N-Methyl-substituted Ethane-1,2-diamine Complexes of Dichlororhodium(III)

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The synthesis and spectroscopic properties of some complexes of the type *trans*-$[RhCl_2(N{-}N')_2]^+$ (N–N' = *N*-methyl-, *NN'*-dimethyl-, *NN*-dimethyl,*NNN'*-trimethyl-, and *NNN'N'*-tetramethyl-ethane-1,2-diamine, men, sdmen, udmen, trimen, and tetmen, respectively) are described and the previously reported route to *trans*-$[RhCl_2(udmen)_2]^+$ is shown to give a *cis*-isomer. The chemical and polarographic-reduction behaviour of the complexes is reported together with a kinetic study of chloride–bromide exchange in *trans*-$[RhCl_2(N{-}N')_2]^+$ (N–N' = men, udmen, trimen, or tetmen). The activation parameters for the reaction of *trans*-$[RhCl_2(tetmen)_2]^+$ with bromide ion have been determined and are discussed in relation to literature data for the analogous reactions of *trans*-$[RhCl_2(en)_2]^+$ and *trans*-$[RhCl_2(NH_3)_4]^+$.

BECAUSE of the unusual reactivity of rhodium(III) complexes of the type *trans*-$[RhL_4X_2]^+$ [L = pyridine (py) or ½ ethane-1,2-diamine (en); X = halide] in the presence of reducing agents,[1] we have extended these studies to analogous complexes containing *N*-methylated ethane-1,2-diamines and now describe their preparation, spectroscopic properties, and reduction behaviour, together with a kinetic study of their chloride–bromide exchange reactions.

RESULTS AND DISCUSSION

Preparation and Spectroscopic Properties of Rhodium(III) Complexes containing N-Methyl-substituted Ethane-1,2-diamines.—Previous work showed that the products resulting from the reaction of rhodium trichloride with excesses of *N*-methylated ethane-1,2-diamines were dependent on the degree of *N*-methylation of the ligand.[2] Thus, whereas en and *N*-methylethane-1,2-diamine (men) give trischelated complexes $[Rh(N{-}N')_3]^{3+}$ (N–N' = en or men), complexes of the type *trans*-$[RhCl_2(N{-}N')_2]^+$ were reported to be formed with the more substituted diamines (N–N' = *NN'*-dimethyl-, *NN*-dimethyl-, *NNN'*-trimethyl-, and *NNN'N'*-tetramethyl-ethane-1,2-diamine, sdmen, udmen, trimen, and tetmen respectively [2]). We have confirmed these results except for the reaction involving udmen, which gave exclusively *cis*-$[RhCl_2(udmen)_2]^+$. Authentic *trans*-$[RhCl_2(udmen)_2]^+$, together with the previously unreported complex *trans*-$[RhCl_2(men)_2]^+$, can be prepared using a procedure similar to that described [3] for the preparation of *trans*-$[RhCl_2(en)_2]^+$, and there is no evidence for the formation of *cis*-isomers under these conditions. It was not possible to convert *trans*-$[RhCl_2(udmen)_2]^+$ into the *cis*-isomer, even *via* the recently described route [4] for the conversion of *trans*-$[RhCl_2(en)_2]^+$ into *cis*-$[RhCl_2(en)_2]^+$, and we have no explanation for the atypical formation of the *cis*-isomer when rhodium trichloride reacts directly with an excess of udmen.

The complexes described above were isolated as chloride or perchlorate salts and their formulations are supported by elemental analysis and by conductivity (Table 1) and spectroscopic measurements (see below). Further confirmation of the formulation *cis*-$[RhCl_2(udmen)_2]^+$ was provided by the partial resolution of the complex (see Experimental section) and by a study of its base hydrolysis. Thus, the electronic spectrum of *cis*-$[RhCl_2(udmen)_2]^+$ in sodium hydroxide solution (0.1 mol dm^{-3}) undergoes a change, from $\lambda_{max.}$ 377 and 312 to 349 and 290 nm, which is essentially complete within 15 min at 25 °C and which is consistent with the formation of *cis*-$[Rh(udmen)_2(OH)_2]^+$. However, a solution of *trans*-$[RhCl_2(udmen)_2]^+$ under the same conditions exhibited no change in electronic spectrum within 15 min. This differing behaviour of the two isomers towards base hydrolysis is thus very similar to that of *cis*- and *trans*-$[RhCl_2(en)_2]^+$.[5]

The electronic spectra of the complexes described above are in Table 2, together with those of *cis*- and *trans*-$[RhCl_2(en_2)]^+$ and some butane-2,3-diamine analogues. Inspection of Table 2 shows that the electronic spectrum of *cis*-$[RhCl_2(udmen)_2]^+$ is not consistent with the *trans*-configuration proposed previously,[2] whereas the electronic spectrum of authentic *trans*-$[RhCl_2(udmen)_2]^+$ is clearly in keeping with the shift to lower energy of the ligand-field bands which is observed on progressive *N*-methylation of *trans*-$[RhCl_2(en)_2]^+$. The decrease in ligand-field strength with increasing methylation is much more pronounced for the *N*-substituted than for the *C*-substituted ethane-1,2-diamines, and space-filling molecular models suggest that this is due to greater steric overcrowding and non-bonded interaction of the methyl substituents with the chloride ligands produced on *N*- as opposed to *C*-methylation of *trans*-$[RhCl_2(en)_2]^+$. The same trend was observed [6] for the ligands en, men, sdmen, and udmen in a series of complexes of the type $[Ni(N{-}N')_3]^{2+}$, and tetmen exhibited a low ligand-field strength in some square-planar palladium(II) complexes.[7] The particularly low ligand-field strength observed in the present work for the fully *N*-methylated ligand, tetmen, is probably attributable to a combination of its relatively low σ-donor strength (pK_{a1} 9.28) [8] and the steric overcrowding in *trans*-$[RhCl_2(tetmen)_2]^+$. That the Rh–N

[1] R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc.* (*A*), 1971, 1840 and refs. therein.
[2] G. W. Watt and P. W. Alexander, *J. Amer. Chem. Soc.*, 1967, **89**, 1814.
[3] S. A. Johnson and F. Basolo, *Inorg. Chem.*, 1962, **1**, 925.
[4] A. W. Addison, R. D. Gillard, P. S. Sheridan, and L. R. H. Tipping, *J.C.S. Dalton*, 1974, 709.
[5] S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 1741.
[6] S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, 1965, **4**, 20.
[7] D. W. Meek, *Inorg. Chem.*, 1965, **4**, 250.
[8] P. Paoletti, R. Barbucci, A. Vacca, and A. Dei, *J. Chem. Soc.* (*A*), 1971, 310.

TABLE 1

Analytical and conductivity data for complexes of the type $[RhCl_2(N{-}N')_2]X$ (X = ClO_4 or Cl)

Complex	Found (%) C	H	N	Calc. (%) C	H	N	Λ * / S cm² mol⁻¹
trans-$[RhCl_2(men)_2][ClO_4]$	17.4	4.6	13.6	17.1	4.8	13.3	85
trans-$[RhCl_2(sdmen)_2]Cl{\cdot}0.5H_2O$	24.3	6.4	14.3	24.3	6.4	14.2	96
trans-$[RhCl_2(sdmen)_2][ClO_4]$	21.3	5.5	12.4	21.4	5.4	12.5	
trans-$[RhCl_2(udmen)_2][ClO_4]$	21.3	5.5	12.4	21.4	5.4	12.5	79
cis-$[RhCl_2(udmen)_2][ClO_4]$	21.6	5.7	12.6	21.4	5.4	12.5	88
trans-$[RhCl_2(trimen)_2][ClO_4]$	25.1	6.4	11.9	25.1	5.9	11.7	80
trans-$[RhCl_2(tetmen)_2][ClO_4]$	28.2	6.5	11.1	28.5	6.4	11.1	82
trans-$[RhCl_2(tetmen)_2]Cl{\cdot}2H_2O$	30.5	7.4	11.8	30.1	7.6	11.7	

* Conductivity of 10^{-3} mol dm^{-3} aqueous solutions at 25 °C.

TABLE 2

Electronic spectra of rhodium(III) complexes of *C*- and *N*-methylated ethane-1,2-diamine (in water)

Complex	$\lambda_{max.}$/nm	$10^{-3}\bar{\nu}_{max.}/cm^{-1}$	$\varepsilon_{max.}/dm^3\ mol^{-1}\ cm^{-1}$	Ref.
trans-$[RhCl_2(en)_2]^+$	406, 286	24.6, 35.0	75, 130	3
trans-$[RhCl_2(rbd)_2]^+$ [a]	405, 283 (sh)	24.7, 35.3	75, 120	3
trans-$[RhCl_2(mbd)_2]^+$ [b]	409, 290 (sh)	24.4, 34.5	75, 120	3
trans-$[RhCl_2(dmbd)_2]^+$	412	24.3	75	3
trans-$[RhCl_2(men)_2][ClO_4]$	413, 293	24.2, 34.1	81, 149	*c*
trans-$[RhCl_2(sdmen)_2]Cl{\cdot}0.5H_2O$	419, 300	23.9, 33.3	72, 162	*c*
trans-$[RhCl_2(sdmen)_2]Cl$	418, 300	23.9, 33.3	72, 171	2
trans-$[RhCl_2(udmen)_2][ClO_4]$	434, 315	23.0, 31.7	87, 120	*c*
cis-$[RhCl_2(udmen)_2][ClO_4]$	377, 313	26.5, 31.9	246, 181	*c*
cis-$[RhCl_2(udmen)_2]I$ [d]	377, 312	26.5, 32.0	260, 200	2
cis-$[RhCl_2(en)_2]^+$	352, 295	28.4, 33.9	155, 180	3
trans-$[RhCl_2(trimen)_2][ClO_4]$	444, *ca.* 348 (sh), 322	22.5, 28.7, 31.0	112, 114, 198	*c*
trans-$[RhCl_2(trimen)_2]Cl$	444, 322	22.5, 31.0	102, 150	2
trans-$[RhCl_2(tetmen)_2][ClO_4]$	467, 363, 335	21.4, 27.5, 29.9	61, 134, 134	*c*
trans-$[RhCl_2(tetmen)_2]Cl{\cdot}2H_2O$	467, 364, 334	21.4, 27.5, 29.9	51, 113, 107	*c*
trans-$[RhCl_2(tetmen)_2]Cl$	460, 259, 330 (sh)	21.7, 27.9, 30.3	63, 157, 172	2

[a] rbd = *rac*-Butane-2,3-diamine. [b] mbd = *meso*-Butane-2,3-diamine. [c] This work. [d] Previously described as *trans*.[2]

bonds in *trans*-$[RhCl_2(tetmen)_2]^+$ are not very strong is indicated by the fact that when an aqueous solution of the complex is heated under reflux with an excess of pyridine, the bidentate tetmen is readily displaced by the unidentate py to give *trans*-$[RhCl_2(py)_4]^+$. The analogous reaction with *trans*-$[RhCl_2(en)_2]^+$ does not occur.

A correlation with the extent of *N*-methylation of the N–N′ ligands may also be made for the symmetric Rh–Cl stretching mode of *trans*-$[RhCl_2(N{-}N')_2]X$ (X = NO_3, Cl, or ClO_4), which is readily identified as a strong sharp band in the Raman spectrum of the crystalline salt. Thus, increasing *N*-methylation is associated with a progressive decrease in ν(Rh–Cl) (Table 3).

TABLE 3

Symmetric rhodium–chlorine stretching frequencies and polarographic half-wave potentials for complexes of the type *trans*-$[RhCl_2(N{-}N')_2]X$

N–N′	X	$\bar{\nu}$(Rh–Cl)/ cm^{-1}	$-E_{\frac{1}{2}}$/V *versus* s.c.e.
en	NO_3	309	0.70 [a]
en	ClO_4	305 [b]	
men	ClO_4	303	0.58
sdmen	Cl	301	0.54
udmen	ClO_4	297	0.47
trimen	ClO_4	290	0.49 [a]
tetmen	Cl	283	0.34 [a]

[a] Refs. 10 and 13. [b] C. Burgess, F. R. Hartley, and D. E. Rogers, *Inorg. Chim. Acta*, 1975, **13**, 35.

The complexes *trans*-$[RhCl_2(N{-}N')_2]^+$ (N–N′ = men, udmen, or trimen) can, in principle, exist as *trans,trans*- and *trans,cis*-isomers. However, steric considerations suggest that the *trans,trans*-isomers should be preferred, and a previous study [9] of the isomers formed in the synthesis of *trans*-$[Co(men)_2(NO_2)_2]^+$ showed that, under a variety of conditions, only *trans,trans*-isomers were obtained. Additionally, the asymmetry of the co-ordinated secondary nitrogen atoms in *trans*-$[RhCl_2(N{-}N')_2]^+$ (N–N′ = men, sdmen, or trimen) gives rise to the possibility of *meso*- and *rac*-isomers. In an attempt to gain some insight into which isomers are formed under the preparative conditions employed here, we recorded the ^1H n.m.r. spectra of the complexes in D_2O solution (Table 4). Only for *trans*-$[RhCl_2(men)_2]^+$ is there evidence for the presence of more than one isomer, the ^1H n.m.r. spectrum exhibiting two methyl resonances (at τ 7.31 and 7.35, and of intensity ratio *ca.* 1 : 2) which appeared as sharp doublets in acid solution [$^3J(HNCH_3)$ 6 Hz] and collapsed to sharp singlets in alkaline solution. From the above discussion, together with the observation [9] that the methyl resonances of pure *meso*- and (±)-*trans,trans*-$[CoCl_2(men)_2]^+$ in D_2O solution occur at τ 7.60 and 7.63, respectively, we conclude that the pH-controlled synthesis of *trans*-$[RhCl_2(men)_2]^+$ used in this work yields a mixture of *meso*- and (±)-*trans,trans*-isomers and it is these isomers which give rise to the ^1H n.m.r. signals at τ 7.31 and 7.35, respectively.

The ^1H n.m.r. spectrum of *cis*-$[RhCl_2(udmen)_2]^+$ clearly tends to exclude structure (I) which possesses four inequivalent methyl groups, and, since (II) should be the

[9] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 1968, **7**, 915.

sterically less favoured of the two remaining possible isomers, the two sharp methyl resonances observed are tentatively assigned to the two inequivalent pairs of

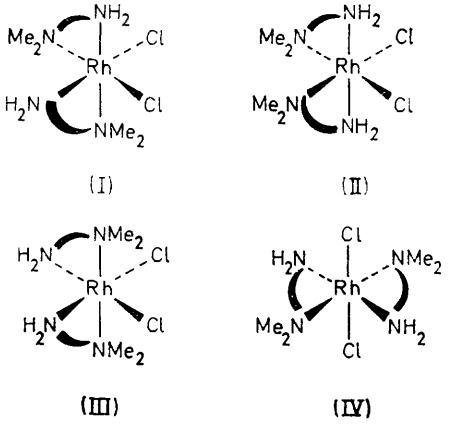
TABLE 4

Methyl resonances in the ^{1}H n.m.r. spectra [a] of rhodium(III) complexes of *N*-methylated ethane-1,2-diamines in D_2O solution

Complex	pD	τ(CH$_3$) [b]	^3J(HNCH$_3$)/ Hz
trans-[RhCl$_2$(men)$_2$]$^+$	*ca.* 3.5	7.35 (d) (2)	6
		7.31 (d) (1)	6
	ca. 12	7.35 (s) (2),	
		7.31 (s) (1)	
trans-[RhCl$_2$(sdmen)$_2$]$^+$	*ca.* 4	7.39 (d)	6
	ca. 12	7.39 (s)	
trans-[RhCl$_2$(udmen)$_2$]$^+$	*ca.* 6	7.19 (5)	
cis-[RhCl$_2$(udmen)$_2$]$^+$	*ca.* 6	7.39 (s) (1),	
		7.14 (s) (1)	
trans-[RhCl$_2$(trimen)$_2$]$^+$	*ca.* 4	7.40 (d) (3),	6
		7.25 (s) (3),	
		7.09 (s) (3)	
	ca. 12	7.40 (s) (3),	
		7.25 (s) (3),	
		7.09 (s) (3)	
trans-[RhCl$_2$(tetmen)$_2$]$^+$	*ca.* 6	7.27 (s)	

[a] 100-MHz Data except for those of the trimen and tetmen complexes which are at 60 MHz. [b] d = Doublet, and s = singlet; figures in parentheses are relative intensities.

methyl groups in (III). Similarly, the presence of only one methyl resonance in the ^{1}H n.m.r. spectrum of *trans*-[RhCl$_2$(udmen)$_2$]$^+$ is consistent with the presence of only one isomer, presumably the sterically more favoured



trans,trans-isomer, (IV). The ^{1}H n.m.r. spectra of *trans*-[RhCl$_2$(N–N′)$_2$]$^+$ (N–N′ = sdmen or trimen) are consistent with the *trans*-configuration but give no additional information regarding stereochemistry.

Polarographic and Chemical Reduction of trans-[RhCl$_2$(N–N′)$_2$]$^+$ (N–N′ = N-*methylated en*).—The complexes *trans*-[RhX$_2$(py)$_4$]$^+$ (X = Cl or Br) undergo halide exchange which is accelerated by mild reducing agents such as primary and secondary alcohols, whereas acceleration of halide exchange in *trans*-[RhX$_2$(en)$_2$]$^+$ requires the presence of much stronger reducing agents.[1] This difference in behaviour has been discussed in relation to the polarographic half-wave potentials, $E_{\frac{1}{2}}$, for the complexes.[10] Thus, *trans*-[RhX$_2$(py)$_4$]$^+$ has a more positive $E_{\frac{1}{2}}$ than *trans*-[RhX$_2$(en)$_2$]$^+$ (X = Cl or Br) and is presumably, therefore, more easily reduced to the active rhodium(I) species which is believed to catalyse halide exchange in the rhodium(III) complex.[1] However, because of equilibrium (1), the concentration of the

$$Rh^{I} + H_2O \rightleftharpoons Rh^{III}\text{–}H + OH^- \qquad (1)$$

rhodium(I) species is dependent on pH. Thus, in the bis(ethylenediamine) system the formation of [Rh(en)$_2$]$^+$ is definitely incomplete at pH 13,[11] whereas with the tetrakis(pyridine) system the above equilibrium appears to lie essentially completely in favour of [Rh(py)$_4$]$^+$ at pH 4, although py dissociation tends to occur in the latter case.[12] Since $E_{\frac{1}{2}}$ for *trans*-[RhCl$_2$(tetmen)$_2$]$^+$ is intermediate between those of *trans*-[RhCl$_2$(en)$_2$]$^+$ and *trans*-[RhCl$_2$(py)$_4$]$^+$,[10,13] it seemed possible that halide substitution in *trans*-[RhCl$_2$(tetmen)$_2$]$^+$ might be accelerated by ethanol and that the formation of [Rh(tetmen)$_2$]$^+$ *via* equilibrium (1) would be essentially complete at a readily accessible pH, thereby making the isolation of the latter feasible. Because of this we have investigated the chemical reduction of *trans*-[RhCl$_2$(tetmen)$_2$]$^+$ in water and ethanol, and the chloride–bromide exchange of the latter, in the presence and absence of reducing agents, is described in the next section. The previously unreported $E_{\frac{1}{2}}$ values for *trans*-[RhCl$_2$(N–N′)$_2$]$^+$ (N–N′ = men, sdmen, or udmen) are also given together with related $E_{\frac{1}{2}}$ values in Table 3. As found previously,[14] there is a shift of $E_{\frac{1}{2}}$ to more positive values as the first *d–d* singlet–singlet transition ($^1A_{1g} \rightarrow {}^1T_{1g}$) moves to lower energy.

Previous work [11] has shown that electrochemical reduction of *trans*-[RhCl$_2$(en)$_2$]$^+$ in aqueous solution at 25 °C gives *trans*-[RhH(en)$_2$(OH)]$^+$, whereas reduction of the former with sodium tetrahydroborate in aqueous solution at 0 °C has been reported [15] to give initially *trans*-[RhCl(H)(en)$_2$]$^+$. We find that reduction of *trans*-[RhCl$_2$(tetmen)$_2$]$^+$ with Na[BH$_4$] in aqueous solution at 25 °C under anaerobic conditions results in formation of *trans*-[RhH(tetmen)$_2$X]$^{n+}$ (X = OH, n = 1; X = H_2O, n = 2), where X varies with the pH of the solution. Thus, *trans*-[RhH(tetmen)$_2$(OH$_2$)][BPh$_4$]$_2$·3H$_2$O could be precipitated in good yield from solutions of pH 6. The spectroscopic properties of this and related hydridorhodium(III) complexes are in Table 5. The apparent difference in the nature of the products resulting on Na[BH$_4$] reduction of *trans*-[RhCl$_2$(N–N′)$_2$]$^+$ (N–N′ = en or tetmen) in aqueous solution is probably simply a result of the different reaction temperatures employed (0 °C for en, 25 °C for tetmen), since we have found that

[10] A. W. Addison, R. D. Gillard, and D. H. Vaughan, *J.C.S. Dalton*, 1973, 1187.
[11] R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc.* (*A*), 1970, 3126.
[12] H. Shaw, Ph.D. Thesis, University of Kent at Canterbury, 1971.
[13] M. P. Hancock, Ph.D. Thesis, University of Kent at Canterbury, 1972.
[14] A. A. Vlček, *Discuss. Faraday Soc.*, 1958, **26**, 164; D. R. Crow, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 291.
[15] J. A. Osborn, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 1964, 3168.

$Na[BH_4]$ reduction of *trans*-$[RhCl_2(en)_2]^+$ and *trans*-$[RhCl_2(NH_3)_4]^+$ in anaerobic aqueous solution at 25 °C gives products with very similar spectroscopic properties to those reported for *trans*-$[RhH(en)_2(OH)]^+$ [11] and *trans*-$[RhH(NH_3)_4(OH_2)]^{2+}$,[16] respectively (Table 5). This

TABLE 5

Infrared Rh–H stretching frequencies and high-field ^1H n.m.r. doublet positions for some rhodium(III) hydride complexes

Complex	τ	^1J(Rh–H)/ Hz	$\bar{\nu}$(Rh–H) [a]/ cm^{-1}
trans-$[RhCl(H)(tetmen)_2]^+$	28.9 [b]	13	2 158
trans-$[RhCl(H)(en)_2]^+$			2 100 [c]
trans-$[RhCl(H)(py)_4]^+$	24.7 [b]	21	2 160 [d]
trans-$[RhH(tetmen)_2(OH_2)]^{2+}$	31.6 [e]	17	2 166
trans-$[RhH(en)_2(OH_2)]^{2+}$	32.2 [e]	30 [f]	
trans-$[RhH(en)_2(OH)]^+$	30.6 [e]	30	2 058 [g]
trans-$[RhH(NH_3)_4(OH_2)]^{2+}$	32.0 [e]	25	2 146 [h]

[a] Infrared spectra measured as Nujol mulls. [b] In ethanol. [c] $[BPh_4]^-$ Salt, ref. 15. [d] $[ClO_4]^-$ Salt, ref. 12. [e] In aqueous solution. [f] Ref. 16. [g] $[BPh_4]^-$ Salt, ref. 11. [h] $[SO_4]^{2-}$ Salt, ref. 17.

lability of chloride *trans* to hydride is to be expected [17] and we have shown that dissolution of *trans*-$[RhCl(H)(tetmen)_2][PF_6]$ {which can be isolated following $Na[BH_4]$ reduction of an ethanolic solution of *trans*-$[RhCl_2(tetmen)_2]^+$} in water results in rapid aquation and the formation of *trans*-$[RhH(tetmen)_2(OH_2)]^{2+}$.

There is a dramatic change in the electronic spectrum of an aqueous solution of *trans*-$[RhH(tetmen)_2(OH_2)]^{2+}$ [$\lambda_{max.}$ 330 and 274(sh) nm, $\varepsilon_{max.}$ *ca.* 500 and *ca.* 420 dm^3 mol^{-1} cm^{-1}] as the pH is increased to *ca.* 9.5 by addition of anaerobic sodium hydroxide solution. This change, which is attributed to the formation of $[Rh(tetmen)_2]^+$ [equation (1)], is complete at pH *ca.* 10 and the final spectrum consists of two bands of much higher intensity [$\lambda_{max.}$ 298(sh) and 274 nm, $\varepsilon_{max.}$ *ca.* 1.7×10^3 and *ca.* 2.2×10^3 dm^3 mol^{-1} cm^{-1}]. Addition of anaerobic aqueous HCl to give pH 6 reverses this change and the whole process is repeatedly reversible. However, attempts to isolate the species present in basic solution were unsuccessful.

Kinetics of Replacement of Chloride by Bromide in trans-$[RhCl_2(N\text{–}N')_2]^+$.—For the reactions (2) (N–N′ = men,

$$trans\text{-}[RhCl_2(N\text{–}N')_2]^+ + 2Br^- \longrightarrow trans\text{-}[RhBr_2(N\text{–}N')_2]^+ + 2\,Cl^- \quad (2)$$

udmen, trimen, or tetmen) in aqueous solution no intermediate mixed complexes were observed and there was no evidence of *trans* ⟶ *cis* isomerisation. The rate law was established only for complexes with men or tetmen, where the rate was independent of the bromide concentration (Table 6). This observation is in accord with the results obtained in studies of other *trans*-tetraaminedichlororhodium(III) complexes [5,18,19] which undergo rate-determining replacement of the first chloride ligand by water followed by relatively rapid anation; the replacement of the second chloride ligand is thought to occur by a similar mechanism but at a higher rate than replacement of the first.

The relative rates of chloride replacement by bromide in *trans*-$[RhCl_2(N\text{–}N')_2]^+$ as a function of N–N′ are, at 80 °C, tetmen ⋙ en > udmen > trimen > men (Table 6). Activation parameters, which are available only for the first two members of the series, show that the reaction involving tetmen has a slightly higher enthalpy of activation but a distinctly more positive entropy of activation than that for en (Table 7). Space-filling

TABLE 6

Kinetic data for the reaction *trans*-$[RhCl_2(N\text{–}N')_2]^+ + 2Br^- \longrightarrow$ *trans*-$[RhBr_2(N\text{–}N')_2]^+ + 2Cl^-$ (N–N′ = en or *N*-methylated en). I = 0.2 mol dm^{-3} with $Na[ClO_4]$ and [Rh] = 10^{-3} mol dm^{-3}; aqueous solution unless stated otherwise

N–N′	θ_c/°C	[Br$^-$]/mol dm^{-3}	10^5k/s^{-1}
men	80	0.2	0.67
		0.1	0.74
		0.05	0.71
tetmen	61	0.2	6.63, 6.52, 6.58, 6.55
		0.1	6.57
		0.05	6.55
	64.5	0.2	9.9
	64.5	0.2	3.3 [a]
	73	0.2	27.3, 26.8
		0.1	27.0
		0.05	26.7
	82	0.2	60.6, 66.3, 63.6
		0.1	66.6
		0.05	65.1
en	80	0.2	4.20 [b]
men	80	0.2	0.67
udmen	80	0.2	2.5
trimen	80	0.2	1.21
tetmen	80	0.2	56.0 [c]

[a] In aqueous ethanol (9 : 1). [b] Ref. 18. [c] Calculated from data at 61, 73, and 82 °C.

TABLE 7

Activation parameters [a] for the reaction *trans*-$[RhCl_2(N\text{–}N')_2]^+ + 2Br^- \longrightarrow$ *trans*-$[RhBr_2(N\text{–}N')_2]^+ + 2Cl^-$ at 80 °C in aqueous solution

N–N′	$\Delta H^\ddagger$/kcal mol^{-1}	$\Delta S^\ddagger$/cal K^{-1} mol^{-1}
$2NH_3$ [b]	24.11 ± 0.39	−9.2 ± 1.1
en [b]	24.81 ± 0.56	−8.7 ± 1.6
tetmen [c]	25.4 ± 0.7	−1.92 ± 2.1

[a] Uncertainties are standard deviations; 1 cal = 4.184 J. [b] Ref. 19. [c] This work.

models indicate that the chloride ligands in *trans*-$[RhCl_2(tetmen)_2]^+$ are tightly surrounded by methyl groups, thus tending to rule out an associative (S_N2) mechanism. A dissociative mechanism, when N–N′ = tetmen, would be expected to result in high relief of steric strain accompanied by a low gain in solvation energy on formation of the highly alkylated intermediate, whereas the reverse should prevail when N–N′ = en. Another factor of possible importance in determining the activation parameters is the loss of ligand-field stabilisation energy (l.f.s.e.). Poë and Twigg [19] argued that the latter

[16] K. Thomas and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 356.
[17] K. Thomas, J. A. Osborn, A. R. Powell, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 1801.
[18] H. L. Bott, E. J. Bounsall, and A. J. Poë, *J. Chem. Soc.* (*A*), 1966, 1275.
[19] A. J. Poë and M. V. Twigg, *Canad. J. Chem.*, 1972, **50**, 1089.

is unimportant compared with solvation effects for chloride replacement in *trans*-$[RhCl_2(en)_2]^+$ and *trans*-$[RhCl_2(NH_3)_4]^+$, which have similar ligand-field splittings ($^1A_{1g} \rightarrow {}^1T_{1g}$ occurs at 24 600 [3] and 24 100 cm^{-1},[19] respectively). However, for tetmen a greater difference in loss of l.f.s.e., relative to en, is involved {$^1A_{1g} \rightarrow {}^1T_{1g}$ for *trans*-$[RhCl_2(tetmen)_2]^+$ occurs at 21 400 cm^{-1}} and probably needs to be considered. Thus, although there should be a smaller gain in solvation energy on forming the activated state when N–N′ = tetmen rather than en, there should be a considerably smaller loss of l.f.s.e. in the former case. This is possibly why the enthalpy of activation for *trans*-$[RhCl_2(tetmen)_2]^+$ is not very much greater than that for *trans*-$[RhCl_2(en)_2]^+$. Similarly, the more positive entropy of activation for the reaction of the former complex is in keeping with the dissociative relief of steric rigidity and lesser solvation expected in the formation of the activated state.

No evidence has been obtained for rhodium(I) catalysis in the reaction of *trans*-$[RhCl_2(tetmen)_2]^+$ with bromide. Thus, none of the kinetic runs in aqueous solution showed an induction period, and the prediction, based on a consideration of half-wave potentials, that this reaction should be accelerated by ethanol [10] has not been fulfilled (Table 6). Similarly, addition of $Na[BH_4]$ (0.03 equiv.) to an anaerobic aqueous solution containing *trans*-$[RhCl_2(tetmen)_2]^+$ (1 equiv.) and a large excess of sodium bromide did not result in any chloride–bromide exchange, whereas *trans*-$[RhCl_2(en)_2]^+$ reacts rapidly under the same conditions to give *trans*-$[RhBr_2(en)_2]^+$.[20] It therefore seems probable that the potential catalyst in the tetmen system, $[Rh(tetmen)_2]^+$, is unable to catalyse halide exchange in *trans*-$[RhCl_2(tetmen)_2]^+$ because the steric bulk of the methyl groups around the metal centre hinders formation of the bridged intermediate, Rh^{I}–Cl–Rh^{III}–Cl. Support for this conclusion comes from a study [21] of the reaction of halides with *trans*-$[PtCl_2(en)(tetmen)]^{2+}$ in the presence of added $[Pt(en)(tetmen)]^{2+}$ and from a similar study [22] on *trans*-$[PtCl_2(dmbd)_2]^{2+}$ (dmbd = 1,4-dimethylbutane-2,3-diamine), in which steric inhibition of the normal platinum(II)-catalysed substitution mechanism [23] was observed in each case.

EXPERIMENTAL

Materials.—Rhodium trichloride trihydrate was obtained from Johnson, Matthey Ltd. The *N*-methyl-substituted ethane-1,2-diamine ligands used were the highest purity grades obtainable from B.D.H. or Koch–Light Ltd. *N*-Methylethane-1,2-diamine dihydrochloride and *NN*-dimethylethane-1,2-diamine dihydrochloride were prepared by titrating aqueous solutions of the free diamines with 4 mol dm^{-3} HCl. After evaporating the resulting solutions to dryness, the products were recrystallised from aqueous ethanol and dried *in vacuo*. The complex *trans*-$[RhCl_2(NH_3)_4]Cl$ was prepared by the method of Poë and Twigg [19] and recrystallised from hot water containing a little concentrated HCl. Samples of *trans*-$[RhCl_2(en)_2]X$ (X = NO_3 or Cl) and *trans*-$[RhCl_2(py)_4][ClO_4]$ were kindly provided by Drs. P. S. Sheridan and P. M. Gidney, respectively. Reagent grade $Na[BH_4]$ was recrystallised from diglyme before use. All other chemicals were of reagent grade and were used without further purification.

Instrumentation.—Raman spectra of crystalline samples, in glass capillary tubes, were recorded using a Coderg Raman spectrophotometer with an O.I.P. 181B helium–neon continuous laser as source. Polarography was made with a Radiometer POLARITER PO4 two-electrode polarograph fitted with an adjustable mercury drop-life timer operating at 1.54 drop s^{-1} and using a mercury column height of 50 cm. Other spectroscopic and conductivity measurements were made using instruments described previously.[24] Elemental microanalyses were by the University of Kent microanalytical laboratory, using standard procedures.

Preparation of Complexes.—trans-*Dichlorobis*(N-*methylethane*-1,2-*diamine*)*rhodium*(III) *perchlorate and* trans-*dichlorobis*(NN-*dimethylethane*-1,2-*diamine*)*rhodium*(III) *perchlorate*, *trans*-$[RhCl_2(men)_2][ClO_4]$ *and trans*-$[RhCl_2(udmen)_2][ClO_4]$. These complexes were prepared using a procedure similar to that described [3] for the synthesis of *trans*-$[RhCl_2(en)_2]^+$. Rhodium trichloride trihydrate (1.06 g, 4 mmol) and the appropriate *N*-methyl-substituted ethane-1,2-diamine dihydrochloride (8 mmol) were dissolved in water (40 cm^3). Sodium hydroxide solution (8 cm^3, 1 mol dm^{-3}) was added to the agitated solution, whereupon a red-brown precipitate was formed. The mixture was then heated under reflux, giving a clear cherry-red solution. Aliquot portions of 1 mol dm^{-3} NaOH (*ca.* 1 cm^3) were added to the boiling solution at *ca.* 2 min intervals until the pH of the solution remained steady at *ca.* 7. The golden-yellow solution was filtered while hot, treated with a solution of sodium perchlorate monohydrate (1.4 g) in water (10 cm^3), and concentrated on a rotary evaporator to a volume of 50—60 cm^3. On cooling, the solution deposited a crop of salts which was removed by filtration and discarded. The remaining solution was concentrated further to *ca.* 25 cm^3 and cooled at *ca.* 0 °C, when orange-yellow crystals of the desired complex were obtained. The product was recrystallised twice from hot water and dried *in vacuo*. Yields: for N–N′ = men, 47%; for udmen, 50%. The electronic spectra of the mother liquors showed no evidence for the presence of the *cis*-isomers.

cis-*Dichlorobis*(NN-*dimethylethane*-1,2-*diamine*)*rhodium*-(III) *perchlorate*, *cis*-$[RhCl_2(udmen)_2][ClO_4]$. The crude chloride salt of this complex was prepared by the procedure described by Watt and Alexander [2] for the synthesis of their '*trans*'-isomer. The complex was precipitated from the udmen solvent on addition of diethyl ether, filtered off, and washed with ethanol, and redissolved in a small volume of aqueous ethanol (1 : 1). The perchlorate salt was obtained in good yield by adding an excess of lithium perchlorate in aqueous ethanol (1 : 1) and cooling the solution at 0 °C. The resulting feathery yellow crystals were recrystallised from hot water, washed with ethanol, and dried *in vacuo*, yield 59%. The *cis*-isomer was also obtained when ethanol was added to the udmen–rhodium trichloride mixture and the reaction carried out as before. In neither case was there

[20] A. W. Addison, Ph.D. Thesis, University of Kent at Canterbury, 1970.

[21] A. J. Poë and D. H. Vaughan, *J. Amer. Chem. Soc.*, 1970, **92**, 7537.

[22] F. Basolo, M. L. Morris, and R. G. Pearson, *Discuss. Faraday Soc.*, 1960, **29**, 80; H. R. Ellison, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1961, **83**, 3943.

[23] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, pp. 237—238 and 494—497.

[24] P. M. Gidney, R. D. Gillard, B. T. Heaton, P. S. Sheridan, and D. H. Vaughan, *J.C.S. Dalton*, 1973, 1462.

any spectroscopic evidence for formation of the *trans*-isomer.

trans-*Dichlorobis*(NN′-*dimethylethane*-1,2-*diamine*)*rhodium*(III) *chloride hemihydrate and perchlorate, trans*-$[RhCl_2(sdmen)_2]Cl\cdot 0.5H_2O$ *and trans*-$[RhCl_2(sdmen)_2][ClO_4]$. The chloride hemihydrate was prepared by the method of Watt and Alexander,[2] and was recrystallised from hot aqueous ethanol (1 : 1) and dried *in vacuo*, yield 54%. The perchlorate was obtained in high yield by addition of an excess of $Li[ClO_4]$ to an aqueous ethanol (1 : 1) solution of the chloride salt. The very sparingly soluble yellow solid was isolated by filtration, washed with water and ethanol, and dried *in vacuo*.

trans-*Dichlorobis*(NNN′-*trimethylethane*-1,2-*diamine*)*rhodium*(III) *perchlorate, trans*-$[RhCl_2(trimen)_2][ClO_4]$. The procedure used for the synthesis of this complex is a modification and extension of the method described previously.[3] A mixture of $RhCl_3\cdot 3H_2O$ (0.73 g), trimen (11 cm^3), absolute ethanol (40 cm^3), and diethyl ether (40 cm^3) was heated under gentle reflux with vigorous magnetic stirring for 2.5 h. The orange-yellow solution was filtered while hot and treated with a solution of $Li[ClO_4]$ (0.5 g) in ethanol (10 cm^3), giving a precipitate of the orange perchlorate salt. This was filtered off, washed with ethanol, recrystallised from hot water, and dried *in vacuo*, yield 0.93 g (70%).

trans-*Dichlorobis*(NNN′N′-*tetramethylethane*-1,2-*diamine*)*rhodium*(III) *perchlorate and chloride dihydrate, trans*-$[RhCl_2(tetmen)_2][ClO_4]$ *and trans*-$[RhCl_2(tetmen)_2]Cl\cdot 2H_2O$. The perchlorate salt was synthesised by a slight modification and extension of the previously published [2] route to the chloride. A mixture of finely ground $RhCl_3\cdot 3H_2O$ (1.06 g), tetmen (20 cm^3), absolute ethanol (25 cm^3), and sodium-dried diethyl ether (50 cm^3) was heated under reflux with magnetic stirring for 3 h. The perchlorate salt was precipitated from the warm filtered solution on addition of an excess of $Li[ClO_4]$ dissolved in absolute ethanol. After filtering off and washing with ethanol, the product was recrystallised from hot aqueous ethanol (1 : 9) and dried *in vacuo*, yield 0.98 g (48%).

The chloride salt was obtained by passing an aqueous solution of the perchlorate down a column of Dowex anion-exchange resin in the chloride form. The column was eluted with distilled water and the eluate evaporated to dryness on a rotary evaporator. The resulting orange flakes were dried *in vacuo*.

Preparation of Samples for ^1H *N.m.r. Measurements.*—The chloride salts of *trans*-$[RhCl_2(men)_2]^+$ and *trans*-$[RhCl_2(trimen)_2]^+$, which were required to prepare solutions of sufficiently high concentration for ^1H n.m.r. measurements, were generated by anion exchange of aqueous solutions of the perchlorate salts (*ca.* 0.1 g). The eluates were evaporated to dryness and the solid chloride salts thus obtained were dissolved in D_2O (*ca.* 1 cm^3). Chloride salts were also used for measuring the ^1H n.m.r. spectra of *trans*-$[RhCl_2(sdmen)_2]^+$ and *trans*-$[RhCl_2(tetmen)_2]^+$, whereas the perchlorate salts were used for both the *trans*- and *cis*-isomers of $[RhCl_2(udmen)_2]^+$. Where appropriate (Table 4), D_2O was pre-acidified with drops of 0.01 mol dm^{-3} HCl, and any subsequent basification was achieved with drops of 1 mol dm^{-3} NaOH. Solutions quoted in Table 4 as having pD *ca.* 6 were those obtained by dissolving the pure complexes in D_2O (equilibrated with atmospheric carbon dioxide).

Resolution of cis-$[RhCl_2(udmen)_2]^+$.—A partial resolution of this complex was achieved by cation-exchange chromatography of an aqueous solution of *cis*-$[RhCl_2(udmen)_2][ClO_4]$ on SP Sephadex C-25 resin in the lithium form, using a procedure similar to that described previously.[24a] The first fractions eluted off the column exhibited positive rotations at 328 nm, whilst the last fractions showed negative rotations at 328 nm.

Reaction of trans-$[RhCl_2(tetmen)_2]^+$ *with Pyridine.*—A solution of *trans*-$[RhCl_2(tetmen)_2]Cl\cdot 2H_2O$ (0.04 g) and pyridine (1.5 cm^3) in water (10 cm^3) was heated under reflux for 2 h. The resulting yellow solution was filtered while hot and then treated with a solution of $Na[ClO_4]\cdot H_2O$ (0.5 g) in water (5 cm^3). The solution was boiled briefly (to remove excess of pyridine) and then cooled, giving yellow crystals of *trans*-$[RhCl_2(py)_4][ClO_4]$ which were isolated by filtration, washed with water and ethanol, and dried *in vacuo* (Found: C, 41.9; H, 3.3; N, 9.8. $C_{20}H_{20}Cl_3N_4O_4Rh$ requires C, 40.7; H, 3.4; N, 9.5%). The i.r. spectrum of the complex was identical with that of authentic *trans*-$[RhCl_2(py)_4][ClO_4]$.

trans-*Aquahydridobis*(NNN′N′-*tetramethylethane*-1,2-*diamine*)*rhodium*(III) *Bis*(*tetraphenylborate*) *Trihydrate, trans*-$[RhH(tetmen)_2(OH_2)][BPh_4]_2\cdot 3H_2O$.—All the following manipulations were made under an argon atmosphere. To a stirred solution of *trans*-$[RhCl_2(tetmen)_2][ClO_4]$ (0.25 g) in deoxygenated water at *ca.* 0 °C was added, dropwise, a solution of $Na[BH_4]$ in diglyme ($[BH_4]^-$: Rh = 1 : 1). This solution was then stirred for 30 min at 25 °C and filtered. After acidification of the yellow-brown filtrate with deoxygenated 0.1 mol dm^{-3} HCl to pH *ca.* 6, a deoxygenated aqueous solution (5 cm^3) of $Na[BPh_4]$ (0.3 g) was added. The dense white precipitate of the product which immediately formed was filtered off, washed with deoxygenated water (2 × 10 cm^3), and dried *in vacuo* (Found: C, 68.7; H, 7.5; N, 5.4. $C_{60}H_{81}B_2N_4O_4Rh$ requires C, 68.8; H, 7.8; N, 5.4%). A Lassaigne test for halogen was negative.

trans-*Chlorohydridobis*(NNN′N′-*tetramethylethane*-1,2-*diamine*)*rhodium*(III) *Hexafluorophosphate, trans*-$[RhCl(H)tetmen)_2][PF_6]$.—The complex *trans*-$[RhCl_2(tetmen)_2]Cl\cdot 2H_2O$ (0.25 g, 0.525 mmol) was reduced in deoxygenated ethanol (15 cm^3) with $Na[BH_4]$ using the same procedure as described above. The filtered solution was treated with a freshly prepared saturated solution of hydrogen chloride in ethanol (0.1 cm^3, *ca.* 0.03 mol HCl per mol Rh). The resulting solution was filtered to remove a little precipitated brown solid and to the pale yellow filtrate was added an excess of sodium hexafluorophosphate (0.17 g) in deoxygenated ethanol (10 cm^3). A pale yellow crystalline solid was gradually deposited over *ca.* 2 h and was filtered off under argon, washed with ethanol (2 × 5 cm^3), and dried *in vacuo* (Found: C, 27.7; H, 6.3; Cl, 7.0; N, 10.9. $C_{12}H_{33}ClF_6N_4PRh$ requires C, 27.9; H, 6.4; Cl, 6.8; N, 10.8%). Care should be taken not to add larger quantities of hydrogen chloride to the above reduced solution otherwise an insoluble unidentified brown precipitate is formed.

Polarographic and Kinetic Studies.—These were made essentially as described previously.[1,10,24] The replacement of chloride by bromide in *trans*-$[RhCl_2(N{-}N')_2]^+$ was monitored by following the increase in absorbance at the wavelengths given below:

Complex	Wavelength/nm
trans-$[RhCl_2(men)_2]^+$	295
trans-$[RhCl_2(udmen)_2]^+$	300
trans-$[RhCl_2(trimen)_2]^+$	310
trans-$[RhCl_2(tetmen)_2]^+$	315

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