The Relative Stabilities of Halogeno-complexes. Part V.[1] The *trans*-Rh $en_2Cl_2^+$–I^- and *trans*-Rh $en_2Br_2^+$–I^- Systems

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Equilibrium constants have been obtained spectrophotometrically for the stepwise replacement by iodide of the chloride in *trans*-Rh $en_2Cl_2^+$, and of the bromide in *trans*-Rh $en_2Br_2^+$. At 90° $K_1(Cl^-:I^-) = K_1(Br^-:I^-) = 7{\cdot}0$. Extrapolation to 90° of data obtained at lower temperatures gives $K_2(Cl^-:I^-) = 2{\cdot}2$ and $K_2(Br^-:I^-) = 1{\cdot}9$. The temperature-dependence of the equilibrium constants lead to the following enthalpy data. $\Delta H_1^\circ(Cl^-:I^-) = -0{\cdot}1 \pm 0{\cdot}9$, $\Delta H_2^\circ(Cl^-:I^-) = -6{\cdot}2 \pm 9{\cdot}4$, $\Delta H_1^\circ(Br^-:I^-) = -2{\cdot}6 \pm 0{\cdot}4$, and $\Delta H_2^\circ(Br^-:I^-) = 3{\cdot}4 \pm 0{\cdot}3$ kcal./mole.

From these, and other data obtained previously, it is possible to obtain the relative enthalpies of bonding of the dihalogeno-complexes in aqueous solution. These are in the order di-iodo > iodobromo > iodochloro > dibromo > bromochloro > dichloro. The values are discussed in terms of class (a) or (b) character of these complexes and the extent to which this is affected by the nature of the halide in the *trans*-position.

The preparation and ultraviolet and visible absorption spectra of some new *trans*-bisethylenediaminediacido-rhodium(III) complexes are reported.

PRECEDING Papers [1,2] in this Series have been concerned with the ease with which one halide in a complex can be replaced by another, as indicated by the equilibrium constant for the interchange or, better, by the enthalpy change involved. We now describe further studies involving some *trans*-bisethylenediaminedihalogeno-complexes of rhodium(III). These studies provide a measure of the class (a) or (b) character,[3] or of the "hardness" or "softness,"[4] of the complexes involved, and thermodynamic effects transmitted from a halide across the rhodium to the *trans*-position have also been estimated. The measurements were made spectrophotometrically at constant ionic strength, and temperature variation was used to obtain enthalpy and entropy data.

RESULTS

Ultraviolet and Visible Absorption Spectra.—The main features of the spectra of the unmixed dihalogeno-complexes have already been reported.[1,5] Table 1 records our results for the di-iodo-complex and for the newly prepared iodobromo- and iodochloro-complexes. The extinction coefficient which we obtained for the **340**-mμ absorption maximum of the di-iodo-complex is considerably greater than that reported by Johnson and Basolo,[5] but the high value was obtained consistently from several independently prepared samples and from many samples produced *in situ* by the reaction of known amounts of the *trans*-dichloro- and *trans*-dibromo-complexes with varying excesses of iodide. The spectra of the mixed-halide complexes are intermediate between those of the corresponding well-characterised unmixed *trans*-complexes.[5] When considered together with the observation that no *trans* ⟶ *cis* re-arrangement has been detected in any of the reactions of these *trans*-diacido-complexes of rhodium(III), this fact confirms the *trans*-configuration of the mixed complexes.

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[1] Part IV, H. L. Bott and A. J. Poë, *J. Chem. Soc.*, **1965**, **5931**.

[2] (*a*) A. J. Poë and M. S. Vaidya, *J. Chem. Soc.*, **1960**, **3431**; (*b*) *idem.*, *ibid.*, **1961**, **1023**; (*c*) A. J. Poë, *ibid.*, **1964**, **676**.

[3] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

[4] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533; Proc. 8th Internat. Conf. Co-ordination Chem., Springer-Verlag, Vienna, **1964**, p. 315.

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

TABLE 1

Visible and ultraviolet absorption spectra of *trans*-Rh en_2XY^+ complexes

		λ (mμ)	ε (cm.$^{-1}$ l. mole^{-1})
X = Y = I	(This work)	462, 340, 269, 222	260, 14,300, 31,000, 20,000
	(Ref. 5)	462, 341, 269, 222	260, 10,000, 30,000, 20,000
X = I, Y = Br		455, 311, 253	260, 7500, 41,500
X = I, Y = Cl		440, 300, 242	154, 4350, 38,500

The trans-Rh en_2ICl^+–I^- *and* trans-Rh en_2IBr^+–I^- *Equilibria*.—The equilibria were studied by mixing suitably dilute solutions of the di-iodo-complex with solutions containing a fixed total concentration (0·5 or 0·6M) of potassium iodide and potassium chloride or bromide, the ratio of the individual concentrations being varied. The solutions were kept in a thermostat-bath and their spectra were examined periodically. When the spectra were unchanging with time the solutions were assumed to be at equilibrium. This study involving the *trans*-iodo-complexes was simplified by the large labilising effect of the iodide [6] which ensured that equilibrium between the di-iodo- and iodobromo- or iodochloro-complexes was attained well before any dibromo- or dichloro-complex was formed. This was shown by the excellent isosbestic points obtained at 55° and below during the reactions of the di-iodo-complex with bromide or chloride and also after the di-iodo-complex had reacted for about 8 half-lives with various I^- : Cl^- or I^- : Br^- mixtures. A typical set of spectra is shown in Figure 1. Equilibrium was attained after 12 hr. and spectra remained constant for at least 12 hr. thereafter. The calculation of the equilibrium constants was easily performed by the direct use of experimental absorbance values which were inserted in equation (1).

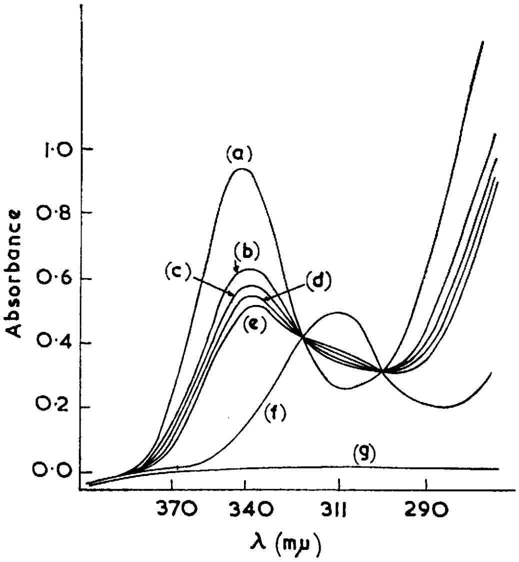

FIGURE 1. Ultraviolet spectra of *trans*-Rh en_2BrI^+–*trans*-Rh $en_2I_2^+$ equilibrium mixtures at 55°, μ = 0·5M. $[I^-]/[Br^-]$ ratios are (a) ∞, (b) 2·0, (c) 2·5, (d) 3·0, (e) 3·5, and (f) 0·0. (g) is the base-line

$$K_2 = (A - A_1)R/(A_2 - A) \qquad (1)$$

K_2 is the equilibrium constant for replacement of X^- in Rh en_2IX^+ by I^- (X = Cl or Br), A is the measured absorbance of the solution at a given wavelength and at particular concentrations of X^- and I^- ($R = [X^-]/[I^-]$), and A_1 and A_2 are the absorbances when all of the complex is present as *trans*-Rh en_2IX^+ ($[I^-] = 0$) and *trans*-Rh $en_2I_2^+$ ($[X^-] = 0$), respectively. The results, which

TABLE 2

The *trans*-Rh $en_2ICl^+ + I^- \underset{}{\overset{K_2}{\rightleftharpoons}}$ *trans*-Rh $en_2I_2^+ + Cl^-$ equilibrium (absorbances obtained at 340 mμ)

	$[Cl^-]/[I^-]$	A	$A - A_1$	$A_2 - A$	K_2
(*a*) 45°	∞	0·043			
(μ = 0·6M)	5·00	0·480	0·437	0·337	6·49
	4·50	0·500	0·457	0·317	6·50
	4·00	0·531	0·488	0·286	6·82
	3·50	0·553	0·510	0·264	6·76
	0	0·817			
					$\bar{K}_2 = 6·64 \pm 0·13$
(*b*) 50°	∞	0·047			
(μ = 0·6M)	5·00	0·460	0·413	0·365	5·65
	4·50	0·479	0·432	0·346	5·62
	4·00	0·505	0·458	0·320	5·72
	3·50	0·535	0·488	0·290	5·88
	0·00	0·825			
					$\bar{K}_2 = 5·72 \pm 0·11$
(*c*) 55°	∞	0·038			
(μ = 0·5M)	4·00	0·437	0·399	0·322	4·96
	3·50	0·461	0·423	0·298	4·97
	3·00	0·482	0·444	0·277	4·81
	2·50	0·505	0·467	0·254	4·60
	2·00	0·562	0·524	0·197	5·32
	0·00	0·759			
					$\bar{K}_2 = 4·93 \pm 0·08$

$\Delta H° = -6·18 \pm 0·41$ kcal./mole; $\Delta S° = -15·6 \pm 1·3$ cal. deg.$^{-1}$ mole^{-1}.

TABLE 3

The *trans*-Rh $en_2IBr^+ + I^- \overset{K_2}{\rightleftharpoons}$ *trans*-Rh $en_2I_2^+ + Br^-$ equilibrium (absorbances obtained at 340 mμ, μ = 0·5M)

	$[Br^-]/[I^-]$	A	$A - A_1$	$A_2 - A$	K_2
(*a*) 45°	∞	0·130			
	3·50	0·518	0·388	0·399	3·40
	3·00	0·557	0·427	0·360	3·56
	2·50	0·585	0·465	0·332	3·43
	2·00	0·640	0·510	0·277	3·68
	0·00	0·917			
					$\bar{K}_2 = 3·52 \pm 0·05$
(*b*) 50°	∞	0·120			
	3·50	0·460	0·340	0·377	3·16
	3·00	0·487	0·367	0·350	3·14
	2·50	0·525	0·405	0·312	3·22
	2·00	0·570	0·450	0·267	3·37
	0·00	0·837			
					$\bar{K}_2 = 3·22 \pm 0·05$
(*c*) 55°	∞	0·130			
	3·50	0·505	0·375	0·437	3·00
	3·00	0·533	0·403	0·409	2·96
	2·50	0·570	0·440	0·372	2·96
	2·00	0·620	0·490	0·322	3·04
	0·00	0·942			
					$\bar{K}_2 = 2·99 \pm 0·05$

$\Delta H° = -3·38 \pm 0·34$ kcal./mole^{-1}; $\Delta S° = -8·1 \pm 1·0$ cal. deg.$^{-1}$ mole^{-1}.

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[6] F. Basolo, E. J. Bounsall, and A. J. Poë, *Proc. Chem. Soc.*, 1963, 366.

were obtained at a wavelength of 340 mμ (corresponding to an absorption peak of *trans*-Rh $en_2I_2^+$), are shown in Tables 2 and 3. The limits quoted are standard deviations calculated by using a statistical method which is described in the Experimental section. These standard deviations correspond to a standard deviation in the experimental absorbance measurements of about $\pm 0{\cdot}005$ units.

The trans-*Rh* $en_2Cl_2^+$*–*I^- *and* trans-*Rh* $en_2Br_2^+$*–*I^- *Equilibria.*—Solutions of the dichloro- and dibromo-complexes were mixed with solutions containing iodide and chloride, and iodide and bromide mixtures, respectively, in various concentration ratios and allowed to come to equilibrium at $\geqslant 70°$. Under these conditions equilbrium was established between the Rh $en_2I_2^+$, Rh en_2IX^+, and Rh $en_2X_2^+$ complexes (X = Cl or Br). As was found with the *trans*-Rh en_2Cl_2–Br^- system,[1] decomposition competed with the slow establishment of the replacement equilibria so that reproducible data were difficult to obtain at lower temperatures. Thus no consistent data were obtainable for the Rh $en_2Cl_2^+$–I^- system below about 85° but for the Rh $en_2Br_2^+$–I^- system satisfactory data were obtainable down to 70° although many of the solutions had to be discarded when decomposition was clearly indicated by the nature of the spectra. The decomposition occurred rather haphazardly but the fact that it was more prevalent at lower temperatures suggests that it has a lower activation energy than those reactions involved in the attainment of equilibrium.

Since these solutions contained all three species *trans*-Rh $en_2X_2^+$, -Rh en_2IX^+, and -Rh $en_2I_2^+$ in equilibrium, values of K_1 (the equilibrium constant for the replacement of one X^- in *trans*-Rh $en_2X_2^+$ by I^-) could not be calculated directly from experimentally measured absorbance data, as could values of K_2. Values of K_1 had rather to be calculated from the more complicated expression:

$$K_1 = (\varepsilon - \varepsilon_0)/\{(\varepsilon_1 - \varepsilon)R + (\varepsilon_2 - \varepsilon)K_2R^2\} \qquad (2)$$

ε_0, ε_1, and ε_2 represent the extinction coefficients of *trans*-Rh $en_2X_2^+$, -Rh en_2IX^+, and -Rh $en_2I_2^+$, respectively, at a particular wavelength. ε is the apparent extinction coefficient obtained from the absorbances, measured at the same wavelength, of the solutions at a given $[I^-]/[X^-]$ ratio, R. Values of K_2 were obtained by extrapolation from lower temperatures of the previously determined K_2 values by means of a plot of log K_2 against $1/T$. The K_2 values were corrected for differences in ionic strengths by multiplying them by ratios of experimentally determined activity coefficients of the appropriate halide salts at the two ionic strengths concerned.[7] The temperature-dependence of these ratios was assumed to be negligible since the individual activity coefficients change in the same way with temperature. No significant errors were introduced by the approximate nature of these corrections because the calculation of K_1 is not greatly affected by the value of K_2 and the corrections are small. [A 15% error in $K_2(Cl^- : I^-)$ at 90° introduces an error of only 2% into the value obtained for K_1.] Higher ionic strengths (1·5 or 2·0M) were used in the determination of K_1 because of the high $[X^-]/[I^-]$ ratios needed to produce sufficient of the *trans*-Rh $en_2X_2^+$ and -Rh en_2IX^+ species and because inconsistent results were obtained if $[I^-]$ dropped below about 0·1M. Results for the $Br^- : I^-$ system at 70 and 90° are given in Table 4, the quoted limits being obtained as before. Absorbances were measured at 311 mμ, an absorption maximum of *trans*-Rh en_2IBr^+ and a wavelength at which the contribution of the term $(\varepsilon_2 - \varepsilon)R^2$ in equation (2) was minimised. Results for the $Cl^- : I^-$ system at 90° are given in Table 5. Absorbances were measured at 300 mμ, an absorption maximum of *trans*-Rh en_2ICl^+.

Recently it has been found [8] that the spectrum of *trans*-Rh $en_2I_2^+$ is sensitive to excess of free iodide at about 300 mμ. The effect on the values obtained for K_1 in Table 5 is negligible, however. Table 6 presents some measurements made [8] on the $Cl^- : I^-$ system at 85 and 96°. Equilibrium was attained after 24 and 8 hr., respectively. The data were obtained over a wider range of $[Cl^-] : [I^-]$ ratios than those in Table 5, and the effects of errors in the extrapolated values of K_2 were also more serious. Calculation of the constants sometimes involved the difference between two terms of similar size and the standard deviations are therefore larger. The values ε'_2 are the extinction coefficients of the di-iodo-complex in the given $Cl^- : I^-$ mixtures at room temperature before any chemical reaction had occurred. The extinction coefficients of the dichloro- and iodochloro-

TABLE 4

The *trans*-Rh $en_2Br_2^+ + I^- \underset{}{\overset{K_1}{\rightleftharpoons}}$ *trans*-Rh $en_2IBr^+ + Cl^-$ equilibria

[Complex] = $3{\cdot}01 \times 10^{-4}$M, λ = 311 mμ, μ = 1·50M, ε_0 = 260; ε_1 = 7500; ε_2 = 3740 cm.$^{-1}$ l. mole^{-1}; K_2 = 1·88 at 90° and 2·48 at 70°.

	$[Br^-]/[I^-]$	ε	$\varepsilon - \varepsilon_0$	$\varepsilon_1 - \varepsilon$	$\varepsilon_2 - \varepsilon$	K_1
(*a*) 90·0°	14·0	2640	2380	4860	1100	6·64
	12·0	2960	2700	4540	780	6·96
	12·0	2945	2685	4555	795	6·89
	11·0	3140	2880	4360	600	7·10
	9·0	3440	3180	4060	300	6·94
	8·0	3700	3440	3800	40	7·21
						$\bar{K}_1 = 6{\cdot}96 \pm 0{\cdot}13$
(*b*) 70·0°	11·0	3590	3330	3910	150	9·30
	9·0	3705	3445	3795	35	8·16
	8·0	3960	3700	3540	−220	8·35
						$\bar{K}_1 = 8{\cdot}60 \pm 0{\cdot}22$

$\Delta H°$ = $-2{\cdot}62 \pm 0{\cdot}39$ kcal./mole^{-1}; $\Delta S°$ = $-3{\cdot}4 \pm 1{\cdot}1$ cal. deg.$^{-1}$ mole^{-1}.

TABLE 5

The *trans*-Rh $en_2Cl_2 + I^- \overset{K_1}{\rightleftharpoons}$ *trans*-Rh $en_2ICl^+ + Cl^-$ equilibrium

[Complex] = $6{\cdot}07 \times 10^{-4}$M, λ = 300 mu, K_2 = 2·18, T = 90°, μ = 2·0M; ε_0 = 107; ε_1 = 4150; ε_2 = 4260 cm.$^{-1}$ l. mole^{-1}.

$[Cl^-]/[I^-]$	ε [a]	$\varepsilon - \varepsilon_0$	$\varepsilon_1 - \varepsilon$	$\varepsilon_2 - \varepsilon$	K_1
19·0	1270	1163	2880	2990	6·95
	1281	1174	2869	2979	6·86
17·0	1360	1253	2790	2900	6·78
	1392	1285	2758	2868	6·99
15·0	1579	1472	2571	2681	7·47
	1608	1501	2542	2652	7·71 [b]
13·0	1692	1585	2458	2568	7·14
	1675	1568	2475	2585	7·01
12·0	1760	1653	2390	2500	6·98
	1762	1655	2388	2498	6·98
					$\bar{K}_1 = 7{\cdot}01 \pm 0{\cdot}07$

[a] The first value of each pair was obtained 13 hr. after mixing the solutions and the second value was obtained from the same solution 3 hr. later. [b] This value was not included in the average.

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[7] G. F. Kortüm and J. O'M. Bockris, " Electrochemistry," Elsevier Publishing Co., London, 1951, vol. 2, p. 670.

[8] H. L. Bott, unpublished observations.

complexes, at 300 mμ, were unaffected by the presence of free iodide at the concentrations used in all these experiments. The differences between the values of K_2 in Table 6 and that given in Table 5 are only slightly larger than would be expected on the basis of the standard deviations quoted. This can be accounted for by small systematic errors due, for example, to the greater dependence (when $[X^-]/[I^-]$ is low) of the values in Table 6 on the extrapolated values of K_2, and to $[I^-]$ being less than 0·1M when $[X^-]/[I^-]$ is large.

TABLE 6

The *trans*-Rh $en_2Cl_2^+ + I^- \underset{}{\overset{K_1}{\rightleftharpoons}}$ *trans*-Rh $en_2ICl^+ + Cl^-$ equilibrium (data obtained by Mr. H. L. Bott)

[Complex] = $3·05 \times 10^{-4}$M; λ = 300 mμ; K_2 = 2·31 at 85° and 1·78 at 96°; μ = 1·5M; ε_0 = 107; ε_1 = 4150 cm.$^{-1}$ l. mole^{-1}.

	$[Cl^-]/[I^-]$	ε	ε'_2	$\varepsilon - \varepsilon_0$	$\varepsilon_1 - \varepsilon$	$\varepsilon'_2 - \varepsilon$	K_1
85·0°	2·6	3510	4500	3403	640	990	5·85
	4·2	3015	4220	2908	1135	1205	6·81
	7·0	2116	4020	2009	2034	1904	5·27
	12·0	1658	3880	1551	2492	2222	6·36
	20·0	1160	3820	1053	2990	2660	6·37
	30·0	776	3750	669	3374	2974	5·57
							$\bar{K}_1$ = 6·04 ± 0·32
96·0°	2·6	3502	4500	3395	648	998	6·63
	4·2	3018	4220	2911	1132	1202	7·47
	7·0	2278	4020	2171	1872	1742	6·56
	12·0	1537	3880	1431	2613	2343	5·66
	20·0	850	3820	743	3300	2970	4·15
	30·0	711	3750	604	3439	3039	5·00
							$\bar{K}_1$ = 6·26 ± 0·36

$\Delta H°$ = +0·9 ± 1·9 kcal./mole. $\Delta S°$ = 6 ± 5 cal. deg.$^{-1}$ mole^{-1}.

DISCUSSION

The relative stabilities of halogeno-complexes can be discussed in terms of class (a) and class (b) character. Ahrland, Chatt, and Davies[3] classified the metals on the basis of the relative stability of complexes containing donor atoms which are in the first short row of the periodic table compared with those containing donor atoms from the second or later periods. The greater the relative stability of the complexes containing the heavier donor atoms the greater was the class (b) character. Metals of greatest class (b) character are those at the end of the transition-metal series. Class (b) character also increases on descending a group so that elements of highest class (b) character are found in a triangle in the periodic table with a base which extends from iridium to mercury and with an apex at copper. The borderline between the classes is ill-defined, primarily because the classification depends on the oxidation state of the metal ion. Ahrland *et al.* associated class (b) character largely with the ability of the metal ion to " back-donate " d_π-electrons to the ligands but this has been criticised, at least when applied to halogeno-complexes.[2b, 9] The class (b) character of halogeno-complexes depends on a balance between solvation effects, which always favour class (b) behaviour, and bond-strength effects which probably always favour class (a) behaviour. The less difference there is between the strengths of the M–Cl and M–I bonds the greater will be the class (b) character.[2b]

Not only will the classification depend on the oxidation state of the metal but it will also depend on the other ligands joined to the metal. Thus, the introduction of a second iodide into $PtCl_6^{2-}$ or $PtBr_6^{2-}$ is several times easier than the introduction of the first.[10] The replacement of four of the chloride ligands in $PtCl_6^{2-}$ by two ethylenediamine groups arranged *trans* to each other makes the replacement of a chloride by a bromide about four times easier.[2c] Replacement of chloride by bromide in *trans*-Pt en_2XCl^+ is about 50% easier when X = Br than when X = Cl.[2c]

Pearson[4] has considered class (a) and (b) character as part of a general interaction between Lewis acids and bases. He has suggested a classification into " hard " and " soft " acids or bases such that hard acids tend to react more completely with hard bases and soft acids more completely with soft bases. Hardness and softness corresponds largely with low and high polarisability, respectively. Class (b) metals are soft because, for example, they tend to react more completely with the heavier and softer halides.

In the present work we have obtained results which give a measure of the class (b) character or softness of rhodium(III) in the *trans*-bisethylenediaminedilhalogeno-complexes. In addition, the variation with X^- of the class (b) character of the five-co-ordinate Lewis acid Rh en_2X^{-2+} is also obtained. Thus, at 90° the equilibrium constant for replacement of both chloride ligands in *trans*-Rh $en_2Cl_2^+$ by bromide[1] is 1·6 and that for replacement of two bromide ligands by iodide is 13·3. There is, therefore, a small but definite increase in stability from the dichloro- through the dibromo- to the di-iodo-complex and so the bisethylenediaminedihalogenorhodium(III) system is slightly class (b). After allowing for statistical effects, the chloride in *trans*-Rh en_2ICl^+ is replaced by iodide about 25% more easily than a chloride in *trans*-Rh $en_2Cl_2^+$. Although equilibrium constants frequently have to be accepted as measures of class (a) or (b) character, the possible temperature-dependence of the resulting classification, and the tendency to interpret the classification in terms of bond strengths, makes enthalpy changes a better basis when they are available. The enthalpy changes for the complete replacement of chloride by bromide, and of bromide by iodide, are 0 ± 1 (ref. 1) and −6·0 ± 0·5 kcal./mole, respectively. This behaviour is not dissimilar to the hexahalogenoplatinum(IV) system in which the complete replacement of chloride by bromide is slightly endothermic whereas the replacement of bromide by iodide is strongly exothermic.[2a]

The effect of changing the halide X^- on the class (b) character of the five-co-ordinate Lewis acid Rh en_2X^{-2+} is shown by the enthalpy data in Table 7. Where the equilibria were not studied directly the values were obtained from suitable combinations of measured values. With the possible exception of the Cl^- : Br^- interchange, the class (b) character increases as the group in the *trans*-position changes from chloride through bromide

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[9] R. J. P. Williams, *Proc. Chem. Soc.*, 1960, 20.

[10] A. J. Poë, unpublished calculations based on data in ref. 2.(*a*)

to iodide. The enthalpy values include the change in solvation enthalpy which results from the interchange of the free halide ions and it is necessary for a more unambiguous comparison to correct the values for these solvation effects. When the free halide changes from iodide to chloride, or from iodide to bromide, the solvation enthalpy changes by −18·5 or −10·4 kcal./mole, respectively.[11] Correcting the enthalpies of reaction for these changes leads to the relative enthalpies of the complex ions in solution. These values are a combination of the enthalpies of bonding of the ligands to the metal ion and of the solvent to the complex. If the highest value is taken arbitrarily as zero the enthalpies of these *trans*-complexes are: Rh $en_2I_2^+$, 0; Rh en_2IBr^+, −7·0 ± 0·3; Rh en_2ICl^+, −12·3 ± 0·4; Rh $en_2Br_2^+$, −14·8 ± 0·5; Rh en_2BrCl^+, −22·9 ± 0·7; Rh $en_2Cl_2^+$, −31·0 ± 0·9 kcal./mole. The trends in these values are most clearly shown in Figure 2 which reveals linear enthalpy relationships. Enthalpies of *trans*-Rh en_2XY^+ are plotted against the enthalpies of *trans*-Rh en_2ClY^+ where X^- and Y^- are chloride, bromide, or iodide. The smaller the increase in enthalpy along the series Y = Cl, Br, I the greater is the class (b) character of Rh en_2X^{-2+}. The class (b) character of the Lewis acid Rh en_2X^{-2+} therefore increases steadily along the series X = Cl, Br, I. These enthalpy effects which are transmitted across the rhodium ion are quite appreciable, unlike the free-energy effects which are very much smaller. This implies that the effects on the entropy are just counter-balanced by those on the enthalpy. Thus, it is found that the higher the enthalpy of the solvated complex ion the higher is the entropy. The systematic changes show that the " softness " of a Lewis acid can be a function not only of the ion to which the Lewis base becomes directly attached but also of the softness of other groups already attached to that ion. In this case an iodide ion makes the rhodium ion to which it is attached appreciably more soft than does the relatively hard chloride ion.

TABLE 7

$\Delta H°$ Values for the reactions *trans*-Rh $en_2XY^+ + Z^- \longrightarrow$ *trans*-Rh $en_2XZ^+ + Y^-$

X	Cl[a]	Br[a]	I[b]	Cl[b]	Br[a]	I[a]	Cl[a]	Cl[b]	Br[b]	I[a]
Y	Cl	Cl	Cl	Br	Br	Br	Cl	Cl	Cl	Cl
Z	Br	Br	Br	I	I	I	I	I	I	I
$\Delta H°$ (kcal./mole)	0	0	−2·8	−0·1	−2·6	−3·4	0·9	−0·1	−2·6	−6·2
Standard deviation (kcal./mole)	~0·5	~0·5	0·5	0·8	0·4	0·3	1·9	1·0	0·8	0·4

[a] Direct measurement. [b] Indirect estimate.

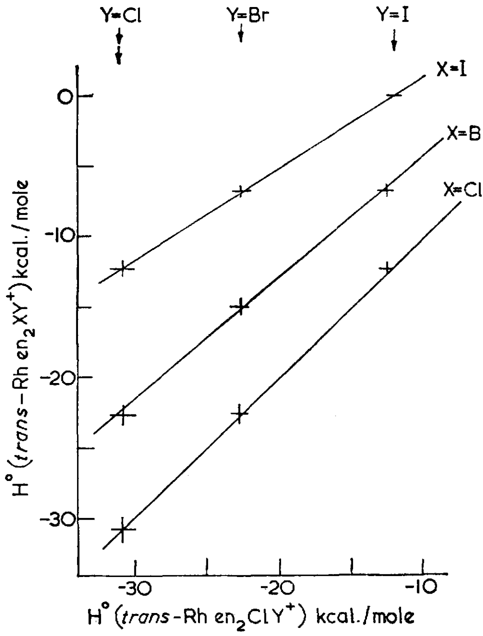

FIGURE 2 Linear enthalpy relationships for the *trans*-Rh en_2XY^+ complexes in aqueous solution. Enthalpies are measured relative to $H°$(*trans*-Rh $en_2I_2^+$) taken arbitrarily as zero. The gradients for the lines when X = Cl, Br, and I are in the ratios 1·00 : 0·85 : 0·65

The enthalpy effects should not necessarily be ascribed entirely to changes in the strengths of the bonds of Rh en_2X^{-+} to halide ions as X^- is changed. Since X^- is itself a halide ion, the Rh en_2X^{-2+} unit must not be considered as a rigid entity unaffected by what is bonded to it. The mutual interactions can be accounted for if (*a*) a halide ion weakens the bond in the position *trans* to it, (*b*) the *trans* weakening effect increases along the series Cl^-, Br^-, I^-, and (*c*) the magnitude of this effect is smaller the smaller the strength of the bond affected, *i.e.*, the effect on the Rh–Y bond decreases along the series Y = Cl, Br, or I. These interactions are such that the mixed complexes always have a higher enthalpy than the average of the appropriate unmixed ones. Since corresponding data are not yet available for the *cis*-complexes the effects are not necessarily specifically *trans* effects.

These thermodyanic effects are paralleled by kinetic effects observed in the same complexes.[12] The labilising effect of the halides increases along the series Cl^-, Br^-, I^- and is presumably, at least in part, a consequence of weakening the *trans*-bond. Other evidence for weakening of the *trans*-bond is provided by the infrared absorption data shown in Table 8. These were kindly obtained for us by Dr. David Adams of the University of Leicester. The frequencies shown for the *trans*-dichloro- and *trans*-dibromo-complexes are presumably the asymmetric stretching frequencies and, as such, are not directly

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[11] L. Benjamin and V. Gold, *Trans. Faraday Soc.*, 1954, **50**, 797.

[12] E. J. Bounsall and A. J. Poë, Proc. 8th Internat. Conf. Co-ordination Chem., Springer-Verlag, Vienna, 1964, p. 313.

comparable with the frequencies quoted for the mixed complexes. The two values given for the Rh–Cl stretching frequency in $\text{Rh en}_2\text{BrCl}^+$ arise from difficulties of assignment. It is clear that the replacement of chloride by iodide in the *trans* position significantly lowers the Rh–Br stretching frequency, and the replacement of bromide by iodide similarly lowers the Rh–Cl stretching frequency. Although there will be some coupling of the vibrations of the two halides we conclude tentatively that these frequencies are a rough indication of the relative force constants of the individual bonds.

TABLE 8

Rhodium–halide stretching frequencies in solid *trans*-$[\text{Rh en}_2\text{XY}]\text{ClO}_4$

	$\nu_{\text{Rh–Cl}}$ (cm.$^{-1}$)	$\nu_{\text{Rh–Br}}$ (cm.$^{-1}$)
$[\text{Rh en}_2\text{Cl}_2]\text{ClO}_4$	343·0	—
$[\text{Rh en}_2\text{Br}_2]\text{ClO}_4$	—	222·7
$[\text{Rh en}_2\text{BrCl}]\text{ClO}_4$	343·0 or 333·4	212·7
$[\text{Rh en}_2\text{IBr}]\text{ClO}_4$	—	195·6
$[\text{Rh en}_2\text{ICl}]\text{ClO}_4$	311·4	—

These effects are not consistent with the back-bonding hypothesis. This would predict that a Rh–Cl bond *trans* to an iodide would be weakened less than a Rh–I bond and the presence of one iodide in the complex should decrease the relative affinity for another.[13] Johnson, Basolo, and Pearson have also argued, on the basis of kinetic evidence, that π-bonding is not important in such rhodium(III) complexes.[14] The data are qualitatively consistent with a polarisation theory involving greater electron transfer towards the rhodium the greater the polarisability of the halide. This results in a decreased effective ionic charge on the rhodium and a consequent *trans*-bond weakening which will be greater the greater the strength of the bond affected. A purely ionic model is not able to provide even a rough quantitative explanation, however. The greater size of the more polarisable iodide ion ensures that there is less charge–charge repulsion between the halide ions *trans* to each other in the chloroiodo-complex than in the dichloro-complex. This source of extra stability in the former is not outweighed by the greater charge–dipole repulsions found in the mixed complex.[8] A significant amount of covalency must therefore be invoked so that charge transfer from the iodide is sufficiently great to lead to the bond-weakening effects observed. Charge transfer of this type is also indicated by, for example, the increasing back-donation to carbon monoxide in XMn(CO)_5 as X changes along the series Cl, Br, I. This results in decreasing C–O stretching frequencies, decreasing lability of the CO ligands, and certain changes in the ultraviolet absorption spectra.[15]

EXPERIMENTAL

The *trans*-bisethylenediaminedichloro- and -dibromo-rhodium(III) ions were prepared in solution by Johnson and Basolo's method [5] and were isolated as the perchlorate salts by addition of ice-cold concentrated perchloric acid (10 ml.) to the mixture (50 ml.). Yields were generally 10—15% higher than when isolation was effected as the nitrate salt. *trans*-Bisethylendiaminedi-iodorhodium(III) iodide was also prepared by Johnson and Basolo's method.[5] Purity was judged by elemental analyses and the reproducibility of the ultraviolet and visible spectra of samples from different preparations. The configuration of these compounds and of those described below was inferred from the ultraviolet and visible absorption spectra (Tables 1 and 9) and from the methods of preparation, no *trans* ⟶ *cis* rearrangements having been observed so far in these systems.

trans-*Bisethylenediaminechloroiodorhodium*(III) *perchlorate* was prepared by reacting the *trans*-di-iodo-iodide complex (0·6 g.) with a 160-fold excess of aqueous sodium chloride (9·35 g. in 50 ml.) at 55° for 12 hr. after which the colour of the solution had changed from a dark red-brown to a bright orange-red. The solution was filtered, cooled in an ice-bath and cold, concentrated perchloric acid (4 ml.) was added. The precipitate was collected and reacted for a further 5 hr. with aqueous sodium chloride (4·5 g. in 50 ml.) after which the compound was precipitated as before, filtered off, and dissolved in a minimum of warm water. This solution was cooled and the compound reprecipitated by addition of cold concentrated perchloric acid. It was filtered off, washed with separate portions of cold dilute perchloric acid, ethanol, and ether, and dried *in vacuo* at room temperature. Yield 80% (Found: C, 9·9; H, 3·2; I, 25·9; N, 11·7. $\text{C}_4\text{H}_{16}\text{Cl}_2\text{IN}_4\text{O}_4\text{Rh}$ requires C, 9·9; H, 3·3; I, 26·2; N, 11·4%).

trans-*Bisethylenediaminebromoiodorhodium*(III) *perchlorate* was prepared in an exactly analogous manner to the chloroiodo-complex. Yield 55% (Found: C, 9·1; H, 3·1; N, 10·5. $\text{C}_4\text{H}_{16}\text{BrClIN}_4\text{O}_4\text{Rh}$ requires C, 9·2; H, 3·0; N, 10·6%).

trans-*Bisethylenediamineazidochlororhodium*(III) *perchlorate* was prepared from the diazido-complex.[5] *trans*-Bisethylenediaminediazidorhodium(III) perchlorate (0·54 g.) was heated under reflux for 1 hr. with one equivalent of aqueous perchloric acid (20 ml.). The acid was present to catalyse the removal of one azide ion, thereby producing the *trans*-aquoazido-complex *in situ*. An additional hour under reflux did not change the ultraviolet absorption spectrum of the solution. This showed peaks at 360 and 257 mμ with extinction coefficients of about 600 and 6000 cm.$^{-1}$ l. mole^{-1}, respectively. Sodium chloride (5·85 g.) was then added and the solution maintained at 50° for 16 hr., filtered, and cooled to room temperature. On addition of cold, concentrated perchloric acid (5 ml.) a bright yellow compound crystallised. This was collected, dissolved in a minimum of warm water, and the compound reprecipitated by addition of cold concentrated perchloric acid (3 ml.). After collection on a filter the compound was washed with cold dilute perchloric acid, ethanol, and ether, and was finally dried *in vacuo*. Yield 62% (Found: C, 12·2; H, 4·0; Cl, 17·9. $\text{C}_4\text{H}_{16}\text{Cl}_2\text{N}_7\text{O}_4\text{Rh}$ requires C, 12·0; H, 4·0; Cl, 17·7%).

trans-*Bisethylenediamineazidobromorhodium*(III) *perchlorate* was prepared in a way exactly analogous to that for the azidochloro-complex. Yield 40% (Found: C, 11·1; H, 3·7; Cl + Br, 26·2. $\text{C}_4\text{H}_{16}\text{BrClN}_7\text{O}_4\text{Rh}$ requires C, 10·8; H, 3·6; Cl + Br, 26·0%).

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[13] S. Ahrland, J. Chatt, N. R. Davies, and A. A. Williams, *J. Chem. Soc.*, 1958, 276.

[14] S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 1741.

[15] H. B. Gray, E. Billig, A. Wojcicki, and M. Farona, *Canad. J. Chem.*, 1963, **41**, 1281.

An attempt was made to prepare *trans*-bisethylenediamineazidoiodorhodium(III) perchlorate in a similar way but mixtures consisting mainly of the di-iodo-complex were always obtained. Attempted preparation from the di-iodo-complex *via* the aquoiodo-complex were more successful but the product was always contaminated with some di-iodo-complex as was shown by the absorption spectrum. Absorption maxima were observed at 408 and 292 mμ in addition to those for the di-iodo-complex and these were presumably due to the azidoiodo-complex.

Sodium trans-*bisethylenediaminedithiosulphatorhodium*(III) was prepared by treating *trans*-bisethylenediaminedichlororhodium(III) nitrate (0·5 g.) with a five-fold excess of sodium thiosulphate pentahydrate (3·5 g.) in water (20 ml.) under reflux. The solution rapidly turned brown and a light brown precipitate was slowly deposited. After 30 min. this precipitate was filtered off and the greenish-yellow filtrate was refluxed for a further 2 hr. with no further change in colour and no further formation of a precipitate. The solution was cooled and saturated sodium chloride solution (20 ml.) was added. After several hours at −5° a pale greenish-yellow precipitate was formed and this was separated and recrystallised by dissolving in the minimum amount of warm water and adding an equal volume of cold saturated sodium chloride solution. The precipitate was collected by filtration, washed successively with small amounts of cold dilute sodium chloride solution, ethanol, and ether, and dried *in vacuo*. Yield 16% (Found: C, 10·4; H, 3·5; N, 12·3; S, 27·7. $C_4H_{16}N_4NaO_6RhS_4$ requires C, 10·2; H, 3·4; N, 11·9; S, 27·3%).

Visible and Ultraviolet Absorption Spectra.—Absorption spectra of solutions of the compounds in silica cells were obtained with a Perkin-Elmer (model 350) recording spectrophotometer. The main features of the spectra are given in Tables 1 and 9.

TABLE 9

Visible and ultraviolet absorption spectra of some *trans*-bisethylenediaminediacidorhodium(III) complexes

		λ (mμ)	ε (cm.$^{-1}$ l. mole^{-1})
trans-Rh $en_2(N_3)_2^+$	(This work)	375, 282	740, 13,000
	(Ref. 5)	375, 282	780, 12,000
trans-Rh $en_2(H_2O)N_3^{2+}$ [a]		360, 257	~600, ~6000
trans-Rh $en_2ClN_3^+$		377, 263	560, 9600
trans-Rh $en_2BrN_3^+$		388, 272	580, 15,100
trans-Rh $en_2IN_3^+$ [b]		408, 292	—, —
trans-Rh $en_2(S_2O_3)_2^-$		415, 340sh, 263	60, ~330, 14,200

[a] Prepared *in situ*. [b] Samples contaminated with *trans*-Rh $en_2I_2^+$.

Equilibrium Measurements.—Aliquot portions of stock solutions of the complexes were diluted to 25 or 50 ml. in standard flasks with solutions of (*a*) potassium iodide only, (*b*) potassium bromide or chloride only, and (*c*) potassium iodide and potassium chloride or bromide in various ratios. The total halide concentration, and therefore the ionic strength, was kept constant and was so large that the amount of halide which entered the complex was negligible in comparison. The flasks were wrapped in aluminium foil and kept in an oil-bath at a temperature which was constant to within ±0·1°. Periodically absorption spectra of cooled aliquot portions were measured in 1-cm. silica cells. The reactions of the complexes are sufficiently slow that no readjustment of equilibrium occurred between the time of removal from the thermostat bath and the time of measurement of the spectra. Reference solutions were used which contained the same amounts of all reagents other than the rhodium complex. When successive measurements of the same solutions were identical the spectra were used to calculate the equilibrium constants. The halide solutions were made up by weighing finely powdered and dried AnalaR potassium salts into standard volumetric flasks.

Estimation of Standard Deviations of Thermodynamic Parameters.—For any given equilibrium the equilibrium constants are assumed to be random variables which have the same standard deviations (expressed as a percentage of the constant) irrespective of the temperature. This is a reasonable assumption on theoretical grounds and also when the standard deviations of groups of constants obtained at different temperatures are compared. The standard deviation, σ_K, of an individual value for a constant is then calculated from all the values of the constants by the method of pooled variances[16] and the standard deviation, $\sigma_{\bar{K}}$, of the average of N values obtained at any one temperature is given by $\sigma_K/N^{\frac{1}{2}}$.

The standard deviation of log $\bar{K}$ is given by log $(1 + \sigma_{\bar{K}}/100)$ or $\sigma_{\bar{K}}/230{\cdot}3$ so that the standard deviations of the enthalpy values are obtainable from equation (3).

$$\sigma_{\Delta H^\circ} = \{4{\cdot}58\ T_1T_2/230{\cdot}3(T_1 - T_2)\}\{(\sigma^2{}_{\bar{K}})_{T_1} + (\sigma^2{}_{\bar{K}})_{T_2}\}^{\frac{1}{2}}\text{cal./mole} \quad (3)$$

When the equilibrium constants were measured at three different temperatures the best enthalpy value is taken as the weighted mean of the three values found from constants at the three pairs of temperatures as shown in equation (4).[17]

$$\overline{\Delta H}^\circ = \frac{\Delta H^\circ{}_{12}/(\sigma^2{}_{\Delta H^\circ})_{12} + \Delta H^\circ{}_{23}/(\sigma^2{}_{\Delta H^\circ})_{23} + \Delta H^\circ{}_{13}/(\sigma^2{}_{\Delta H^\circ})_{13}}{1/(\sigma^2{}_{\Delta H^\circ})_{12} + 1/(\sigma^2{}_{\Delta H^\circ})_{23} + 1/(\sigma^2{}_{\Delta H^\circ})_{13}}\ \text{cal./mole} \quad (4)$$

$\sigma_{(\overline{\Delta H}^\circ)}$ is given by the square root of the inverse of the denominator in equation 4. In all these estimations we have ignored any errors which are caused by uncertainties in the temperatures. This is justified since any difference in the temperature between two measurements of a constant will be reflected in the variations in the constants obtained which in turn is reflected by the values of σ_K. The uncertainty in ΔH° caused by uncertainty in the value of $T_1 - T_2$ will be less than 1 or 2% which is considerably less than the deviations obtained by the above procedure.

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[17] Ref. 16, ch. 7.