Synthesis, Structure, and Electrochemical Reduction of 2-(Arylazo)pyridine Complexes of Rhodium(III)

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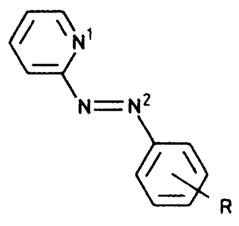
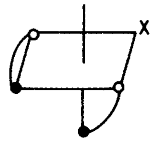
The synthesis of new halogenorhodium(III) 2-(arylazo)pyridine(L) complexes of the type $[RhX_2L_2]ClO_4{\cdot}H_2O$ (X = Cl, Br, or I; aryl = Ph, C_6H_4Me-*m* or -*p*) are described. From their spectral data it has been shown that the complexes are *cis, trans, cis* in the following sequence: Cl,Cl; N(pyridine), N(pyridine); and N(azo),N(azo). They are electroactive and display several cyclic voltammetric reductive responses on the negative side of a saturated calomel electrode. E.s.r. studies of the electrolysed solutions indicate that the electrons are added successively to the ligand centre.

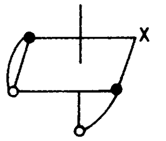
In recent years complexes of the 2-(arylazo)pyridine ligand system, L, with platinum-group metal ions have been intensively studied.[1–5] Important phenomena like catalysis,[1] organic hydroxylation,[2] isomerisation,[3] and reactions at electrodes[4] are some of the current research activities in this area. In comparison, the chemistry of rhodium with L is scarce. As part of our interest in such complexes we report here the synthesis, characterisation, structural elucidation, and electron-transfer behaviour of a group of dihalogenocomplexes of rhodium(III).



R
H :L¹ = pap
m-Me :L² = *m*-tap
p-Me :L³ = *p*-tap



(1)



(2)

X=Cl, Br, or I; ●=N²

Results and Discussion

Synthesis and Formulation of Chelates.—The reaction between hydrated RhX_3 (X = Cl, Br, or I) and L proceeds smoothly in boiling methanol. The cationic dihalogenorhodium(III) complexes have been isolated as perchlorate salts. Recrystallisation from dichloromethane–hexane (1:1) yielded highly crystalline products. While the chloro complexes have generally been prepared, the bromo and iodo complexes were synthesised only in the case of ligand L^2. The yields of the chloro and bromo complexes are quite high (70—90%) but that of the iodo is low (25%). It is believed that the steric crowding of the two bulky *cis* iodide ligands (see below) is the controlling factor in the synthetic reaction.

The complexes are all diamagnetic, and are soluble in polar organic solvents. All behave as 1:1 electrolytes[6] in acetonitrile. These along with the analytical data lead unequivocally to the formulation of the rhodium(III) chelates as $[RhX_2L_2]ClO_4{\cdot}H_2O$.

Spectra and Stereochemistry.—The stereochemistry of the RhX_2 moiety in the rhodium(III) complexes has been determined by i.r. data. The dichloro species show moderately strong bands at *ca.* 340 and *ca.* 325 cm^{-1} (Table), which are absent for the dibromo and di-iodo analogues. These bands are evidently due to ν(Rh–Cl). The doublet nature of ν(Rh–Cl) indicates[7] that the two chlorides are *cis* to each other. These *cis* dihalogeno complexes of L^2 and L^3 uniformly display a single methyl signal in CD_3CN each at δ *ca.* 2.3 in ^1H n.m.r. spectra. These facts taken collectively imply that the gross stereochemistry of the dichlororhodium(III) complex could be either (**1**) or (**2**). Here we note that isomer (**2**) does not exist[3,5] in the cases of ruthenium(II) and osmium(II). Thus we propose that the gross stereochemistry of the present dihalogenorhodium† complexes is as shown in (**1**).

All the complexes show strong i.r. bands at *ca.* 1 300 cm^{-1}, assignable[3] to ν(N=N), and at *ca.* 1 600 cm^{-1} due to ν(C=N) + ν(C=C) vibrations.[3] Electronic spectra of acetonitrile solutions were recorded in the region 800—220 nm. Highly intense allowed charge-transfer transitions, which have been observed in the visible and u.v. region, are tabulated.

Redox Reactions.— *Cyclic voltammmetry.* The electron-transfer behaviour in acetonitrile solution of representative cases was examined by cyclic voltammetry in the range 2.0 to −1.5 V, *versus* a saturated calomel electrode (s.c.e.), using

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† The dibromo and di-iodo analogues have virtually identical i.r. spectra in the range 4 000—400 cm^{-1}.

Table. Physical and electrochemical data for the rhodium complexes

Compound	I.r. (cm^{-1})[a]		U.v.–visible[b]	^{1}H N.m.r.[c]	Cyclic voltammetry
	ν(N=N)	ν(Rh–Cl)	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})	δ_{Me}	$E^{\circ\prime}_{298}$/V (ΔE_p/mV)[d]
$[RhCl_2L^1{}_2]ClO_4 \cdot H_2O$	1 305	340, 330	360(21 560), 305(11 190),[e] 220(38 160)[e]		−0.02(70), −0.34(120), −1.05[f]
$[RhCl_2L^2{}_2]ClO_4 \cdot H_2O$	1 310	340, 325	370(16 645), 305(9 010),[e] 225(29 990)[e]	2.20	0.03(70), −0.24(130), −1.36[f,g]
$[RhCl_2L^3{}_2]ClO_4 \cdot H_2O$	1 310	350, 320	385(19 220), 295(11 560), 230(27 050)[e]	2.33	0.00(60), −0.35(90), −0.99[f]
$[RhBr_2L^2{}_2]ClO_4 \cdot H_2O$	1 310		375(21 390), 230(43 850)[e]	2.20	[h]
$[RhI_2L^2{}_2]ClO_4 \cdot H_2O$	1 310		360(17 820), 245(34 780)	2.40	[h]

[a] In KBr disc. [b] In MeCN. [c] In CD_3CN. [d] In MeCN using 0.1 mol dm^{-3} $[NEt_4][ClO_4]$ as supporting electrolyte. [e] Shoulder. [f] Irreversible cathodic response. [g] Two more irreversible cathodic responses at −0.58 and −1.0 V with small current height were also observable. [h] Not examined.

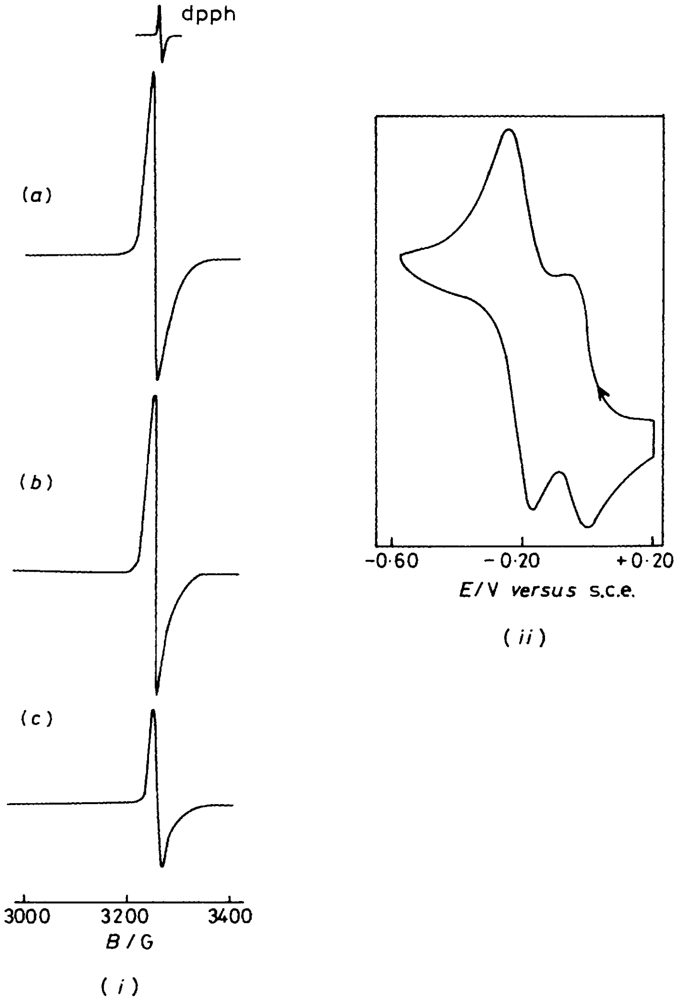

Figure. (*i*) E.s.r. spectra (G = 10^{-4} T) of frozen acetonitrile (0.1 mol dm^{-3} $[NEt_4][ClO_4]$) solutions at 77 K: (*a*) $[RhCl_2L^2{}_2]$, (*b*) $[RhCl_2L^2{}_2]^-$, and (*c*) $[RhCl_2L^2{}_2]^+$ in a dilute acetonitrile solution of hydrazine. (*ii*) Segmented cyclic voltammogram of $[RhCl_2L^2{}_2]ClO_4 \cdot H_2O$ at a scan rate of 50 mV s^{-1}

platinum as the working electrode. A typical cyclic voltammogram of complex (**1**) is displayed in the Figure. All the observed responses are reductive in nature.

The colour of the acetonitrile solution of complex (**1**) at the initial potential (+0.3 V) was pale yellow but a purple colour was observed to develop at the electrode surface shortly after passing the potential corresponding to the least negative reversible wave, $E^{\circ\prime}(1)$ at *ca.* 0.0 V. At more negative potentials two more responses at *ca.* −0.3 and *ca.* −1.0 V were also observable, of which the response at most negative potential was irreversible.

Properties of the reduced solution. The coulometrically produced solutions obtained by electrolysis of $[RhCl_2L^2{}_2]ClO_4 \cdot H_2O$ at −0.1 and −0.4 V are respectively purple and brown. Hydrazine also reduces $[RhCl_2L^2{}_2]^+$ to a purple solution. The reduced products are unstable and their isolation in the pure state has not been possible. However, we have managed to record the e.s.r. spectra of the reduced solutions by performing the electrolysis at 260 K and quickly freezing (acetonitrile, 77 K) the electrolysed solutions. The parent complex $[RhCl_2L^2{}_2]^+$ is diamagnetic and e.s.r. silent. However, the solutions of the reduction products obtained by electrolysis at two different potentials (at −0.1 and −0.4 V) showed highly intense, symmetric, and sharp e.s.r. signals with '*g*' values at 1.9975 and 2.0006 respectively, as shown in the Figure. In the presence of an aqueous solution of hydrazine, $[RhCl_2L^2{}_2]^+$ showed a similar e.s.r. spectrum (Figure). These results strongly suggest that the unpaired electrons in the reduced products, $[RhCl_2L^2{}_2]$ and $[RhCl_2L^2{}_2]^-$, are localised[8,9] in orbitals of predominantly ligand character. The electrons are believed to be added[4] successively to the two azo functions.

Experimental

Materials.—The ligand was synthesised as before.[5c] Dinitrogen was purified by bubbling it through an alkaline dithionite reducing solution. The purification/preparation of solvents and supporting electrolyte for electrochemical work was done as before.[4] Reagents were used as received. The salt $RhCl_3 \cdot 3H_2O$ was obtained from Loba-Chemie Indoaustranal Co. All other chemicals and solvents used for preparative work were of reagent grade used without further purification.

Physical Measurements.—Spectroscopic data were obtained with the use of the following instruments: electronic spectra, Hitachi 330 spectrophotometer, i.r. spectra (KBr disc, 4 000—600 cm^{-1}), Perkin-Elmer IR-983 spectrophotometer (4 000—300 cm^{-1}), ^{1}H n.m.r. spectra (CD_3CN), Varian EM 390. Solution electrical conductivity was measured using an Elico CM 82T conductivity bridge with a solution concentration of *ca.* 10^{-3} mol dm^{-3}. Magnetic susceptibilities were measured with a PAR vibrating-sample magnetometer (model 155) fitted with a Walker Scientific Magnet (model L 75 FBAL). *X*-band e.s.r. spectra were recorded with a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at 77 K. The spectra were calibrated with the help of diphenylpicrylhydrazyl (dpph) (*g* = 2.0037). Electrochemical measurements were done with the help of a PAR model 370-4 electrochemistry system: a model 174A polarographic analyser, model 175 universal programmer, model RE0074 XY recorder, model 173 potentiostat, model 179 digital coulometer, and a model 377A cell system. All experiments were done under a dinitrogen atmosphere in a three-electode configuration by using a planar Beckman model 39273 platinum electrode as the working electrode. All results were collected at 298 ± 1 K and are referenced to a s.c.e. The reported potentials are uncorrected for junction contribution.

Syntheses.—Dichlorobis[2-*(phenylazo)pyridine*]*rhodium*(III) *perchlorate*, [Rh(pap)$_2$Cl$_2$]ClO$_4$·H$_2$O. A sample of RhCl$_3$·3H$_2$O (0.103 g, 0.4 mmol) was dissolved in methanol (20 cm^3) and to it 2-(phenylazo)pyridine (0.209 g, 1.1 mmol) was added. The mixture was heated to reflux for 3 h. It was then cooled to room temperature and filtered. An aqueous solution of NaClO$_4$ (2 g in 50 cm^3 water) was added to the filtrate with stirring. A green-yellow precipitate appeared. The mixture was then concentrated to half its initial volume by heating on a water-bath. The cooled solution was filtered and the precipitate was collected and washed thoroughly with water. Recrystallisation of the precipitate from dichloromethane–hexane (1:1) yielded the greenish yellow crystalline product (yield 84%) (Found: C, 40.65; H, 2.65; N, 12.95. Calc. for $C_{22}H_{20}Cl_3N_6O_5Rh$: C, 40.15; H, 3.05; N, 12.80%); Λ_M(MeCN) 120 ohm^{-1} cm^2 mol^{-1}.

Dichlorobis[2-(*m*-tolylazo)pyridine]rhodium(III) perchlorate, [Rh(*m*-tap)$_2$Cl$_2$]ClO$_4$·H$_2$O and dichlorobis[2-(*p*-tolylazo)pyridine]rhodium(III) perchlorate, [Rh(*p*-tap)$_2$Cl$_2$]ClO$_4$·H$_2$O. were prepared similarly using the appropriate ligand: [Rh(*m*-tap)$_2$Cl$_2$]ClO$_4$·H$_2$O (yield 89%) (Found: C, 43.20; H, 3.25; N, 12.10. Calc. for $C_{24}H_{24}Cl_3N_6O_5Rh$: C, 42.00; H, 3.50; N, 12.25%), Λ_M(MeCN) 110 ohm^{-1} cm^2 mol^{-1}; [Rh(*p*-tap)$_2$Cl$_2$]ClO$_4$·H$_2$O (yield 85%) (Found: C, 41.15; H, 3.25; N, 12.10. Calc. for $C_{24}H_{24}Cl_3N_6O_5Rh$: C, 42.00; H, 3.50; N, 12.25%), Λ_M(MeCN) 120 ohm^{-1} cm^2 mol^{-1}.

Dibromobis[2-(m-*tolylazo)pyridine*]*rhodium*(III) *perchlorate*, [Rh(*m*-tap)$_2$Br$_2$]ClO$_4$·H$_2$O. To a solution of RhCl$_3$·3H$_2$O (0.100 g, 0.40 mmol) in methanol (20 cm^3) was added LiBr (1.0 g). The mixture was heated to reflux for 1 h. 2-(*m*-tolylazo)pyridine was added (0.24 g, 1.20 mmol) and heated to reflux for another 2 h. The solution then cooled to room temperature and was filtered. An aqueous NaClO$_4$ solution (2 g in 50 cm^3 water) was added to the filtrate with stirring. A reddish brown precipitate appeared. The mixture was then concentrated to half its initial volume by heating on a water-bath. The cooled solution was filtered and the precipitate was collected and washed thoroughly with water. Recrystallisation of the brown precipitate from dichloromethane–hexane (1:1) yielded an orange crystalline compound (yield 68%) (Found: C, 38.50; H, 2.90; N, 11.35. Calc. for $C_{24}H_{24}Br_2ClN_6O_5Rh$: C, 37.20; H, 3.10; N, 10.85%); Λ_M(MeCN) 110 ohm^{-1} cm^2 mol^{-1}.

Di-iodobis[2-(*m*-tolylazo)pyridine]rhodium(III) perchlorate, [Rh(*m*-tap)$_2$I$_2$]ClO$_4$·H$_2$O was prepared similarly to the dibromo analogue using KI (1 g) instead of LiBr. A dark brown crystalline compound was obtained (yield 25%) (Found: C, 33.05; H, 2.95; N, 10.25. Calc. for $C_{24}H_{24}ClI_2N_6O_5Rh$: C, 33.15; H, 2.75; N, 9.65%); Λ_M(MeCN) 115 ohm^{-1} cm^2 mol^{-1}.

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