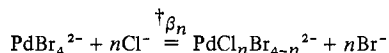


Mixed-Ligand Complexes of Palladium(II) with Bromide and Chloride in Acetonitrile¹

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A computer and a graphical method are used to evaluate equilibrium constants and extinction coefficients from spectrophotometric data for the system



The measurements were performed in acetonitrile at an ionic strength maintained at 1.5 with tetrabutylammonium halide. The results obtained by both techniques are in reasonably good agreement. The computer-determined values for the constants are $\log \dagger\beta_1 = 1.24 \pm 0.07$, $\log \dagger\beta_2 = 1.84 \pm 0.06$, $\log \dagger\beta_3 = 2.50 \pm 0.06$, and $\log \dagger\beta_4 = 2.39 \pm 0.05$. These constants yield a distribution of mixed-halide species which approximates that which would be predicted on a statistical basis. The stability of PdCl_4^{2-} is $10^{2.4}$ times greater than that of PdBr_4^{2-} in acetonitrile. This is not only an inversion of the relative stability in water but a change of 6.5 orders of magnitude. The measurement of mixed-ligand complexation appears to be a better method of determining the relative stability of simple ligand complexes than measurements involving the individual systems.

Introduction

It has been shown that palladium(II) forms a series of mixed-halide complexes $\text{PdY}_n\text{X}_{4-n}^{2-}$. The stability constants of all the tetracoordinate mixed-halide complexes with chloride and bromide,^{2,3} bromide and iodide,⁴ and chloride and iodide⁵ in aqueous media have been evaluated in this laboratory. A number of interesting correlations have been delineated.^{5,6} The relative stabilities of the simple tetracoordinate complexes were obtained and it was found that iodide is $\sim 10^{8.2}$ times more stable than bromide which is $\sim 10^{4.1}$ times more stable than chloride.⁶ As in a number of other systems,⁷ it was observed in the case of palladium that the greater the difference in the stability of the parent complexes the more stable are the mixed complexes.

The object of this investigation is to measure the equilibrium constants of the $\text{PdCl}_n\text{Br}_{4-n}^{2-}$ system in acetonitrile instead of water. It is also of interest to test further the general applicability of our newly developed computer technique³ for data evaluation and to compare the results with our former graphical method.²

Experimental Section

Reagents. Acetonitrile. Fisher Certified grade acetonitrile was contacted with calcium hydride for several days and then distilled from fresh calcium hydride through a 10-plate Oldershaw distillation column. The purified acetonitrile was stored over molecular sieves under an atmosphere of dry nitrogen in a dark glass bottle fitted with Teflon stopcocks. Pressurization with nitrogen was used to dispense the solvent.

Bis(tetrabutylammonium) Tetrachloropalladate(II). Stoichiometric amounts of anhydrous palladium chloride (Engelhard Industries, Inc.) and tetrabutylammonium chloride (Eastman White Label) were stirred for 1 day in a minimum amount of acetone. The solvent was evaporated from the filtered solution

and the residue was recrystallized from fresh acetone, dried under vacuum, and stored in a vacuum desiccator over CaSO_4 . Palladium stock solutions were prepared by adding weighed amounts of the salt to an appropriate volume of acetonitrile.

Tetrabutylammonium Chloride and Tetrabutylammonium Bromide. Eastman White Label salts were used as received. Acetonitrile solutions of each salt were prepared by weight and standardized by silver nitrate titration.

Apparatus. A Cary Model 14 recording spectrophotometer was used to record the absorption spectra. The 1-cm silica absorption cells used in this study were constructed so that a titration experiment could be performed in the cell in a closed system. A 200-ml reservoir which contained two openings was fused on top of the cell. The first cell opening was used for the addition of the solution to be titrated and consisted of a 14/35 outer joint which after the addition was sealed with a Teflon stopper for the remainder of the experiment. The second opening was sealed by a rubber serum bottle stopper through which the titrant solution was added. In order to prevent the solution in the cell from contacting this stopper, a Teflon stopcock was inserted between them. As an added precaution the rubber stoppers had been boiled in acetonitrile for several hours in order to remove extractable impurities which might affect the absorbance measurements.

The titrant solutions were added from a syringe microburet (Micro-Metric Instruments, Model SB2).

Method. In acetonitrile the effect caused by the addition of chloride to a palladium bromide solution or by bromide to a palladium chloride solution was examined spectrophotometrically. The additions proceeded in each case until the ratios of the halide concentrations overlapped. A titration technique was used in which both the titrant and titrated solutions contained 1.5×10^{-4} M palladium and either 1.5 M chloride or bromide. The blank solutions were identical except that no palladium was present. The halide concentrations of these solutions were verified by silver nitrate titrations.

After addition of the solution to be titrated, the cell was closed and all additions of the titrant were made using the microburet with a syringe needle attached. The needle was inserted through the rubber stopper and the bore of the stopcock. Identical procedures were employed in dealing with the blank solutions except conventional syringes were used for volume additions. The solutions were mixed by shaking the cells by hand. After each addition, it was necessary to wait approximately 45 min for the system to reach equilibrium. Prior to recording the spectra of each palladium solution against its blank, the instrument was zeroed at 450 nm with air in both compartments.

Results

The halide concentration used in this study was dictated by the solubility of the tetrabutylammonium salts. The spectra still change slightly with increases in chloride or bromide. However, with the ligand to palladium(II) ratio of 10^4 there was sufficient halide present to saturate coord-

(1) This work was performed under the auspices of the United States Atomic Energy Commission.

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

(3) S. Feldberg, P. Klotz, and L. Newman, *Inorg. Chem.*, **11**, 2860 (1972).

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(5) S. C. Srivastava and L. Newman, *Inorg. Chem.*, **11**, 2855 (1972).

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(7) Y. Marcus and I. Eliezer, *Coord. Chem. Rev.*, **4**, 273 (1969).

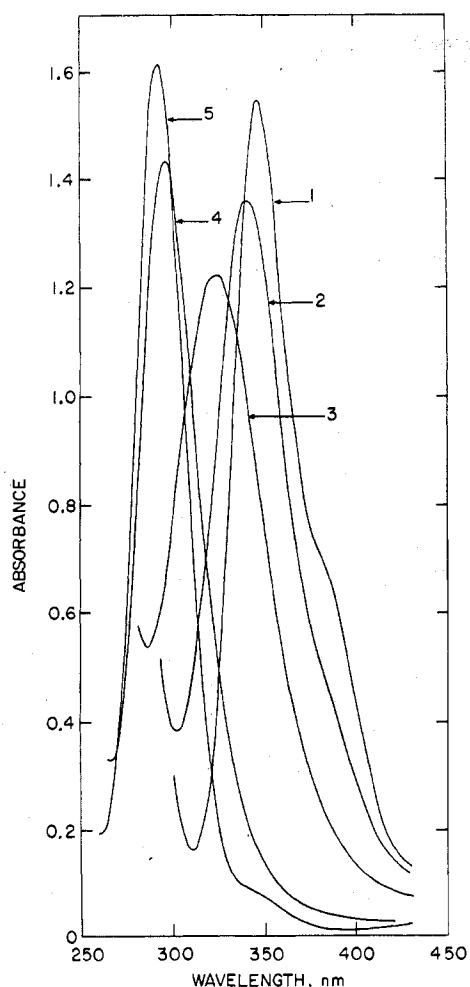


Figure 1. Selected ultraviolet absorption spectra of a system containing $1.5 \times 10^{-4} M$ palladium(II) in acetonitrile at a constant halide concentration of $1.5 M$. The ligand concentration ratios ($R = [\text{Cl}]/[\text{Br}]$) of the curves are: $R = 0.000$ (no chloride present), 0.0741 , 0.275 , 2.79 , ∞ (no bromide present) for curves 1-5, respectively.

dinately greater than 95% of the palladium as PdCl_4^{2-} and PdBr_4^{2-} .

Figure 1 shows some typical absorption spectra each of which is identified in the figure legend. Since the intermediate spectra cannot be explained by the simple mixing of the tetrachloride and tetrabromide species, they can only be attributed to the existence of mixed-ligand complexes. A total of 65 intermediate spectra were recorded in order to evaluate the formation constants for the mixed-ligand complexes.

The presence of an isosbestic point is generally taken as an indication that only two species are in equilibrium while a deviation from the isosbestic point indicates the formation of a third species. In going from PdCl_4^{2-} to PdBrCl_3^{2-} , deviations from the isosbestic point occur at a bromide to chloride ratio of 0.36 indicating a beginning of the formation of $\text{PdBr}_2\text{Cl}_2^{2-}$. However, a chloride to bromide ratio of only 0.052 is all that is needed to give similar indications in going from PdBr_4^{2-} to PdClBr_3^{2-} . This observation suggests that the simple complex PdCl_4^{2-} will prove to be more stable than PdBr_4^{2-} . This is in contrast to the observation in the aqueous system where chloride is more readily displaced by bromide and PdBr_4^{2-} is more stable than PdCl_4^{2-} .

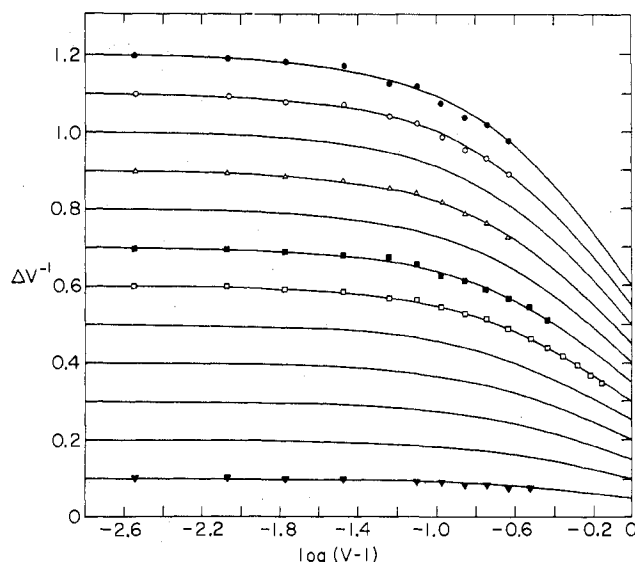
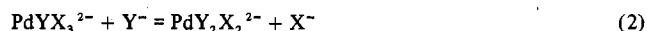


Figure 2. The family of normalized curves: $\Delta V^{-1} = A - A_1$; $\log(V-1) = \log R + \log \dagger K_1$. Formation of PdClBr_3^{2-} from PdBr_4^{2-} . Some plots of A vs. $\log R$ at various wavelengths fitted on the appropriate curves: \bullet , 325 nm; \circ , 320 nm; \triangle , 315 nm; \blacksquare , 360 nm; \square , 390 nm; \blacktriangledown , 300 nm.

Analysis of the Data

Graphical Method. The normalized-curve technique was used exactly as previously described.² Starting with either PdCl_4^{2-} or PdBr_4^{2-} , only the following two stepwise reactions need be studied to characterize the system completely



The method consists of initially obtaining the formation constant and relevant extinction coefficients for the first replacement step. This is accomplished by choosing from a family of normalized curves the one which best fits a plot of the data as absorbance vs. $\log \{[\text{Y}^-]/[\text{X}^-]\}$. Typical plots used for the determination of a formation constant for the first replacement step are shown in Figure 2. An elaboration of the terminology is given in a paper dealing with mixed-ligand complexes of nickel(II) with bromide and chloride in acetonitrile.⁸

The constants for the second replacement step are obtained by utilizing the parameters obtained from Figure 2 and by guessing at values for the extinction coefficient for $\text{PdY}_2\text{X}_2^{2-}$. A plot is then made utilizing a functional form derived from the appropriate equilibria. When the correct value for the guessed extinction coefficient is selected, a straight-line relationship exists. A typical plot used for the determination of the constant for the second replacement is shown in Figure 3. Once again reference should be made to previous publications for a definition of the terminology and a more detailed description of the technique.^{2,8} The results obtained for the stepwise equilibrium constants are shown in Table I.

Computer Method. The equilibrium constants can be written as

$$\dagger\beta_n = \frac{[\text{PdCl}_n\text{Br}_{4-n}^{2-}][\text{Br}^-]^n}{[\text{PdBr}_4^{2-}][\text{Cl}^-]^n} \quad (1 \leq n \leq 4) \quad (3)$$

The details of a computer method for evaluating the equi-

(8) T. W. Gilbert and L. Newman, *Inorg. Chem.*, 9, 1705 (1970).

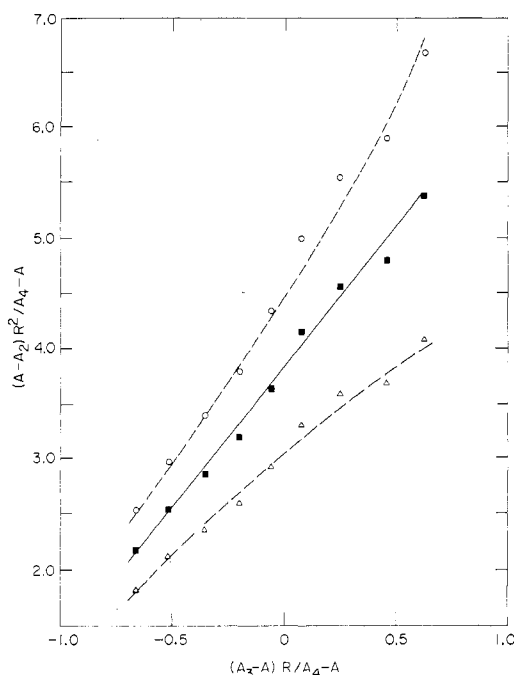


Figure 3. A typical plot used in determining the constant for the reaction $\text{PdYX}_3^{2-} + \text{Y}^- = \text{PdY}_2\text{X}_2^{2-} + \text{X}^-$. Determination of the formation constant for $\text{PdBrCl}_3^{2-} + \text{Br}^- = \text{PdBr}_2\text{Cl}_2 + \text{Cl}^-$ at 340 nm. The assumed values of A_2 for the curves shown: Δ , 1.3; \blacksquare , 1.5; \circ , 1.7.

Table I. Comparison of the Stepwise Constants^a

Equilibrium	Log $\dagger K_n$	
	Graphical	Computer ^b
$\text{PdBr}_4^{2-} + \text{Cl}^- \xrightleftharpoons{\dagger K_1} \text{PdClBr}_3^{2-} + \text{Br}^-$	0.85	1.24 ± 0.05
$\text{PdClBr}_3^{2-} + \text{Cl}^- \xrightleftharpoons{\dagger K_2} \text{PdCl}_2\text{Br}_2^{2-} + \text{Br}^-$	0.50	0.60 ± 0.01
$\text{PdCl}_2\text{Br}_2^{2-} + \text{Cl}^- \xrightleftharpoons{\dagger K_3} \text{PdCl}_3\text{Br}^{2-} + \text{Br}^-$	0.50	0.66
$\text{PdCl}_3\text{Br}^{2-} + \text{Cl}^- \xrightleftharpoons{\dagger K_4} \text{PdCl}_4^{2-} + \text{Br}^-$	0.0	-0.11 ± 0.01

^a Ionic strength maintained at 1.5 with tetrabutylammonium halide in acetonitrile. ^b Error estimate based on error in log $\dagger\beta_n$ (Table III). $\sigma_{\log \dagger K_n} = \sigma_{\log \dagger\beta_n} - \sigma_{\log \dagger\beta_{n-1}}$ (see ref 3, eq 26). Log $\dagger\beta_0 = 0$ and $\sigma_{\log \dagger\beta_0} = 0$.

librium constants and the extinction coefficients from spectrophotometric data have been published.³ Since it is possible explicitly to calculate the extinction coefficients if values of $\dagger\beta_n$ are given, we can discuss the nature of the error, σ , as a function of the $\dagger\beta_n$ values alone. Several facts emerge describing the error surface. (1) In the region of the minimum the error surface is highly skewed. (2) The computer program converges rapidly to a set of

values of $\dagger\beta_n$ corresponding to a value of σ in the vicinity of the minimum. Different sets of rapid convergence values (RCV's) will be obtained if different initial guessed values (IGV's) are selected for the $\dagger\beta_n$'s. (3) Convergence to the minimum from a set of RCV's is impractically slow. (4) Each set of RCV's has the relationship (in the vicinity of the minimum)

$$\dagger\beta_j = a_j \dagger\beta_4 + b_j \quad (j = 1, 2, 3) \quad (4)$$

Since several sets of RCV's are obtained, a plot of $\dagger\beta_j$ vs. its corresponding $\dagger\beta_4$ gives a straight line of slope a_j and intercept b_j . A plot of σ vs. log $\dagger\beta_4$ provides an estimate of an optimum value for $\dagger\beta_4$ (corresponding to the minimum value of σ). The remaining values of $\dagger\beta_n$ corresponding to the optimum $\dagger\beta_4$ are calculated from eq 4. The constants may be given a final refinement by reinserting these values into the computer program.

Given in Table II are the IGV's and RCV's for the $\dagger\beta_n$'s and the corresponding value which was obtained for the error, σ . The sets of $\dagger\beta_n$'s corresponding to the four lowest values of σ are used to evaluate the parameters a_j and b_j (Figure 4). A plot of σ vs. log $\dagger\beta_4$, shown in Figure 5, allows evaluation of the optimum value of $\dagger\beta_4$ and the remaining β_n 's are obtained using eq 4. These values after the final readjustment are virtually unchanged and are given in Table III. The error assigned to each of these values was estimated by dividing the data into four subsets (see ref 3 for details) and noting the variation in the optimum $\dagger\beta_4$. The four values obtained were 2.5, 2.2, 2.5, and 2.4, averaging 2.4. The standard deviation of the mean is

$$\sigma_{\log \dagger\beta_4} = \sqrt{\frac{\sum (\log \dagger\beta_4 - 2.4)^2}{3}} / \sqrt{4} = 0.07 \quad (5)$$

The errors in the remaining $\dagger\beta_n$'s are estimated using the equation

$$\sigma_{\log \dagger\beta_n} \approx \sigma_{\log \dagger\beta_4} \left(\frac{a_n \dagger\beta_4}{\dagger\beta_n} \right) \quad (6)$$

The equilibrium constants written in the form of eq 1 and 2 are included in Table I.

Discussion

When the graphical method is used to evaluate $\dagger K_1$ and $\dagger K_4$, only absorption curves passing through the isobestic are used; *i.e.*, only two species are present. When $\dagger K_2$ and $\dagger K_3$ are evaluated, only three species are present. In the computer method all the data are used for the calculation of all the constants but even then the data contributing most significantly to the evaluation of a given constant will be roughly the same as in the graphical method. Thus, it

Table II. Initial Guesses (IGV) and Rapid Convergence Values (RCV) of $\dagger\beta$'s

	IGV		RCV		IGV		RCV		IGV		RCV		IGV		RCV	
	IGV	RCV	IGV	RCV	IGV	RCV	IGV	RCV	IGV	RCV	IGV	RCV	IGV	RCV	IGV	RCV
$\dagger\beta_4$	1000	2.58×10^3	200	4.45×10^2	150	3.23×10^2	100	2.01×10^2	66	1.40×10^2	10	3.82×10^1	1	2.86×10^1		
$\dagger\beta_3$	1000	2.74×10^3	200	5.49×10^2	150	4.05×10^2	100	2.69×10^2	66	1.92×10^2	10	7.32×10^1	1	6.26×10^1		
$\dagger\beta_2$	1000	6.48×10^2	200	1.20×10^2	150	8.86×10^1	100	5.89×10^1	66	4.31×10^1	10	2.48×10^1	1	2.01×10^1		
$\dagger\beta_1$	1000	1.36×10^2	200	2.88×10^1	150	2.21×10^1	100	1.55×10^1	66	1.16×10^1	10	6.99	1	6.41		
σ	.065	.012461		.012083	.056	.012049	.053	.012042	.050	.012080	.026	.012478	.046	.012599		
Iterations	30		33		32		25		43		50		50			
Real Time	112		123		120		95		162		187		187			

Four lowest values

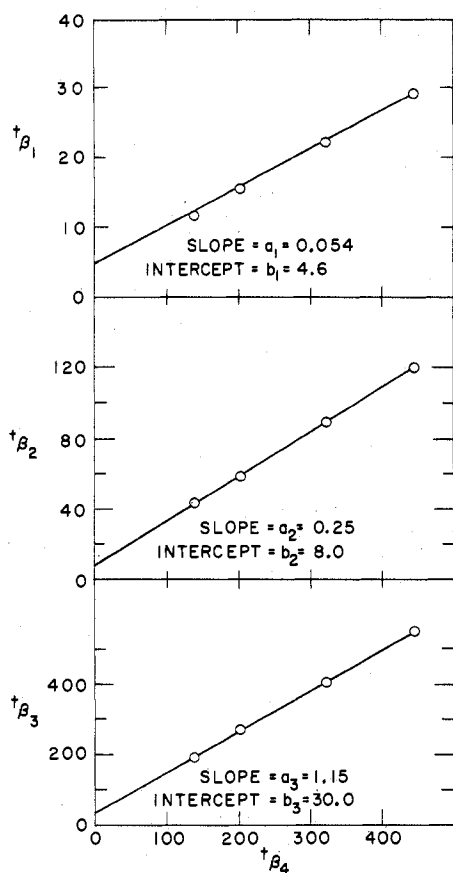


Figure 4. The straight-line relationships between the formation constants.

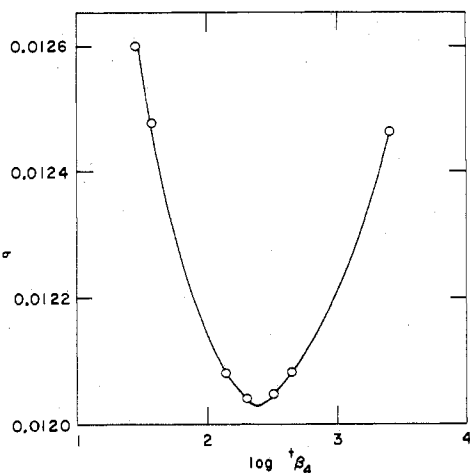


Figure 5. Variation of the standard deviation with $\log \beta_4$.

is not too surprising that the results of the two methods of analysis are in reasonable agreement except possibly for the measurement of the first constant. The low uncertainty of the stepwise constants, $\log \beta_2$, $\log \beta_3$, and $\log \beta_4$, is clearly indicated by the RCV's in Table II. In the four sets of data (corresponding to low σ), the variation of β_n/β_{n-1} ($n = 2, 3, 4$) is clearly less pronounced than the variation in β_n .

The statistical interrelationship of the equilibrium constants has been calculated for a tetrahedral system.^{6,7} Comparison of these values with the appropriately normalized experimental constants is shown in Table IV. The equilibria written in this fashion are possibly more useful in comparing the results from the graphical and computer analysis. The

Table III. Optimum Values of $\log \beta_n$ and the Estimated Uncertainties

n	$\log \beta_n \pm \sigma_{\log \beta_n}$	n	$\log \beta_n \pm \sigma_{\log \beta_n}$
1	1.24 ± 0.05	3	2.50 ± 0.06
2	1.84 ± 0.06	4	2.39 ± 0.07

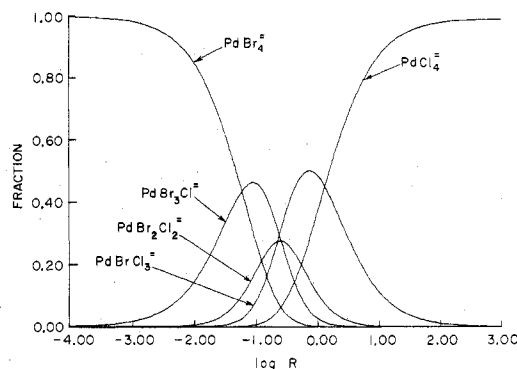


Figure 6. The fractional distribution of palladium(II) chloride-palladium(II) bromide complexes in acetonitrile as a function of the log of the halide concentration ratio ($R = [\text{chloride}]/[\text{bromide}]$). This distribution is based on the formation constants calculated using the least-squares computer technique.

constants obtained using the computer analysis are closest to the statistical values. In the aqueous system an almost perfectly statistical distribution was observed.³ A plot of the fractional distribution obtained from the computer-measured constants is shown in Figure 6. The distributions are essentially statistical in position.^{5,6} The obvious difference is that the middle species, $\text{PdCl}_2\text{Br}_2^{2-}$, attains a maximum value of only ~ 0.28 as opposed to the statistical value of ~ 0.37 .

Some interesting comparisons can be made between the palladium system in water and that in acetonitrile. In water the peak for PdCl_4^{2-} occurs at 279 nm and for PdBr_4^{2-} at 332 nm, a separation of 53 nm. The spectra in acetonitrile are almost identical except for a slight shift toward longer wavelengths with PdCl_4^{2-} occurring at 293 nm and PdBr_4^{2-} at 348 nm. The molar absorptivities of these species are also quite similar in both solvents but with the bromide peak being slightly higher than the chloride in the aqueous system and the chloride peak higher when the solvent is acetonitrile.

Despite these similarities there is a startling difference in their chemistry. In the aqueous system, PdBr_4^{2-} is more stable than PdCl_4^{2-} by a factor of $10^{4.1}$. The relative stability in acetonitrile is given by the value of $\log \beta_4 = 2.39$,⁶ indicating that the chloride is more stable than the bromide by a factor of $10^{2.4}$. This is an inversion of stability of 6.5 orders of magnitude in going from a water to an acetonitrile solvent. Palladium would appear to go from a class b soft acceptor with respect to the halides as donors in an aqueous system to a class a hard acceptor in acetonitrile. The solvation of palladium by water is probably significantly different from acetonitrile but it is not clear why this should lead to an inversion in the relative stability toward bromide and chloride. A somewhat similar situation presented itself in the case of nickel(II): in acetonitrile, NiCl_4^{2-} is more stable than NiBr_4^{2-} ⁸ but in dimethyl sulfone, NiBr_4^{2-} is more stable than NiCl_4^{2-} .⁹ In this situation there is an inversion of more than 8 orders of magnitude but the more weakly coordinating solvent, dimethyl sulfone, in-

(9) C. H. Liu, L. Newman, and J. Hasson, *Inorg. Chem.*, **7**, 1868 (1968).

Table IV. Comparison of Theoretical Statistical Constants with Normalized Experimental Equilibrium Constants

Equilibrium	Log (statistical)	Log (normalized experimental) ^a	
		Graphical	Computer
$\frac{3}{4}\text{PdBr}_4^{2-} + \frac{1}{4}\text{PdCl}_4^{2-} = \text{PdBr}_3\text{Cl}^{2-}$	0.60	0.39	0.64
$\frac{1}{2}\text{PdBr}_4^{2-} + \frac{1}{2}\text{PdCl}_4^{2-} = \text{PdBr}_2\text{Cl}_2^{2-}$	0.78	0.43	0.64
$\frac{1}{4}\text{PdBr}_4^{2-} + \frac{3}{4}\text{PdCl}_4^{2-} = \text{PdBrCl}_3^{2-}$	0.60	0.46	0.71

^a Log (normalized experimental) = $\log \beta_n^\dagger - (n/4) \log \beta_4^\dagger$, where n (=1, 2, 3) is the number of chlorides in the product.

verts the system in the opposite sense from what occurred with palladium.

The study of mixed-ligand complexes not only gives information about the nature of the mixed-ligand complexes but is possibly the best means of obtaining information on the relative stabilities of complex systems. As an example, it is almost impossible to decide upon the relative stabilities of the halide complexes of palladium by going to the literature.¹⁰ Using measurements of the type performed

(10) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964; Supplement No. 1, 1971.

in this investigation one has the advantage of evaluating the constants under identical conditions and the relative stabilities are obtained by determining only half of the number of constants that are required by the conventional approach.⁶

Clearly many other systems should be studied in order to understand the relative stabilities of ligand complexes in various solvents. Studies of mixed-ligand complexes should prove most valuable.

Registry No. PdCl₄²⁻, 14349-67-8; PdBr₄²⁻, 14127-70-9; PdClBr₃²⁻, 36673-40-2; PdCl₂Br₂²⁻, 36673-07-9; PdCl₃Br²⁻, 36655-12-6.

Contribution from the Chemistry Department, New Mexico State University, Las Cruces, New Mexico 88001

Cobalt(III) Complexes of Linear Tetramines. VI. Stereochemistry of Dichloro(4,8-diaza-2,10-undecanediamine)cobalt(III) Complexes

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The ligand 4,8-diaza-2,10-undecanediamine (diMe-2,3,2) has been prepared as an isomeric mixture containing the *RS* (meso) isomer and the *RR,SS* racemate. The pure *SS* isomer has been prepared, also. The ligand is a dimethyl derivative of 3,7-diaza-1,9-nonanediamine (2,3,2). *cis*- and *trans*-dichloro(4,8-diaza-2,10-undecanediamine)cobalt(III) complexes have been isolated containing the optically active ligand while only a *trans*-dichloro complex has been prepared containing the meso ligand. The optically active ligand coordinates stereospecifically in both the *cis* and *trans* complexes such that the *SS* ligand coordinates with the secondary nitrogen atoms exhibiting the *RR* configuration in both complexes. In the case of the *cis* complex the Λ - β topography is produced. The *RS* (meso) ligand coordinates in the *trans* complex with the secondary nitrogen atoms in the *SR* configuration.

Introduction

Transition metal complexes of the tetramine ligand 3,7-diaza-1,9-nonanediamine, NH₂(CH₂)₂NH(CH₂)₃NH(CH₂)₂NH₂ (2,3,2), have been under investigation in our laboratory and others in recent years.²⁻¹⁰ A notable result of these investigations is the isolation of three isomers of the *trans*-[Co(2,3,2)Cl₂]⁺ complex which differ in the configuration

of the asymmetric secondary nitrogen atoms, *RS* (meso), *RR*, and *SS*.⁴⁻⁶ There is good evidence that the *RS* (meso) isomer is thermodynamically more stable than the optically active isomers (*RR* and *SS*) since the latter isomerize to the former in methanolic solution, and the former is prepared by the air oxidation technique.^{4,11} This behavior is consistent with predictions based upon the assumption that the conformational behavior of the six-membered chelate ring of the complex parallels that of cyclohexane. In the *RS* (meso) isomer the six-membered ring can assume the chair conformation with the aminoethyl groups occupying equatorial positions on the ring allowing the primary amines to coordinate readily to positions coplanar with the six-membered ring (Figure 1a). In the case of the *RR* (*SS*) isomer if the ring assumes the chair conformation, one aminoethyl group occupies an axial site on the ring and its primary amine function cannot readily coordinate to a position coplanar with the ring but instead can coordinate only to a position perpendicular to the ring yielding a *cis*- β topography (Figure 1b). In order for this primary amine to coordinate readily in a

- (1) NDEA predoctoral fellow.
- (2) H. G. Hamilton, Jr., and M. D. Alexander, *Inorg. Chem.*, **5**, 2060 (1966).
- (3) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc. A*, 1331 (1966).
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- (11) M. D. Alexander and P. C. Harrington, unpublished results.