Preparation and Properties of the Geometric Isomers of the Dichloro(3,6-diazaoctane-1,8-diamine)rhodium(III) Cation, $[Rh(trien)Cl_2]^+$

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The *cis*-α, *cis*-β, and *trans*-isomers of $[Rh(trien)Cl_2]^+$ have been isolated and characterised. The physical properties of the $[Rh(trien)Cl_2]^+$ isomers are compared with those of the corresponding $[Co(trien)Cl_2]^+$ and $[Rh(en)_2Cl_2]^+$ isomers. Optically active samples of each of the *cis*-isomers were obtained. The differing reactivities of the *cis*-isomers toward photo-induced hydrolysis, and a kinetic study of nucleophilic substitution of *cis*-α-$[Rh(trien)Cl_2]^+$ are reported.

TRIETHYLENETETRAMINE,3,6-DIAZAOCTANE-1,8-DIAMINE (trien), when occupying four co-ordination sites, is capable of arrangement around a six-co-ordinate metal ion in three ways (Figure 1) and all three geometric isomers of $[Co(trien)Cl_2]^+$ have been isolated.[1,2] The ion of corresponding formula containing rhodium, $[Rh(trien)Cl_2]^+$, was first prepared by Johnson and Basolo,[3] and, to date, no effort to prepare, separate, and characterise all three geometric isomers has been reported. There is renewed interest in the mechanism of catalysed substitutions at rhodium(III) centres,[4] and for preparative and kinetic studies, we needed to know the geometric configuration

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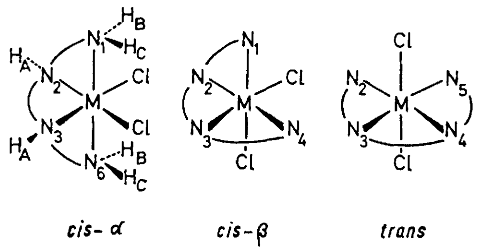
[1] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 1967, **6**, 787.

[2] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 1965, **4**, 45.

[3] S. A. Johnson and F. Basolo, *Inorg. Chem.*, 1962, **1**, 925.

[4] R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc. (A)*, 1971, 1840 and references therein.

of the $[Rh(trien)Cl_2]^+$ ion. We report here the basic chemistry of the complex ions with this stoicheiometry.



cis-α *cis*-β *trans*

FIGURE 1 A representation of the three possible geometric isomers of $[M(trien)Cl_2]$

RESULTS

Characterisation of the Geometric Isomers of $[Rh(trien)Cl_2]^+$.—The reaction described by Johnson and Basolo [3] was used to prepare $[Rh(trien)Cl_2]Cl$. The first isolated product has an electronic spectrum similar to that of *cis*-$[Rh(en)_2Cl_2]^+$ and, in the original work, was assigned *cis*-geometry. More recently, on the basis of its i.r. spectrum, it was suggested [5] that it had the *cis*-α-configuration; our work supports that assignment. After removal of the *cis*-α-isomer, further concentration of the filtrate gives the more soluble chloride salt of the *cis*-β-cation. The remaining mother liquor gives small amounts of *trans*-$[Rh(trien)Cl_2]^+$, (see Experimental section).

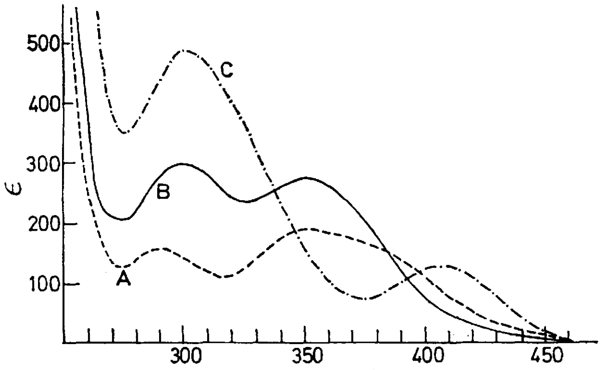


FIGURE 2 Electronic spectra of A, *cis*-α-; B, *cis*-β-; and C, *trans*-$[Rh(trien)Cl_2]^+$ in water

The analyses and conductivities (Table 1) support the above formulations, and the electronic spectra (Figure 2) are similar to those [3] of the analogous *cis*- and *trans*-$[Rh(en)_2Cl_2]^+$ complexes. We further find that the *X*-ray powder photographs of *cis*-α-$[Rh(trien)Cl_2]Cl,H_2O$ and of *cis*-α-$[Co(trien)Cl_2]Cl,2H_2O$ are essentially identical.

N.m.r. spectra provide a good method for distinguishing the two *cis*-isomers. *cis*-α-$[Rh(trien)Cl_2]^+$ has three pairs of equivalent *N*-bonded protons, (H_A, H_B, and H_C *in Figure* 1), and, consistent with this configuration, the 100 MHz n.m.r. spectrum, in [$^2H_6$]dimethyl sulphoxide (dmso), shows resonances of equal intensity at τ 3·0, 4·30, and 4·90. The resonance at τ 3·0 is considerably sharper than the other two and spin-decoupling either of these broad resonances causes the other resonance to sharpen. It is thus possible to assign the resonance at τ 3·0 to H_A and the resonances at τ 4·30 and 4·90 to H_B and H_C [$^2J(H_BH_C)$ *ca.* 10 Hz]. This spectrum is to be contrasted with the 60 MHz n.m.r. spectrum of *cis*-β-$[Rh(trien)Cl_2]Cl$ which shows resonances at τ 2·2(1), 3·3(1), 4·5(1), 4·7(1), and 5·3(2) due to the six inequivalent *N*-bonded protons.

The i.r. spectrum of *cis*-α-$[Rh(trien)Cl_2]Cl,H_2O$ is virtually identical to that of *cis*-α-$[Co(trien)Cl_2]Cl,2H_2O$, and the spectra of the *trans*-isomers of $[Rh(trien)Cl_2]ClO_4$ and $[Co(trien)Cl_2]ClO_4$ are also similar {although we find that the ν(NH) bands in $[Co(trien)Cl_2]ClO_4$ occur *ca.* 50 cm^{-1} lower than previously reported [5]}. We were unable, however, to correlate the i.r. spectrum of *cis*-β-$[Rh(trien)Cl_2]Cl,2H_2O$ with that of either of the known forms of the chloride salt of the corresponding cobalt complex. Anhydrous *cis*-β-$[Co(trien)Cl_2]Cl$, prepared by the method of Sargeson and Searle,[1] has an i.r. spectrum significantly different from that reported [5] by Buckingham and Jones for the hydrate *cis*-β-$[Co(trien)Cl_2]Cl,H_2O$. The i.r. spectrum of *cis*-β-$[Rh(trien)Cl_2]Cl,2H_2O$, a dihydrate, is significantly different from the spectra of both these cobalt complexes, and this difference is assumed to be due to variation of crystal (not molecular) structure for varying degrees of hydration.

Partial separations of both *cis*-α- and *cis*-β-$[Rh(trien)Cl_2]^+$ into optical isomers were achieved on Sephadex SP-C-25 cation exchange columns, using a procedure like that described by Legg and Douglas.[6] The chiroptical spectra in the region of the *d*–*d* transitions for the resolved rhodium complexes (Figures 3 and 4) resemble those of the corresponding cobalt complexes,[2] although, of course, the Cotton effects for the rhodium complexes occur at higher energy.

Hydrolysis of $[Rh(trien)Cl_2]^+$.—Johnson and Basolo found [3] that the base hydrolysis of *cis*-$[Rh(en)_2Cl_2]^+$ was much faster than that of *trans*-$[Rh(en)_2Cl_2]^+$. Similarly,

TABLE 1

Physical properties and analytical results (%) for $[Rh(trien)Cl_2]Y,xH_2O$

	Ref.	λ_{max}/nm	ε	Λ [a]		C	H	N	Cl
cis-α-$[Rh(trien)Cl_2]Cl,H_2O$	*b*	352,288	240,210	125	Found	19·0	6·0	14·7	
cis-$[Rh(trien)Cl_2]Cl,H_2O$	*c*	352,293	250,200		Found	19·1	5·5		28·8
					Calc.	19·3	5·4	15·0	28·5
cis-β-$[Rh(trien)Cl_2]Cl,2H_2O$	*b*	350,300	270,290	98	Found	18·4	5·2	14·3	27·1
					Calc.	18·4	5·6	14·3	27·3
trans-$[Rh(trien)Cl_2]ClO_4$	*b*	406,286	128,490	94	Found	17·3	4·3	13·5	25·1
					Calc.	17·2	4·3	13·4	25·4
cis-$[Rh(en)_2Cl_2]NO_3$	*c*	352,295	155,180						
trans-$[Rh(en)_2Cl_2]NO_3$	*c*	406,286	75,130						

[a] Conductivity of 10^{-3}M aqueous solutions at 25° in Ω^{-1} cm^2 mol^{-1}. [b] This work. [c] Ref. 3.

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[5] D. A. Buckingham and D. Jones, *Inorg. Chem.*, **1965**, **4**, 1387.

[6] J. I. Legg and B. E. Douglas, *Inorg. Chem.*, 1968, **7**, 1452.

we find that hydrolysis of both *cis*-α- and *cis*-β-[Rh(trien)-Cl_2]$^+$ at room temperature (0·1N-sodium hydroxide solution) is complete within 5 min whereas *trans*-[Rh(trien)Cl_2]$^+$ remained unchanged under the same conditions.

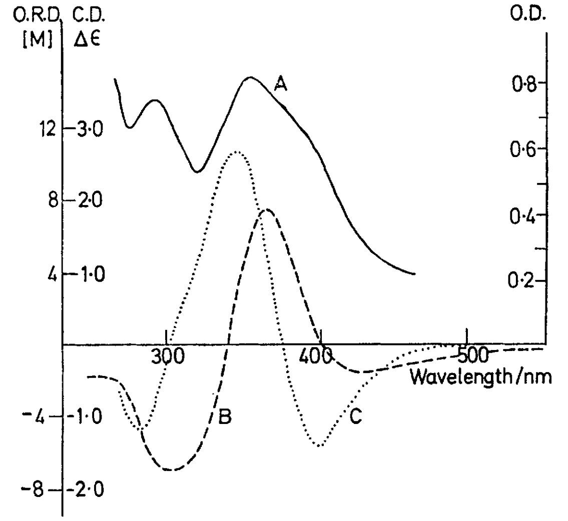

FIGURE 3 Spectra of *cis*-α-[Rh(trien)Cl_2]$^+$; A, electronic; B, o.r.d.; C, c.d.

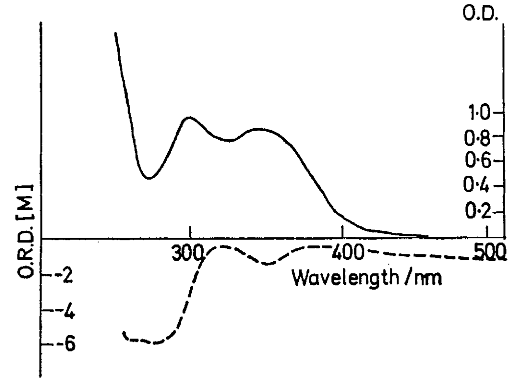

FIGURE 4 Spectra of *cis*-β-[Rh(trien)Cl_2]$^+$; electronic (——), o.r.d. (– – – –)

There is no evidence for photo-induced hydrolysis of *cis*-α-[Rh(trien)Cl_2]$^+$ at pH 7, in that a solution of *cis*-α-[Rh(trien)Cl_2]Cl ($5{\cdot}35 \times 10^{-3}$M; Λ 125 Ω^{-1} cm^2 mol^{-1}) was essentially unchanged upon irradiation for 240 min ([Cl^-] = $3{\cdot}8 \times 10^{-3}$M; Λ 96 Ω^{-1} cm^2 mol^{-1}, $\lambda_{max.}$ 350 and 288 nm).

The resolved *cis*-α-[Rh(trien)Cl_2]$^+$ is optically stable. After 6 months at room temperature only half of its initial activity is lost, and irradiation of a solution containing (+)-*cis*-α-[Rh(trien)Cl_2]$^+$ ($1{\cdot}0 \times 10^{-2}$M) and sodium chloride (*ca.* 0·1M) for 90 min resulted in only a 5% loss of optical activity.

This contrasts with the behaviour of *cis*-[Rh(en)$_2Cl_2$]NO_3 ($1{\cdot}0 \times 10^{-3}$M; Λ 84 Ω^{-1} cm^2 mol^{-1}) which upon irradiation for 20 min gave a solution ($\lambda_{max.}$ 375 and 280 mm, Λ 193 Ω^{-1} cm^2 mol^{-1}; [Cl^-] $0{\cdot}8 \times 10^{-3}$M) which contained *ca.* 80% of *trans*-[Rh(en)$_2$Cl(OH_2)]$^{2+}$. Boiling this solution with hydrochloric acid for 1 h gave quantitative conversion to *trans*-[Rh(en)$_2Cl_2$]$^+$ ($\lambda_{max.}$ 407 nm). Irradiation of (+)-*cis*-[Rh(en)$_2Cl_2$]$^+$ ($1{\cdot}4 \times 10^{-3}$M) in sodium chloride (*ca.* 0·1M) solution for 16 min resulted in complete loss of optical activity and the resultant solution had an electronic spectrum ($\lambda_{max.}$ 395 and 283 nm) which indicates the presence of *trans*-[Rh(en)$_2Cl_2$]$^+$ and *trans*-[Rh(en)$_2$Cl(OH_2)]$^{2+}$.

For *cis*-β-[Rh(trien)Cl_2]$^+$, irradiation causes loss of optical activity and a small change in the electronic spectrum. Heating this irradiated solution with an excess of hydrochloric acid gives only partial reconversion to *cis*-β-[Rh-(trien)Cl_2]$^+$.

Kinetic Results.—*cis*-α-[Rh(trien)(Cl_2)]$^+$ + Y (Y = Br^-, I^-, or N_3^-). The reaction of *cis*-α-[Rh(trien)Cl_2]$^+$ with nucleophiles Y (Y = Br^-, I^-, and N_3^-) gives *cis*-α-[Rh(trien)Y_2]$^+$. The electronic spectra of the final solutions are identical to those of the independently prepared *cis*-α-[Rh(trien)Y_2]$^+$ samples (see Experimental section), and the *cis*-α-configuration of these substitution products is based upon the following i.r., c.d., and n.m.r. results. Their i.r. spectra are virtually identical to the i.r. spectrum of authentic *cis*-α-[Rh(trien)Cl_2]$^+$, except for Y = N_3^-, when additional bands due to the azide group are observed at *ca.* 2050 cm^{-1}. The c.d. spectrum of the dibromo-substituted product is similar to that of *cis*-α-[Rh(trien)Cl_2]$^+$ except that the spectrum is shifted to lower energy. The 100 MHz ^{1}H n.m.r. spectrum of the bis-azido complex in [$^2H_6$]dmso solution shows three equally intense peaks due to the *N*-bonded protons at τ 3·45 (H_A, Figure 1), 4·40, and 4·98 (H_B and H_C). The ^{1}H n.m.r. spectra of the dibromo- and di-iodo-complexes are less definitive since both spectra contain only two resonances (in the ratio 1 : 2) attributable to *N*-bonded protons [Y = Br, τ 3·39(1), 4·72(2); Y = I, 3·46(1), 4·82(2)]. However, it seems more reasonable to assign these spectra to a *cis*-α-configuration, with the resonances due to H_B and H_C being coincident, than to a *cis*-β-configuration.

TABLE 2

Kinetic results for the reaction of *cis*-α-[Rh(trien)Cl_2]$^+$ with Y in water. Y = Br^-, I^-, or N_3^-. [Rh] = 10^{-3}M, μ = 0·5M, T = 70°

Y	[Y]/mol l^{-1}	10^4k_1/s^{-1} [a]	10^4k_2/s^{-1} [b]	k_1/k_2 [c]
Br^-	0·5	7·97	2·48	3·3
	0·4	8·15	2·47	
	0·3	8·35	2·48	
	0·5 [d]	8·20	2·20	
I^-	0·5	7·13	2·42	2·8
	0·4	6·90	2·55	
	0·3	6·85	2·63	
N_3^-	0·5	9·53	3·97	2·4
	0·4	9·59	3·87	
	0·3	9·48	3·93	
NCS^-	0·5	7·75	*e*	*e*
	0·4	7·47		
	0·3	6·85		

[a] Rate constant for replacement of first chloride. [b] Rate constant for replacement of second chloride. [c] k_1, k_2 Are the average of the three values of k_1 and k_2 given in the Table. [d] Ethanol 30%. [e] Anation of second chloride by thiocyanate was not observed; see Discussion section.

The pseudo-first-order rate plots for the above substitutions, obtained by plotting log(A − A_t) *vs.* time, were clearly resolvable into two consecutive reactions, which were assumed to correspond to the consecutive replacement of the two chlorides. Using the method of Corain and Poë,[7] rate

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[7] B. Corain and A. J. Poë, *J. Chem. Soc.* (*A*), 1967, 1633.

constants for these two stages were obtained: these are given in Table 2.

The substitution by bromide ion was also monitored in ethanol–water (3 : 7) solution; this modification of solvent had no significant effect upon the rate of reaction (Table 2).

cis-α-$[\mathrm{Rh(trien)Cl_2}]^+ + \mathrm{NCS}^-$. Substitution by thiocyanate ion gave $[\mathrm{Rh(trien)(NCS)Cl}]^+$ which did not undergo further thiocyanate substitution, since no evidence of $[\mathrm{Rh(trien)(NCS)_2}]^+$ was found (see Experimental section). Heating an aqueous solution of $[\mathrm{Rh(trien)(NCS)Cl}]^+$ with an excess of thiocyanate ion led to the slow formation of an uncharacterised hydrolysis product. The pseudo first-order rate plot of the first part of the reaction gave a rate constant which is assumed to correspond to replacement of the chloride ion. The rate of this replacement is similar to the rate observed for the other reactions (Table 2).

DISCUSSION

Photo-induced Hydrolysis of cis-$[\mathrm{Rh(trien)Cl_2}]^+$ and $[\mathrm{Rh(en)_2Cl_2}]^+$.—The results of the photo-induced hydrolysis for the *cis*-α- and *cis*-β isomers of the ion $[\mathrm{Rh(trien)Cl_2}]^+$ and for *cis*- and *trans*-$[\mathrm{Rh(en)_2Cl_2}]^+$, are consistent with Adamson's rules,[8] originally developed to account for the photo-induced hydrolysis in complexes of chromium(III). They have been applied, with a degree of success, to rhodium(III) and iridium(III) complexes,[9,10] and the results reported here are not inconsistent with these rules. Thus, irradiation of an aqueous solution of *trans*-$[\mathrm{Rh(en)_2Cl_2}]^+$ yields *trans*-$[\mathrm{Rh(en)_2Cl(H_2O)}]^{2+}$ as a primary photochemical process.

The observed isomerisation and hydrolysis of *cis*-$[\mathrm{Rh(en)_2Cl_2}]^+$ to *trans*-$[\mathrm{Rh(en)_2Cl(H_2O)}]^{2+}$ suggest a more complex process than the photo-induced hydrolysis predicted by Adamson's rules. In the case of *cis*-$[\mathrm{Ir(en)_2Cl_2}]^+$, Basolo and Bauer noted a photolysis product which appeared to contain a unidentate ethylenediamine ligand. Such a ring opening may be the primary photochemical process for *cis*-$[\mathrm{Rh(en)_2Cl_2}]^+$, which is followed by thermal displacement of chloride by the unco-ordinated end of the ethylenediamine, with chelate reformation. Such a reaction would be much slower for the thermally more inert iridium(III) complex.

For *cis*-α-$[\mathrm{Rh(trien)Cl_2}]^+$, Adamson's rules predict that either N^2 or N^3 (Figure 1) should be labilised upon irradiation. The geometry of the trien ligand makes hydrolysis of these secondary amine nitrogens difficult, so the observed inertness of *cis*-α-$[\mathrm{Rh(trien)Cl_2}]^+$ toward photolysis is consistent with these rules. The unchanged electronic spectrum and optical stability of *cis*-α-$[\mathrm{Rh(trien)Cl_2}]^+$ also suggest that there is no significant amount of labilisation of the terminal primary amine nitrogens (N^1 and N^6 in Figure 1).

The situation is less clear for *cis*-β-$[\mathrm{Rh(trien)Cl_2}]^+$. The change in the electronic spectrum, and the optical instability upon irradiation, suggest that photo-induced hydrolysis does occur in the *cis*-β-isomer. Inspection of the geometry of the *cis*-β-isomer shows that a terminal amine nitrogen (N^1 in Figure 1) is ***trans*** to a chloride so that its displacement would not be inhibited by steric constraints as in the *cis*-α-isomer.

Kinetics of Nucleophilic Substitutions of cis-α-$[\mathrm{Rh(trien)Cl_2}]^+$.—The reactions of *cis*-α-$[\mathrm{Rh(trien)Cl_2}]^+$ with Y ($\mathrm{Y = Br^-, I^-,}$ or $\mathrm{N_3^-}$) are two-stage processes corresponding to the successive replacement of the two chloride ligands. In all the cases studied, the rate of replacement of the first chloride is virtually independent of the nature and concentration of the incoming nucleophile. These results are similar to those observed for the halide substitutions in ***trans***-$[\mathrm{Rh(en)_2X_2}]^+$ (X = halide) and suggest that a similar mechanism operates in both systems,[11] *i.e.* the reaction proceeds according to the scheme below, in which

$$[\mathrm{Rh(trien)Cl_2}]^+ + \mathrm{H_2O} \rightleftharpoons [\mathrm{Rh(trien)Cl(H_2O)}]^{2+} + \mathrm{Cl}^- \text{ slow}$$

$$[\mathrm{Rh(trien)Cl(H_2O)}]^{2+} + \mathrm{Y}^- \longrightarrow [\mathrm{Rh(trien)ClY}]^+ + \mathrm{H_2O} \text{ fast}$$

the rate-determining replacement of chloride by water is followed by relatively rapid anation. There is still doubt concerning the degree of assistance rendered by the incoming ligand for substitutions at rhodium(III) centres. A recent report[12] suggests that the anation of $[\mathrm{Rh(NH_3)_5(H_2O)}]^{3+}$ by $\mathrm{Cl^-}$ and $\mathrm{Br^-}$ involves nucleophilic assistance by the entering halide ions, classifying these mechanisms as I_a.[13]

The rates of replacement of the second chloride by various nucleophiles are also virtually independent of the concentration of the nucleophile, suggesting a mechanism similar to that proposed for the replacement of the first chloride. Statistically, the ratio k_1/k_2 should be 2·0, but in these two-step substitutions, a value slightly greater than 2·0 is obtained. This ratio of rate constants (k_1/k_2) might be used as a measure of the effect of the co-ordinated ligand on the rate of substitution of the second chloride, *i.e.* as a measure of the *cis*-effect of the ligands. Thus since k_1/k_2 is greater than 2·0, chloride accelerates the rate of nucleophilic substitution more than any of the nucleophiles studied. This order of decreasing ability to labilise the second chloride ligand is thus $\mathrm{Cl^- > N_3^- > I^- > Br^-}$. Although there is no obvious intramolecular explanation for this order, it should be noted that the observed *cis*-effects are small when compared to the ***trans***-effects of the same nucleophiles. For example, the rate of replacement of $\mathrm{Cl^-}$ by $\mathrm{I^-}$ in ***trans***-$[\mathrm{Rh(en)_2ClI}]^+$ is 200 times that for $\mathrm{I^-}$ substitution in ***trans***-$[\mathrm{Rh(en)_2Cl_2}]^+$ after allowing for statistical effects.[11] The lack of such large *cis*-effects reinforces the proposal that the ***trans***-effect is truly a ***trans***-directional effect of

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[8] A. W. Adamson, *J. Phys. Chem.*, 1967, **71**, 798.

[9] F. Basolo and R. A. Bauer, *J. Amer. Chem. Soc.*, 1968, **90**, 2437.

[10] F. Basolo and R. A. Bauer, *Inorg. Chem.*, 1969, **8**, 2231.

[11] H. L. Bott, E. J. Bounsall, and A. J. Poë, *J. Chem. Soc.* (*A*), 1966, 1275.

[12] F. Monacelli, *Inorg. Chim. Acta*, 1968, **2**, 263; H. L. Bott, A. J. Poë, and K. Shaw, *J. Chem. Soc.* (*A*), 1970, 1745.

[13] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1966, ch. 1.

the co-ordinated ligand since it does not affect *cis*- and *trans*-ligands equally. Although it would be desirable to have activation enthalpies for these reactions, in order to confirm that these *cis*-effects are small, the ratios of rate constants parallel the behaviour of activation enthalpies in other substitutions at rhodium(III). Thus, it seems likely that similar effects are important for substitutions in *cis*-α-$[Rh(trien)Cl_2]^+$.

The lack of catalysis by ethanol in the substitution by bromide into *cis*-α-$[Rh(trien)Cl_2]^+$ suggests that catalysis by Rh^I does not play an important role in these reactions. This is consistent with the observation that *trans*-$[Rh(en)_2Cl_2]^+$ does not undergo ethanol-catalysed halide interchange under similar conditions, while *trans*-$[Rh(py)_4Cl_2]^+$ (py = pyridine), with a more positive polarographic half-wave potential, has been found to undergo ethanol-catalysed halide interchanges.[4] Thus the ethylenediamine- and triethylenetetramine-rhodium(III) complexes are very poor oxidants relative to the pyridine analogues. However, on using a stronger reducing agent, *cis*-α-$[Rh(trien)Cl_2]^+$ has been shown to undergo catalysed substitutions without isomerisation and with a high degree of retention of optical activity. These experiments will be reported in more detail separately.

The inertness of the chloride ion in $[Rh(trien)(NCS)Cl]^+$ toward replacement by thiocyanate suggests that the co-ordinated thiocyanate prevents replacement of the second chloride ligand. This behaviour is consistent with the observation of Johnson and Basolo[3] that thiocyanate substitution of *trans*-$[Rh(en)_2Cl_2]^+$ leads to *trans*-$[Rh(en)_2(NCS)Cl]^+$ which is also inert to further thiocyanate substitution. {Thiocyanate substitution of *cis*-$[Rh(en)_2Cl_2]^+$ leads to an uncharacterised species which was believed, however, to contain the $[Rh(en)_2(NCS)Cl]^+$ cation.} Since a rate constant for the replacement of the second chloride by thiocyanate cannot be obtained for any of these reactions, an estimate of the relative *cis*- and *trans*-labilising effects of the co-ordinated thiocyanate ligand is impossible; but the list giving the order of decreasing ability to labilise the second chloride ligand can be expanded to read $Cl^- > N_3^- > I^- > Br^- \gg NCS^-$, regardless of the geometry of the complex.

EXPERIMENTAL

^1H n.m.r. spectra were recorded on a Perkin-Elmer R 10 spectrometer at 60 MHz and on a JEOL PS 100 spectrometer at 100 MHz. I.r. spectra were measured as Nujol mulls on Perkin-Elmer 457 and 225 grating spectrometers and *X*-ray powder photographs were obtained using a Phillips Debye–Scherrer powder camera, type PW 1024/10. C.d. measurements were made on a Roussel–Jouan Dichrographe model 1B, with a sensitivity of $1{\cdot}5 \times 10^{-4}$ mm^{-1}. O.r.d. spectra were recorded on a Bendix–Bellingham Stanley Polarmatic spectropolarimeter. Conductivities were determined on a Phillips PR 9500 conductivity bridge with a dipping cell.

Triethylenetetramine tetrahydrochloride was prepared from 'technical grade' triethylenetetramine by the method of Jonassen and Strickland.[14]

Resolution of Complexes.—Partial resolution of *cis*-α- and *cis*-β-$[Rh(trien)Cl_2]^+$ was achieved using a Sephadex SP-C-25 cation exchange resin in the lithium form. An aqueous solution of the complex (*ca.* 100 mg) was loaded on to a column (2·0 × 30 cm) and eluted with lithium chloride (0·2M) at a flow rate of 40 ml h^{-1}. The first fractions eluted from the column had positive rotations at 365 nm while the latter fractions had negative rotations at 365 nm. Evaporation of an optically active solution of *cis*-α-$[Rh(trien)Cl_2]^+$, caused precipitation of racemic *cis*-α-$[Rh(trien)Cl_2]Cl$. This left a filtrate with enhanced optical activity. Attempts to repeat this enhancement procedure with optically active *cis*-β-$[Rh(trien)Cl_2]^+$ were unsuccessful.

Preparation of Complexes.—cis-α-*Dichlorotriethylenetetraminerhodium*(III) *chloride dihydrate,* cis-α-$[Rh(trien)Cl_2]Cl,2H_2O$. The method used is essentially that used by Basolo and Johnson,[3] but we do find that pH control is essential.

Rhodium trichloride trihydrate (1·0 g) was dissolved in warm water (20 ml) and treated with a solution of triethylenetetramine tetrahydrochloride (4 ml of a 0·5M solution). This mixture was refluxed for 30 min, when more sodium hydroxide (3 ml of a 0·5M solution) was added dropwise to the boiling solution over 30 min. Further sodium hydroxide was then added to the boiling solution until the pH had settled at 8. The boiling was continued for an additional 20 min, and the solution was then cooled in an ice bath. After several hours, the yellow precipitate was collected by filtration and washed with cold water, ethanol, and acetone, and air dried. Yield 0·25 g.

cis-β-*Dichlorotriethylenetetraminerhodium*(III) *chloride dihydrate,* cis-β-$[Rh(trien)Cl_2]Cl,2H_2O$. The mother liquor from the above preparation, kept at 0° overnight, deposited a pale yellow solid which was removed. Concentration of the filtrate to *ca.* 5 ml gave more solid. These two crops were combined and recrystallised twice from aqueous sodium hydroxide solution (pH 8) to give the *cis*-β-isomer; yield 0·1 g.

The pure *cis*-complexes, once separated from the reaction solution, are stable in acidic solution. The reaction solution, however, often deposits a very finely divided yellow solid if it remains under acidic conditions. This yellow solid is quite insoluble in water, and is as yet uncharacterised, but its presence can make crystallisation of the pure *cis*-isomer of $[Rh(trien)Cl_2]^+$ difficult.

trans-*Dichlorotriethylenetetraminerhodium*(III) *perchlorate,* trans-$[Rh(trien)Cl_2]ClO_4$. The mother liquor after isolation of *cis*-β-$[Rh(trien)Cl_2]^+$ was evaporated to *ca.* 2 ml. Any further precipitate was removed and the filtrate was acidified (pH 1) by addition of dilute HCl. One drop of concentrated perchloric acid was then added and, after standing for several days at 5°, yellow crystals were deposited which were recrystallised from water to give the *trans*-isomer (0·01 g).

A slightly higher yield was obtained as follows. The mother liquor after isolation of *cis*-α-$[Rh(trien)Cl_2]^+$ was evaporated nearly to dryness. The yellow solid was removed by filtration and the syrupy orange-brown filtrate was discarded. The yellow solid was dissolved in water (10 ml) and the pH adjusted to *ca.* 7 by the addition of dilute HCl. This solution was put on a Sephadex G.10

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[14] H. B. Jonassen and G. T. Strickland, *J. Amer. Chem. Soc.*, 1958, **80**, 312.

chromatographic column (2·0 × 30 cm), and elution with water led to a partial separation of the initial yellow band into orange and yellow bands. The orange material is uncharacterised, but the yellow material was collected, and the solution evaporated to *ca.* 2 ml and treated with concentrated perchloric acid (0·1 ml). After standing for several days at 5°, yellow crystals were deposited which were collected and recrystallised from water to give the pure *trans*-isomer (yield 0·05 g).

cis-α-*Dibromotriethylenetetraminerhodium*(III) *bromide trihydrate*, cis-α-$[Rh(trien)Br_2]Br,3H_2O$. The procedure used for the preparation of *cis*-α-$[Rh(trien)Cl_2]Cl$ was used, with rhodium tribromide and triethylenetetramine tetrahydrobromide used as starting materials. The first isolated product had an electronic spectrum ($\lambda_{max.}$ 366 nm, ε 306, shoulder 280 nm, ε 1330) similar to that observed after bromide substitution of *cis*-α-$[Rh(trien)Cl_2]^+$. (Found: C, 13·3; H, 3·5; N, 10·3. $C_6H_{24}Br_3N_4O_3Rh$ requires C, 13·3; H, 4·4; N, 10·3%).* A more convenient synthesis of $[Rh(trien)Br_2]Br$ involves bromide anation of $[Rh(trien)Cl_2]Cl$; see preparation of $[Rh(trien)(N_3)_2]N_3$ for experimental details.

cis-α-*Diazidotriethylenetetraminerhodium*(III) *azide*, cis-α-$[Rh(trien)(N_3)_2]N_3$. *Cis*-α-$[Rh(trien)Cl_2]Cl,H_2O$ (0·19 g, 0·5 mmol) and sodium azide (1·6 g, 25 mmol) were dissolved in water (25 ml). The solution was heated for 6 h on a steam bath, and then kept in the refrigerator for a week. The large orange crystals which formed were separated by filtration, washed with cold water, ethanol, and air dried. It was recrystallised from warm water (Found: C, 19·2; H, 4·9; N, 48·1. $C_6H_{18}N_{13}Rh$ requires C, 19·2; H, 4·8; N, 48·5%). The electronic spectrum [$\lambda_{max.}$ 335 nm (shoulder), ε = 1130; 257 nm, ε = 12 700] is essentially identical to that observed after azide substitution of *cis*-α-$[Rh(trien)Cl_2]^+$ in the kinetic experiments.

As reported by Johnson and Basolo[3] for *trans*-$[Rh(en)_2(N_3)_2]^+$, the trien complex is stable at room temperature in the dark, but is discoloured by daylight within a few hours.

cis-α-*Di-iodotriethylenetetraminerhodium*(III) *iodide*, cis-α-$[Rh(trien)I_2]I$. *cis*-α-$[Rh(trien)Cl_2]Cl,H_2O$ in aqueous solution was heated with a fifty fold excess of sodium iodide in a procedure analogous to the above preparation. The dark red crystals of $[Rh(trien)I_2]I$ were separated by filtration and recrystallised from water (Found: C, 11·4; H, 3·3; N, 8·8. $C_6H_{18}N_4I_3Rh$ requires C, 11·4; H, 3·2; N, 8·8%). The electronic spectrum ($\lambda_{max.}$ 370 nm, ε 1100; 295 nm, ε 4600) is essentially identical to that observed after iodide anation of *cis*-α-$[Rh(trien)Cl_2]Cl$ in the kinetic experiments.

Chlorothiocyanatotriethylenetetraminerhodium(III) *thiocyanate*, $[Rh(trien)(NCS)Cl]NCS$. An aqueous solution of *cis*-α-$[Rh(trien)Cl_2]Cl$ with a four fold excess of sodium thiocyanate was heated on a steam bath for *ca.* 15 min. The solution was reduced in volume to *ca.* 5 ml, carefully filtered, and cooled in a salt–ice bath for several hours. The yellow solid, which formed, was collected by filtration, washed with ethanol, and dried over phosphorus pentoxide. The i.r. spectrum showed peaks at 2120 and 2050 cm^{-1}, which are attributable to ν(CN) in ionic and *N*-bonded thiocyanate respectively. However, elemental analysis (Found: C, 21·0; H, 4·0; N, 18·5; Cl, 12·6%), is not that required for $[Rh(trien)Cl(NCS)]NCS$ (Calc.: C, 24·0; H, 4·5; N, 21·0; Cl, 8·9%) and suggests the presence of *ca.* 50% $[Rh(trien)Cl_2]NCS$ (Calc.: C, 16·5; H, 4·15; N, 16·1; Cl, 16·3%). However, repeated attempts to purify this product were unsuccessful. Longer reaction times, or an increase in the thiocyanate concentration, gave a pale yellow solution from which a solid could not be isolated. The solution had a broad, featureless, electronic spectrum, with major absorbances centred at 300 and 325 nm. An identical spectrum was produced when an aqueous solution of $[Rh(trien)(NCS)Cl]NCS$ was heated on a steam bath for 30 min, or when a solution of $[Rh(trien)Cl_2]Cl$ was heated with a hundred fold excess of thiocyanate ion (as in the thiocyanate anation kinetic runs). In these cases, a solid product could not be isolated.

Irradiations.—These were carried out by irradiating aqueous solutions thermostatted at *ca.* 20° in silica u.v. cells by means of a 150 W high pressure Bendix xenon lamp which was fitted with a lens so that a narrow beam of light (0·1 cm diameter) passed through the sample. No filters were used. Optically active *cis*-β-$[Rh(trien)Cl_2]^+$ was not treated in this way, for its loss of optical activity was noted during exposure to light while running chiroptical spectra.

Hydrolysis Experiments.—The electronic spectra of *cis*-$[Rh(en)_2Cl_2]Cl$, *cis*-α-, and *cis*-β-$[Rh(trien)Cl_2]Cl$ (*ca.* 5 × 10^{-3}M) in sodium hydroxide solution (0·1N) at room temperature were monitored with time. After 5 min no further change occurred even on heating to 80° for 15 min, and the electronic spectra of the resultant solutions had $\lambda_{max.}$ 327, 277; 326, 275; 323, 280sh nm respectively. The electronic spectra of the hydrolysates of *cis*-$[Rh(trien)Cl_2]^+$ are significantly different (suggesting that hydrolysis occurs without stereochemical change) but $\lambda_{max.}$ values are similar to those of *cis*-$[Rh(en)_2(OH)_2]^+$. As expected, the electronic spectra show reversible changes with pH, due, presumably, to conversion to the diaquo-species in acid. The spectra of the above hydrolysates at pH 1 show $\lambda_{max.}$ at 316, 270sh; 320, 269; 312sh, 276 nm respectively.

Kinetic Studies on cis-α-$[Rh(trien)Cl_2]^+$.—All the reactions were studied by observing absorbance changes in the electronic spectra of the reaction mixture either by scanning the whole spectrum at known time intervals or by continually following absorbance changes at a constant wavelength. The substitutions were monitored by following the increase in absorbance at 280 nm (for Br^- substitution), 380 nm (I^-), and 330 nm (N_3^-). Electronic spectra were recorded on a Unicam SP 800 spectrophotometer fitted with a constant wavelength attachment and a thermostatted cell block capable of holding cells of up to 10 mm path length. It was possible to control the temperature of the cell block to better than ±0·5°. The reaction mixtures were maintained in the thermostatted cells throughout the whole of the reaction. The quoted rate constants are, in all cases, the average of at least three separate determinations and the individual values are all within 5% of the average value shown in Table 2.

Standard solutions of the sodium salts of all the nucleophiles used were prepared from reagent-grade materials and distilled water. The concentration of *cis*-α-$[Rh(trien)Cl_2]^+$ was *ca.* 10^{-3}M for the kinetic runs and the ionic strengths of the solutions were maintained at 0·5M with sodium perchlorate. Slight hydrolysis of the complex occurs on standing for a few days as shown by the accompanying small

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* With such highly hydrated species, it has been found in these laboratories that the loosely held water molecules are volatilised in the preheating stage of analysis, so the hydrogen analysis is consistently lower than the calculated value. Correction for this effect leads to a hydrogen value (calculated) of 3·3%, in good agreement with the 3·5% found.

changes in the electronic spectrum, so the stock solution of the complex was stored at 5 °C but no solution older than one week was used in the kinetic runs. After storing for one week at 5 °C the decrease in the absorbance at 350 nm of a 2×10^{-3}M solution was less than 5% of its original value.

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