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The Isolation and Characterization of Halo- and Aquo-Complexes of Rhodium(III) of the Type *Trans*-$[Rh(en)_2XY]^{n+}$

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The preparations of trans-$[Rh(en)_2X_2]ClO_4$ *(X = Cl, Br or I), trans-*$[Rh(en)_2XY]ClO_4$ *(X ≠ Y = Cl, Br or I), trans-*$[Rh(en)_2X(H_2O)](ClO_4)_2$ *(X = F, Cl, Br or I) and trans-*$[Rh(en)_2(H_2O)_2](ClO_4)_3$ *are described. The cis–trans stereochemistries of the complexes are assigned on the basis of infrared and U/V–visible spectra. The U/V–visible spectra are reported and the bands due to the spin-allowed d–d transitions are identified. The infrared and Raman spectra are reported and the rhodium–halogen stretching vibrations assigned.*

Introduction

The kinetics of the substitution reactions of *trans*-$[Rh(en)_2XY]^{n+}$ complexes, where en = ethylenediamine and X and Y are unidentate ligands have been studied previously and shown to be first order in substrate but independent of the concentration of the entering ligand[1–5] and independent of the ionic strength of the medium[2] over the limited range 0.1–0.5*M*. Furthermore the reactions occur with retention of the *trans*-configuration. A number of mechanisms have been put forward that are consistent with these results. As part of our general interest in inorganic reaction mechanisms we set out to completely characterize the replacement of one ligand (Y) by another (L) from *trans*-$[Rh(en)_2XY]^{n+}$ and *trans*-$[Rh(en)_2Y_2]^{n+}$ cations. In order to achieve this and to avoid merely observing either the loss of starting material or the formation of the product in the presence of a large excess of L (pseudo first-order conditions) we required to isolate and characterise as many of the possible intermediate species as we could. Soon after we commenced this work it became apparent that there were a number of errors and inconsistencies in the literature describing the preparation of the mixed halo-complexes, some of which have been corrected[5] since the present work was undertaken. Accordingly we present a full report of the preparation of *trans*-$[Rh(en)_2X_2]ClO_4$ (X = Cl, Br and I) and *trans*-$[Rh(en)_2XY]ClO_4$ (X = Cl, Y = Br and I; X = Br, Y = I). In addition we describe for the first time the isolation of *trans*-$[Rh(en)_2X(H_2O)](ClO_4)_2$ (X = F, Cl, Br and I) and *trans*-$[Rh(en)_2(H_2O)_2](ClO_4)_3$. Furthermore we have taken advantage of the availability of such a complete series of complexes to record and assign their electronic and vibrational spectra.

Experimental

All the compounds reported were recrystallized until their quantitative ultra-violet and visible spectra showed no further change.

Cis and *trans*-$[Rh(en)_2Cl_2]NO_3$ were prepared as described previously[6](Found (*cis*-), C, 13.5; H, 4.5; N, 19.8; $C_4H_{16}Cl_2N_5O_3Rh$ requires C, 13.5; H, 4.5; N, 19.7%). *Trans*-$[Rh(en)_2Cl_2]ClO_4$ was prepared either by recrystallising the corresponding nitrate in the presence of perchloric acid or by passing the nitrate down an anion exchange column containing Dowex AG1-X8 resin in the perchlorate form (Found, C, 12.4; H, 4.0; N, 14.5; $C_4H_{16}Cl_3N_4O_4Rh$ requires C, 12.2; H, 4.1; N, 14.2%).

Trans-$[Rh(en)_2Br_2]ClO_4$ was prepared as described previously[7] (Found, C, 10.1; H, 3.5; N, 11.8; $C_4H_{16}ClBr_2N_4O_4Rh$ requires C, 10.0; H, 3.3; N, 11.6%). *Trans*-$[Rh(en)_2I_2]ClO_4$: *Trans*-$[Rh(en)_2I_2]I$, prepared as described previously,[6] yielded the perchlorate salt on repeated recrystallization from sodium perchlorate solution. However, addition of one molar equivalent of silver perchlorate was a quicker and more convenient route for its preparation (Found C, 8.3; H, 2.9; N, 9.7; $C_4H_{16}ClI_2N_4O_4Rh$ requires C, 8.3; H, 2.8; N, 9.7%). An attempt to use a Dowex AGl-X8 anion exchange resin was only partially successful as it proved difficult to remove the complex from the resin.

Trans-$[Rh(en)_2ClBr]ClO_4$. The method reported previously[7] in which *trans*-$[Rh(en)_2Br(H_2O)](ClO_4)_2$ prepared *in situ* by treating the dibromide with silver perchlorate, was treated with a mixture of hydrochloric and perchloric acids was found to be unsatisfactory. A solution of *trans*-$[Rh(en)_2Cl_2]ClO_4$ (0.46 g; 1.17 mmol) and silver perchlorate (0.24 g; 1.16 mmol) in distilled water (25 ml) was refluxed for two hours. After cooling to room temperature the precipitated silver chloride was filtered off. The filtrate was treated with sodium bromide (1 g; 9.75 mmol) overnight at room temperature. Sodium perchlorate (1 g) was added to this solution which was then evaporated to half-volume on a water-bath before cooling in an ice-bath to deposit a mass of orange–red crystals in 50% yield. Double recrystallization from dilute perchloric acid had no effect on the quantitative ultra-violet and visible spectrum (Found, C, 10.8_5; H, 3.6; N, 12.7_5; $C_4H_{16}BrCl_2N_4O_4Rh$ requires C, 11.0; H, 3.7; N, 12.8%).

Trans-$[Rh(en)_2ClI]ClO_4$ and *trans*-$[Rh(en)_2BrI]ClO_4$ were prepared in 58% and 60% yields respectively by the method described previously[8] (Found C, 9.9; H, 3.4; N, 11.5; $C_4H_{16}Cl_2IN_4O_4Rh$ requires C, 9.9; H, 3.3; N, 11.55%. Found C, 9.1_5; H, 3.1; N, 10.6; $C_4H_{16}BrClIN_4O_4Rh$ requires C, 9.1; H, 3.0_5; N, 10.6%).

Trans-$[Rh(en)_2X(H_2O)](ClO_4)_2$ (X = Cl, Br, I) were prepared by refluxing *trans*-$[Rh(en)_2X_2]ClO_4$ with 1 mol equivalent of $0.1M$ aqueous silver perchlorate (2 hours for X = Cl; 15 minutes for X = Br, 10 minutes for X = I). After filtering off the precipitated silver halide the solutions were evaporated almost to dryness on a boiling water bath to yield the halo-aquo-complexes in virtually quantitative yields. The products, which were dried *in vacuo* over phosphorus pentoxide for 12 hours, could be recrystallized with difficulty from acetone in which they were very soluble. *Anal.* *Trans*-$[Rh(en)_2Cl(H_2O)](ClO_4)_2$, found C, 9.7; H, 3.6; N, 11.3; $C_4H_{18}Cl_3N_4O_9Rh$ requires C, 10.1; H, 3.8; N, 11.8%. *Trans*-$[Rh(en)_2Br(H_2O)](ClO_4)_2$, found C, 9.3; H, 3.3; N, 10.7_5; $C_4H_{18}BrCl_2N_4O_9Rh$ requires C, 9.2; H, 3.5; N, 10.8%. *Trans*-$[Rh(en)_2I(H_2O)](ClO_4)_2$, found C, 8.1; H, 3.0; N, 9.5; $C_4H_{18}Cl_2IN_4O_9Rh$ requires C, 8.5; H, 3.2; N, 9.9%.

Trans-$[Rh(en)_2I(H_2O)](BPh_4)_2$ was prepared by treating *trans*-$[Rh(en)_2I(H_2O)](ClO_4)_2$ with sodium tetraphenylborate. The product was soluble in acetone (Found C, 62.7; H, 5.9_5; N, 5.1; $C_{52}H_{58}B_2IN_4ORh$ requires C, 62.0_5; H, 5.8; N, 5.6%).

Reaction of trans-$[Rh(en)_2Cl_2]ClO_4$ with Silver Fluoride

A solution of *trans*-$[Rh(en)_2Cl_2]ClO_4$ (0.39 g; 1.0 mmol) and silver fluoride (0.30 g; 2.5 mmol) in water (5 ml) was refluxed for 12 hours. The precipitated silver chloride was removed by filtering the hot solution into an aqueous solution of sodium perchlorate (2 g in 5 ml). On cooling this solution in ice 0.37 g of a very pale yellow crystalline compound was obtained. Microanalyses and the ultraviolet and visible spectrum were consistent with the product being *trans*-$[Rh(en)_2F(H_2O)](ClO_4)_2$ (Found, C, 10.2; H, 3.9; N, 12.0; $C_4H_{18}Cl_2FN_4O_9Rh$ ($[Rh(en)_2F(H_2O)](ClO_4)_2$) requires C, 10.5; H, 4.0; N, 12.0%; $C_4H_{16}ClF_2N_4O_4Rh$ ($[Rh(en)_2F_2]ClO_4$) requires C, 13.3; H, 4.5; N, 15.5%).

Trans-$[Rh(en)_2(H_2O)_2](ClO_4)_3$

An aqueous solution (25 ml) of *trans*-$[Rh(en)_2I_2]I$ (0.50 g; 0.87 mmol) was refluxed with silver perchlorate (25 ml of a $0.1M$ aqueous solution) for 30 minutes. After cooling the precipitated silver iodide was filtered off to yield a near colourless filtrate which was treated with 72% perchloric acid (0.1 ml), reduced in volume to about 3 ml and left in a desiccator over concentrated sulphuric acid for three days. The resultant very sticky mass of pale yellow crystals was filtered under suction and washed firstly with a little absolute ethanol to remove any perchloric acid and secondly with diethylether. The crystals were then air dried to give a 50% yield of *trans*-$[Rh(en)_2(H_2O)_2](ClO_4)_3$ (Found, C, 8.5; H, 3.5; N, 10.0_5; $C_4H_{20}Cl_3N_4O_{14}Rh$ requires C, 8.6; H, 3.6; N, 10.0_5%).

Trans-$[Rh(en)_2(OH)_2]ClO_4$ was prepared in situ by dissolving *trans*-$[Rh(en)_2(H_2O)_2](ClO_4)_3$ in $0.1M$ sodium hydroxide solution.

Spectra

Ultra-violet and visible spectra were recorded in aqueous solution on a Perkin–Elmer model 450 spectrophotometer. Where indicated the spectra were resolved into their component Gaussian bands using a Du Pont 301 curve resolver. Infrared spectra were recorded on Perkin–Elmer model 225 and Beckman IR11 spectrometers. Above 200 cm^{-1} samples were run as nujol mulls encased in thin polythene sheets held between caesium iodide plates. Below 200 cm^{-1} the caesium iodide plates were replaced by thick polythene plates. The Raman spectra were recorded on crystalline samples on a Cary 82 spectrometer using a krypton laser (15448 cm^{-1} line). Nmr spectra were recorded on both a Perkin–Elmer R12 and a Varian HA-100.

Microanalyses

Microanalyses were carried out by the microanalytical department at University College London.

Results and Discussion

The starting material for the preparation of all the complexes described in the present paper was $[Rh(en)_2Cl_2]NO_3$ which was obtained as a mixture of *cis*- and *trans*-isomers that were easily and cleanly separated by fractional recrystallisation. It has been reported that the use of perchloric rather than nitric acid leads to the preparation of $[Rh(en)_2Cl_2]ClO_4$ in higher yield than the nitrate.[8] However we were unable to confirm the higher yield and in addition found that the separation of the *cis*- and *trans*-isomers was more difficult for the perchlorates than for the nitrates.

All the aquo-complexes reported in this paper have been isolated for the first time, although they have previously been studied in solution.[3] As we found earlier with platinum(II)[9] it appears that the major difficulty in the isolation of aquo complexes is their high solubility in water; the solubility of the haloaquo-complexes being very much higher than that of the dihalo-complexes. Perhaps surprisingly the solubility of the diaquo-complex was similar to that of the halo-aquo-complexes. All the haloaquo-complexes were assigned a *trans*-structure on the basis of their ultraviolet and visible spectra (see below). Previously we found that platinum(II)–aquo complexes may react with sodium tetraphenylborate to give phenyl complexes.[9] Accordingly, *trans*-$[Rh(en)_2I(H_2O)](ClO_4)_2$ was treated with sodium tetraphenylborate; however the product was the anticipated *trans*-$[Rh(en)_2I(H_2O)](BPh_4)_2$ and not a rhodium(III)–phenyl complex.

The isolation of the mixed fluoroaquo-complex rather than the difluoro-complex when *trans*-$[Rh(en)_2Cl_2]ClO_4$ was treated with 2 equivalents of silver fluoride was unexpected but presumably indicates that fluoride is a very weak ligand with an affinity for rhodium(III) that is comparable to or even less than that of water, as has been found in the case of platinum(II).[10]

The properties of the present compound described as *trans*-$[Rh(en)_2ClBr]ClO_4$ and that described previously[7] are not identical. Both give excellent analyses. However, the present sample exhibits a band, due to the $^1A_1 \rightarrow {}^1T_1$ transition, at 23,870 cm^{-1}, which is essentially midway between the bands for this transition in the corresponding dichloro- (24,360 cm^{-1}) and dibromo- (23,360 cm^{-1}) complexes as expected.[11] By contrast the earlier sample had[7] a band at 24,210 cm^{-1} which is rather closer to that of the dichloro-complex than expected, and which may perhaps indicate that the earlier product was a mixture of the chloro–bromo- and dichloro-complexes, which would be difficult to detect from the microanalytical results.

TABLE I. Comparison of the Position of the $^1A_1 \rightarrow {}^1T_1$ Observed in *cis*- and *trans*-$[Rh(en)_2XY]^{n+}$ with that Predicted Using Equation 1[a].

X	Y	Observed Position (cm^{-1})		Predicted Position (cm^{-1})
		cis	*trans*	
Cl	Cl	28490	24630	28570
Br	Br	27620[b]	23360	28170
H_2O	H_2O	31750[c]	29240	30630
Cl	Br		23870	28370
Cl	H_2O		26110	29600
Br	H_2O		24690	29400

[a] Literature values for $E([RhL_6])$ where L = Cl, Br and H_2O or L_2 = en were taken from reference 13. [b] From reference 6. [c] From reference 14.

Stereochemistry of the Complexes

This *cis–trans* nature of the dihalo-complexes was established firstly from their infrared and secondly from their U/V–visible spectra. Thus the infrared spectra of the *trans*-complexes exhibited only a single band at around 1600 cm^{-1} due to the $-NH_2$ deformation mode, whereas in the *cis*-complexes a doublet was observed in agreement with the literature.[6,12] In the U/V–visible spectra the $^1A_1 \rightarrow {}^1T_1$ transition (see below for the assignment of the spectra), was observed at higher energy in *cis*-$[Rh(en)_2X_2]^+$ where X = Cl and Br, than in the corresponding *trans*-isomers. Furthermore, the position of this band in the *trans*-isomers was always at lower energy than predicted on the basis of the principle of average environment[11] using equation 1, whilst in the *cis*-isomers its position was essentially that predicted (see Table I). This interesting observation is perhaps not unexpected

$$E([Rh(en)_2XY]^{1+}) = \frac{2}{3}E([Rh(en)_3]^{3+}) + \frac{1}{6}E([RhX_6]^{m+}) + \frac{1}{6}E([RhY_6]^{n+}) \quad (1)$$

since the conformations of the ethylenediamine rings in $[Rh(en)_3]^{3+}$ and *cis*-$[Rh(en)_2XY]^{1+}$ complexes are the same. It also provides a very useful method for determining the *cis–trans* nature of bis(ethylenediamine)rhodium(III) complexes.

The infrared method for assigning stereochemistry could not be applied to the aquo-complexes because of the presence of a band due to coordinated water in the region of interest. The chloroaquo- and bromoaquo-complexes were, however, assigned a *trans*-geometry on the basis of the position of the $^1A_1 \rightarrow {}^1T_1$ transition as compared to that calculated from equation 2 (Table II).

$$E(cis\text{- or } trans\text{-}[Rh(en)_2X(H_2O)]^{2+}) = E(cis\text{- or } trans\text{-}[Rh(en)_2X_2]^{+}) - \frac{1}{6}E([RhX_6]^{3-}) + \frac{1}{6}E([Rh(H_2O)_6]^{3+}) \quad (2)$$

The $[Rh(en)_2(H_2O)_2](ClO_4)_3$ prepared here was assigned a *trans*-stereochemistry on the basis of the

TABLE II. Comparison of the Position of the $^1A_1 \rightarrow {}^1T_1$ Band Observed in $[Rh(en)_2X(H_2O)]^{2+}$ with Those Calculated for the *cis*- and *trans*- Isomers According to Equation 2[a].

X	Band Positions (cm^{-1})		
	Observed	Calculated for *trans*-isomer	Calculated for *cis*-isomer
Cl	26,110	25,664	29,444
Br	24,690	24,594	28,634

[a] Literature values for $E([RhL_6])$ where L = Cl, H_2O were taken from ref. 13.

agreement of its U/V–visible spectrum with that reported by Gendernalik[14] who prepared both isomers in solution, but did not isolate either of them. $[Rh(en)_2F(H_2O)](ClO_4)_2$ was assigned a *trans*-stereochemistry on the basis of our failure to observe any *trans* → *cis* isomerisation in any of the other interconversions that we carried out, together with the fact that its U/V–visible spectrum fits nicely into the series of *trans*-$[Rh(en)_2X(H_2O)]^{n+}$ in accordance with the position of X in the spectrochemical series[11], *i.e.* $X = I < Br < Cl < F < H_2O$ (see Table III and Figure 1).

TABLE III. The Ultraviolet and Visible Spectra of *trans*-$[Rh(en)_2XY]^{n+}$ Complexes in Aqueous Solution[a].

X	Y	Bands (cm^{-1})			Other bands (cm^{-1})			Previous Workers (cm^{-1})
		1	2	3				
Cl	Cl		24630^b (84)	34970 (130)	41670 (1350)	48540 (38900)		24630(75), 34970(130) (ref. 6) 24570(75), 34970(125) (ref. 7) 21300(sh∼1.5), 25000(82), 35200(123) (at 80° K, ref. 16)
Br	Br		23360^b (107)		36230 (2720)	42920 (37600)		23530(100), 36230(1800) (ref. 6) 23530(120), 36230(3000), 43290(∼31000) (ref. 7)
I	I		21650 (322)		29500 (21780)	37170 (47450)	45450 (sh∼16820)	21650(260), 29330(10000), 37170(30000), 45050(20000), (ref. 6) 21650(260), 29410(14300), 37170(31000), 45050(20000) (ref. 8)
Cl	Br	20580 (sh∼18)	23870 (94)		37040 (1590)	45050 (31700)		20580(sh∼10), 24210(95), 38170(∼1600) (ref. 7)
Cl	I	20580 (243)	22730^b (151)		33560 (3870)	41320 (38100)		22730(154), 33330(4350), 41320(38500) (ref. 8) 20410(260), 22730(160), 33220(4300), 41490(38300) (ref. 5)
Br	I	20490 (162)	22080 (172)		32260 (4540)	39530 (25700)	44250 (17600)	21980(260), 32150(7500), 39530(41500) (ref. 8)
F	H_2O		28900 (80)	35710^b (131)				
Cl	H_2O		26110^b (46)	35340 (143)				26320–28570(26),^{c} 35340(73)^c (ref. 3)
Br	H_2O	21280 (32)	24690^b (55)	35710 (520)	42550 (5260)			∼21500(26),^{c} ∼25300(48)^c (ref. 3)
I	H_2O	21010 (150)	∼24400^d	30120 (sh∼760)	33330 (sh∼1240)	37040 (sh∼2030)	44250 (15100)	21050(95)^c, 33330(1000)^c (ref. 3)
H_2O	H_2O^e		29240^b (66)	36760 (125)				29240(64)^c, 38170(148)^c (ref. 4)
OH	OH^f		29590 (136)	34480 (136)				29760(94)^c, 34600(154)^c (ref. 4)
F	OH^f		28820 (124)	33780 (159)				

TABLE III. (Cont.)

X	Y	Bands (cm^{-1}) 1	2	3	Other bands (cm^{-1})		Previous Workers (cm^{-1})
Cl	OH^f		27550 (123)	35090 (172)			
Br	OH^f		27030 (138)		36360 (sh∿1066)		
I	OH^f	22470 (149)	25600^d (v.wh. sh∿120)		29590 (1195)	37040 (6072)	

[a] Band maxima in cm^{-1}, molar absorptivities ($l\ mol^{-1}cm^{-1}$) in parenthesis (sh = shoulder). [b] Band distorted in shape, suggesting that it results from two transitions. [c] Estimated for complex prepared in solution, but not isolated. [d] Band located by Gaussian analysis. [e] Obtained by dissolving *trans*-$[Rh(en)_2(H_2O)_2](ClO_4)_3$ in 0.1 *M* $HClO_4$. [f] Obtained by dissolving *trans*-$[Rh(en)_2X(H_2O)](ClO_4)_n$ in 0.1 *M* NaOH.

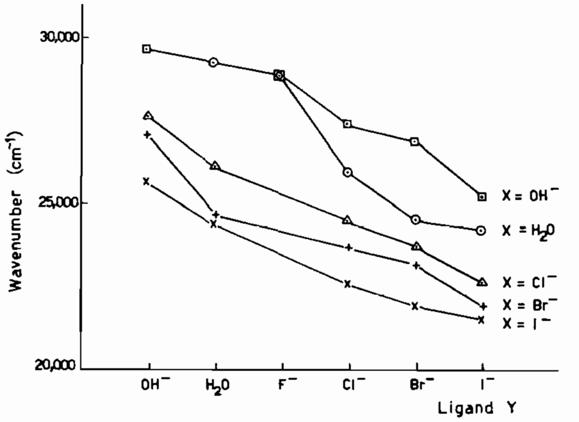

Figure 1. Position of the ${}^1A_1 \rightarrow {}^1T_1$ transition in *trans*-$[Rh(en)_2XY]^{n+}$.

An attempt was made to use ^1H NMR as a further technique for distinguishing between *cis*- and *trans*-isomers since in the analogous cobalt(III) complexes the *cis*-isomer has a more complex spectrum than the *trans*-isomer.[15] however saturated solutions of *cis*- and *trans*-$[Rh(en)_2Cl_2]ClO_4$ in 2*M* DCl in D_2O had virtually identical ^1H NMR spectra.

Ultraviolet and Visible Spectra

The ultraviolet and visible spectra of the present complexes are given in Table III, together with the spectra reported by previous workers. In general the agreement is reasonable except in the case of *trans*-$[Rh(en)_2ClBr]ClO_4$ where, as mentioned above, we suspect that the previous workers had some *trans*-$[Rh(en)_2Cl_2]ClO_4$ present as impurity.

The two lowest spin-allowed *d–d* bands in octahedral low spin d^6 complexes arise from ${}^1A_1 \rightarrow {}^1T_1$ and ${}^1A_1 \rightarrow {}^1T_2$ transitions, and the lowest spin forbidden band is due to the ${}^1A_1 \rightarrow {}^3T_1$ transition. In *trans*-$[Rh(en)_2Cl_2]ClO_4$ we have observed two bands (bands 2 and 3 in Table III) with molar absorptivities consistent with spin-allowed *d–d* transitions. We assign these to the ${}^1A_1 \rightarrow {}^1T_1$ and ${}^1A_1 \rightarrow {}^1T_2$ transitions respectively in agreement with the independent assignment of DeArmond and Hillis.[16] The spin-forbidden ${}^1A_1 \rightarrow {}^3T_1$ transition in *trans*-$[Rh(en)_2Cl_2]ClO_4$ was too weak to be observed in the present work, although it has been observed as a weak shoulder at about 21300 cm^{-1} in a glassy solution of *trans*-$[Rh(en)_2Cl_2]Cl$ at −189° C.[16] The position of the ${}^1A_1 \rightarrow {}^1T_1$ transition in the other complexes (band 2 in Table III) was identified on the basis of the spectrochemical series (Figure 1) which in these complexes was found to be $OH^- > H_2O > Cl^- > Br^- > I^-$. The ${}^1A_1 \rightarrow {}^1T_2$ transition (band 3) was only observed in those complexes where it was not obscured by intense charge transfer transitions. Band 1, which was often too weak to be observed, was assigned to the ${}^1A_1 \rightarrow {}^3T_1$ spin-forbidden *d–d* transition.

It is noteworthy that in a number of the complexes band 2 is distorted in shape suggesting that the ${}^1T_1$ level is split. Such a splitting of the ${}^1T_1$ state, due to the reduction in symmetry from O_h, has been observed previously in *trans*-$[Co(en)_2F_2]^+$ [17] and *trans*-$[Rh(oxalate)_2Cl_2]^{3-}$ [18] where it gives rise to two distinct bands. Since there is only a very small splitting of the ${}^1T_1$ state in the *cis*-$[Co(en)_2X_2]^+$, this has provided a simple method, based on the number of bands present, for distinguishing between the *cis*- and *trans*-isomers. Unfortunately, the lower splitting of the ${}^1T_1$ state in *trans*-$[Rh(en)_2X_2]^+$ complexes precludes the application of this method to their stereochemical assignment.

Far Infrared and Raman Spectra

There are very few reports of the metal–halogen stretching vibrations of *trans*-$[ML_4XY]$ (X and Y =

halogen) in the literature.[19–23] Accordingly we recorded the infrared and Raman spectra of *trans*-$[Rh(en)_2XY]ClO_4$ (Table IV). Previous work on ethylenediamine–rhodium(III) complexes, particularly $[Rh(en)_3]I_3$, has suggested that the rhodium–nitrogen stretching vibrations[24,25] lie between 555 and 575 cm^{-1}, well outside the likely range for rhodium–halogen stretching vibrations (150–350 cm^{-1}).* However an N–Rh–N deformation mode has been observed[24,25] in this range at about 250 cm^{-1}, and a similar band was found in

TABLE IV. Bands Observed in the Far Infrared (90–350 cm^{-1}) and Raman (20–1000 cm^{-1}) Spectra of *trans*-$[Rh(en)_2XY]ClO_4$[a].

XY	Raman				Infrared			
	ν_{Rh-Cl}	ν_{Rh-Br}	ν_{Rh-I}	Other bands	ν_{Rh-Cl}	ν_{Rh-Br}	ν_{Rh-I}	Other bands
X = Y = Cl	305(vs)	–	–	73(w) 135(w) 145(w) 180(w) 205(s) 254(m) 260(m) 450(m) 503(w) 535(s) 933(s)	344(vs)	–	–	142(m) 260(vs) 314(m)
X = Y = Br	–	194(vs)	–	58(s) 255(w) 267(w) 454(vw) 465(vw) 534(m) 934(m)	–	222(vs)	–	116(s) 170(m) 268(w) (274(w)
X = Y = I[b]	–	–	135(vs)	37(m) 248(vw)	–	–	186(vs)[c]	105(w) 294(m)
X = Cl, Y = Br[b]	310(vw)	210(s)	–	58(m) 193(vs) 265(s) 255(s) 450(w) 534(s) 931(m)	316(w)	213(s) 222(s)	–	270(s) 330(m)
X = Cl, Y = I[b]	317(vw)	–	172(s)	27(w) 37(w) 265(w) 530(vw)	312(s)	–	168(s)	134(s) 264(s)
X = Br, Y = I[b]	–	207(vw)	157(vs)	26(w) 36(w) 258(w) 530(vw)	–	200(s)	158(w)	110(m) 118(m) 125(m) 256(m) 295(s)

[a] Infrared spectra were recorded as nujol mulls, Raman spectra were recorded on powdered solids. [b] Compound exhibited fluorescence in the Raman spectrum. [c] Adams and Chandler[16] reported this at 178 cm^{-1}.

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* It must be remembered that in many atom systems such as the present complexes no observed frequency arises from changes in a single internal coordinate. In assigning a particular band to an Rh–X vibration we mean that this band arises principally from a change in this internal coordinate with lesser contributions from changes in other internal coordinates.

TABLE V. Comparison of the Computer Simulated and Assigned Frequencies in *trans*-[Rh(en)$_2$XY]$^+$ Complexes[a].

X	Y			ν_{Rh-Cl}	ν_{Rh-Br}	ν_{Rh-I}
Cl	Br		Simulated	323	220	
		Observed	Raman	310	210	
			Infrared	316	213, 222	
Cl	I		Simulated	325		164
		Observed	Raman	317		172
			Infrared	312		168
Br	I		Simulated		222	155
		Observed	Raman		207	157
			Infrared		200	158

[a] The stretching force constants, f_{Rh-X}, were calculated from the stretching frequencies observed in *trans*-[Rh(en)$_2$X$_2$]$^+$ (Table IV) assuming that the interaction force constant, $f_{Rh-X/Rh-X}$, was 10% of f_{Rh-X}. These values of f_{Rh-X} ($f_{Rh-Cl} = 1.71$, $f_{Rh-Br} = 1.34$ and $f_{Rh-I} = 1.05$ mdyn Å^{-1}) were then used to simulate the frequencies in *trans*-[Rh(en)$_2$-XY]$^+$ on the assumption that $f_{Rh-X/Rh-Y}$ was equal to the arithmetic mean of $f_{Rh-X/Rh-X}$ and $f_{Rh-Y/Rh-Y}$.

the present spectra. More recent work, including normal vibrational analysis, on the related palladium(II) complexes [Pd(en)$_2$]$^{2+}$ X^{2-}, where X^{2-} = [PdCl$_4$]$^{2-}$ or 2Cl$^-$, supports these assignments.[26,27]

If the non-planarity of the ethylenediamine rings is neglected then *trans*-[Rh(en)$_2$X$_2$]$^+$ has D_{2h} symmetry and accordingly should give rise to two Rh–X stretching modes, one an infrared active–Raman inactive antisymmetric mode and the other an infrared inactive–Raman active symmetric mode. The antisymmetric mode would be expected to lie at the higher frequency. Our present assignments (Table IV) are in agreement both with this and with earlier assignments where these are available.[20,23]

In the mixed complexes where $X \neq Y$ the idealised symmetry (considering ethylenediamine to be planar) drops to C_{2v} and now the two X–Rh–Y stretching modes are both of A_1 symmetry and accordingly in addition to interacting strongly are both infrared and Raman active. It is, however, possible to divide the two observed frequencies into one to which the Rh–X stretch makes the greater contribution and one to which the Rh–Y stretch makes the greater contribution.[28] To decide which is which for X–Rh–Y in which X is the lighter group we used three criteria: (i) The lighter group contributes more to the out-of-phase X–Rh–Y mode (Figure II-3, ref. 28) that gives rise to the more intense infrared and less intense Raman band. (ii) The intensities of the Raman bands increase as the atomic weights of the contributing elements increase because the polarisability of the bond between the heavier elements is greater. (iii) The force constants for the Rh–X stretching modes in *trans*-[Rh(en)$_2$-X$_2$]$^+$ complexes were calculated[29] assuming that the system could be represented by a linear triatomic X–Rh–X system. These force constants were then used to simulate the band positions expected for the mixed halo-species *trans*-[Rh(en)$_2$XY]$^+$. The agreement between the assigned and simulated frequencies (Table V) is excellent in view of the approximations inherent in the calculation.

The full assignments obtained using these three criteria are given in Table IV. It is noteworthy that the "Rh–Cl" assignments obtained here for *trans*-[Rh-(en)$_2$ClY]$^+$, where Y = Br or I, on the basis of both infrared and Raman data differ from those given previously[20] on the basis of infrared data alone.

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