Polarography of Some Rhodium(III) Complexes

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The redox behaviour of a number of rhodium(III) complexes has been examined by d.c. polarography. The complexes undergo two-electron reduction at the dropping mercury electrode (d.m.e.), those with aza-aromatic ligands being reduced at significantly more positive potentials than their counterparts with amine or acyclic amine ligands. Superoxo- and peroxo-bridged dirhodium(III) complexes exhibit polarographic behaviour comparable to μ-peroxodicobalt(III) complexes. Replacement of two ethylenediamine ligands by four pyridine ligands increases the $E_{\frac{1}{2}}$ value for Co^{III}, Rh^{III}, and Ir^{III} complexes and renders the Rh^{III} complexes susceptible to ethanol acceleration of their substitutions.

SALTS of complexes of the type *trans*-dihalogenotetrapyridinerhodium(III) inhibit cell division at sublethal levels in *Escherichia coli* whereas the formally related ethylenediamine (en) complexes, *trans*-$[Rh(en)_2X_2]^+$ (X = Cl or Br), are completely inactive.[1] To assist in establishing the causes of this biological action at the molecular level, we have been engaged in a comprehensive study of the chemical properties of these and

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[1] R. J. Bromfield, R. H. Dainty, R. D. Gillard, and B. T. Heaton, *Nature*, 1969, **223**, 735.

similar rhodium complexes with nitrogen-containing bases. In addition to the contrast in biological activity, a further distinction between the complexes exists; halide exchanges in *trans*-[Rh(py)$_4$X$_2$]$^+$ (X = Cl or Br, py = pyridine) complexes are accelerated by mild reductants such as primary and secondary alcohols whereas no corresponding effect has been found with *trans*-[Rh(en)$_2$Cl$_2$]$^+$. However, catalytic halide exchange in the latter complex has been induced by the presence of stronger reducing agents. We suggested[2] that this difference in behaviour between the pyridine and ethylenediamine complexes arises from the difference in their redox properties; the polarographic half-wave reduction potentials for the pyridine complexes are less negative than those of the corresponding ethylenediamine complexes, *i.e.* the former are good oxidants relative to the latter. The reason for the difference in anti-bacterial activity between the two types of complex may also arise from this difference in redox properties. We therefore investigated the polarographic behaviour of some rhodium(III) complexes in order to gain further insight into the general chemistry of this metal.

EXPERIMENTAL

Preparations.—The starting materials used in all the preparations were ' RhCl$_3$,3H$_2$O ' or ' RhBr$_3$,xH$_2$O ' (Johnson, Matthey). All other chemicals used were of reagent grade purity. Substituted pyridines were obtained from Reilly Tar & Chemical Co., thiazole from Fluka A.G., 1-methylimidazole from R. N. Emanuel Co., and other heterocyclic compounds and amines from Koch–Light Laboratories and B.D.H. Ltd. The complexes were all obtained by known methods;[3-6] preparations which differed from those in the literature are given below.

Hexa-amminecobalt(III) *hexacyanorhodate*(III). Rhodium trichloride trihydrate (0·5 g) was fused (10 min) with potassium cyanide (10 g). The cooled melt was dissolved in warm water (20 cm^3), filtered, and hexa-amminecobalt(III) chloride (1 g) in warm water (10 cm^3) was added to the colourless solution. The desired salt crystallised rapidly as orange prisms which were filtered off, washed with water (in which they are slightly soluble), and air-dried. The electronic spectrum [λ 225 (ε 540), λ 255 nm (ε 295 l mol^{-1} cm^{-1})] of hexacyanorhodate(III) [after subtraction of the absorbance of hexa-amminecobalt(III)] agreed essentially with that reported previously,[7] although our ε values were slightly higher.

Hexa-amminecobalt(III) *hexathiocyanatorhodate*(III). Rhodium trichloride trihydrate (0·26 g) was fused with sodium thiocyanate (5 g) at *ca*. 100—120 °C until the mixture was dehydrated (*ca*. 10 min), when it was dissolved in warm water (15 cm^3) and activated charcoal was added. After filtration, a solution (15 cm^3) of hexa-amminecobalt(III) chloride (1 g) was added to the filtrate, whereupon the desired salt precipitated. The orange crystals were washed with water and air-dried. The electronic spectrum, after subtracting that of the hexa-amminecobalt(III) ion, was in agreement with that in the literature.[7]

Tetraethylammonium hexanitrorhodate(III). Rhodium trichloride trihydrate (0·52 g) was fused (10 min) with sodium nitrite (15 g) just above the melting point of the latter. The yellow melt when cooled was dissolved in hot water (30 cm^3), activated charcoal added, and the solution was filtered to remove impurities. To the warm filtrate was added a warm aqueous solution (10 cm^3) of tetraethylammonium chloride (1 g). The required salt crystallised from the cooled solution and was recrystallised from water and air-dried to give white prisms. The electronic spectrum was in good agreement with that in the literature.[7]

Polarography.—Polarograms were obtained on a Beckman Electroscan 30 instrument which incorporated a three-electrode system. The anode consisted of a platinum spiral in sodium nitrate solution and was separated from the working compartment by an agar gel–sodium nitrate salt bridge. The reference electrode was saturated calomel with a fibre junction and all $E_{\frac{1}{2}}$ values are reported in volts relative to this electrode. A dropping mercury electrode (d.m.e.) was used which had a flow rate of 1·41 mg s^{-1} and a drop time of 4·56 s at −0·6 V in a 0·1M-KCl solution. The complexes were made up as 10^{-4}M-solutions (100 cm^3) in 0·1M-KCl, except for the superoxo-complexes, which were in 0·1M-KNO$_3$, and the bromo-complexes, which were in 0·1M-KBr. The polarogram of the μ-peroxo-rhodium(III) complex was measured in 0·1M-KNO$_3$ at pH 10·5. Oxygen was removed from the solutions by bubbling White Spot nitrogen through them for at least 15 min.

Polarograms were run down to *ca*. −1·5 V where K$^+$ reduction begins. A steep rise in the anodic current at potentials more positive than *ca*. 0·0 V, presumably due to mercury oxidation * (*e.g.* in acidic solutions), sometimes prevented the full wave for the complex, *e.g. trans*-[Rh(py)$_4$(H$_2$O)Cl]$^{2+}$, from being obtained because the bottom of the wave was ' lost ' in the region below −0·1 V in the anodic current due to the mercury oxidation $2Hg + 2Cl^- \longrightarrow Hg_2Cl_2 + 2e^-$. Pronounced maxima occurred with many of the complexes especially at [Rh^{III}] > *ca*. 2 × 10^{-4}M. These maxima could be suppressed by the addition of aqueous gelatin solution (<0·005% final concentration) followed by further degassing for 1 min. The addition of gelatin tended to alter the $E_{\frac{1}{2}}$ values slightly, and it was advantageous to use low rhodium(III) concentrations, as less gelatin was needed to suppress the maxima. Some of the complexes were not sufficiently soluble, because of the high counterion concentration of the supporting electrolyte. In such cases, either a saturated solution was filtered and used, *e.g.* with *trans*-[Rh(3-Clpy)$_4$Cl$_2$]Cl (3-Clpy = 3-chloropyridine), or aqueous methanol (up to 50% v/v MeOH) was used as solvent as in the case of *trans*-[Rh(iquin)$_4$Cl$_2$]Cl (iquin = isoquinoline). Polarograms of *trans*-[Rh(py)$_4$-Cl$_2$]Cl in methanol (0, 10, and 80% v/v)–water were identical;

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* In fact, a blue aqueous solution of μ-superoxo-dirhodium(III) perchlorate, when shaken with metallic mercury, rapidly decolorised; this effect may underly the anomaly in superoxo-complex behaviour mentioned later.

[2] R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *Chem. Comm.*, 1969, 976.

[3] A. W. Addison and R. D. Gillard, *J. Chem. Soc.* (*A*), 1970, 2523.

[4] A. W. Addison, K. Dawson, R. D. Gillard, B. T. Heaton, and H. Shaw, *J.C.S. Dalton*, 1972, 589.

[5] G. W. Watt and P. W. Alexander, *J. Amer. Chem. Soc.*, 1967, **89**, 1814; A. Werner, *Chem. Ber.*, 1912, **45**, 1230; S. K. Hall and B. E. Douglas, *Inorg. Chem.*, 1968, **7**, 530; W. C. Wolsey, C. A. Reynolds, and J. Kleinberg, *ibid.*, 1963, **2**, 463; M. Delepine, *Bull. Soc. chim. France*, 1929, **45**, 235.

[6] E. D. McKenzie and R. A. Plowman, *J. Inorg. Nuclear Chem.*, 1970, **32**, 199.

[7] H. H. Schmidtke, *Z. phys. Chem.* (*Frankfurt*), 1964, **40**, 96.

the $E_{\frac{1}{2}}$ value was not affected by increasing the acidity of the solution (pH 2), but a maximum appeared which was not suppressed by gelatin.

Electronic spectra were recorded on a Unicam SP 800 spectrophotometer, wavelengths being calibrated against a rare-earth element filter.

RESULTS

Table **1** summarises the results of the polarographic reduction of the monomeric rhodium(III) complexes studied at 25 °C together with data, taken from the literature, on other monomeric rhodium(III) complexes. The majority of the complexes gave well defined waves which were shown to be diffusion controlled by the linearity of plots of the limiting current against the square root of the height of the mercury head and concentration of the depolariser. Also given in Table 1 are the positions of the first spin-allowed transition for these complexes.

The value of n, the number of electrons involved in the reduction process, has been determined previously as two for a few rhodium(III) complexes by analyses of the Ilkovic equation.[8,9] Also, it has been shown in a few cases that the controlled-potential electrolysis of a rhodium(III) complex produces Rh^I as an intermediate, and that not more than two electrons per rhodium ion were involved in the reduction.[9,10] It was, therefore, possible to assign the number of electrons involved in the reduction of these rhodium(III) complexes by comparing the height of the observed polarographic wave with those of the waves obtained for the complexes *trans*-$[Rh(py)_4Cl_2]^+$, *trans*-$[Rh(py)_4Br_2]^+$, or *trans*-$[Rh(en)_2Cl_2]^+$ of known n. *Ceteris paribus*, the ratio of the wave heights is given by $n_1D_1^{\frac{1}{2}} : n_2D_2^{\frac{1}{2}}$. Diffusion coefficients, D, vary very little so that to a good approximation the ratio of the wave heights is given by $n_1 : n_2$. It was found that, for rhodium(III) complexes which gave a well defined wave, the value of n was two. No attempt was made to assign values of n to complexes which gave ill defined polarographic waves.

TABLE 1

Polarographic results and data for rhodium(III) complexes

Complex	$-E_{\frac{1}{2}}$/V	$\lambda_{max.}$/nm
trans-$[Rh(py)_4Cl_2]^+$	0·21	410
trans-$[Rh(py)_4ClBr]^+$	0·22	426
trans-$[Rh(py)_4Br_2]^+$	0·27	441
trans-$[Rh(py)_4I_2]^+$	0·25 [a]	488
trans-$[Rh(py)_4Cl(OH)]^+$	0·34 [b]	360
trans-$[Rh(py)_4Br(OH)]^+$	0·26 [b]	370
trans-$[Rh(py)_4(N_3)_2]^+$	0·32	408
trans-$[Rh(lut)_4Cl_2]^+$	0·11 [a]	410
trans-$[Rh(4\text{-}Etpy)_4Cl_2]^+$	0·36	410
trans-$[Rh(pic)_4Cl_2]^+$	0·39	410
trans-$[Rh(pic)_4Br_2]^+$	0·31	439
trans-$[Rh(3\text{-}Mepy)_4Cl_2]^+$	0·24	410 [c]
trans-$[Rh(3\text{-}Mepy)_4Br_2]^+$	0·26	441 [c]
trans-$[Rh(3\text{-}Etpy)_4Cl_2]^+$	0·27	410 [c]
trans-$[Rh(4\text{-}NH_2py)_4Cl_2]^+$	0·47	410 [c]
trans-$[Rh(3\text{-}NH_2py)_4Cl_2]^+$	0·20	410 [c]
trans-$[Rh(3\text{-}Clpy)_4Cl_2]^+$	0·14	408
trans-$[Rh(iquin)_4Cl_2]^+$	0·22	410
trans-$[Rh(pzl)_4Cl_2]^+$	0·24	407
trans-$[Rh(thz)_4Cl_2]^+$	0·15	408
trans-$[Rh(thz)_4Br_2]^+$	0·18	439
trans-$[Rh(prm)_4Cl_2]^+$	0·12	408
trans-$[Rh(im)_4Cl_2]^+$	0·37	410 [c]
trans-$[Rh(im)_4Br_2]^+$	0·34 [a]	439 [c]
trans-$[Rh(5\text{-}NO_2im)_4Cl_2]^+$	0·32 [d]	*e, c*
trans-$[Rh(5Cl\text{-}im)_4Cl_2]^+$	0·50 [f]	409 [c]
$[Rh(im)_5Br]^{2+}$	0·61 [a]	370
$[Rh(im)_5Cl]^{2+}$	0·57	350
mer-$[Rh(pic)_3Cl(ox)]$	0·41 [a]	388
trans-$[Rh(NH_3)_4Cl_2]^+$	0·56	408
trans-$[Rh(en)_2Cl_2]^+$	0·70	406
trans-$[Rh(Me_3en)_2Cl_2]^+$	0·49	444
trans-$[Rh(Me_4en)_2Cl_2]^+$	0·34	460
trans-$[Rh(en)_2Br_2]^+$	0·76 [g]	425 [h]
trans-$[Rh(en)_2I_2]^+$	0·60 [g]	463 [h]
trans-$[Rh(en)_2Cl(NCS)]^+$	0·82 [g]	362 [h]
trans-$[Rh(en)_2(NO_2)_2]^+$	1·16 [g]	300 [h]
cis-$[Rh(en)_2Cl_2]^+$	0·76	352 [h]
cis-$[Rh(trien)Cl_2]^+$	0·70	352
$[Rh(en)_3]^{3+}$	0·72 [a]	301
$[Rh(pn)_3]^{3+}$	0·54	301
$[Rh(NH_3)_5Cl]^{2+}$	0·94 [i]	348 [e]
$[Rh(NH_3)_5(OH)]^{2+}$	1·10 [j]	321 [k]
$[Rh(H_2edta)Cl_2]^-$	0·73	402
cis-$[Rh(py)_2Cl_4]^-$	0·08	446
$[Rh(phen)Cl_4]^-$	0·41	445sh [m]
$[Rh(bipy)Cl_4]^-$	0·37 [l]	445 [n]
$[Rh(ox)_3]^{3-}$	0·83 [o]	385
$[Rh(CN)_6]^{3-}$	Not reduced above −2·0 V [p]	225
$[Rh(SCN)_6]^{3-}$	Not reduced above −1·5 V	510
$[Rh(NO_2)_6]^{3-}$	Not reduced above −1·5 V	335
$[RhCl_6]^{3-}$	*ca.* 0	521
trans-$[Rh(H_2O)_4Cl_2]^+$	*ca.* 0	451
$[Rh(H_2O)_3Cl_3]$	*ca.* 0	472
$[Rh(H_2O)_6]^{3+}$	0·35	397

py = Pyridine; lut = lutidine; 4-Etpy = 4-ethylpyridine; pic = picoline; 3-Mepy = 3-methylpyridine; 3-Etpy = 3-ethylpyridine; 4-NH_2py = 4-aminopyridine; 3-NH_2py = 3-aminopyridine; 3-Clpy = 3-chloropyridine; iquin = isoquinoline; pzl = pyrazole; thz = thiazole; prm = pyrimidine; im = 1-methylimidazole; 5-NO_2im = 5-nitro-1-methylimidazole; 5-Clim = 5-chloro-1-methylimidazole; ox = oxalate; en = ethylenediamine; Me_3en = *NNN′*-trimethylethylenediamine; Me_4en = *NNN′N′*-tetramethylethylenediamine; trien = triethylenetetramine; pn = 1,2-diaminopropane; H_4edta = ethylenediaminetetra-acetic acid; phen = 1,10-phenanthroline; bipy = 2,2′-bipyridine.

[a] Not a well defined wave. [b] 0·1M-KNO_3, pH 8. [c] Ref. 4. [d] Second wave with $E'' = -0{\cdot}54$ V. [e] Obscured by charge-transfer bands. [f] The $E_{\frac{1}{2}}$ value changed slightly with time, probably because of some decomposition of the solute. [g] Ref. 16. [h] S. A. Johnson and F. Basolo, *Inorg. Chem.*, 1962, **1**, 925. [i] Ref. 17. [j] pH 9·40; $E_{\frac{1}{2}}$ varies with pH (ref. 9). [k] H. H. Schmidtke, *Z. phys. Chem.* (*Frankfurt*), 1965, **45**, 305. [l] There is also a cathodic–anodic wave at $E_{\frac{1}{2}}$ *ca.* −0·07 V. [m] There is another, weaker, band at 538 nm; ref. 21. [n] $\varepsilon = 158$ l mol^{-1} cm^{-1}. [o] D. M. Wagnerova, *Coll. Czech. Chem. Comm.*, 1961, **26**, 2076. [p] In 0·1N-tetraethylammonium chloride. [q] This has been attributed to a charge-transfer transition (K. C. Caulton and R. F. Fenske, *Inorg. Chem.*, 1967, **6**, 562).

Plots of log $(i/i_d - i)$ against E (i is the diffusion current at a potential E and i_d the limiting diffusion current) for the well defined waves were approximately linear but the gradients were considerably larger than the theoretical gradient (for a reversible wave the gradient $2{\cdot}3RT/nF$, for $n = 2$ at 25 °C, is 0·0295 V), thus indicating the irreversible nature of the electrode process. The irreversible nature of the reduction of the complex *trans*-$[Rh(en)_2Cl_2]^+$ has also

[8] R. D. Gillard, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, 1965, 4107.

[9] L. E. Johnstone and J. A. Page, *Canad. J. Chem.*, 1969, **47**, 2123; *ibid.*, p. 4241.

[10] R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc.* (*A*), 1970, 3126.

been shown by the absence of an anodic incision in its oscillopolarogram.[11]

The spectrum of $K_3[RhCl_6]$ in 1·0M-NaCl [$\lambda_{max.}$ 520 (ε 120) and 413 nm (ε 94 l mol^{-1} cm^{-1})] differed slightly from that given in the literature [$\lambda_{max.}$ 518 (ε 112) and 411 nm (ε 94 l mol^{-1} cm^{-1})] for aqueous solutions of $[RhCl_6]^{3-}$. Hydrolysis of this ion is known to be fairly rapid;[12] however, the polarogram was run immediately after making up the solution (in 0·1N-KCl cooled to 5 °C) so that very little hydrolysis could have occurred during the experiment.

The polarographic results for the picoline superoxo- and peroxo-complexes, and the pyridine superoxo-complex of rhodium(III) are given in Table 2 together with some data from the literature on related complexes. Comparison of the currents observed at 0·0 V for the (picoline) μ-peroxo- and μ-superoxo-rhodium(III) complexes revealed that the latter was being reduced at $E > 0{\cdot}0$ V as there was a current generated which was significantly greater than the residual current of the KNO_3 used as supporting electrolyte. In none of the three cases was a reduction wave observed in the region 0·0 to −0·5 V, where most of the pyridine and substituted-pyridine complexes of rhodium(III) as yet studied exhibit a distinct two-electron reduction wave.

TABLE 2

Polarographic properties of some μ-superoxo-complexes

Complex	$E_{\frac{1}{2}}$/V	n	Medium
O_2^- [a]	*ca.* −2	1	Pyridine
[Co(salen)(py)(O_2)] [b]	−0·6	1	Pyridine
$[Co_2(CN)_{10}O_2]^{5-}$ [c]	−0·12	1	Water
	−1·55	6	Water
$[Co_2(en)_4(NH_2)O_2]^{4+}$ [d]	0 [e]	1	Water
	−0·64	4	Water
$[Rh_2(py)_8Cl_2O_2]^{3+}$	0 [e]	1	Water
	−0·58	*f*	Water
$[Rh_2(pic)_8Cl_2O_2]^{3+}$	0 [e]	1	Water
	−0·79	6	Water
$[Rh_2(pic)_8Cl_2O_2]^{2+}$	−0·79	6	Water [g]

[a] M. E. Peover and B. S. White, *Chem. Comm.*, 1965, 183. [b] G. Costa, A. Puxeddu, and L. B. Stefani, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 191; salen = *NN'*-ethylenebis(salicylideneiminato). [c] Ref. 23. [d] Ref. 24. [e] Not a genuine wave, but non-zero current at 0·0 V. [f] Anomalous (see text). [g] pH 10·5; *n* relative to preceding complex.

The polarograms of the picoline complexes enabled an estimate to be made of the relative numbers of electrons involved in the reductions. These complexes incurred a current increase at the −0·79 V wave which was six times the current involved in the continuous reduction from 0·0 V, so the results are in excellent agreement with sequence (1). The relative change in current observed for the

$$[Rh^{3+}O_2^{-}Rh^{3+}] \xrightarrow{e^-} [Rh^{3+}O_2^{2-}Rh^{3+}]^{4+} \xrightarrow{6e^-} 2Rh^+ + 2O^{2-} \qquad (1)$$

pyridine complex was less satisfactory, but of the expected order. The $E_{\frac{1}{2}}$ values for the six-electron reduction wave were relatively ligand sensitive, differing by 0·2 V. The observed ratio of currents at this wave for the pyridine and picoline superoxo-complexes respectively was *ca.* 2·4 : 1, for which we are unable to offer an explanation based on the species described. However, in view of the presence of Hg^{II} ions in ' aged ' solutions of superoxo-complex over mercury metal, there may well be some mercury-catalysed formation of novel rhodium species which give rise to the anomaly. It is also possible that reduction of the co-ordinated pyridine ligands occurs. The data in Table 2 demonstrate that one-electron reduction is characteristic of superoxo-complexes.

DISCUSSION

The interrelation between the polarographic half-wave potentials and the spectroscopic properties of transition-metal complexes has been discussed by Vlcek.[13-15] For complexes of trivalent rhodium and cobalt, distinct correlations have been found between $E_{\frac{1}{2}}$ and the energy of the first spin-allowed transition. Notably, complexes of the type $[Rh(en)_2XY]^+$ have been studied. Crow's data[16] yield a straight line with gradient $4{\cdot}2 \times 10^{-5}$ V cm for the plot of $E_{\frac{1}{2}}$ for the complexes against $\Delta\nu$, the difference between the energy of the first spin-allowed transition in the ion $[Rh(en)_3]^{3+}$ and the first singlet band in the complexes (X, Y = NO_2^-, NCS^-, I^-, Br^-, and Cl^-). For a similar group of *trans*-$[Rh(en)_2XY]^+$ ions, Gillard *et al.*[8] quote a gradient of $-3{\cdot}3 \times 10^{-5}$ V cm, $\Delta\nu$ being relative to the ion $[Rh(NH_3)_6]^{3+}$: related to the ion $[Rh(en)_3]^{3+}$, these results fit well a line of gradient $3{\cdot}0 \times 10^{-5}$ V cm. This previous work revealed also that the complex *trans*-$[Rh(py)_4Cl_2]^+$ and its dibromo-analogue did not fit the line.

A plot of $E_{\frac{1}{2}}$ against ν_1, the energy of the first *d–d* singlet–singlet transition in wave numbers, for the complexes of Rh^{III} listed in Table 1, reveals that the points for bis(ethylenediamine)rhodium complexes do indeed lie approximately on a straight line; other complexes, with presumably innocent ligands, also conform to this line, *e.g.* $[Rh(NH_3)_5Cl]^{2+}$, $[Rh(NH_3)_5(OH)]^{2+}$, $[Rh(ox)_3]^{3-}$, and $[Rh(edta)Cl_2]$ (ox = oxalate and edta = ethylenediaminetetra-acetate). However, the majority of the complexes in Table 1 do not fit this correlation; they have unrelated $E_{\frac{1}{2}}$ and ν_1 values. From the Figure, most of these species have $E_{\frac{1}{2}}$ values significantly more positive than the linear-correlation hypothesis would have predicted. Most pertinently, the complexes *trans*-$[RhL_4XY]^{n+}$ (L is an aza-aromatic ligand) fall into this category, despite their structural and spectroscopic analogy to the *trans*-$[Rh(en)_2XY]^{n+}$ complexes. Indeed, values of $E_{\frac{1}{2}}$ for the simple sequence XY = Cl_2, ClBr, and Br_2 in $[Rh(py)_4XY]^+$ are in the reverse order to that expected from their ν_1 values; nor is the change in $E_{\frac{1}{2}}$ linear with ν_1. One cannot relate the $E_{\frac{1}{2}}$ values to any observed spectroscopic property of the ligands or of the complexes. Occasionally some trends in the ligands lead to the expected $E_{\frac{1}{2}}$ order. Thus, the complexes $[RhCl_6]^{3-}$, *cis*-$[Rh(py)_2Cl_4]^-$, and *trans*-$[Rh(py)_4Cl_2]^+$ are in the expected order, which is related to the degree of substitution of chloride ions by pyridine ligands in these complexes. However, the overall charge of the species is not a factor which affects the variation of $E_{\frac{1}{2}}$ with

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[11] H. W. Munro, personal communication.

[12] W. Robb and G. M. Harris, *J. Amer. Chem. Soc.*, 1965, **87**, 4472.

[13] A. A. Vlcek, *Discuss. Faraday Soc.*, 1958, **26**, 164.

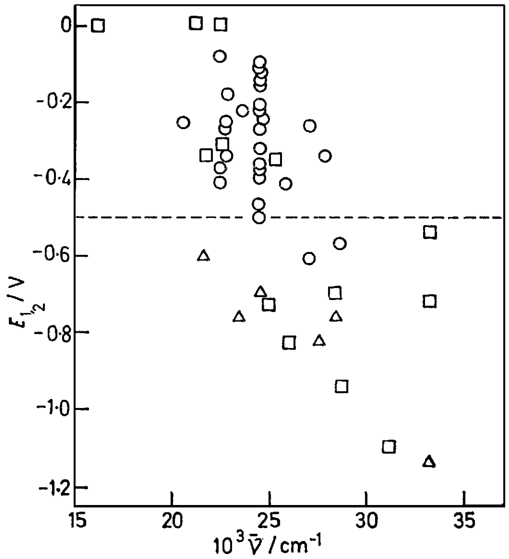
[14] A. A. Vlcek, *Progr. Inorg. Chem.*, ed. F. A. Cotton, Interscience, New York, 1963, vol. 5, p. 211.

[15] A. A. Vlcek, *Electrochim. Acta*, 1968, **13**, 1063.

[16] D. R. Crow, *Inorg. Nuclear Chem Letters*, 1969, **5**, 291.

structure and composition here, there being little parallel observed between $E_{\frac{1}{2}}$ and ionic charge. Co-ordinated water appears to have an anomalous effect, in that the complexes *trans*-$[Rh(py)_4X(OH_2)]^{2+}$ (X = Br or Cl) have no obvious waves. (There may be a wave at *ca.* 0·0 V, but it is almost totally obscured by the anodic mercury wave, only the slightest indication of its top being observable.) Even the species $[Rh(H_2O)_xCl_{6-x}]^{(3-x)-}$ have $E_{\frac{1}{2}}$ values very close to 0·0 V.

The interpretation of polarographic results for some rhodium(III) systems has been complicated by the kinetic inertia of the added rhodium(III) salt in attaining equilibrium with ligands also added to the solution. This is possibly the reason for the discrepancy between our result and the previously determined value $E_{\frac{1}{2}} = -0{\cdot}39$ V [17] for the ion $[Rh(NCS)_6]^{3-}$, which we do not observe to undergo reduction above −1·5 V. The hexanitro- and hexacyano-rhodate(III) anions are also not reduced at the d.m.e. under our experimental conditions. The latter ion has been investigated previously and reduction was reported to occur [17,18] at *ca.* −1·5 V, whereas our result is consistent with that of Rius and Molera [19] who could not induce reduction at the d.m.e. We note that previous workers merely used a fresh solution of 'RhCl$_3$' in aqueous potassium cyanide, a situation which does not yield the ion $[Rh(CN)_6]^{3-}$. Similarly, $[Co(CN)_6]^{3-}$ is not reduced by the d.m.e. in 0·1M-KCl.[14]



Distribution of $E_{\frac{1}{2}}$ against $\bar{\nu}$ for rhodium(III) complexes, complexes not observed to undergo $n \leqslant 2$ reduction (Table 1) being excluded: (○), azo-aromatic ligands; (△), bis(ethylenediamine) complexes; (□), other complexes

Examination of the Figure reveals that there may be a *tendency* for stronger σ-donor ligands to render $E_{\frac{1}{2}}$ more negative; thus, the order of increasingly negative values of $E_{\frac{1}{2}}$ (pyrimidine > thiazole > pyridine > 1-methylimidazole > ethylenediamine, ammonia) is antiparallel to the order of basicities of these ligands. This trend, as a governing factor in the properties of rhodium(III) complexes, has been proposed elsewhere [4] and probably should be related to the preference for 'class a' behaviour of rhodium(III).

The effects of pyridine-ring substituents on $E_{\frac{1}{2}}$ may be summarised thus: (i) 3-substituted pyridines exhibit similar behaviour to pyridine itself; (ii) 4-substitution has a greater effect on $E_{\frac{1}{2}}$ than 3-substitution; (iii) 4-substitution leads to $E_{\frac{1}{2}}$ values which are more negative than those for 3-substituted pyridines; and (iv) the dichloro-complex is less readily reduced than the dibromo complex for the 4-substituted pyridines, whereas the reverse is true for the 3-substituted pyridines and pyridine itself. There is no palpable rationale for this behaviour.

More germane to the issue of mechanism, halide exchange of complexes whose $E_{\frac{1}{2}}$ values are more negative than −0·5 V (*i.e.* those below the broken line in the Figure) is not accelerated by ethanol, whereas the reverse is true for complexes having a value of $E_{\frac{1}{2}}$ more positive than −0·5 V and to which this kinetic test has been applied. Thus for the bis(ethylenediamine) and penta-ammine complexes, ethanol definitely has no accelerative effect on halide exchange, whereas for the pyridine and substituted-pyridine complexes, ethanol has been found to exert such an effect. Similarly ethanol is known to accelerate the halide exchanges of the tetrakis(1-methylimidazole) complexes whereas no corresponding catalysis has been observed with the pentakis(1-methylimidazole) complexes, although this latter reaction can be accelerated by stronger reducing agents such as BH_4^-.

In relating the ease of reduction of the complexes to their structure, two possible effects may be proposed. First, it is possible that the complexes are readily reduced by virtue of their electronic structure only, so that, where there are ligands with a *d* π-delocalising effect, the reducing electrons may enter *via* an orbital which is not localised on the metal ion and the *d–d* transition energies are not representative of the reducibility. This is applicable to the heteroaromatic ligands which have both occupied and unoccupied π systems, so that electron transfer may occur through a pyridine π* orbital, for example. The suggestion [13] that pre-excitation $t_{2g} \longrightarrow e_g$ is required for reduction need not apply if charge is transferred from the electrode *via* a ligand σ orbital into the metal e_g orbitals. The ability of halide ligands to act as electron-transfer bridges is inherent in the mechanism proposed for catalysis in the $[Rh(py)_4X_2]^+$ series. Such transfer could also be facilitated when the e_g orbitals interact with the π orbitals of the aromatic ligands. Indeed the assumption [13,20] that orbital energies are not drastically perturbed by the electrode field may be unwarranted.

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[17] J. B. Willis, *J. Amer. Chem. Soc.*, 1944, **66**, 1067.

[18] W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, 1959, 2757.

[19] A. Rius and M. J. Molera, *Anales Real. Soc. Espan fis. quim.*, 1949, **45B**, 1151 (*Chem. Abs.*, 1952, **46**, 835h).

[20] D. R. Crow, 'Polarography of Metal Complexes,' Academic Press, London, 1969, ch. 8.

The second explanation follows from stereochemical arguments. The ease of reduction of the heterocyclic ligand complexes may be related to the release of constraint applied to the heterocyclic rings by any rotation-restricting effect of the halide ligands; *i.e.* one deduces that process (2), for example, would involve a larger

$$[\mathrm{Rh(py)_4X_2}]^+ + 2e^- \longrightarrow [\mathrm{Rh(py)_4}]^+ + 2X^- \quad (2)$$

entropy increase than cases in which the degree of freedom of the nitrogen ligands is unchanged. Hence ΔS of reduction would be greater than values for similar complexes with ethylenediamine ligands. Restricted rotation of a monocyclic heteroaromatic ligand has been invoked in the past to account for entropy contributions to equilibrium constants involving metal complexes of such ligands, and Vlcek suggested[13] that the relation between polarographic and spectroscopic properties in these complexes may not hold if entropy changes between the oxidised and reduced species are not consistent within a series of spectroscopically related complexes. Ideally, total restriction of a rotational degree of freedom of a single pyridine molecule about its two-fold symmetry axis corresponds to a loss of *ca.* 15 cal K^{-1} mol^{-1} in rotational entropy at room temperature; this would lead to a thermodynamic destabilisation of *ca.* 5·5 kcal mol^{-1} of a complex containing such an entity (equivalent to a redox potential increase of 0·12 V). It is notable that the *N*-methylated ethylenediamine ligands contain a steric constraint also, but this is less important in terms of the entropy argument than in its obvious modification (*cf.* $\lambda_{max.}$) of the electronic structure of the Rh^{III} species.

The greater oxidising power of the heterocyclic base complexes is almost certainly the reason for the acceleration of their reactions by mild reductants, the ethylenediamine complexes being unaffected. However, this interpretation may only be applied qualitatively as $E_{\frac{1}{2}}$ is not necessarily a measure of E^0 for the given reduction process, but is related to it in that the difference between $E_{\frac{1}{2}}$ and E^0 is a measure of the rate of the ' electrode ' process; *i.e.*, $E_{\frac{1}{2}}$ is related to E^0 only for a ' reversible ' wave, for which $(E_{\frac{1}{2}} - E^0) < 0{\cdot}05$ V, and the reduction waves observed for these Rh^{III} complexes are irreversible. Moreover, irreversibility associated with a large activation energy for the reduction process leads to $E_{\frac{1}{2}}$ values which are more negative than E^0, so the values here relate to lower limits for E^0. We would, for example, predict that the bis(*NNN'*-trimethylethylenediamine) and the bis(*NNN'N'*-tetramethylethylenediamine) complexes, unlike the parent bis(ethylenediamine) complexes, should show ethanol acceleration in their halide substitutions. Similarly the complexes $[\mathrm{Rh(phen)Cl_4}]^-$ (phen = 1,10-phenanthroline) and $[\mathrm{Rh(bipy)Cl_4}]^-$ (bipy = 2,2'-bipyridine) should also undergo ethanol accelerated halide exchange.

Complexes of the type $[\mathrm{M(L)_2X_2}]^+$ (M = Ir or Rh; L = 2,2'-bipyridine or 1,10-phenanthroline; X = Cl or Br) were investigated polarographically. In all cases irreversible and ill defined waves with large maxima were obtained. Although it is not strictly correct to compare the heights of these ill defined waves with the waves of complexes for which *n* is known, this procedure indicated that the number of electrons involved in the polarographic reduction was greater than two and was not the same for all complexes. It is known that the rhodium complexes react with BH_4^- or ethanol to give highly coloured products; the exact nature of the species responsible is uncertain, but it has been suggested that they contain rhodium in a low oxidation state which is stabilised by the π-delocalising ligands. The colour of these products has been ascribed to metal ⟶ ligand $d_\pi \longrightarrow p_{\pi^*}$ transitions so that it is not possible to distinguish between Rh^I–L^0 and, *e.g.*, Rh^{II}–L^{-I}. It seems likely that a similar type of behaviour is to be expected polarographically, *i.e.* delocalisation of the reducing electrons over the chelate ligands, which would account for the large and rather ill defined waves obtained. Another contributing factor to the irreversible nature of the waves is that these complexes have a *cis*-geometry and would not therefore be expected to attain the square-planar geometry of Rh^I with ease.

The complexes containing the ion $[\mathrm{Rh(L)Cl_4}]^-$ (L = 2,2'-bipyridine or 1,10-phenanthroline) exhibited two well defined waves; the one at —0·37 V (or —0·41 V for L = phen) was the same height as that of the cathodic–anodic wave occurring at *ca.* —0·07 V. The nature of this cathodic–anodic wave is by no means certain. It is possible that, at this relatively positive potential, mercury is oxidised and there is electron transfer from the electrode to the complex; the electron exchange is probably centred on the ligands rather than on the metal atom. However, the presence of a polarographic reduction wave for these complexes at potentials more positive than —0·5 V would, as previously mentioned, suggest that the halide exchanges of these complexes would be accelerated by ethanol. There is at present no evidence to support this conclusion; on the contrary, Kulasingam *et al.*[21] suggested that the reaction $[\mathrm{Rh(phen)Br_4}]^- \longrightarrow [\mathrm{Rh(phen)_2Br_2}]^+$ was not accelerated by ethanol (based on similar rates of formation of the bis product in aqueous ethanol and aqueous acetone). However, there are contra-indications to the earlier conclusion: (i) the reactions were carried out under reflux with the solutions exposed to the atmosphere; (ii) oxygen is an efficacious inhibitor of the acceleration, despite the effectiveness of diethyl ether in deaerating and hence apparently accelerating an analogous synthesis with pyridine, which is also rapid *in vacuo* with degassed water as solvent; (iii) the complexes $[\mathrm{Rh(phen)_2Cl_2}]^+$ and $[\mathrm{Rh(bipy)_2Cl_2}]^+$ are formed readily from ' $RhCl_3$ ' and the ligand *in vacuo* in degassed water; (iv) McKenzie and Plowman[6] demonstrated that the reaction $[\mathrm{Rh(phen)Cl_4}]^- \xrightarrow{\text{phen}} [\mathrm{Rh(phen)_2Cl_2}]^+$ is inhibited by acid; and (v) rhodium(I) catalysts are deactivated by acid to yield inactive hydridorhodium(III) species.[10] Available data do not therefore unambiguously prove

[21] G. C. Kulasingam, W. R. McWhinnie, and J. D. Miller, *J. Chem. Soc.* (*A*), 1969, 521.

the absence of catalysis in these systems for formation of $[Rh(L)_2Cl_2]^+$ complexes or their subsequent halide exchange. Gidney's[22] evidence strongly favours catalysis in both these types of reaction.

Values of the half-wave potentials for the aquochloro-species could not be determined accurately as they occurred at *ca.* 0·0 V. However, these values of $E_{\frac{1}{2}}$ would again suggest that the halide exchanges of these complexes would be accelerated by ethanol. Unfortunately, there is no direct evidence on this point but several other observations are relevant. Thus it has been observed that '$RhCl_3$', which under the varying experimental conditions probably contains differing amounts of the aquochloro-species, is reduced by ethanol; acetaldehyde is detectable as one of the products by its i.r. spectrum in the gas phase. Similarly ethanol will accelerate the formation of the complex *trans*-$[Rh(py)_4Cl_2]^+$ from $RhCl_3$ in aqueous pyridine, and the formation of $[Rh(phen)Cl_4]^-$ and *cis*-$[Rh(phen)_2Cl_2]^+$ from an aqueous solution of $RhCl_3$ and 1,10-phenanthroline. These results can be interpreted as involving a Rh^I species, formed by reduction of $RhCl_3$ with ethanol, as the active catalyst.

The μ-superoxo-complexes of rhodium(III) undergo one-electron reduction at positive potentials followed by further reduction at more negative potentials. This behaviour is similar to that observed in the polarography of μ-peroxo- and μ-superoxo-dicobalt(III) complexes, in which (after the one-electron reduction of the superoxo-group to the peroxo-group) the μ-peroxo-cobalt dimers are robust toward further reduction in a region where monomeric complexes with similar amine and oxygen-containing ligands undergo the $Co^{III} \longrightarrow Co^{II}$ reduction. The E^0 value for cobalt(III) ammine superoxo-complexes has in fact been estimated to be *ca.* +1·0 V.[23] At a more negative potential, simultaneous reduction of both cobalt(III) and the peroxo-group occurs yielding a large current. For example, $[Co_2(en)_4(NH_2)O_2]^{4+/3+}$ has a four-electron reduction wave at $E_{\frac{1}{2}} = -0{\cdot}64$ V.[24] One dissimilarity between the behaviour of the rhodium(III) and cobalt(III) μ-superoxo-complexes is that the complex $[(NH_3)_5Co{\cdot}\mu(O_2){\cdot}Co(NH_3)_5]^{5+}$ undergoes a one-electron reduction of the superoxo-group but the resulting μ-peroxo-complex then undergoes an intramolecular redox reaction to form Co^{II} and O_2.[25] No such behaviour has been observed with the μ-(su)peroxo-complexes of rhodium(III). Also rhodium(III) itself undergoes two-electron reduction to Rh^I, whereas cobalt(III) may be reduced to Co^{II}. These differences arise simply because Rh^{II} is a stronger reductant than Co^{II} within a comparable ligand environment.

A comparison was made of the polarographic behaviour of two of the rhodium(III) complexes with the analogous Co^{III} and Ir^{III} complexes. The complexes studied were *trans*-$[M(en)_2Cl_2]^+$ and trans-$[M(py)_4Cl_2]^+$ (M = Co, Rh, and Ir), and the results are given in Table 3. Cobalt(III) complexes usually have two reduction waves corresponding to the processes $Co^{III} \longrightarrow Co^{II}$ and $Co^{II} \longrightarrow Co^0$; thus $[Co(NH_3)_6]^{3+}$ has a one-electron wave at $-0{\cdot}26$ V and a two-electron wave at $-1{\cdot}20$ V in 0·1N-KCl, so that the waves occurring at *ca.* $-1{\cdot}0$ V in both these complexes correspond to a two-electron reduction $Co^{II} \longrightarrow Co^0$. The one-electron wave in the complex *trans*-$[Co(py)_4Cl_2]^+$ could not be measured as it occurred at positive potentials. The number of electrons involved in the iridium reduction was not determined as the wave was not well defined but, by analogy with Rh^{III}, one might expect it to involve two electrons. In spite of the differing number of electrons involved in these reductive processes two observations can be made. The bis(ethylenediamine) complex is more difficult to reduce in each case, *i.e.* the tetrapyridine complexes are better oxidising agents than the bis(ethylenediamine) complexes. For analogous complexes, the ease of reduction is $Co^{III} > Rh^{III} > Ir^{III}$, *i.e.* the Ir^{III} complexes tend to be thermodynamically more stable relative to the lower oxidation state than are the Rh^{III} complexes, which are themselves similarly more stable than the Co^{III} complexes. This order may simply be the result of the smallest ion, Co^{III}, having the greatest electron affinity.

TABLE 3

Polarographic half-wave potentials[a] for analogous Co^{III}, Rh^{III}, and Ir^{III} complexes

M^{III}	*trans*-$[M(en)_2Cl_2]^+$	*trans*-$[M(py)_4Cl_2]^+$
Co	$\geqslant -0{\cdot}04$[b]	$>0{\cdot}0$, $-1{\cdot}08_2$
Rh	$-0{\cdot}70$	$-0{\cdot}21$
Ir	Not reduced above $-1{\cdot}5$ V[c]	$-0{\cdot}88$

[a] Values of $E_{\frac{1}{2}}$ are in volts relative to an s.c.e.; 0·1N-KCl as supporting electrolyte. [b] R. Ralea, G, Burlacu, and D. Giurgiu, *Rev. Roumaine Chim.*, 1965, **10**, 211. [c] $E_{\frac{1}{2}} \simeq 2{\cdot}0$ V (F. Basolo and R. A. Bauer, *Inorg. Chem.*, 1969, **8**, 2231).

It is tempting to speculate that the biological effects of the heteroaromatic base complexes of rhodium(III) are, at least in part, attributable to their redox properties. Cobalt(III) and iridium(III) complexes, of very similar geometries but very different redox properties, are completely inactive.

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[22] P. M. Gidney, Ph.D. Thesis, University of Kent at Canterbury, 1972.

[23] A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, 1961, **83**, 509.

[24] H. Graff and W. K. Wilmarth, *Proc. Symp. Co-ordination Chem.*, ed. M. T. Beck, Akademiai Kiado, Budapest, 1965, p. 255.

[25] A. A. Vlcek, *Coll. Czech. Chem. Comm.*, 1960, **25**, 3036.