27. *The Relative Stabilities of Halogeno-complexes. Part III.*[1] *The* trans-Pt $en_2Cl_2^{2+}$–Br^- *Equilibria.*

By A. J. Poë.

Equilibrium constants for successive replacement of chloride in *trans*-Pt $en_2Cl_2^{2+}$ by bromide have been found spectrophotometrically to be $K_1 = 11{\cdot}5$ and $K_2 = 4{\cdot}3$ at ~20° and an ionic strength of 0·5M. The value of K_1/K_2 is only about 70% of that expected on purely statistical grounds, and replacement of the second chloride is therefore thermodynamically easier than that of the first. The relative thermodynamic *trans*-effect of the chloride and bromide is therefore the same as that observed in kinetic studies of platinum(II) complexes.

The ultraviolet absorption spectra of Pt $en_2Cl_2^{2+}$ and Pt $en_2Br_2^{2+}$ are changed by addition of an excess of the corresponding halide ion in a way consistent with a small amount of ion-pair formation.

SUCCESSIVE equilibrium constants for the interchange of halogen in *trans*-Pt $en_2Hal_2^{2+}$ ions (en = ethylenediamine) with different free halide ions in aqueous solution are of interest in giving a thermodynamic, as opposed to a kinetic, measure of the relative *trans*-effect of the halogen ligands in platinum(IV) complexes. The equilibria between the various chloro- and bromo-complexes have been studied spectrophotometrically by measuring the absorption spectra of solutions of *trans*-Pt en_2Cl_4 and *trans*-Pt en_2Br_4 in potassium halide solutions of various chloride : bromide concentration ratios at a constant ionic strength of 0·5M.

RESULTS

Ultraviolet Absorption Spectra of trans-Pt en_2Cl_4 *and* trans-Pt en_2Br_4.—The absorption spectrum of *trans*-Pt en_2Cl_4 was found to have maxima at 332 and 263 mμ with extinction coefficients of 105 and 950 cm.$^{-1}$ l. mole^{-1}, respectively, in agreement with previous work.[2] In addition, a shoulder to the 332 mμ band was observed at 380 mμ ($\varepsilon \gtrsim 20$ cm.$^{-1}$ l. mole^{-1}), and the spectrum measured in 0·5M-potassium chloride solution showed increased absorption below about 300 mμ, although the absorption at the 332 mμ peak remained unchanged.[3] The difference between the absorption with and without additional chloride showed a maximum at about 240 mμ, and the increased absorbance of a solution which was 0·25M in chloride and 0·25M in perchlorate was half that of the 0·5M chloride solutions. The spectra of solutions which were all 0·5M in chloride but were 10^{-2}, 10^{-3}, and 10^{-4}M in the complex were all of the same shape, and the addition of an equivalent of Pt en_2^{2+} had no effect on them.

The spectrum of *trans*-Pt en_2Br_4 had absorption maxima at 320 and 237 mμ, and a shoulder at 370 mμ, with extinction coefficients of 1100, 40,000 and about 150 cm.$^{-1}$ l. mole^{-1}, respectively.

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[1] Part II, *J.*, 1961, 1023.

[2] Basolo, Bailar, and Tarr, *J. Amer. Chem. Soc.*, 1950, **72**, 2433.

[3] Cf. Poë, *Discuss. Faraday Soc.*, 1960, **29**, 133; Basolo and Pearson, "Advances in Inorganic and Radiochemistry," Vol. III, p. 38.

The spectrum changes in the presence of additional free bromide, and the difference between the spectra with and without the excess of bromide has a maximum at about 260 mμ. The change in absorbance is directly proportional to the amount of additional bromide if the solution is maintained at a constant ionic strength by addition of sodium perchlorate. If it is not so maintained, then the increase is faster at lower than at higher bromide concentrations. As with the chloro-complex, the shape of the spectrum in 0·5M free-halide solution is unchanged by a hundred-fold change in the concentration of the complex or by addition of an equivalent of $\text{Pt en}_2{}^{2+}$. Some of the spectra are shown in Figs. 1 and 2.

The observed changes in the spectra cannot be caused by the existence of redox equilibria of the type: $\text{Pt en}_2\text{Hal}_2{}^{2+} + \text{Hal}^- \rightleftharpoons \text{Pt en}_2{}^{2+} + \text{Hal}_3{}^-$, in spite of the fact that the new absorption maxima occur at about the same wavelength[4] as for $\text{Cl}_3{}^-$ and $\text{Br}_3{}^-$. This is so because (i) the addition of $\text{Pt en}_2{}^{2+}$ does not change the shape of the spectra whereas it would greatly distort the redox equilibria, (ii) the growth of the absorbance would be proportional to $[\text{Hal}^-]^{0\cdot5}$ and not to $[\text{Hal}^-]$, and (iii) the unchanging shape of the spectra with changing $[\text{Pt en}_2\text{Hal}_2{}^{2+}]$, but constant $[\text{Hal}^-]$, is inconsistent with the redox equilibria since the ratio of the concentrations of the two absorbing species would remain constant only if all the reactants were diluted equally. This also eliminates complete replacement of one ethylenediamine ligand by two halide ions as the cause of the changes. Finally, (iv) the equilibrium constant for the reduction of the bromo-complex can be calculated from published data[5] to be about 10^{-16} which is far too small to explain the observed results.

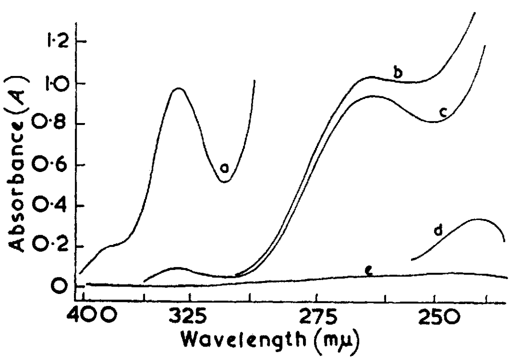

FIG. 1.

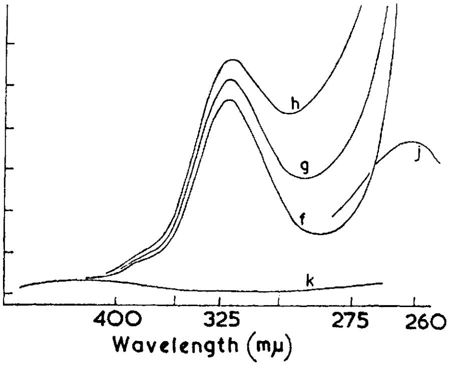

FIG. 2.

FIG. 1. Ultraviolet absorption spectra of 0·01M-$\text{Pt en}_2\text{Cl}_4$: (a) 1 cm. cell, no excess of Cl^-; (b) 1 mm. cell, 0·5M-excess of Cl^-; (c) 1 mm. cell, no excess of Cl^-; (d) = (b) — (c); (e) = zero absorbance.

FIG. 2. Ultraviolet absorption spectra of $\text{Pt en}_2\text{Br}_4$ in 1 cm. cells: (f), (g), and (h) are for 8×10^{-4}M-$\text{Pt en}_2\text{Br}_4$ in 0M-, 0·2M-, and 0·5M-bromide, respectively; (j) is $10 \times$ difference between 8×10^{-5}M-$\text{Pt en}_2\text{Br}_4$ in 0M- and 0·5M-bromide; (k) = zero absorbance.

The results are, however, consistent with association equilibria of the type: $\text{Pt en}_2\text{Hal}_2{}^{2+} + \text{Hal}^- \rightleftharpoons \text{Pt en}_2\text{Hal}_2,\text{Hal}^+$.

The apparent extinction coefficient, ε′, would then be given by

$$\varepsilon' = (\varepsilon_2 + K_a\varepsilon_a[\text{Hal}^-])/(1 + K_a[\text{Hal}^-])$$

where K_a is the association constant, ε_2 is the extinction coefficient of $\text{Pt en}_2\text{Hal}_2{}^{2+}$, and ε_a that of the associated species. Since ε′ is proportional to $[\text{Hal}^-]$ up to $[\text{Hal}^-]$ = 0·5M, K_a must be less than about 0·1 l. mole^{-1} and, from the gradient, ε_a for $\text{Pt en}_2\text{Cl}_2,\text{Cl}^+$ at 242 mμ is not less than ~8000 cm.$^{-1}$ l. mole^{-1} and ε_a for $\text{Pt en}_2\text{Br}_2,\text{Br}^+$ at 270 mμ is not less than ~24,900 cm.$^{-1}$ l. mole^{-1}. Since the complexes are stable at room temperature[6] towards their

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[4] Katzin, *J. Chem. Phys.*, 1952, **20**, 1165.

[5] (*a*) Grinberg and Orlova, *Zhur. priklad. Khim.*, 1949, **22**, 441 (*Chem. Abs.*, 1951, **45**, 2358i); (*b*) Latimer, " Oxidation Potentials," Prentice-Hall Inc., New York, 2nd edn., 1952, p. 60.

[6] Drew, *J.*, 1932, 2328.

corresponding concentrated halogen hydracids it is unlikely that the formation of the associated species involves displacement of one end of an ethylenediamine ligand with formation of a third Pt–Hal bond. Some form of ion-pairing is therefore indicated and the increased effect of additional bromide with decreasing ionic strength is consistent with this. Ion-pairing between dipositive and uninegative ions is electrostatically unlikely [7] but, in this case, close association of the outer-sphere halide ion with an inner-sphere halide might occur in an analogous way to that of Cl^- in Cl_3^- and Br^- in Br_3^-, the platinum(IV) ion being highly electronegative. In this case the close similarity between the wavelength of absorption of the associated species and that of the trihalide ion might not be a coincidence.

For solutions of *trans*-Pt en_2Cl_4 in an excess of iodide an absorption peak at 360 mμ grows with increasing $[I^-]$ in a way consistent with ion-pair formation.[3] The growth is in excellent quantitative agreement with $K_a = 1{\cdot}28$ l. mole^{-1} and $\varepsilon_a = 2{\cdot}25 \times 10^4$ cm.$^{-1}$ l. mole^{-1}. In this case, however, decrease of the concentration of complex ion, but not that of iodide, does change the shape of the spectrum, and addition of Pt en_2^{2+} greatly decreases the absorption at 360 mμ. Formation of Pt en_2^{2+} and I_3^- must therefore be occurring. An analysis of the data suggests that the redox equilibrium cannot alone cause the changes and the product *trans*-Pt $en_2I_2^{2+}$ appears to be considerably hydrolysed.

The Pt $en_2Cl_2^{2+}$–Br^- *Equilibria.*—Spectra were measured of Pt en_2Cl_4 or Pt en_2Br_4 dissolved in solutions of chloride and bromide in various proportions, the sum of the salt concentrations always being 0·5M. The associated species, Pt en_2Cl_2,Cl^+ and Pt en_2Br_2,Br^+, are formed only in negligible concentrations even in 0·5M-chloride and -bromide solutions, respectively, and the equilibrium constants for the replacement reactions can be derived if it is assumed that the Pt $en_2Cl_2^{2+}$–Br^-, Pt en_2ClBr^{2+}–Br^- or –Cl^-, and Pt $en_2Br_2^{2+}$–Cl^- association products are also formed in negligible amounts and that they do not affect the absorption spectra above 300 mμ. The association products involving outer-sphere bromide and inner-sphere chloride are likely to be thermodynamically unstable towards interchange, and those involving outer-sphere chloride ions are unlikely, by analogy with the Pt en_2Cl_2,Cl^+ species, to affect the spectra above about 300 mμ. The effect of the Pt $en_2Br_2^{2+}$–Br^- interaction is known and can be allowed for. The absorbance of the solutions is then given by:

$$A = \varepsilon_0[\text{Pt en}_2\text{Cl}_2^{2+}] + \varepsilon_1[\text{Pt en}_2\text{ClBr}^{2+}] + \varepsilon'[\text{Pt en}_2\text{Br}_2^{2+}] \qquad (1)$$

where ε' is the apparent extinction coefficient of the dibromo-complex at the bromide concentration of the particular solution under consideration, and ε_0 and ε_1 are the extinction coefficients of the dichloro- and the chlorobromo-complex, respectively. It follows that:

$$(\varepsilon - \varepsilon_0) + K_1(\varepsilon - \varepsilon_1)[\text{Br}^-]/[\text{Cl}^-] + K_1K_2(\varepsilon - \varepsilon')[\text{Br}^-]^2/[\text{Cl}^-]^2 = 0 \qquad (2)$$

where $K_1 = [\text{Pt en}_2\text{ClBr}^{2+}][\text{Cl}^-]/[\text{Pt en}_2\text{Cl}_2^{2+}][\text{Br}^-]$,

and $K_2 = [\text{Pt en}_2\text{Br}_2^{2+}][\text{Cl}^-]/[\text{Pt en}_2\text{ClBr}^{2+}][\text{Br}^-]$,

and ε is the apparent extinction coefficient of the solution as a whole.

If we assume that at higher bromide concentrations [Pt $en_2Cl_2^{2+}$] is negligible, K_2 can be obtained approximately from the gradient of a plot of ε against $(\varepsilon' - \varepsilon)[Br^-]/[Cl^-]$. Such a plot, involving data at 320 mμ, was a straight line of gradient 4·5 down to $[Br^-]/[Cl^-] = 0{\cdot}1$, but it was later found that this was a chance result of the constancy of the terms in equation (2) which involved K_1, rather than a result of a negligible value of [Pt $en_2Cl_2^{2+}$] over this wide range.

With K_2 known, it is possible to obtain K_1 graphically after suitably rearranging equation (2). At 320 mμ, however, the relative sizes of the terms involved are such that only a very approximate value of K_1 can be obtained, although the relation between K_1 and ε_1 is accurately obtainable. As a result of this, K_2 can be found accurately at this wavelength, independently of the exact value of K_1 which is used, provided that K_1 and ε_1 lie in the ranges suggested by the approximate graphical determinations and also that their interdependence is allowed for. Thus, K_2 lies between 3·8 and 4·1 for K_1 and ε_1 varying, respectively, from 15 and 200 cm.$^{-1}$ l. mole^{-1} to 6 and 450 cm.$^{-1}$ l. mole^{-1}. Use of $K_2 = 4{\cdot}0$ enabled a more accurate estimate of K_1 to be made graphically from data at 300 mμ where the relative sizes of the terms were much more favourable.

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[7] Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley and Sons, New York, 1958, p. 381.

TABLE 1.

Calculation of K_1 from results at 300 mμ by assuming various values for ε_1 and taking $K_2 = 4{\cdot}0$ and $\varepsilon_0 = 90$ cm.$^{-1}$ l. mole^{-1}.

$$K_1 = \{(\varepsilon - \varepsilon_0)[\mathrm{Cl}^-]/[\mathrm{Br}^-]\}/\{\varepsilon_1 - \varepsilon + K_2(\varepsilon' - \varepsilon)[\mathrm{Br}^-]/[\mathrm{Cl}^-]\}$$

			K_1 when ε_1 is:					
[Cl⁻]/[Br⁻]	ε	ε′	550	590	600	610	620	650
49	200	580	14·2	12·8	12·5	12·2	12·0	11·2
24	275	590	13·6	12·1	11·8	11·5	11·2	10·4
15·7	335	600	12·7	11·2	10·9	10·6	10·3	9·5
11·5	385	608	13·9	12·0	11·4	11·2	10·8	9·9
9·00	430	615	15·1	12·7	12·1	11·7	11·2	10·1
7·33	465	625	16·0	13·0	12·4	11·8	11·4	10·1
6·14	490	632	14·6	11·8	11·3	10·7	10·3	9·2
5·25	515	640	17·2	13·1	12·4	11·7	11·1	9·7
4·57	530	650	16·1	12·2	11·5	10·9	10·3	8·9
4·00	550	658	17·1	12·4	11·6	11·0	10·3	8·9
Average K_1 ($\overline{K}_1$)			15·1	12·3	11·8	11·3	10·9	9·7
$\sum(\overline{K}_1 - K_1)^2$			21·22	3·15	2·68	2·53	3·13	4·67
Probable error					0·11	0·11		

Values of ε and ε′ were obtained from smooth curves drawn through the experimental points.

An accurate value of K_1 was finally obtained by assuming values for ε_1 which lay in a range suggested by the graphical plots and by calculating a value of K_1 from the apparent extinction coefficients obtained for each [Cl⁻] : [Br⁻] and [ClO$_4^-$] : [Br⁻] ratio. These coefficients were obtained from curves drawn through the plotted results. The set of constants corresponding to a particular value of ε_1 was averaged and the deviations were calculated. The average of the set which had the minimum deviation was accepted as the best value of K_1 obtainable. The " least-squares " procedure is illustrated in Table 1 and the best value of K_1 from those results is 11·5, with a probable error of ±0·1. This error is a measure only of the internal consistency of the results and does not take systematic errors into account. Thus, when the procedure was applied to data at 355 mμ, K_1 was found to be 14·5 with almost equally good internal consistency. The systematic errors, however, were much greater because of (i) lower values of absorbances measured, (ii) less accurately known variation of ε′, and (iii) the much greater dependence on (ε − ε′) which is also much smaller.

When $K_1 = 11{\cdot}5$ was used in calculating K_2 from data at 320 mμ (Table 2) and 335 mμ,

TABLE 2.

Calculation of K_2 from data at 320 mμ by assuming various values for ε_1 and taking $K_1 = 11{\cdot}5$ and $\varepsilon_0 = 80$ cm.$^{-1}$ l. mole^{-1}.

$$K_2 = \{\varepsilon - \varepsilon_1 + (\varepsilon - \varepsilon_0)[\mathrm{Cl}^-]/[\mathrm{Br}^-]K_1\}/\{(\varepsilon' - \varepsilon)[\mathrm{Br}^-]/[\mathrm{Cl}^-]\}$$

			K_2 when ε_1 is:				
[Cl⁻]/[Br⁻]	ε	ε′	180	190	200	210	220
49·0	120	1107	5·19	4·72	4·25	3·78	3·30
24·0	180	1110	5·36	5·10	4·85	4·59	4·34
15·7	235	1113	4·73	4·55	4·37	4·19	4·01
11·5	295	1120	4·59	4·45	4·30	4·16	4·03
9·00	355	1122	4·57	4·45	4·34	4·22	4·10
7·33	420	1126	4·74	4·63	4·53	4·42	4·32
6·14	470	1130	4·60	4·51	4·41	4·32	4·23
5·25	515	1133	4·51	4·43	4·34	4·26	4·17
4·57	555	1138	4·41	4·34	4·25	4·18	4·10
4·00	605	1141	4·52	4·45	4·38	4·30	4·23
2·33	780	1160	4·55	4·50	4·43	4·36	4·31
1·50	890	1180	4·21	4·17	4·11	4·07	4·01
$\overline{K}_2$			4·67	4·53	4·38	4·24	4·10
$\sum(\overline{K}_2 - K_2)^2$			1·12	0·57	0·36	0·43	0·85
Probable error					0·035	0·038	

Values of ε and ε′ were obtained from smooth curves drawn through the experimental points.

values of $4{\cdot}35 \pm 0{\cdot}04$ and $4{\cdot}20 \pm 0{\cdot}04$ were obtained. The effect of changing K_2 from 4·0 to 4·28 in the calculations of K_1 was negligible. Thus $K_1/K_2 = 2{\cdot}7$ with 95% confidence limits, based on internal consistency, of $\pm 0{\cdot}1$. The effect of systematic errors is difficult to estimate but it seems unlikely that K_1/K_2 can be significantly greater than 3 and it is certainly less than 4.

Use of the values of K_1 and K_2 enables the variation of ε_1 with wavelength to be calculated. ε_1 has a maximum of 215 cm.$^{-1}$ l. mole^{-1} at 365 mμ and then rises steadily to ~600 cm.$^{-1}$ l. mole^{-1} at 300 mμ, below which our figures do not give accurate results. The 365 mμ peak was also observed, clearly resolved, during the reaction of Pt $en_2Br_2^{2+}$ with chloride before equilibrium was attained.

DISCUSSION

The value of K_1/K_2 would be expected to be 4 if statistical factors were the only ones involved.[8] That it is only 2·7 shows that the replacement of a chloride by a bromide is thermodynamically easier if there is a bromide rather than a chloride in the *trans*-position. This effect is quantitatively expressed by a difference of 0·23 kcal. mole^{-1} in the free-energy changes.

No unambiguous measure of the relative *trans*-effect of chloride and bromide in platinum(IV) complexes has been obtained from kinetic studies.[9] The thermodynamic *trans*-effect observed here is qualitatively the same as, but considerably smaller than, the kinetic effect observed for platinum(II) complexes.[10] Even this qualitative identity would not necessarily be expected since the equilibrium *trans*-effect is a measure of the ratio of the kinetic *trans*-effect as measured by two different reactions. Thus it is related to:

$$K_2/K_1 = \frac{\text{Rate const. of (Br)PtCl–Br}^-\text{ reaction}}{\text{Rate const. of (Br)PtBr–Cl}^-\text{ reaction}} \Big/ \frac{\text{Rate const. of (Cl)PtCl–Br}^-\text{ reaction}}{\text{Rate const. of (Cl)PtBr–Cl}^-\text{ reaction}}$$

$$= (k_2/k'_2)/(k_1/k'_1) = (k_2/k_1)/(k'_2/k'_1)$$

where the *trans*-directing groups are written in parentheses. Thus the results show that the relative kinetic *trans*-effect of bromide and chloride would be slightly greater if measured by the replacement of a chloride in the complex by a bromide than if measured by the reverse interchange.

A case where the equilibrium *trans*-effect is quite different from the kinetic one is that involving the species $(PEt_3)_3PtCl^+$ which is postulated as an intermediate[11] in the *cis*–*trans*-isomerisation of $(PEt_3)_2PtCl_2$. This isomerisation is catalysed by small amounts of triethylphosphine, and the $(PEt_3)_3PtCl^+$ formed appears to react rapidly with chloride ions to form an equilibrium mixture of the *cis*- and the *trans*-complex, the latter being formed in much larger amounts. In view of the strong kinetic *trans*-effect of triethylphosphine, its replacement by chloride is presumably kinetically easier when a phosphine ligand is in the *trans*-position, but clearly it is thermodynamically easier when chloride is in the *trans*-position. This appears to be a result of solvation. For the ethylenediamine complexes described here the equilibrium *trans*-effect is so small that it is not possible to ascribe it exclusively either to solvation or to bond-energy effects.

The average free-energy change on replacement of a chloride ligand by a bromide is $-1{\cdot}2$ kcal. mole^{-1}. This decrease is about 0·8 kcal. mole^{-1} larger than that for the $PtCl_6^{2-}$–Br^- equilibria[1] and this may indicate an average difference between Pt–Cl and Pt–Br bond energies in the ethylenediamine complexes smaller than the 6 kcal. mole^{-1} for the hexahalogeno-complexes. The results also show that the standard reduction potential

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[8] Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1957, p. 24.

[9] Zvyagintsev and Karandasheva, *Proc. Acad. Sci.* (*U.S.S.R.*), 1956, **108**, 277; Basolo and Pearson, "The Trans-Effect," Progress in Inorganic Chemistry, 1962, Vol. IV, to be published.

[10] Zvyagintsev and Karandasheva, *Proc. Acad. Sci.* (*U.S.S.R.*), 1955, **101**, 93.

[11] Chatt and Wilkins, *J.*, 1952, 273.

of the half-cell, $\mathrm{Pt\,en_2Cl_2^{2+} + 2e = Pt\,en_2^{2+} + 2Cl^-}$, is 0·05 v more positive than for the corresponding bromide system. This is to be compared with a value of 0·017 v obtained by Grinberg *et al.*[12] for the corresponding systems involving $\mathrm{Pt(NH_3)_4^{2+}}$.

EXPERIMENTAL

The complexes $\mathrm{Pt\,en_2Cl_4}$ and $\mathrm{Pt\,en_2Br_4}$ were prepared by methods previously described.[2, 13] The former was also prepared by the oxidation of the compound $\mathrm{Pt\,en_2Cl_2}$ with hydrogen peroxide in concentrated hydrochloric acid; and the latter by repeated evaporation to dryness of the complex $\mathrm{Pt\,en_2Cl_4}$ with concentrated hydrobromic acid on a steam-bath. The chloro-complex was recrystallised several times from water by addition of concentrated hydrochloric acid and/or alcohol until the ultraviolet absorption spectrum remained constant and the sample had a pale cream colour. (The impure product had too large an absorption below 330 mμ.) The bromo-complex in 0·5M-bromide had a spectrum identical with that of $\mathrm{Pt\,en_2Cl_4}$ in 0·5M-bromide, after equilibrium had been attained.

Analyses were performed by the departmental microanalytical section with the following results. (*a*) Found: Pt, 42·6, 42·6; C, 10·7; N, 11·7; H, 3·8. Calc. for $\mathrm{C_4H_{16}Cl_4N_4Pt}$: Pt, 42·7; C, 10·5; N, 12·3; H, 3·5%. (*b*) Found: Pt, 30·4; Br, 49·8; C, 8·2; N, 9·2; H, 2·4%. Calc. for $\mathrm{C_4H_{16}Br_4N_4Pt}$: Pt, 30·7; Br, 50·4; C, 7·6; N, 8·8; H, 2·5%.

Standard salt solutions were made up by dissolving weighed amounts of finely powdered and dried "AnalaR" reagents and spectra were measured with a Unicam S.P. 500 spectrophotometer or a Perkin-Elmer (model 4000) Spectracord. Reference solutions were used which contained the same amounts of all reagents, other than the platinum complex under investigation. 10, 1, and 0·1 cm. quartz cells were used as convenient but most of the measurements from which the constants were eventually calculated were obtained from 0·001M- or 0·002M-solutions of the complex, the same pair of 1 cm. cells being used throughout. Since the samples were slightly hygroscopic the exact strength of each of the $\mathrm{Pt\,en_2Cl_4}$ and $\mathrm{Pt\,en_2Br_4}$ solutions was not always accurately known, and the results were combined where possible by setting the apparent extinction coefficients of the solutions of the complexes in 0·5M-bromide equal to 1300 $\mathrm{cm.^{-1}\,l.\,mole^{-1}}$. The solutions were left at a room temperature of ~20° until the spectra no longer changed, then they were assumed to be at equilibrium. In some cases this took as long as a week, which indicated the absence of appreciable amounts of $\mathrm{Pt\,en_2Cl_2}$ in the samples since this is known [14] to induce rapid exchange and replacement in these systems. $\mathrm{Pt\,en_2Cl_4}$ is not hydrolysed, and $\mathrm{Pt\,en_2Br_4}$ is hydrolysed only slowly, in aqueous solution; so little or no hydrolysis will have occurred in the quite strong bromide and chloride solutions used. Smooth curves were drawn through all the combined results and, although at any given $[\mathrm{Br^-}] : [\mathrm{Cl^-}]$ ratio the spread of values was sometimes as high as ±10%, it was generally much less than this and the choice of possible curves was severely restricted.

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[12] Ref. 5*a*; and Grinberg, Lavrent'ev, and Ptitsyn, *Compt. rend. Acad. Sci.* (*U.R.S.S.*), 1940, **26**, 52 (*Chem. Abs.*, 1940, **34**, 6153).

[13] Watt and McCarley, *J. Amer. Chem. Soc.*, 1957, **79**, 3315.

[14] Basolo, Wilks, Pearson, and Wilkins, *J. Inorg. Nuclear Chem.*, 1958, **6**, 161.