Mixed Ligand Complexes of Palladium(II) with Chloride and Bromide[1]

BY SURESH C. SRIVASTAVA AND LEONARD NEWMAN

A series of mixed ligand complexes of palladium with chloride and bromide has been studied spectrophotometrically. The limiting metal halide species are $PdBr_4^{2-}$ and $PdCl_4^{2-}$, each of which shows two predominant peaks in the ultraviolet region, the former at 246 and 332 mμ and the latter at 222 and 279 mμ. The studies have been performed using data near the peaks at 279 and 332 mμ. The formation constants (log K) for the various equilibria involved have been determined as follows: $[PdCl_3Br^{2-}][Cl^-]/[PdCl_4^{2-}][Br^-] = 1.55 \pm 0.05$; $[PdCl_2Br_2^{2-}][Cl^-]/[PdCl_3Br^{2-}][Br^-] = 1.09 \pm 0.07$; $[PdClBr_3^{2-}][Cl^-]/[PdCl_2Br_2^{2-}][Br^-] = 0.95 \pm 0.07$, and $[PdBr_4^{2-}][Cl^-]/[PdClBr_3^{2-}][Br^-] = 0.55 \pm 0.05$, at 25° and at an ionic strength of 4.5. A relationship is derived whereby a family of normalized curves could be used for the evaluation of the constant for the first step from either direction, employing only the measured absorbance. The constants for the second step have been determined using another relationship requiring only the knowledge of the absorbance of the parent species and the first mixed ligand complex. The individual spectra for the various mixed species have been resolved on the basis of the different constants obtained.

Introduction

Mixed ligand complexes are best studied by methods which introduce the fewest parameters and which readily provide the values for the concentration variables. When trying to obtain stability constants by a spectrophotometric method, one is always faced with the additional problem of having to determine the constants for the extinction coefficients of various species. Moreover, when the successive formation constants in a system are quite close to each other, resulting in the presence of more than two species at a time, the conventional methods for treating the spectrophotometric data using straight-line plots often do not give a satisfactory analysis. The detection of errors in such cases becomes very difficult since the functions that are used for treating the experimental measurements are often quite complicated. Consequently, we thought that it would be desirable to derive simple functions which would employ minimum manipulation of the data and minimum use of previously determined parameters. A spectrophotometric investigation of a series of consecutive mixed ligand complexes of palladium(II) with chloride and bromide using such newly derived functions is described in this paper.

Experimental Section

Apparatus.—A Cary Model 14 recording spectrophotometer was used to obtain the absorption curves. A cell assembly was devised allowing the use of a titration-type procedure in a closed system. Quartz cells with a 10-mm path length were employed. A glass reservoir of 200-ml capacity provided with a Teflon stopper was fused on top of the cells.

Materials.—A standard solution containing 8.51 mg/ml of palladium was prepared by dissolving 7.104 g of Engelhard Industries, Inc., anhydrous palladium chloride in 500 ml of 1.0 M hydrochloric acid. Suitable dilutions of this stock solution were made with a standard solution of perchloric acid (Baker Analyzed reagent). Other appropriate stock solutions were made using the following reagents: reagent grade anhydrous

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lithium chloride (Baker and Adamson), reagent grade anhydrous lithium bromide (Matheson Coleman and Bell), and anhydrous lithium perchlorate (G. Frederick Smith Co.).

Absorption Curves.—Experiments were performed to investigate the effect of increasing chloride and bromide concentrations on the absorbance of solutions of palladium. A solution containing 1.5×10^{-4} M Pd, at an ionic strength of 4.0, was found to be in its fully complexed state with a concentration of 0.5 M bromide or 1.0 M chloride. This was indicated by the fact that solutions containing higher halide concentrations showed no further change in absorbance. The spectra of both $PdCl_4^{2-}$ and $PdBr_4^{2-}$ show two predominant peaks in the ultraviolet region, the positions of the peaks being at 222 and 279 mμ in the case of chloride and at 246 and 332 mμ for the bromide. The separation between the two corresponding peaks at 279 and 332 mμ is more than 50 mμ, and, hence, this region of the spectrum was chosen for the study of the mixed ligand complexes. A series of spectra were run with solutions containing 1.5×10^{-4} M Pd, 0.5 M $HClO_4$, 2.0 M $LiClO_4$, and varying ratios of chloride to bromide. The total halide was kept constant at 2.0 M. The ionic strength thus was maintained at 4.5. The blanks that were used had the same composition, except that the metal ion was absent. Thirty-five closely spaced mixtures were examined, and the absorption curves obtained are shown in Figure 1. The bromide to chloride ratios are given in Table I.
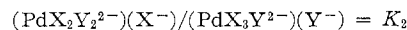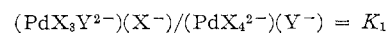
Results and Discussion

At 2.0 M total halide ion, palladium is fully coordinated by halide ion, and the equilibria which need be considered are

$$PdCl_4^{2-} + nBr^- \rightleftarrows PdCl_{4-n}Br_n^{2-} + nCl^- \qquad (1)$$
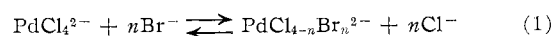
with

$$\beta_n = \frac{[PdCl_{4-n}Br_n^{2-}][Cl^-]^n}{[PdCl_4^{2-}][Br^-]^n}$$

Starting with either $PdCl_4^{2-}$ or $PdBr_4^{2-}$, only the following two stepwise reactions need be studied to characterize the system completely.

$$(PdX_3Y^{2-})(X^-)/(PdX_4^{2-})(Y^-) = K_1$$

$$(PdX_2Y_2^{2-})(X^-)/(PdX_3Y^{2-})(Y^-) = K_2$$

In Figure 1, the uppermost curve on the right-hand side represents $PdBr_4^{2-}$ by itself and the uppermost on the left-side represents $PdCl_4^{2-}$ by itself. Solutions having a mixture of chloride and bromide show spectra
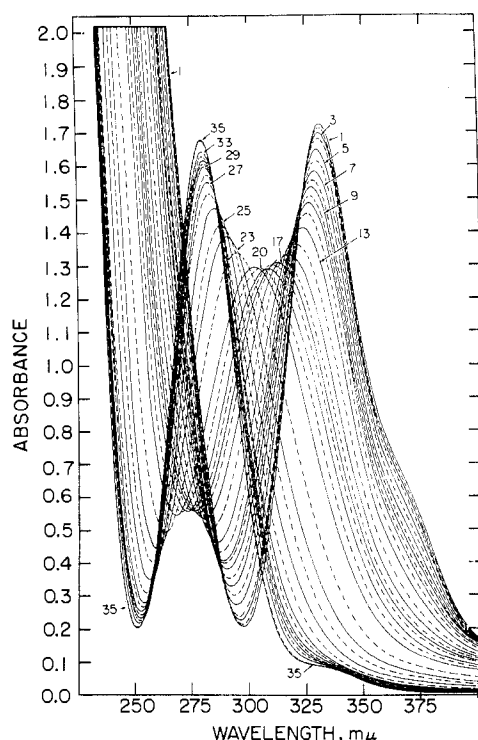
Figure 1.—Absorption spectra of 1.5×10^{-4} M Pd(II) at ionic strength of 4.5. Each solution is 0.5 M in HClO$_4$, 2.0 M in LiClO$_4$, and 2.0 M in halide (LiBr + LiCl); ratios of bromide to chloride (log R) in various curves are given in Table I.

TABLE I

RATIO OF BROMIDE TO CHLORIDE (LOG R)
IN VARIOUS CURVES

Curve	Log R	Curve	Log R
1	No chloride	19	-0.854
2	1.398	20	-0.921
3	0.921	21	-1.000
4	0.699	22	-1.222
5	0.398	23	-1.398
6	0.222	24	-1.523
7	0.097	25	-1.699
8	0.000	26	-1.854
9	-0.079	27	-2.000
10	-0.146	28	-2.097
11	-0.222	29	-2.222
12	-0.301	30	-2.301
13	-0.398	31	-2.398
14	-0.523	32	-2.523
15	-0.620	33	-2.699
16	-0.699	34	-3.398
17	-0.745	35	No Br$^-$
18	-0.796		

which can only be accounted for by the formation of new complexes.

The shifts in the spectra take place more readily when bromide replaces chloride than when the converse occurs. The first isosbestic point on either side indicates the formation of the first mixed species PdX$_3$Y^{2-}. The first curve not passing through these points indicates the beginning of the formation of the second mixed species PdX$_2$Y$_2$$^{2-}$. The ratio ($R$) of Y$^-$ to X$^-$ on the right-hand side for the last curve that passes through the isosbestic point is 1.2 ([Cl$^-$] = 1.1 M, [Br$^-$] = 0.9 M) whereas the ratio at which deviation occurs on the left side is 0.01 ([Br$^-$] = 0.02 M, [Cl$^-$] =

1.98 M). Thus, it would appear that bromide can replace chloride much more easily than chloride can replace bromide.

For the calculation of the different step equilibria, suitable mixtures were selected where no more than three species were present at any time. There is usually some regularity to the shift of the absorption spectrum as the absorbance becomes dependent on different species. For example, from the existence of the first isosbestic point, we can conclude that the first nine curves on both sides arise predominantly from the parent species and the first mixed species. A second mixed species, PdX$_2$Y$_2$$^{2-}$, begins to form upon degeneration of the isosbestic point. The presence of the third mixed species is indicated when deviations from the regular nature of the plots, applicable to two mixed species absorbing, begin to be observed.

Evaluation of the First-Step Constant.—If random experimental errors are to be easily detected, systematic errors recognized, and the data corrected for their presence, the ordinate and abscissa should be very simple functions of the experimental data giving equal weight to each point. The most convenient plots for this purpose are those of the measured absorbance A against R, the ratio of ligand concentrations. A relationship was derived whereby a family of normalized curves could be used for the evaluation of the constant for the first replacement reaction.

Using the common definitions of spectrophotometry, it can be shown that

$$A = \frac{\sum_0^4 A_n \beta_n R^n}{\sum_0^4 \beta_n R^n} \tag{2}$$

where R is the ratio Y$^-$/X$^-$ equal to Br$^-$/Cl$^-$ when starting with PdCl$_4$$^{2-}$ and equal to Cl$^-$/Br$^-$ when starting with PdBr$_4$$^{2-}$; A, the measured absorbance; A_n, the absorbance if all the palladium were as PdX$_{4-n}$Y$_n$$^{2-}$. As a consequence of this definition, β_0 equals unity and A_0 equals the absorbance if Pd were all as PdX$_4$$^{2-}$. If only the first replacement reaction is taking place, eq 2 reduces to

$$A = \frac{A_0 + A_1 \beta_1 R}{1 + \beta_1 R} \tag{3}$$

and if we define a term $\Delta = A_0 - A_1$, we obtain upon substitution in the above

$$\Delta(1 + \beta_1 R)^{-1} = A - A_1 \tag{4}$$

A technique for normalized curves described by Sillén[2] was adopted. An auxiliary variable, V, was defined as

$$V = 1 + \beta_1 R \tag{5}$$

whereupon we can obtain

$$\log (V - 1) = \log R + \log \beta_1 \tag{6}$$

(2) L. G. Sillén, *Acta Chem. Scand.*, **10**, 186 (1956).
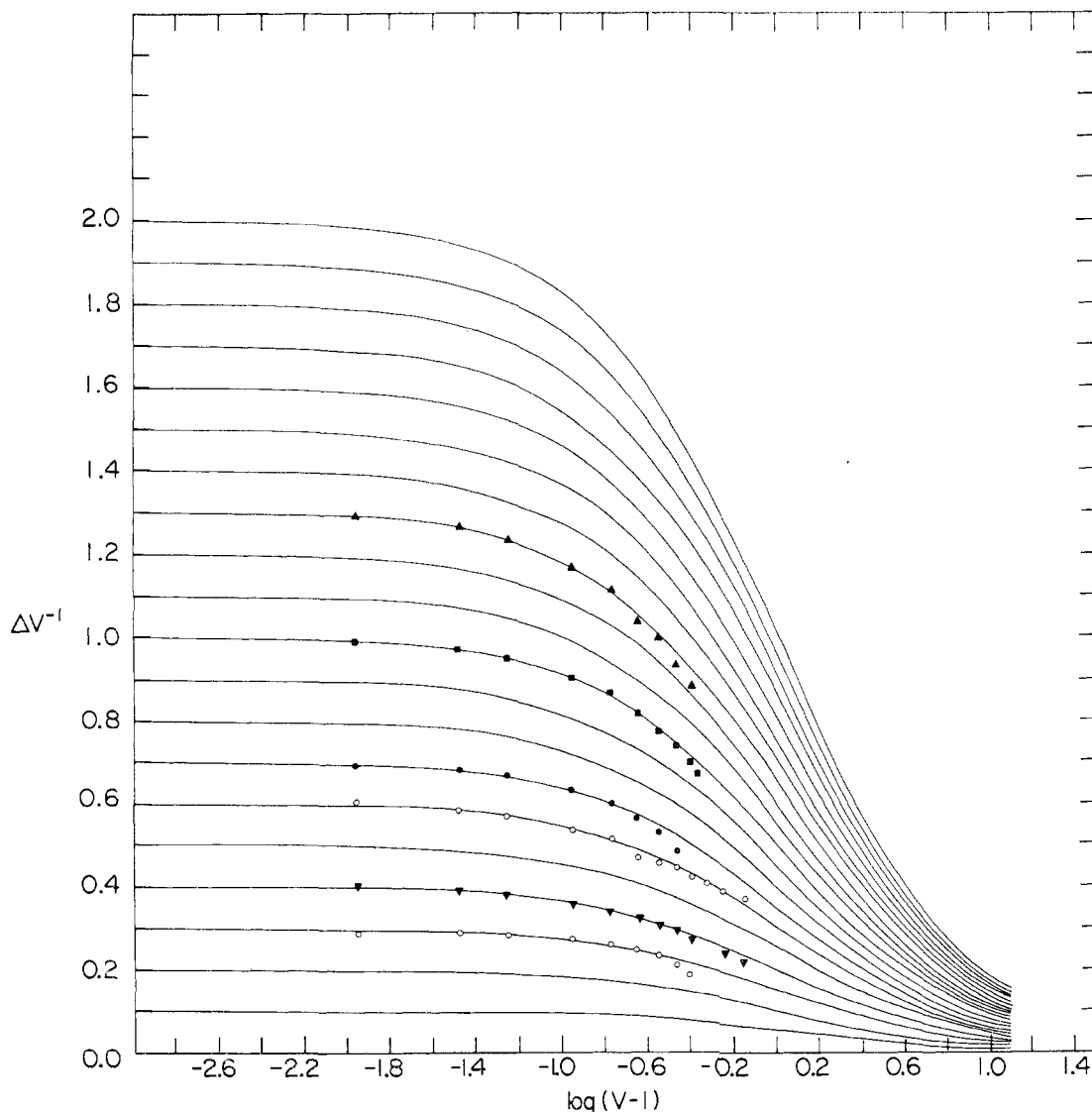
Figure 2.—The family of normalized curves: $\Delta V^{-1} = A - A_1$; $\log (V - 1) = \log R + \log \beta_1$. Formation of $PdBr_3Cl^{2-}$ from $PdBr_4^{2-}$: Plots of A *vs.* $\log R$ at various wavelengths shown fitted into appropriate curves. From above: ▲, 305; ■, 335; ●, 295; O, 280; ▼, 380; O (bottom set), 290 mμ.

and upon substitution in (4) we get

$$\Delta V^{-1} = A - A_1 \qquad (7)$$

A set of normalized curves was calculated for different values of Δ ranging from 0.1 to 2.0 and those of V ranging between 1 and 10. They were plotted as ΔV^{-1} *vs.* $\log (V - 1)$. These curves were compared to the original data plotted as A *vs.* $\log R$ (for these plots, the first nine curves from Figure 1 were used starting with either $PdCl_4^{2-}$ or $PdBr_4^{2-}$). The data were superimposed on the normalized curve which gave the best fit. The value of β_1 was obtained from the translation in the abscissa, and A_1 from the translation in the ordinate. Finally, β_1 was fixed as the average of the values obtained at various wavelengths. In Figure 2 are shown the normalized curves plus a few typical plots of A *vs.* $\log R$ at different wavelengths (using the fixed value of β_1) fitted on the appropriate curves. The permissible vertical and horizontal movement of the data plotted as A *vs.* $\log R$ on the appropriate normalized curve

gives the maximum limits of error in the values of $\log \beta_1$ and A_1. The values of the constants obtained at different wavelengths were found to be in close agreement.

This treatment allows the experimental data to be used directly without any manipulation and is to be preferred over more conventional methods[3] because the experimental errors can be most easily recognized and the appearance of the second replacement reaction can be detected. By contrast, the usual functions which are derived for the treatment of the data, A and R, are so complicated that the interpretations can sometimes be questioned.[4]

Evaluation of the Second-Step Constant.—Direct solution of sets of simultaneous equations for the parameters A_0, A_1, A_2, β_1, and β_2 from eq 2 is usually unsatisfactory. A better procedure is to substitute the preliminary values of β_1, A_0, and A_1 into eq 2, which

(3) L. Newman and D. N. Hume, *J. Am. Chem. Soc.*, **79**, 4571, 4581 (1957).

(4) G. P. Haight, Jr., C. H. Springer, and O. J. Heilmann, *Inorg. Chem.*, **3**, 195 (1964).
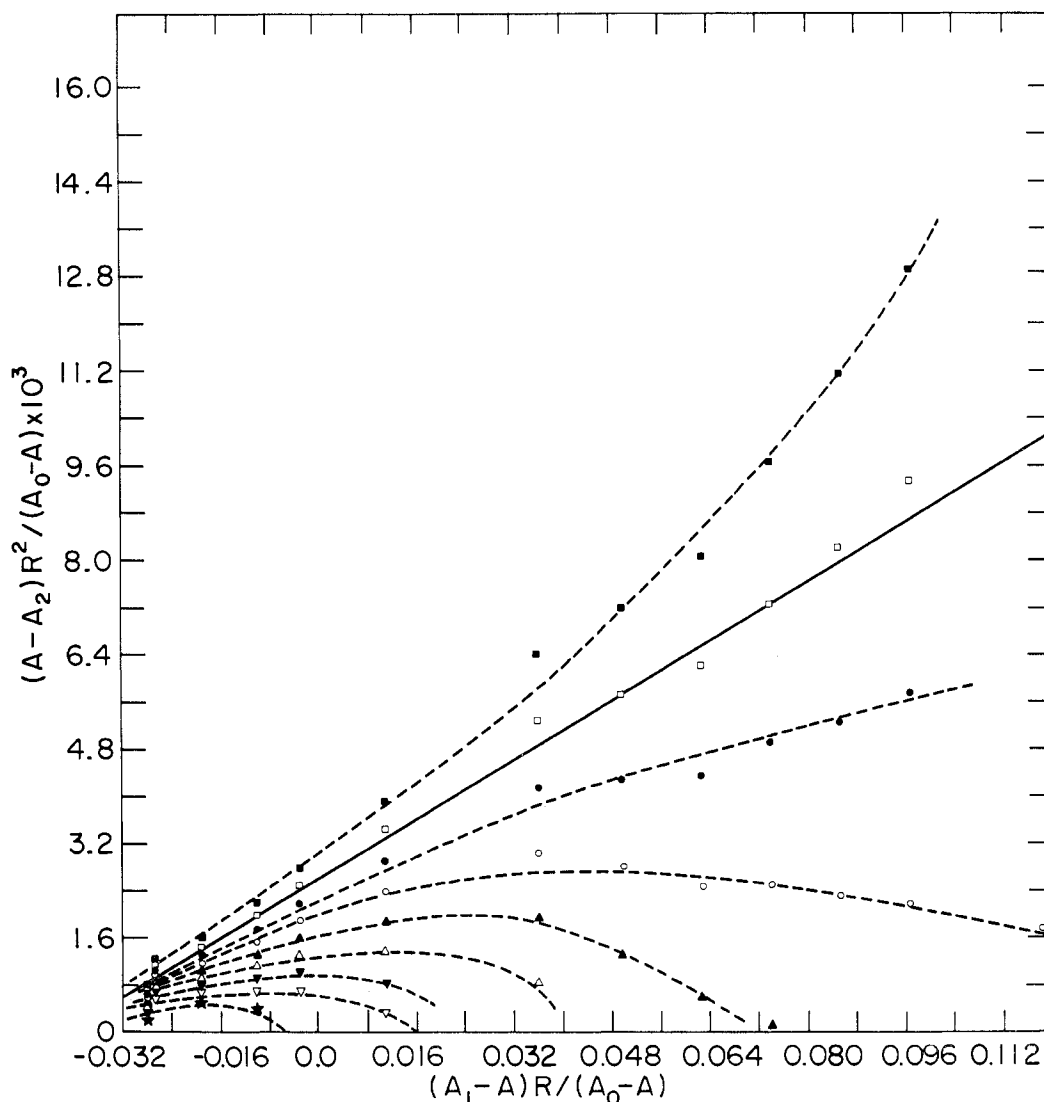
Figure 3.—Determination of the formation constant for the reaction $PdCl_4{}^{2-} + 2Br^- \rightleftarrows PdCl_2Br_2{}^{2-} + 2Cl^-$ at 280 mμ. Various assumed values of A_2: ■, 0.2; □, 0.3; ●, 0.4; ○, 0.5; ▲, 0.6; △, 0.7; ▼, 0.8; ▽, 0.9; ★, 1.0.

may then be solved graphically for β_2 and A_2.[3] However, these types of plots when used did not give very consistent values and the scatter in the data was appreciable, probably owing to the accumulation of errors from the previously determined parameters.

It was observed that small changes in the previously derived value of A_1 did not have a marked effect on the nature of such plots. Consequently, it was thought desirable to derive an expression which only made use of the determined value of A_1 for the calculation of β_2. Upon rearrangement of eq 2, the following expression can be derived

$$\frac{(A - A_2)R^2}{(A_0 - A)} = \beta_2{}^{-1} + \frac{R(A_1 - A)}{(A_0 - A)}\beta_1\beta_2{}^{-1} \quad (8)$$

Different values of A_2 were assumed at regular intervals (~0.025 absorbance unit apart, or less). Plots of the left-hand term vs. $R(A_1 - A)/(A_0 - A)$, gave a straight line only when the appropriate value of A_2 was selected. From this straight line the value of β_2 was obtained from the intercept and the ratio of β_1 to β_2 from the slope. Thus, these plots also provided, in addition to

the value of β_2, values of β_1 which checked with the values obtained when PdX_3Y^{2-} was the predominant species.

Figure 3 shows typical plots of this type used for the calculation of the formation constant for $PdX_2Y_2{}^{2-}$, starting from $PdCl_4{}^{2-}$. Such plots were made at a number of wavelengths and the values of β_2 thus obtained were found in close agreement.

The final values of the stepwise formation constants ($\log K$) for the various equilibria are

$$[PdCl_3Br^{2-}][Cl^-]/[PdCl_4{}^{2-}][Br^-] \overset{K_1}{=} 1.55 \pm 0.05$$

$$[PdCl_2Br_2{}^{2-}][Cl^-]/[PdCl_3Br^{2-}][Br^-] \overset{K_2}{=} 1.09 \pm 0.07$$

$$[PdClBr_3{}^{2-}][Cl^-]/[PdCl_2Br_2{}^{2-}][Br^-] \overset{K_3}{=} 0.95 \pm 0.07$$

$$[PdBr_4{}^{2-}][Cl^-]/[PdClBr_3{}^{2-}][Br^-] \overset{K_4}{=} 0.55 \pm 0.05$$

Conclusions

The individual spectra of the various mixed species were calculated on the basis of the constants thus obtained. The various maxima and the molar absorp-

tivities are shown in Table II. Figure 4 shows the resolved spectra of all the various species.

<div align="center">TABLE II</div>

<div align="center">Absorption Maxima and Molar Absorptivities of the Palladium–Chloride–Bromide Mixed Species</div>

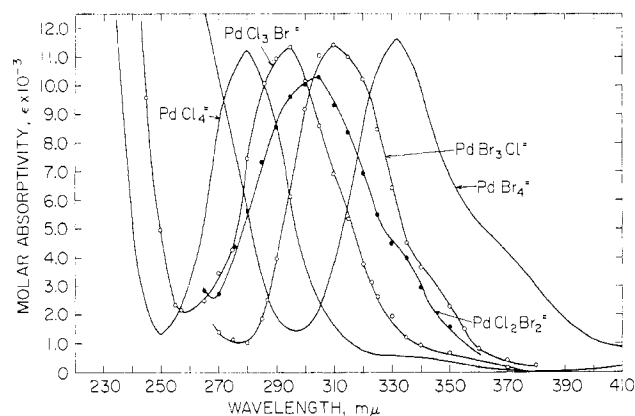| Species	Absorption maxima, $m\mu$	Molar absorptivity, $\epsilon_{max} \times 10^{-3}$
$PdCl_4{}^{2-}$	279 ± 1	11.2 ± 0.05
	222 ± 1	33.1 ± 0.1
$PdCl_3Br^{2-}$	295 ± 5	11.3 ± 0.2
$PdCl_2Br_2{}^{2-}$	305 ± 5	10.3 ± 0.2
$PdClBr_3{}^{2-}$	310 ± 5	11.4 ± 0.2
$PdBr_4{}^{2-}$	332 ± 1	11.5 ± 0.05
	246 ± 1	32.1 ± 0.1

Figure 4.—Resolved spectra of palladium–chloride–bromide mixed complexes.

The constants for the formation of the three mixed species from the parent reactants along with the statistically predicted values are shown in Table III.

<div align="center">TABLE III</div>

<div align="center">Statistical and Observed Values of the Formation Constants</div>

Reaction	Log K (found)	Log K (statistical)
$^3/_4PdCl_4{}^{2-} + ^1/_4PdBr_4{}^{2-} \rightleftharpoons PdCl_3Br^{2-}$	0.52 ± 0.05	0.60
$^1/_2PdCl_4{}^{2-} + ^1/_2PdBr_4{}^{2-} \rightleftharpoons PdCl_2Br_2{}^{2-}$	0.57 ± 0.06	0.78
$^1/_4PdCl_4{}^{2-} + ^3/_4PdBr_4{}^{2-} \rightleftharpoons PdClBr_3{}^{2-}$	0.49 ± 0.05	0.60

In many other systems the stabilities of the mixed ligand complexes are greater than would be predicted on a statistical basis.[5] However, in this system, it appears that the statistical constants are slightly higher than or, within experimental error, equal to the measured values.

Future studies will be made on the palladium system with Cl⁻ and I⁻ and with Br⁻ and I⁻. It will be interesting to see if the stability constants in these systems are greater or smaller than the statistically predicted values.

(5) (a) Y. Marcus and I. Eliezer, *J. Phys. Chem.*, **66**, 1661 (1962); (b) Y. Marcus, I. Eliezer, and M. Zangen, "Proceedings of the Symposium on Coordination Chemistry, Tihany, Hungary, Sept 1964," Akademiai Kiado, Publishing House of the Hungarian Academy of Sciences, Budapest, 1965, pp 409–418.

Synthesis and Vibrational Spectra of $[Co(N_3)_4]^{2-}$, $[Zn(N_3)_4]^{2-}$, and $[Sn(N_3)_6]^{2-}$ [1]

By DENIS FORSTER and WILLIAM DeW. HORROCKS, Jr.

The tetraethylammonium salts of the complex anions $[Co(N_3)_4]^{2-}$, $[Zn(N_3)_4]^{2-}$, and $[Sn(N_3)_6]^{2-}$ were synthesized and the infrared spectra of the solids and of solutions were recorded in the 200–4000-cm⁻¹ region. The Raman spectra of the zinc and tin compounds were measured. A vibrational analysis of a hypothetical T_d $Zn(N_3)_4{}^{2-}$ ion was carried out as an aid in making the assignments. The spectra indicate a nonlinear M–N–N linkage. Vibrational assignments were made on the basis of D_{2d} symmetry for the tetracoordinated species and D_{3d} symmetry for the hexacoordinated tin complex.

Introduction

Very little information is available on the vibrational spectra of azido complexes. This is principally because many of the simple metal azides, *e.g.*, AgN_3 and $Hg(N_3)_2$, are highly explosive compounds. The herein reported preparation of stable complex anions containing azide groups allows a more thorough investigation of the vibrational spectra of coordinated azide ions.[2a] Of particular interest is the determination

of whether the coordination is such that the M–N–N configuration is linear or bent. As typical of tetrahedral complexes of divalent metals, the salts $[(C_2H_5)_4N]_2[M(N_3)_4]$ where M = Co, Zn were synthesized. $[(C_2H_5)_4N]_2[Sn(N_3)_6]$ provides an example of octahedral hexacoordination by the azide ion. The colorless zinc and tin complexes were chosen because of their suitability for Raman investigation.

Experimental Section

Preparation of the Complexes. $[(C_2H_5)_4N]_2[Co(N_3)_4]$.—$[(C_2H_5)_4N]_2[CoCl_4]$ (1.0 g) was shaken with an excess of finely powdered sodium azide (~1 g) in acetone (~20 ml) for about 4 hr. The resulting blue solution was filtered, and diethyl ether was added to the filtrate. The precipitated solid was purified

(1) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, through Contract AF-49(638)-1492.

(2) (a) The apparent stability of the compounds described here has not prevented the authors from exercising great care in their handling. Similar caution is advocated in any further work with these compounds. (b) P. Senise, *J. Am. Chem. Soc.*, **81**, 4196 (1959).