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Mixed-Ligand Complexes of Palladium(II) with Bromide and Iodide[1a]

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A spectrophotometric study of a series of consecutive mixed-ligand complexes of palladium(II) with bromide and iodide has been carried out. The limiting halide species $PdBr_4^{2-}$ and PdI_4^{2-} show well-defined peaks at 246, 332, and 510 mμ and at 268, 317, 407, and 487 mμ, respectively. The following formation constants ($\log {}^{\dagger}K$) have been determined: 2.75 ± 0.05 for $[PdBr_3I^{2-}][Br^-]/[PdBr_4^{2-}][I^-]$, 3.00 ± 0.15 for $[PdBr_2I_2^{2-}][Br^-]/[PdBr_3I^{2-}][I^-]$, 1.70 ± 0.15 for $[PdBrI_3^{2-}][Br^-]/[PdBr_2I_2^{2-}][I^-]$, and 0.80 ± 0.05 for $[PdI_4^{2-}][Br^-]/[PdBrI_3^{2-}][I^-]$. The spectra of the individual mixed species have been resolved.

Introduction

In a previous publication,[2] functions were derived for treating spectrophotometric data for the calculation of stepwise formation constants and their use was demonstrated by determining the constants for the various mixed-ligand complexes of palladium(II) with chloride and bromide. The method allows the calculation of the successive-step equilibrium constants with a minimum use of the previously determined parameters and manipulation of the data, thus minimizing the possibility of cumulative errors in the determination of higher constants. The present paper describes the application of this method to the determination of formation constants of the mixed-ligand complexes of palladium with bromide and iodide.

Experimental Section

Apparatus.—Spectra of various solutions were obtained with a Cary Model 14 recording spectrophotometer. A special closed H cell was devised to keep air out of the system and thus minimize the problem of oxidation of iodide in acidic media. An acidic solution containing palladium, perchlorate, and bromide was placed in one limb of the cell and an acid-free iodide solution in the other limb. The closures were provided with special pressure clamps, so that a slight positive pressure of nitrogen could be maintained inside the cell assembly. Nitrogen was flushed through the solutions in both limbs for about 5 min, and then the spectra were recorded immediately after mixing. Even employing this technique, a slight oxidation of iodide was observed to occur after prolonged periods of time. Consequently, each level of iodide had to be studied with fresh solutions, except in cases where the iodide concentration was extremely low and then a continuous titration procedure could be employed.[2] Silica cells with path lengths of 10 or 100 mm were used to obtain optimum absorbances.

Materials.—A standard solution containing 8.51 mg/ml of palladium was prepared as described earlier.[2] A standard solution of perchloric acid (Baker Analyzed reagent) was used as required to make suitable dilutions of the palladium stock solution. The following reagents were used to prepare other appropriate stock solutions: reagent grade anhydrous lithium bromide (Matheson Coleman and Bell) and anhydrous lithium perchlorate (G. Frederick Smith Co.). Solutions of lithium iodide were made using Mallinckrodt Chemical Works $LiI \cdot 3H_2O$. The compound was dissolved in water, preflushed with nitrogen, filtered quickly, and stored under an atmosphere of nitrogen. The ultraviolet spectrum of this solution was checked from time to time, and fresh solutions were prepared whenever the previous solution showed an absorption due to iodine more than 0.02 absorbance unit in the region 260–380 mμ.

Absorbance Curves.—The absorbance of a 5.0×10^{-5} M palladium solution at an ionic strength of 4.5 showed no further change in absorbance after the addition of 1.0 M iodide. The spectra of these solutions indicated the presence of PdI_4^{2-}, with well-defined peaks at 487, 407, 317, and 268 mμ. In the case of bromide, solutions approached a limiting absorbance at 0.5 M bromide. The spectra of $PdBr_4^{2-}$ showed sharp peaks at 246 and 332 mμ and a broad absorption peak around 510 mμ. Unlike the palladium–chloride–bromide system, there are no two corresponding peaks that could be used unequivocally to study the whole system and to determine all of the equilibria involved. Therefore, a variety of wavelengths and a number of metal ion concentrations had to be selected to study the different equilibria.

In addition to the problem of the air oxidation of iodide, another difficulty was encountered owing to the very low solubility of palladium iodide. Even a large excess of bromide failed to prevent the precipitation of palladium iodide at certain low iodide concentrations. Precipitation, however, is not observed when the iodide concentration is $<5 \times 10^{-4}$ M and in the presence of an excess of bromide. The range of iodide concentration over which precipitation occurs could be decreased by using very low palladium concentrations. The compositions of the solutions studied were: palladium (ranging between 2.0×10^{-6} and 4.0×10^{-4} M), 0.1 M H^+ ($HClO_4$), 2.4 M $LiClO_4$, and varying ratios of bromide to iodide (total halide was kept constant at 2.0 M). The ionic strength, thus, was maintained at 4.5. Suitable blanks were employed containing everything but the metal ion. In general, solutions containing low palladium were employed to evaluate the formation constants involving the intermediate species $PdI_2Br_2^{2-}$.

Results and Discussion

The same type of equilibria as in the palladium–chloride–bromide system exist in the bromide–iodide system and can be represented by the replacement reaction

$$MX_4^{2-} + nY^- = MX_{4-n}Y_n^{2-} + nX^- \qquad (1)$$

with

$${}^{\dagger}\beta_n = \frac{[MX_{4-n}Y_n^{2-}][X^-]^n}{[MX_4^{2-}][Y^-]^n} \qquad (2)$$

It is only necessary to study two step equilibria starting with PdI_4^{2-} and two equilibria starting with $PdBr_4^{2-}$ to categorize the system completely.

Evaluation of the First-Step Constant.—The constant for the first replacement reaction was determined using the previously derived equation

$$\Delta(1 + {}^{\dagger}\beta_1 R)^{-1} = A - A_1 \qquad (3)$$

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[2] S. C. Srivastava and L. Newman, *Inorg. Chem.*, **5**, 1506 (1966).

where R is the ratio of the ligand concentrations ([Y]/[X]); A, the measured absorbance; A_1, the absorbance if all the palladium were as PdX_3Y^{2-}; and Δ, the difference in absorbance between PdX_4^{2-} and PdX_3Y^{2-}. A set of normalized curves was calculated as described and the data plotted as A *vs.* log R were fitted on the appropriate curves. Translation in the abscissa gave the value of $^{\dagger}\beta_1$ and the translation in the ordinate gave A_1. A number of wavelengths were employed and data using different suitable concentrations of palladium were used. The calculation of the constant from the bromide side, the formation of $PdBr_3I^{2-}$, was accomplished with the data shown in Figure 1 (curves 1–17). See Table I. A continuous titration type experiment was employed where the total bromide was kept constant at 2.0 M, and iodide was added in small increasing portions. Owing to the presence of extremely low concentrations of iodide, the simple cell assembly as described in the previous publication was used. A number of wavelengths in the range 400–550 mμ were taken for the calculations. Additional spectral curves in Figure 2 were also used for the determination of this constant. See Table II. Curves 1–17 were employed in the wavelength regions of 320–350 and 390–500 mμ.

The formation constant for PdI_3Br^{2-}, starting from PdI_4^{2-}, was calculated using data also shown in Figures 1 and 2. In these experiments (curves numbered with subscripts), the precautions for avoiding air oxidation of iodide had to be taken. The wavelength region 470–540 mμ in Figure 1 employing curves 1a–9a was used for calculating the constant. The usual arguments[2] hold for selecting the proper curves for the calculation. Curves 1a–8a from Figure 2 in the wavelength region 400–420 mμ were also used for the calculation of $^{\dagger}\beta_1$ for PdI_3Br^{2-}.

The values obtained for $^{\dagger}\beta_1$ for $PdBr_3I^{2-}$ were found to be in good agreement at all of the wavelengths selected and the same held true for $^{\dagger}\beta_1$ for PdI_3Br^{2-}. Figure 3 shows a few typical plots of A *vs.* log R each fitted on the normalized curve at the position governed by the average value obtained for $^{\dagger}\beta_1$.

Evaluation of the Second-Step Constant.—For reasons described in the previous publication the expression

$$\frac{(A - A_2)R^2}{(A_0 - A)} = {}^{\dagger}\beta_2{}^{-1} + {}^{\dagger}\beta_1{}^{\dagger}\beta_2{}^{-1}\frac{R(A_1 - A)}{(A_0 - A)} \quad (4)$$

was used for the determination of the formation constant for $PdX_2Y_2^{2-}$. The unknowns in this equation are A_2, the absorbance if all of the palladium is as $PdX_2Y_2^{2-}$, and $^{\dagger}\beta_2$. The values of A_1 and $^{\dagger}\beta_1$ were calculated as described above, A is the absorbance of a particular solution, and A_0 is the absorbance of the parent species. Various assumed values of A_2 at suitable absorbance intervals were substituted into this equation and the left-hand term was plotted against $R(A_1 - A)/(A_0 - A)$. Only when the proper value of A_2 was selected would a straight line plot be obtained. The slope would give the value of $^{\dagger}\beta_1{}^{\dagger}\beta_2{}^{-1}$, and the intercept, the value for $^{\dagger}\beta_2{}^{-1}$. The values of $^{\dagger}\beta_1$ obtained in this manner should check with the previously determined values for this constant. There are two possible values of $^{\dagger}\beta_2$, the formation constant for $PdI_2Br_2^{2-}$ starting either with $PdBr_4^{2-}$ or with PdI_4^{2-}.

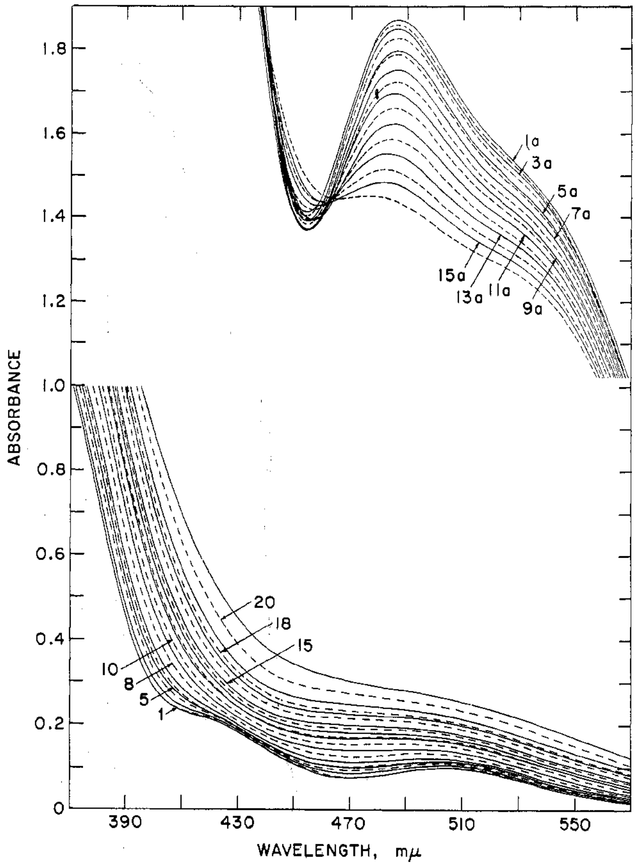

Figure 1.—Absorption spectra of palladium at ionic strength 4.5. Composition of the solutions; 0.1 M $HClO_4$, 2.4 M $LiClO_4$, 2.0 M (LiI + LiBr). See Table I.

TABLE I

LOG R VALUES FOR CURVES OF FIGURE 1

2.5 × 10^{-4} M Pd Path length, 10 mm R = [I^-]/[Br^-]		4.0 × 10^{-4} M Pd Path length, 10 mm R = [Br^-]/[I^-]	
Curve	Log R	Curve	Log R
1	No iodide	1a	No bromide
2	−5.002	2a	−0.9542
3	−4.404	3a	−0.6021
4	−4.111	4a	−0.1761
5	−3.941	5a	0.000
6	−3.823	6a	0.1761
7	−3.730	7a	0.3680
8	−3.572	8a	0.5007
9	−3.462	9a	0.6021
10	−3.380	10a	0.7533
11	−3.315	11a	0.8451
12	−3.262	12a	0.9542
13	−3.218	13a	1.0607
14	−3.179	14a	1.1234
15	−3.146	15a	1.1950
16	−3.091	16a	1.2788
17	−3.047		
18	−3.011		
19	−2.955		
20	−3.865		
21	−2.813		

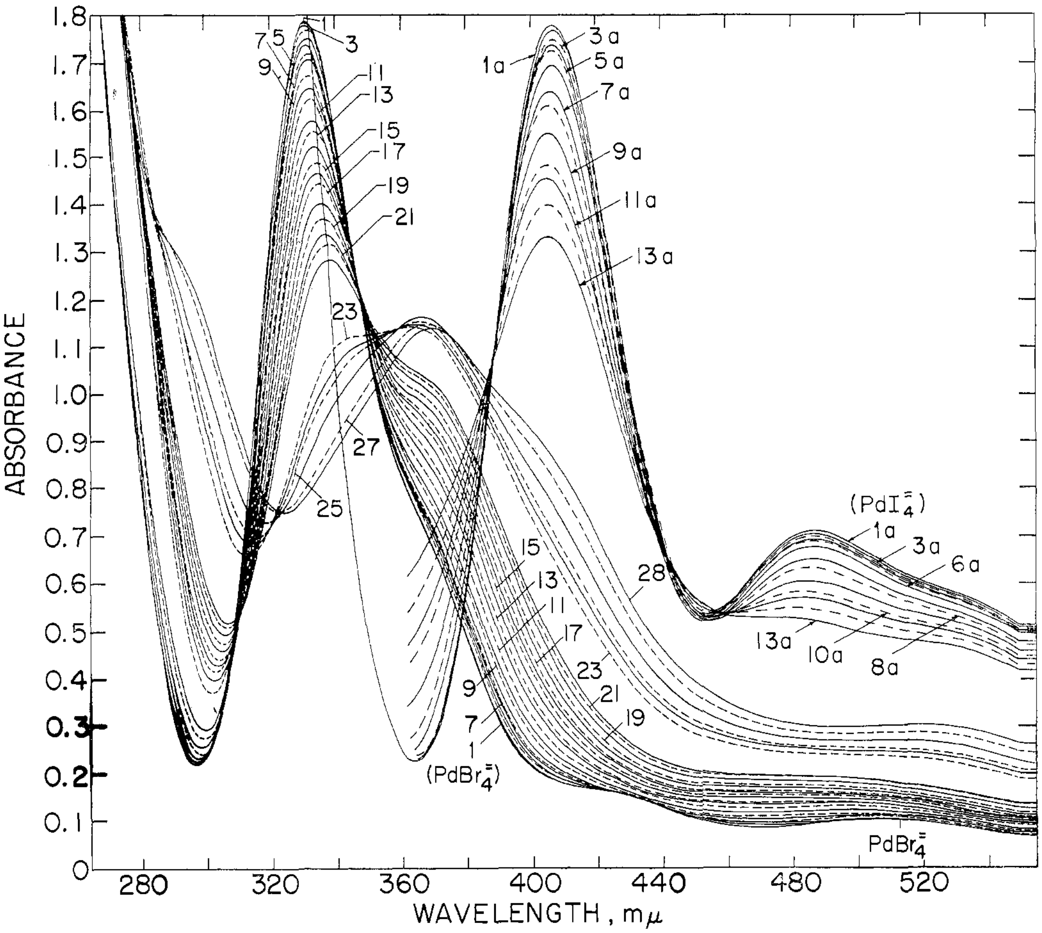

Figure 2.—Absorption spectra of palladium at ionic strength 4.5. Composition of the solutions: 0.1 *M* $HClO_4$, 2.4 *M* $LiClO_4$, 2.0 *M* (LiI + LiBr). See Table II.

Table II

Log *R* Values for Curves of Figure 2

1.5×10^{-5} *M* Pd Path length, 100 mm $R = [I^-]/[Br^-]$		1.5×10^{-4} *M* Pd Path length, 10 mm $R = [Br^-]/[I^-]$	
Curve	Log *R*	Curve	Log *R*
1	No iodide	1a	No bromide
2	−5.544	2a	−0.9547
3	−4.848	3a	−0.6021
4	−4.454	4a	−0.3680
5	−4.253	5a	−0.1761
6	−4.081	6a	0.1761
7	−3.961	7a	0.6021
8	−3.870	8a	0.7536
9	−3.705	9a	0.9542
10	−3.591	10a	1.1234
11	−3.505	11a	1.1950
12	−3.380	12a	1.2788
13	−3.333	13a	1.3802
14	−3.255		
15	−3.195		
16	−3.146		
17	−3.105		
18	−3.041		
19	−2.991		
20	−2.938		
21	−2.894		
22	−2.865		
23	−2.593		
24	−2.540		
25	−2.503		
26	−2.439		
27	−2.352		
28	−2.295		

The high *R* values necessary to obtain curves 18–28 in Figure 2 required the use of the 1.5×10^{-5} *M* Pd in order to avoid precipitation of PdI_2. These curves in the wavelength regions 320–350 mμ and 390–500 mμ were used to calculate ${}^{\dagger}\beta_2$ starting from $PdBr_4^{2-}$. Data in the region 400–420 mμ from Figure 2 employing curves 7a–13a and in the region 470–540 mμ employing curves 9a–16a from Figure 1 were used for the calculation of the constant starting from PdI_4^{2-}. In these experiments the metal ion concentrations were selected such that while starting with PdI_4^{2-} and successively increasing the Br^- concentration, the formation of the species $PdI_2Br_2^{2-}$ was almost complete before the iodide concentration got low enough to cause precipitation. The constants obtained at different wavelengths and different metal ion concentrations gave values of ${}^{\dagger}\beta_2$ which were in essential agreement and the value of ${}^{\dagger}\beta_1$ agreed with that which was previously calculated. Figure 4 shows a typical plot for the calculation of the second-step constant. A number of such plots were made with data starting from either $PdBr_4^{2-}$ or PdI_4^{2-}.

The expression

$$(A - A_2)R = A_1{}^{\dagger}\beta_1{}^{\dagger}\beta_2^{-1} + {}^{\dagger}\beta_2^{-1}[A_0R^{-1} - A({}^{\dagger}\beta_1 + R^{-1})] \quad (5)$$

is a rearrangement of (4) in which use can be made of the previously determined value of ${}^{\dagger}\beta_1$ instead of A_1. Plots of $(A - A_2)R$ *vs.* $[A_0R^{-1} - A({}^{\dagger}\beta_1 + R^{-1})]$ with

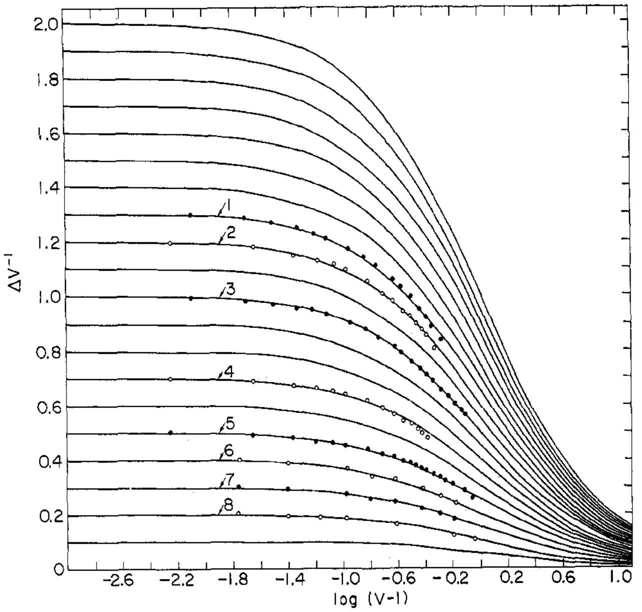

Figure 3.—The family of normalized curves: $\Delta V^{-1} = A - A_1$; $\log (V - 1) = \log R + \log {}^{\dagger}\beta_1$. Some typical plots of A vs. $\log R$ at various wavelengths shown fitted onto appropriate curves. For the formation of $PdBr_3I^{2-}$ from $PdBr_4^{2-}$ the curve numbers and respective wavelengths (mμ) are: 1, 400; 2, 470; 3, 390; 4, 330; 5, 410. For the formation of PdI_3Br^{2-} from PdI_4^{2-} the curve numbers and respective wavelengths are: 6, 485; 7, 520; 8, 400.

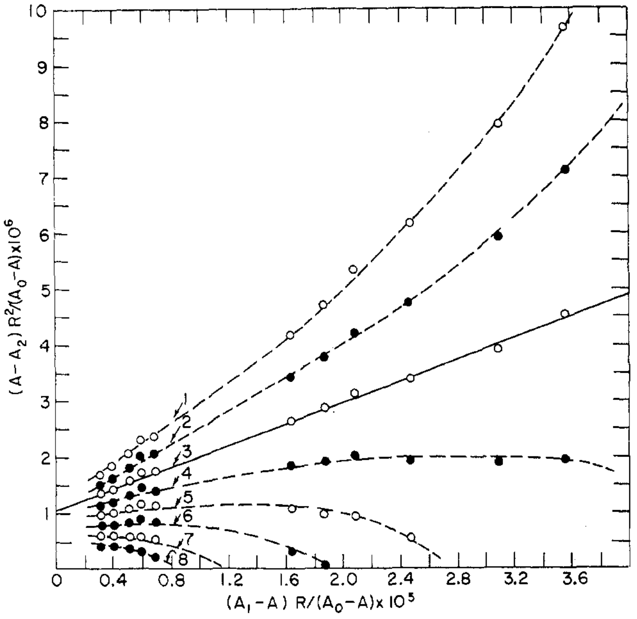

Figure 4.—A typical plot for the determination of the constant for the reaction $PdX_4^{2-} + 2Y^- \rightleftarrows PdX_2Y_2^{2-} + 2X^-$. Determination of the formation constant for $PdBr_4^{2-} + 2I^- \rightleftarrows PdBr_2I_2^{2-} + 2Br^-$ at 330 mμ. Curve numbers with their various assumed values of A_2 are: 1, 0.4; 2, 0.5; 3, 0.6; 4, 0.7; 5, 0.8; 6, 0.9; 7, 1.0; 8, 1.1.

various assumed values of A_2 were also found satisfactory for the calculation of ${}^{\dagger}\beta_2$.

Conclusions

The constants thus obtained allowed a calculation of the spectra of the various individual mixed species. The wavelength maxima and the molar absorptivities of different species are shown in Table III. Figure 5 shows the resolved spectra of all of the species.

TABLE III

ABSORPTION MAXIMA AND MOLAR ABSORPTIVITIES OF THE PALLADIUM–BROMIDE–IODIDE MIXED SPECIES

Species	Absorption max, mμ	Molar absorptivity, $10^{-3}\ \epsilon_{max}$
$PdBr_4^{2-}$	332 ± 1	11.50 ± 0.05
	246 ± 1	32.10 ± 0.10
$PdBr_3I^{2-}$	375 ± 5	11.83 ± 0.20
$PdBr_2I_2^{2-}$	370 ± 5	8.73 ± 0.20
$PdBrI_3^{2-}$	407 ± 5	9.75 ± 0.20
PdI_4^{2-}	487 ± 1	4.68 ± 0.05
	407 ± 1	11.87 ± 0.10
	317 ± 1	17.63 ± 0.05
	268 ± 2	22.4 ± 0.20

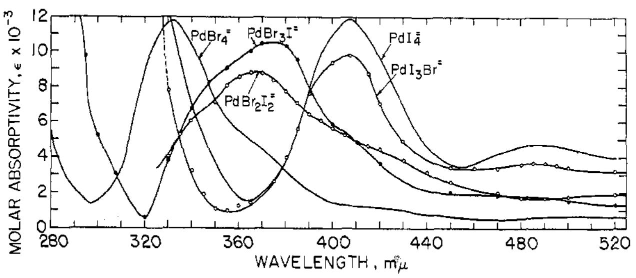

Figure 5.—Resolved spectra of palladium–bromide–iodide mixed complexes.

From the ${}^{\dagger}\beta$ values which were obtained, the stepwise formation constants ($\log {}^{\dagger}K$) for the various equilibria were calculated as 2.75 ± 0.05 for $[PdBr_3I^{2-}]\cdot[Br^-]/[PdBr_4^{2-}][I^-]$, 3.00 ± 0.15 for $[PdBr_2I_2^{2-}]\cdot[Br^-]/[PdBr_3I^{2-}][I^-]$, 1.70 ± 0.15 for $[PdBrI_3^{2-}]\cdot[Br^-]/[PdBr_2I_2^{2-}][I^-]$, and 0.80 ± 0.05 for $[PdI_4^{2-}]\cdot[Br^-]/[PdBrI_3^{2-}][I^-]$.

The formation constants of the three mixed species starting from the parent reactants and the statistically predicted values for the reactions are shown in Table IV.

TABLE IV

STATISTICAL AND THE OBSERVED VALUES OF THE FORMATION CONSTANTS

Reaction	Log †K (found)	Log †K[a] (statistical)
$^3/_4PdBr_4^{2-} + {}^1/_4PdI_4^{2-} \rightleftarrows PdBr_3I^{2-}$	0.69	0.60
$^1/_2PdBr_4^{2-} + {}^1/_2PdI_4^{2-} \rightleftarrows PdBr_2I_2^{2-}$	1.62	0.78
$^1/_4PdBr_4^{2-} + {}^3/_4PdI_4^{2-} \rightleftarrows PdI_3Br^{2-}$	1.26	0.60

[a] These constants are calculated on the assumption that the geometrical isomers of the square-planar complex are present in their statistically expected relative amounts.

It appears that in this system the constants are indeed stronger than the statistically predicted values which is in contrast to the chloride–bromide system.[2] A subject for future work will be the evaluation of the mixed-ligand complexes for the palladium–chloride–iodide system. A complete discussion and comparison of the systems will be reserved until the completion of that work.