Potentials were referenced internally to the ferrocenium–ferrocene couple.[13,27] This couple was measured to be 0.46 V *vs.* the saturated calomel electrode (SCE) in dmf containing NEt$_4$ClO$_4$; values in dmso, CH$_2$Cl$_2$ and MeCN have been reported before.[9,14] Platinum-sheet working and auxiliary electrodes and an Ag–AgCl reference electrode were employed for bulk electrolysis, the auxiliary electrode being separated from the compartment housing the reference and working electrodes by a fine glass frit. The concentrations of the electrolytes (NBu$_4$ClO$_4$ or NEt$_4$ClO$_4$) were ≈0.1 mol dm^{-3} in all electrochemical experiments. Concentrations of the phthalocyanines of between 10^{-6} and 10^{-5} mol dm^{-3} were employed for controlled-potential electrolysis and for cyclic voltammetry the concentrations were *ca.* 10^{-3} mol dm^{-3}.

Infrared spectra (KBr discs) were recorded with a Perkin Elmer model 180 spectrometer, electronic absorption spectra with a Beckman UV/VIS spectrophotometer model UV 5240.

Magnetic susceptibility data were collected on approximately 5 mg pure samples with a Faraday balance by Cahan Instrument Company. Proton NMR spectra ($CDCl_3$ or C_6D_6) were obtained with a Bruker EMX 400 (400 MHz) spectrometer. Elemental analyses were performed by M. Somaru, University of Natal.

Results and Discussion

Spectral Characterization.—The IR spectra observed for the Rh(pc) complexes are typical of metallophthalocyanines. The cyanide vibration observed at 2145 cm^{-1} for $K[Rh(pc)(CN)_2]$ is in the range reported for M–CN vibrations.[14,15,28] The band at 925 cm^{-1} of [Rh(pc)Cl(dmso)] is in the range reported for *O*-bonded dmso.[16,29] Bands for *S*-bonded dmso are normally observed in the 1100 cm^{-1} region;[16,29] the bands in this region of the spectrum of [Rh(pc)Cl(dmso)] are typical of the phthalocyanine moiety. Hence the IR spectra gave no evidence for the existence of *S*-bonded dmso. The IR bands observed at 350 and 345 cm^{-1} for [Rh(pc)Cl(py)] and [Rh(pc)Cl(dmso)] respectively are assigned to the Rh–Cl vibrations. This vibration is observed at 345 cm^{-1} for rhodium(III) porphyrin complexes.[22]

The electronic absorption spectra of the Rh(pc) complexes vary only very slightly with the solvent or axial ligand, Table 1. The Q band is centred near 650 nm, typical of such complexes.[30] The present complexes are soluble in a variety of solvents and possess absorption coefficients that are typical of M(pc) complexes.[30] The spectra for the dicyano complex showed a split in the Soret region, observed previously in cyano complexes of metallophthalocyanines.[31,32]

The absorption spectra of the 'unoxidized' complexes showed slight ring oxidation as evidenced by the presence of a weak band near 700 nm, typical of the presence of phthalocyanine π-cation radical species.[13,16] The magnetic susceptibility of these complexes thus showed weak paramagnetism, $\mu \leqslant 0.5$ μ_B, depending on the extent of oxidation. Weak paramagnetism has also been observed in rhodium(III) prophyrin complexes and was attributed to the presence of small amounts of rhodium(II) porphyrin due to insufficient oxidation of the rhodium(I) starting species.[33] The method of preparation employed for the present complexes precludes the rhodium(II) complex as the source of the weak paramagnetism.

All the present complexes showed proton NMR spectra typical of phthalocyanine complexes, with two sets of resonances near δ 9.5 and 8.2.[26,34–36] These resonances correspond to the inner and outer phthalocyanine ring protons, respectively. The complex [Rh(pc)Cl(py)] showed ^1H NMR resonances due to the bound pyridine at δ 5.37 and 2.00, Table 2. The resonance for bound dmso in [Rh(pc)Cl(dmso)] was observed at δ −1.00.

Oxidation of Rh^{III}(pc) *Complexes.*—Oxidation in M(pc) complexes can occur either at the central metal or at the phthalocyanine ring. Two successive one-electron ring oxidations from the lowest-occupied molecular orbital, a_{1u}, may be observed. Where metal oxidation occurs, the potentials are less positive than those for phthalocyanine ligand oxidation.[11]

Cyclic voltammograms of the present complexes showed oxidation potentials in the range 0.9–1.03 V *vs.* SCE, Table 3. These potentials are in the range reported for phthalocyanine ligand oxidation in M(pc) complexes,[9,11] and hence correspond to the formation of phthalocyanine π-cation radical species. For all the complexes reported here, the oxidation couples were reversible one-electron oxidations with $\Delta E = 60$ mV and $i_a/i_c = 1$ (i_a and i_c are the anodic and cathodic currents, respectively). Cyclic voltammograms for the oxidations of [Rh(pc)Cl(py)] and [Rh(pc)Cl(dmso)] are shown in Fig. 1(*a*) and 1(*b*), respectively.

Controlled potential coulometry of the three complexes at potentials corresponding to the first oxidation couple gave electronic spectral changes shown in Fig. 2 for the electrolysis,

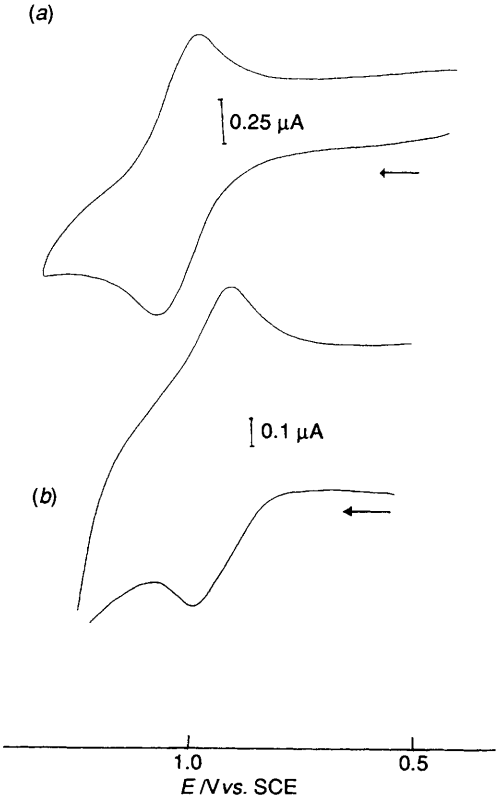


Fig. 1 Cyclic voltammograms for the oxidation of (*a*) [Rh(pc)Cl(py)] in dichloromethane containing NBu_4ClO_4 and (*b*) [Rh(pc)Cl(dmso)] in acetonitrile containing NEt_4ClO_4. Scan rate = 200 mV s^{-1}

Table 1 Electronic absorption spectral data for the complexes

		λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})					
Complex	Solvent	Q band					Soret band
[Rh(pc)Cl(py)]	$CHCl_3$	654(10)	625(3)	590(3)			347(4)
	CH_2Cl_2	650(16)	623(4)	585(4)			345(6)
	dmso	653(24)	625(6)	587(6)			348(8)
	dmf	647(15)	620(4)	585(4)			
[Rh(pc)Cl(dmso)]	MeCN	648(11)	617(2)	584(2)			340(4)
	dmso	653(15)	625(3)	593(3)			345(6)
	dmf	653(19)	623(4)	588(4)			345(7)
$K[Rh(pc)(CN)_2]$	Me_2CO	646(18)	620(4)	584(5)	400(2)	375(2)	
	dmso	655(20)	625(4)	590(6)	405(2)	375(2)	345(19)
	dmf	650(17)	623(4)	587(5)	403(2)	375(2)	342(16)

at 1.0 V, of [Rh(pc)Cl(dmso)] in acetonitrile containing NEt_4ClO_4. The Q band decreased in intensity and two new weaker bands were observed at 700 and 540 nm. The final spectrum was formed with isosbestic points at 665 and 575 nm. The bands centred 540 and 700 nm in the spectra of the final oxidation product are characteristic of the absorption spectra of phthalocyanine π-cation radical species.[13,14,16,37] Controlled-potential coulometry gave $n = 1.0 \pm 0.2$, where n is the number of moles of electrons transferred. The formation of the π-cation radical was reversible for all the complexes. Reduction of the oxidized species at 0 V resulted in regeneration of the starting complex.

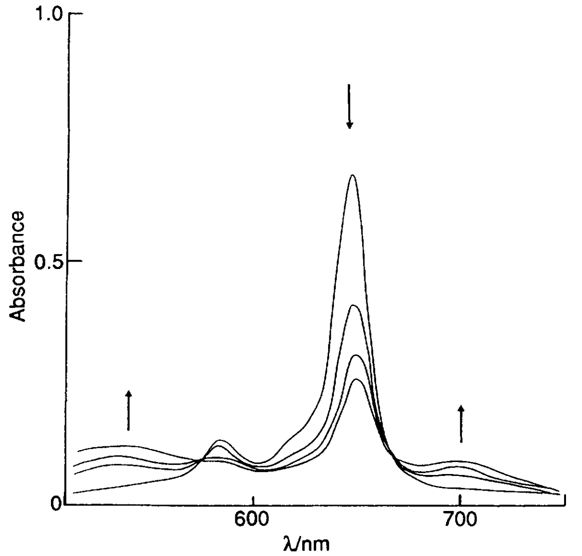


Fig. 2 Electronic absorption spectral changes observed during controlled-potential oxidation, at 1.0 V, of [Rh(pc)Cl(dmso)] in acetonitrile containing 0.1 mol dm^{-3} NEt_4ClO_4

Table 2 Proton NMR data[a]

Compound	pc[b] H²	pc[b] H¹	py or dmso	Ref.
[Rh(pc)Cl(py)]	9.52	8.18	5.37, 2.00	This work
[Rh(pc)Cl(dmso)]	9.54	8.20	−1.00	This work
$[Rh(pc)(CN)_2]^-$ [c]	9.53	8.18		This work
$[Os(pc)(py)_2]$	8.83	7.71	5.27, 3.24	34
$[Ru(pc)(py)_2]$	9.13	7.87	5.21, 2.43	26
$[Ru(pc)(dmso)_2]$	9.32	8.02	−1.18	35

[a] Shifts given in δ *vs.* $CDCl_3$. [b] H² corresponds to the inner ring protons and H¹ to the outer. [c] Solvent C_6D_6.

Chemical oxidation of the Rh(pc) complexes with bromine or iron(III) chloride also resulted in the spectral changes shown in Fig. 2. Exposure of the solid complexes to bromine fumes led to the formation of the π-cation radical species, with a magnetic moment of $\mu = 1.7\ \mu_B$, a value very close that expected for one unpaired electron. It is thus clear from the electrochemical studies and from the electronic absorption spectra that one-electron oxidation of the complexes occurs at the phthalocyanine ring, giving π-cation radical species. Previous studies[19] on the continuous photolysis of some Rh^{III}(pc) complexes also showed oxidation at the phthalocyanine ring. Oxidation in rhodium(III) porphyrin complexes is known to occur exclusively at the porphyrin ligand to give π-cation radicals and dications.[22] The oxidation couples for the removal of the second electron were not observed for the complexes reported here.

Reduction of [Rh(pc)Cl(py)] *and* [Rh(pc)Cl(dmso)].—Fig. 3 shows cyclic voltammograms for these reductions. Each complex shows two reduction processes (1 and 2 in Fig. 3). The first is irreversible since it has no coupled reoxidation peak. This peak was observed in all solvent–electrolyte systems studied for both complexes, with potentials ranging from −0.53 to −0.91 V, Table 3. The value of $E_p - E_{p/2}$ for peak 1 was found to be approximatey 60 mV and $i_c/v^{\frac{1}{2}}$ (where v is the scan rate) was found to be constant, suggesting a diffusion-controlled one-electron reduction. The shape of the peak is consistent with a rapid electron transfer followed by a fast chemical reaction.[22]

Reductions of the phthalocyanine ring in M(pc) complexes are, in general, reversible one-electron processes.[11] The irreversibility of the first reduction in [Rh(pc)Cl(py)] and [Rh(pc)Cl(dmso)] suggests a metal-based reduction rather than the reduction of the phthalocyanine ring. The cyclic voltammograms shown in Fig. 3 are remarkably similar to those reported for the reduction of rhodium(III) porphyrin complexes,[22] where the first irreversible reduction was assigned to the reduction to the rhodium(II) porphyrin complex followed by rapid dimerization of the latter. Porphyrin complexes are structurally similar to phthalocyanine complexes. The striking similarities between the reduction processes of rhodium(III) porphyrins and those of [Rh(pc)Cl(py)] and [Rh(pc)Cl(dmso)] shown in Fig. 3 suggest that the same reduction processes occur in both systems. Thus, the first irreversible reduction peak in the Rh^{III}(pc) complexes is most likely due to reduction of the central metal to Rh^{II} followed by a rapid chemical reaction.

Controlled potential electrolysis of the Rh^{III}(pc) complexes

Table 3 Half-wave potentials for the complexes

		E_p or $E_{\frac{1}{2}}$/V *vs.* SCE				
Complex	Solvent[a]	pc^-–pc^{2-}		pc^{2-}–pc^{3-}	pc^{3-}–pc^{4-}	
$K[Rh(pc)(CN)_2]$	dmso	0.91	0.80[b]	−0.80	−1.33	
	dmf	0.98	0.79[b]	−0.84	−1.37	
	Me_2CO[c]	0.90		−0.90	−1.45	
		pc^-–pc^{2-}		$Rh^{III}(pc^{2-})$–$[Rh^{II}(pc^{2-})]_2^-$ [d]	Rh^{III}–Rh^{II} [d]	$pc^{2-}pc^{2-}$–$pc^{2-}pc^{3-}$
[Rh(pc)Cl(dmso)]	dmso	1.01		−0.02	−0.54	−1.32
	dmf	0.99		−0.08	−0.60	−1.42
	MeCN	0.95		−0.06	−0.91	−1.37
[Rh(pc)Cl(py)]	dmso	0.99		−0.17	−0.53	−1.35
	dmf	1.03		−0.12	−0.64	−1.37
	MeCN	0.96		−0.03	−0.88	−1.39
	CH_2Cl_2[e]	1.00		−0.17	−0.79	−1.47

[a] Electrolyte is NEt_4ClO_4 unless otherwise stated. [b] Sharp cathodic wave due to the reduction of adsorbed species. [c] Data from ref. 15. [d] Irreversible wave. [e] Electrolyte is NBu_4ClO_4.

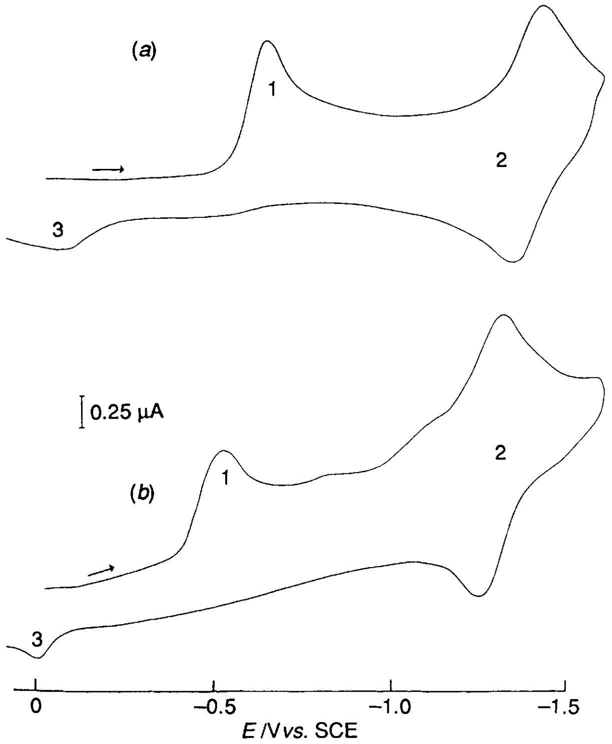


Fig. 3 Cyclic voltammograms for the reduction of (*a*) [Rh(pc)Cl(py)] in dmf and (*b*) [Rh(pc)Cl(dmso)] in dmso containing 0.1 mol dm^{-3} NEt_4ClO_4. Scan rate = 200 mV s^{-1}

was carried out at potentials corresponding to the first reduction and monitored by electronic absorption spectra. Fig. 4 shows the spectral changes observed during the reduction of [Rh(pc)Cl(py)] in dmso, at the potential of the first reduction peak, −0.6 V. The solution turns from blue to green, and the Q band broadens and decreases in intensity. At the end of the reduction the new Q band consists of a broad envelope to high energy of the original Q band, Fig. 4(*b*), with two maxima at 635 and 647 nm. Aggregation is common in phthalocyanine chemistry and the aggregated phthalocyanine complexes show characteristic electronic absorption spectra.[8,30] Monomeric M(pc) complexes show a sharp Q band similar to that in Fig. 4(*a*). The final spectrum obtained on one-electron reduction of [Rh(pc)Cl(py)], Fig. 4(*b*), is typical of dimerized phthalocyanine species. Thus, the spectroelectrochemistry of this complex gives evidence for the formation of a dimeric species on reduction at the potential corresponding to the first reduction peak. Similar spectral changes were observed on reduction of [Rh(pc)Cl(dmso)]. The spectra of the two electroreduced species were similar in dmso solutions, with bands at 647, 635, 587, 460 and 375 nm, hence suggesting the formation of a similar product from both compounds.

The technique of double-potential-step chronoamperometry (DPSCA) has been used successfully to study the kinetics of chemical reactions that follow the electron-transfer step [equations (1) and (2)][38–41]. In this technique (*i*) the working

$$\mathrm{Ox} + ne^- \rightleftharpoons \mathrm{Red} \qquad (1)$$

$$\mathrm{Red} \xrightarrow{k} \mathrm{Z} \qquad (2)$$

electrode is stepped to some potential at which reduction of the electroactive species Ox occurs, (*ii*) the electrode is held at this potential for some time, τ (called the switching time) and (*iii*) the potential is then stepped back, generally to the starting value, with the oxidation of the reduced species, Red. The anodic current from the reoxidation of Red gives information on the reactions of the latter.

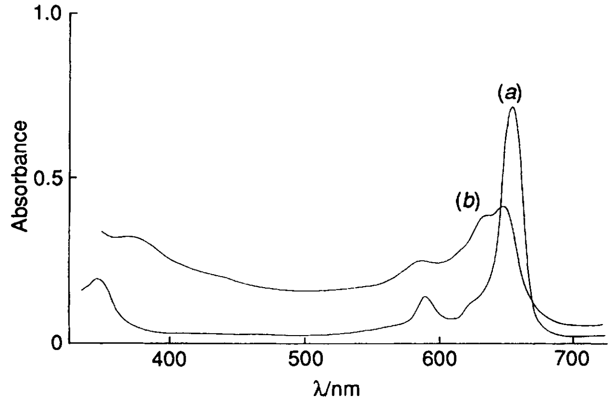


Fig. 4 Electronic absorption spectra obtained before (*a*) and after (*b*) controlled-potential reduction, at −0.7 V, of [Rh(pc)Cl(py)] in dmso containing 0.1 mol dm^{-3} NEt_4ClO_4

Such experiments, Fig. 5, were performed for [Rh(pc)Cl(py)] and [Rh(pc)Cl(dmso)] in order to determine the nature of the product formed following the reduction of these species at potentials corresponding to the first reduction peak (peak 1). Several DPSCA curves were recorded with different switching times and different bulk concentrations of the complexes. The data were analysed[38,40] by determining the cathodic current, i_c, at some time t (where $t < \tau$) in the forward potential step and then determining the anodic current, i_a, at the time $t + \tau$ in the reverse step. The current ratios i_a/i_c were then used to obtain kinetic parameters from the reported working curves[38] and tables,[41] using several t/τ values for each curve. The working curves in ref. 38 (and working tables in ref. 41) treat the chemical step following reduction as a first-order process. Table 4 gives the first-order rate constants derived from DPSCA, for the chemical step following reductions of [Rh(pc)Cl(dmso)] and [Rh(pc)Cl(py)]. The rate constants generally doubled when the bulk concentration was doubled. A decrease with increase in the switching time was also observed. These discrepancies clearly show that the reaction of the electroreduction product is not first order and suggests an order higher than unity. Similar trends in the first-order rate constants were observed for metalloporphyrin complexes in which dimerization occurs following an electron transfer.[40] Second-order rate constants of 30 ± 5 dm^3 mol^{-1} s^{-1} were estimated for Rh(pc) complexes in dmf, from the theoretical working curves for chemical dimerization reactions ($t/\tau = 0.3$).[40] Thus, the kinetic data reported here suggest a dimerization of the electroreduction product.

The electronic absorption spectral changes reveal only the final electroreduction product and give no indication about the site of electron transfer prior to the formation of the dimer. The cyclic voltammograms reported here compare very well with those for the reduction of rhodium(III) porphyrin complexes, where the first reduction occurs at the metal to form a dimeric rhodium(II) porphyrin complex.[22] These similarities suggest that similar reduction processes occur in both rhodium(III) pc and porphyrin complexes. Also, previous studies[19] have shown that laser flash photolysis of Rh^{III}(pc) complexes resulted in reduction to transient Rh^{II}(pc) species. Based on these observations, it is concluded that the first reduction in [Rh(pc)Cl(py)] and [Rh(pc)Cl(dmso)] occurs at the metal and not at the phthalocyanine ligand.

It is quite likely that the anionic ligand is lost during the electrochemical reduction of Rh^{III}(pc) to give a neutral Rh^{II}(pc) complex. The fact that the spectra of the dimeric reduction product showed band positions at exactly the same wavelengths for both [Rh(pc)Cl(py)] and [Rh(pc)Cl(dmso)] suggests the formation of the same complex. It is reasonable to assume that the product is $[Rh^{II}(pc)]_2$, where both the anionic and neutral ligands have been lost.

A small reoxidation peak was observed between −0.03 and −0.17 (peak 3). This is not observed when the cathodic potential scan is terminated before the first reduction, clearly showing that it is due to oxidation of the products formed after the first reduction. Thus, this peak corresponds to the irreversible oxidation of the $[Rh^{II}(pc)]_2$ complex.

Oxidation of the dimeric species at potentials corresponding to peak 3 resulted in regeneration of the $Rh^{III}(pc)$ complexes with a $\leqslant 3$ nm shift of the Q band from the original value. The electronic absorption specrtra of the present complexes are quite similar, Table 1. Any changes in axial ligands on reoxidation of the electroreduction product may not be definitely confirmed by the electronic spectra. It is, however, reasonable to assume that, during the electrooxidation of the $[Rh^{II}(pc)]_2$ complex, anionic and neutral axial ligands are abstracted from the solvent–electrolyte system to form $Rh^{III}(pc)L(L')$ complexes.

The second reduction process (couple 2) is reversible and observed at potentials ranging from −1.32 to −1.47 V; ΔE = 60 mV for this couple, suggesting a one-electron transfer process. No stable electrogenerated anion radical was, however, formed by bulk electrolysis at potentials corresponding to the second reduction. Values of ΔE = 60 mV were also obtained for the oxidation of ferrocene, which was employed as an internal standard in all cyclic voltammetry experiments. The oxidation of ferrocene is a well known one-electron process. The fact that such values were also obtained for ferrocene is a clear indication that the same values obtained for the reduction processes in [Rh(pc)Cl(py)] and [Rh(pc)Cl(dmso)] are a good measure of the number of moles of electrons transferred in each reduction step, and hence confirm the one-electron nature of couple 2. A value of ΔE = 60 mV was also observed for the oxidation of the Rh(pc) complexes, where the one-electron nature of the couple was confirmed by controlled-potential coulometry. The reversibility of couple 2 suggests a ring-based one-electron reduction, giving $[Rh^{II}(pc)]_2^-$, rather than a metal-based reduction.

Table 4 First-order rate constants derived from DPSCA in dmf containing NEt_4ClO_4; τ = 20 s

Concentration mmol dm^{-3}	k/s^{-1} [Rh(pc)Cl(dmso)]	[Rh(pc)Cl(py)]
0.6	1.7×10^{-2}	
0.9		2.5×10^{-2}
1.2	3.5×10^{-2}	
1.9		7.0×10^{-2}
2.3	8.0×10^{-2}	
4.7	1.4×10^{-1}	

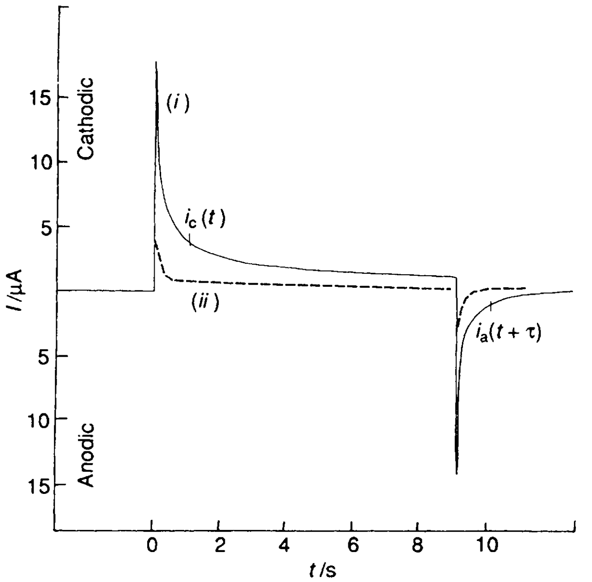


Fig. 5 Double-potential-step chronoamperometry spectrum for (i) [Rh(pc)Cl(dmso)] in dmf containing NEt_4ClO_4, (ii) the electrolyte only; τ = 9 s

Reduction of $K[Rh(pc)(CN)_2]$.—Fig. 6 shows the cyclic voltammogram for the reduction of $K[Rh(pc)(CN)_2]$ in dmf containing NEt_4ClO_4. Two clearly reversible one-electron reduction couples are observed with ΔE = 60 mV and i_c/i_a = 1. The first is observed at −0.84 V in dmf and the second at −1.37 V, Table 3. Comparing the same solvent–electrolyte systems in Table 3, the first reduction for $K[Rh(pc)(CN)_2]$ occurs at potentials at least 200 mV more negative than those for [Rh(pc)Cl(dmso)] and [Rh(pc)Cl(py)]. This is not surprising since metal reductions in M(pc) complexes occur at potentials less negative than those for phthalocyanine ligand reductions. The reversibility of the first (couple 1, Fig. 6) and second (couple 2) reductions suggests phthalocyanine-based ligand reductions. The potentials for both reduction couples are in the range reported for ligand reductions in M(pc) complexes.[7,42] For example, the first ring reduction occurs at −0.755 V for [Mn(pc)] in dmso containing NEt_4ClO_4 and the second at −1.39 V.[7]

Bulk electrolysis of $[Rh(pc)(CN)_2]^-$ solutions at potentials of the first reduction, −0.9 V, resulted in the electronic absorption spectral changes in Fig. 7. The Q band is reduced drastically in intensity and two new bands are formed in the visible region at 643 and 575 nm, Fig. 7(*b*). The spectrum in Fig. 7(*b*) is characteristic of the phthalocyanine anion radical species, whereby one electron has been added to the phthalocyanine ring.[6,37] The spectra of the $[Mg(pc)]^-$ anion radical species, for example, shows characteristic bands at 638, 562 and 420 nm.[37] Thus, from the electronic absorption spectral data it is concluded that the first reduction occurs at the phthalocyanine ligand in $[(Rh(pc)(CN)_2]^-$, forming a $[Rh(pc)(CN)_2]^{2-}$ complex.

The addition of the second electron to the phthalocyanine ring in M(pc) complexes is characterized by a broad absorption band near 520 nm and the disappearance of the band of the

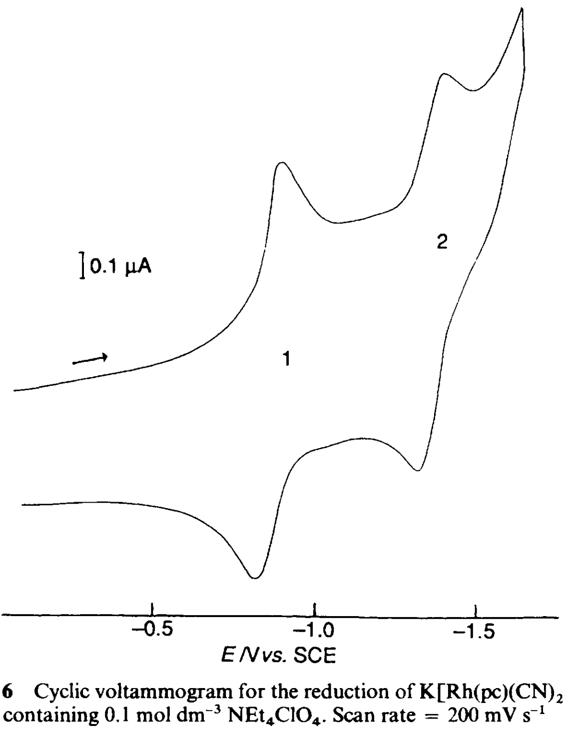


Fig. 6 Cyclic voltammogram for the reduction of $K[Rh(pc)(CN)_2]$ in dmf containing 0.1 mol dm^{-3} NEt_4ClO_4. Scan rate = 200 mV s^{-1}

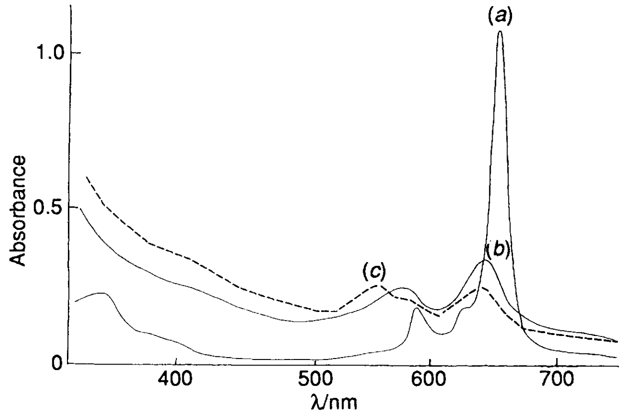
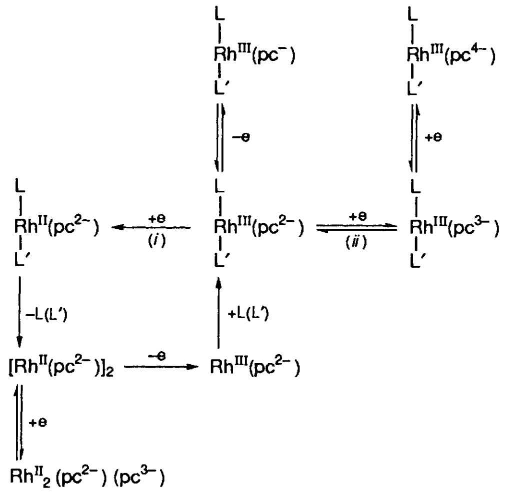


Fig. 7 Electronic absorption spectral changes observed during controlled-potential electrolysis of $K[Rh(pc)(CN)_2]$ in dmso containing 0.1 mol dm^{-3} NEt_4ClO_4: (*a*) before reduction, (*b*) the first reduction at −0.9 V and (*c*) (– – – –) the second reduction, at −1.4 V



Scheme 1 (*i*) L = py or dmso, L′ = Cl; (*ii*) L = L′ = CN

monoanion at 640 nm.[6,37] Bulk electrolysis of $[Rh(pc)(CN)_2]^{2-}$ at potentials corresponding to the second reduction resulted in a decrease in the bands at 643 and 575 nm and the formation of a new band at 550 nm, Fig. 7(*c*). These spectral changes are typical of the formation of the phthalocyanine dianion species,[6,37] and suggest the formation of $[Rh(pc)(CN)_2]^{3-}$ species. The $[Rh(pc)(CN)_2]^{2-}$ and $[Rh(pc)(CN)_2]^{3-}$ species were oxidized back to the starting complex by bulk electrolysis at positive potentials.

Conclusion

Oxidation of the $Rh^{III}(pc)$ complexes occurs at the phthalocyanine ligand with the formation of a phthalocyanine π-cation radical species in all the complexes studied in this work.

Cyclic voltammetric and spectroelectrochemical data show that two possible products are formed after the addition of one electron to the complexes. Addition of one electron to $[Rh(pc)(CN)_2]^-$ results in the formation of a phthalocyanine anion radical $[Rh(pc)(CN)_2]^{2-}$, however, one-electron reduction in [Rh(pc)Cl(py)] and [Rh(pc)Cl(dmso)] occurs at the metal to give a short-lived $Rh^{II}(pc)$ complex, which rapidly dimerizes, Scheme 1. Thus, the nature of the one-electron reduction product depends strongly on the nature of the axial ligands.

Whether reduction occurs at the central metal or at the phthalocyanine ligand will depend on the relative energies of the metal- or ligand-based lowest unoccupied molecular orbitals (LUMOs). The electrochemical data presented show that the LUMO is a metal orbital for the [Rh(pc)Cl(py)] and [Rh(pc)Cl(dmso)] complexes and for $K[Rh(pc)(CN)_2]$ it is a ligand orbital.

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References

1 A. W. Snow and W. R. Barger, in *Phthalocyanines: Properties and Applications*, eds. C. C. Lezoff and A. B. P. Lever, VCH, New York, 1989, vol. 1, ch. 5.
2 J. H. Zagal, *Coord. Chem. Rev.*, 1992, **119**, 89.
3 M. N. Golovin, P. Seymour, K. Jayaraj, Y. S. Fu and A. B. P. Lever, *Inorg. Chem.*, 1990, **29**, 1719.
4 M. El Meray, A. Louati, J. Simon, A. Giraudeau, M. Cross, T. Malinski and K. M. Kadish, *Inorg. Chem.*, 1984, **23**, 2606.
5 P. A. Bernstein and A. B. P. Lever, *Inorg. Chem.*, 1990, **29**, 608.
6 D. W. Clack and J. R. Yandle, *Inorg. Chem.*, 1972, **11**, 1738.
7 A. B. P. Lever, P. C. Minor and J. P. Wilshire, *Inorg. Chem.*, 1981, **20**, 2550.
8 A. B. P. Lever, M. R. Hempstead, C. C. Leznoff, W. Liu, M. Melnik, W. A. Nevin and P. Seymour, *Pure Appl. Chem.*, 1986, **58**, 1467.
9 L. D. Rollman and R. T. Iwamoto, *J. Am. Chem. Soc.*, 1968, **90**, 1455.
10 A. B. P. Lever and J. P. Wilshire, *Can. J. Chem.*, 1976, **54**, 2514.
11 A. B. P. Lever, S. Licoccia, K. Magnell, P. C. Minor and B. S. Ramaswamy, *ACS Symp. Ser.*, 1982, **201**, 237.
12 T. Nyokong, Z. Gasyna and M. J. Stillman, *ACS Symp. Ser.*, 1986, **321**, 309.
13 T. Nyokong, Z. Gasyna and M. J. Stillman, *Inorg. Chem.*, 1987, **26**, 548.
14 T. Nyokong, *Polyhedron*, 1993, **12**, 375.
15 R. Behnisch and M. Hanack, *Synth. Met.*, 1990, **36**, 387.
16 D. Dolphin, B. R. James, A. J. Murray and J. R. Thornback, *Can. J. Chem.*, 1980, **58**, 1125.
17 H. Hanack and X. Munz, *Synth. Met.*, 1985, **10**, 357.
18 X. Munz and M. Hanack, *Chem. Ber.*, 1988, **121**, 239.
19 S. Muralidharan, G. Ferraudi and K. Schmatz, *Inorg. Chem.*, 1982, **21**, 2961.
20 S. Muralidharan and G. Ferraudi, *J. Phys. Chem.*, 1983, **87**, 4877.
21 K. M. Kadish, Y. Hu, T. Boschi and P. Tagliatesta, *Inorg. Chem.*, 1993, **32**, 2996.
22 K. M. Kadish, C.-L. Yao, J. E. Anderson and P. Cocolios, *Inorg. Chem.*, 1985, **24**, 4515.
23 J. Anderson, C.-L. Yao and K. M. Kadish, *Inorg. Chem.*, 1986, **25**, 3224.
24 K. M. Kadish, J. E. Anderson, C.-L. Yao and R. Guilard, *Inorg. Chem.*, 1986, **25**, 1277.
25 L. J. Boucher, in *Coordination Chemistry of Macrocyclic Compounds*, Plenum, New York, 1979, pp. 461–517.
26 N. P. Farrell, A. J. Murray, J. R. Thornback, D. Dolphin and B. R. James, *Inorg. Chim. Acta*, 1978, **28**, L144.
27 R. R. Gagne, C. A. Koval and G. C. Lisensky, *Inorg. Chem.*, 1980, **19**, 2855.
28 Y. Orihashi, H. Ohno, E. Tsuchida, H. Matsuda, M. Nakanishi and M. Kato, *Chem. Lett.*, 1987, 601.
29 P. L. Goggin, in *Comprehensive Coordination Chemistry: Synthesis, Reactions, Properties and Applications of Coordination Compounds*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 2, p. 489.
30 M. J. Stillman and T. Nyokong, in *Phthalocyanines: Properties and Applications*, eds. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989, vol. 1.
31 B. W. Dale, *Trans. Faraday Soc.*, 1969, **65**, 331.
32 M. J. Stillman and A. J. Thomson, *J. Chem. Soc., Faraday Trans. 2*, 1974, 805.
33 P. S. Sheridan and F. Jardine, in *Comprehensive Coordination Chemistry: Synthesis, Reactions, Properties and Applications of Coordination Compounds*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 4, p. 1006.
34 M. Hanack and P. Vermehren, *Inorg. Chem.*, 1990, **29**, 134.
35 W. Kobel and M. Hanack, *Inorg. Chem.*, 1986, **25**, 103.
36 T. J. Marks and D. R. Stojakovic, *J. Am. Chem. Soc.*, 1978, **100**, 1695.

37 P. C. Minor, M. Gouterman and A. B. P. Lever, *Inorg. Chem.*, 1985, **24**, 1894.

38 W. M. Schwarz and I. Shain, *J. Phys. Chem.*, 1965, **69**, 30.

39 M. L. Olmstead and R. S. Nicholson, *Anal. Chem.*, 1969, **41**, 851.

40 J. P. Collman, P. S. Wagenknecht and N. S. Lewis, *J. Am. Chem. Soc.*, 1992, **114**, 5665.

41 E. Gileadi, E. Kirowa-Eisner and J. Penciner, *Interfacial Electrochemistry*, Addison Wesley, London 1975, p. 423.

42 A. B. P. Lever, S. R. Pickens, P. C. Minor, S. Licoccia, B. S. Ramaswany and K. Magnell, *J. Am. Chem. Soc.*, 1981, **103**, 6800.

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