10^{-5} M solution. The determination of k_2 was little more than a rough estimate due to these difficulties, and it was found that any value between 100 and 1000 could be made to fit the data.

Discussion

The above analysis of the spectrophotometric data shows clearly the existence of at least five chloro complexes of bismuth. The data can be interpreted satisfactorily on the assumption that there are only five present and that the highest complex, $BiCl_n^{3-n}$, is $BiCl_5^{--}$. From these data alone it cannot be proved that another species in the middle of the series, present only in small concentrations and having a relatively low extinction coefficient, was not overlooked but this possibility is a very unlikely one. As will be seen in a later publication, quantitative studies of the replacement of chloride ions with bromide ions in the highest chloro complex agree very well with the assumption of a maximum ligand number of five. Accordingly, the most reasonable value to assume for the maximum ligand number of bismuth in chloride medium is five with the sixth coördination position occupied by water. Dr. Sten Åhrland at the University of Lund has kindly made available to us[10] results from a potentiometric study he has been carrying out on the bismuth–chloride system at ionic strength of 2 M which also shows five fairly stable complexes together with indications of a very weak sixth. Dr. Åhrland's value for the over-all formation constant of the ion $BiCl_5^-$, which he estimates as $(4.5 \pm 0.5) \times 10^7$, can be used together with our data to give 900 for k_2 which is a much more reliable value than that obtained directly.

(10) S. Århland, private communication.

With the aid of this datum we calculate from our results

$$270 \pm 5 = \frac{[BiCl^{++}]}{[Bi^{+++}][Cl^-]}$$

$$900 \pm 100 = \frac{[BiCl_2^+]}{[BiCl^{++}][Cl^-]}$$

$$20 \pm 10 = \frac{[BiCl_3]}{[BiCl_2^+][Cl^-]}$$

$$60 \pm 5 = \frac{[BiCl_4^-]}{[BiCl_2^+][Cl^-]^2}$$

$$2.7 \pm 1.0 = \frac{[BiCl_4^-]}{[BiCl_3][Cl^-]}$$

and

$$3.0 \pm 0.5 = \frac{[BiCl_5^{--}]}{[BiCl_4^-][Cl^-]}$$

The wave lengths and extinction coefficients of the peaks were determined as

$BiCl_5^{--}$ =	327 ± 1 mμ;	$(1.61 \pm 0.01) \times 10^4$
$BiCl_4^-$ =	317 ± 2 mμ;	$(0.95 \pm 0.03) \times 10^4$
$BiCl_3$ =	300 ± 10 mμ;	$(0.49 \pm 0.03) \times 10^4$
$BiCl_2^+$ =	$\sim 255 \pm 10$ mμ;	$\sim (0.4 \pm 0.1) \times 10^4$
$BiCl^{++}$ =	238 ± 2 mμ;	$(0.68 \pm 0.01) \times 10^4$
Bi^{+++} =	222 ± 1 mμ;	$(1.10 \pm 0.01) \times 10^4$

The first two formation constants and the absorbance characteristics of $BiCl^{++}$ and $BiCl_2^+$ were determined at an ionic strength of 1.0 obtained with perchloric acid. All other constants were also obtained in 1.0 M perchloric acid but with a salt concentration of 4.0 M yielded an ionic strength of 5.0.

Cambridge, Mass.

A Spectrophotometric Study of the Mixed Ligand Complexes of Bismuth with Chloride and Bromide[1]

By Leonard Newman and David N. Hume

By application of spectrophotometric methods for the study of mixed ligand complexes, developed in a previous paper, the following constants were determined for the bismuth–chloride–bromide system at an ionic strength of 5.00 M: $0.55 \pm 0.05 = [BiBr_5^{--}][Cl^-]/[BiBr_4Cl^{--}][Br^-]$, $3.3 \pm 0.05 = [BiBr_4Cl^{--}][Cl^-]^2/[BiBr_2Cl_3^{--}][Br^-]^2$, $\sim 0.3 \pm 0.2 = [BiBr_4Cl^{--}][Cl^-]/[BiBr_3Cl_2^{--}][Br^-]$, $5.9 \pm 0.9 = [BiBr_2Cl_3^{--}][Cl^-]/[BiBrCl_4^{--}][Br^-]$ and $17 \pm 2 = [BiBrCl_4^{--}][Cl^-]/[BiCl_5^{--}][Br^-]$. All were determined in 1.0 M perchloric acid and 4.0 M halide ion concentration.

Introduction

Quantitative studies in which formation constants are determined for a series of consecutive mixed ligand complex systems appear to be essentially non-existent. The spectrophotometric methods derived in a preceding paper[2] offer an attractive approach to this difficult problem when the absorption spectra of the various complexes involved differ appreciably. Previous workers[2] had

(1) Taken in part from the Doctoral Thesis of Leonard Newman, Massachusetts Institute of Technology, May, 1956.

(2) L. Newman and D. N. Hume, This Journal, **79**, 4576 (1957).

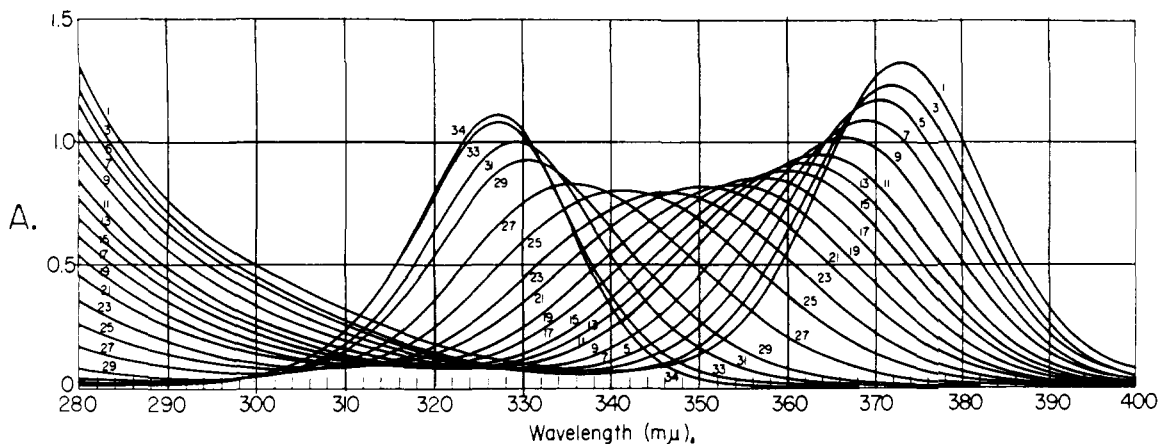(3) C. Merritt, H. M. Hershenson and L. B. Rogers, *Anal. Chem.*, **5**, 572 (1953).

noted a 50 mμ difference in the positions of the absorption peak of bismuth when in 4 M chloride and in 4 M bromide medium. Accordingly, we have studied the spectra of bismuth in chloride–bromide mixtures in which the total halide concentration was maintained at 4 M, which according to previous workers was sufficient to maintain practically all the bismuth in its most complexed state.

From Fig. 1, it can be seen that there is no way of apportioning the spectra of the individual bismuth halide absorption curves to arrive at the spectra observed when both halides are present. Therefore, the spectra observed can only be accounted for by the formation of new complexes.

Fig. 1.—Absorption spectra of 15.0 mg./l. solutions of bismuth at ionic strength of 5.00 M, each solution being 1.00 M in perchloric acid and 4.00 M in halide (sodium bromide plus sodium chloride). The sodium bromide concentrations in moles/l. corresponding to the individual curves are: 1:4.00, 3:3.60, 5:3.20, 7:2.80, 9:2.40, 11:2.00, 13:1.80, 15:1.60, 17:1.40, 19:1.20, 21:1.00, 23:0.80, 25:0.60, 27:0.40, 29:0.20, 31:0.10, 33:0.025 and 34:0.00. The blank is in each instance 1.00 M perchloric acid.

If, as is most likely, these species are mixed ligand complexes, the methods developed in a preceding paper[2] are applicable.

It also can be seen from the figure that shifts in the spectra take place more readily when bromide replaces chloride than when the converse occurs. Qualitatively, therefore, the replacement of chloride by bromide must lead to a stronger complex than the replacement of bromide by chloride.

Experimental

Apparatus and Materials.—The same Cary recording spectrophotometer and general technique were used as described in a previous paper.[4] The chemicals were the same as in previous work with the addition of Mallinckrodt analytical reagent grade sodium bromide. The bismuth solutions studied spectrophotometrically were always 1.00 M in perchloric acid, 4.00 M in total halide (made up from sodium chloride and sodium bromide), and contained 15.00 p.p.m. (mg./l.) of bismuth.

Results

Figure 1 shows 18 of the 34 closely spaced mixtures which were examined. All were measured relative to 1.00 M perchloric acid as a blank. The chloride was found not to absorb appreciably in this region. Sodium bromide does absorb in the lower end of the ultraviolet when present at high concentrations; however, the important portions of the absorption curves of the complexes were at sufficiently long wave lengths to permit this absorption to be neglected.

In attempting a study of the bromide complexes of bismuth, it was found that bromide was oxidized to bromine in the presence of perchloric acid and sodium perchlorate although very slowly in the absence of sodium perchlorate. Although the amount of bromide used up in the oxidation is not significant, the absorbance due to the bromine formed becomes excessive.

The instability of bromide in sodium perchlorate and perchloric acid prevented an extensive study of the bismuth–bromide complexes. However, the absorption spectrum of the highest bromide

complex of bismuth, $BiBr_n^{3-n}$, could be measured in the absence of sodium perchlorate.

Replacement of Bromide by Chloride.—From the shifts in the spectra observed, it was logical to assume that as chloride replaced bromide, a mixed ligand complex was formed which absorbed at lower wave lengths than the simple $BiBr_n^{3-n}$. As a working hypothesis, n was taken equal to 5 in the bromide system and later measurements led to no contradictory result.

Due to the oxidation of bromide in the presence of sodium perchlorate and perchloric acid, the formation constants for the bromide complexes of bismuth could not be obtained at a constant ionic strength. However, it could be ascertained that the highest bromide complex was stronger than the highest chloride complex. The amount ionized in the presence of 4 M sodium bromide was estimated at approximately 1 to 2%. Therefore, the values of A_0 for the bromide complex were actually 1 to 2% higher than the absorbance observed in Fig. 1 for a 4 M sodium bromide solution.

For high bromide-to-chloride ratios, only one mixed ligand complex should be formed. If a long enough wave length were selected, it should be possible to have the $BiBr_5^{--}$ absorbing but not the mixed ligand complex. If this be the condition, then eq. B13[5] for a mixed ligand system of two species present with one absorbing should hold. Application of this equation to the data at 390 mμ gave a straight line plot as indicated in Fig. 2. It should be remembered that since $BiBr_5^{--}$ is the parent complex, X_t now refers to bromide and Y_t to chloride. From the slope, the value of m was found to be one, and the following reaction must be taking place

$$BiBr_4Cl^- + Br^- = BiBr_5^- + Cl^-$$

$$k_1' = \frac{[BiBr_5^-][Cl^-]}{[BiBr_4Cl^-][Br^-]} \tag{6}$$
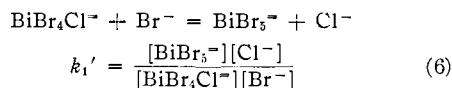
where $k_n = k_1'$ is 0.51.

Although a straight line plot yielding an m of unity indicates the correctness of the assumption

(4) L. Newman and D. N. Hume, THIS JOURNAL, **79**, 4571 (1957).
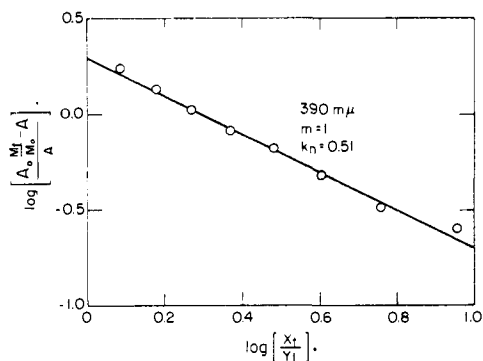
(5) All equations are in ref. 2.

Fig. 2.—Determination of equilibrium constant for reaction $BiBr_5^- + Cl^- \rightarrow BiBr_4Cl^- + Br^-$ at 390 mμ; two species present, one absorbing.

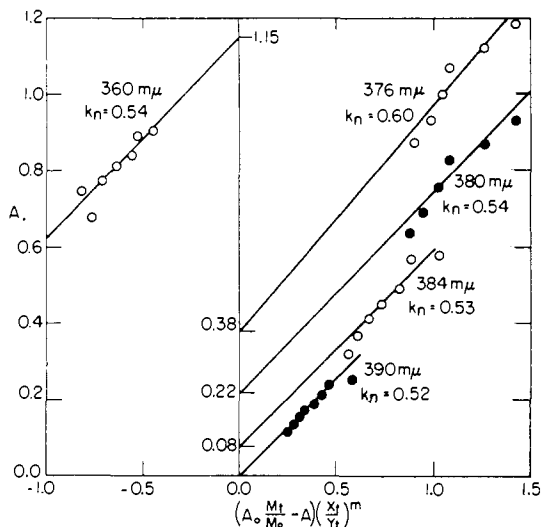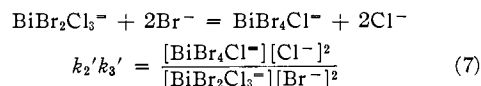
Fig. 3.—Determination of equilibrium constant for reaction $BiBr_5^- + Cl^- \rightarrow BiBr_4Cl^- + Br^-$ at wave lengths where both species absorb.

that the $BiBr_5^=$ was the only absorbing species, it can be further tested by application of eq. B12. This equation assumes two species present and both absorbing. The curve determined in this manner is shown in Fig. 3. Since the intercept is zero, the mixed ligand complex could not be absorbing. The k_1' of 0.52 obtained from this plot agrees quite well with the value obtained from the previous plot.

Equation B12 was then applied at four other wave lengths where the mixed ligand complex does absorb. From the slopes, the average value of k_1' was calculated as 0.55 ± 0.05. Since the intercepts are the absorbance of 15 p.p.m. bismuth in the form of the complex it represents the absorbance of $7.17 \times 10^{-5} M$ of $BiBr_4Cl^=$. As in the simple chloride system, good plots could not be obtained when the extinction coefficients of the species were too similar. However, good results were obtained when either the mixed ligand complex (Fig. 3 at 360 mμ) or the single ligand complex was the absorbing species.

In order to obtain the second formation constant, the data at 390 mμ were once again used, but at lower bromide-to-chloride ratios. Since, as

chloride replaces bromide, there is a spectral shift to shorter wave lengths, it could be assumed that there were three species with one absorbing and eq. B11 was applicable. The results are shown in Fig. 4. Since the slope, p, is two, the following reaction must be taking place

$$BiBr_2Cl_3^- + 2Br^- = BiBr_4Cl^- + 2Cl^-$$

$$k_2'k_3' = \frac{[BiBr_4Cl^-][Cl^-]^2}{[BiBr_2Cl_3^-][Br^-]^2} \tag{7}$$
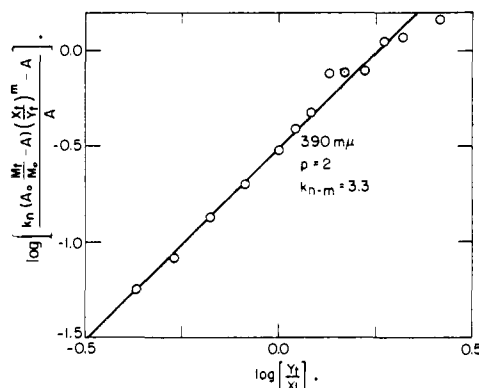
where $k_{n-m} = k_2'k_3'$ was obtained from the intercept as 3.3 ± 0.5.

Fig. 4.—Determination of equilibrium constant for the reaction $BiBr_4Cl^- + 2Cl^- \rightarrow BiBr_2Cl_3^- + 2Br^-$ at 390 mμ, three species present, one absorbing.

At slightly lower wave lengths where 3 species were present and 2 absorbing, eq. B10 became applicable. Once again, the data for lower bromide to chloride ratios were applied and the results at 384 mμ are plotted in Fig. 5. The value of $k_2'k_3'$ equal to 2.0, obtained from the slope, was somewhat lower than observed at 390 mμ.
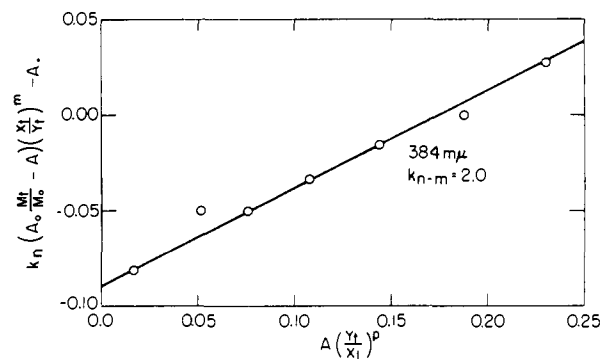

Fig. 5.—Determination of equilibrium constant for the reaction $BiBr_4Cl^- + 2Cl^- \rightarrow BiBr_2Cl_3^- + 2Br^-$ at 384 mμ where two of the three species present absorb.

At still lower wave lengths there would be 3 species present with all 3 absorbing and eq. B9 becomes valid. The results at 380 mμ are shown in Fig. 6. Once again from the slope, $k_2'k_3'$ was determined, in this instance, as 1.9.

As in the chloride case, when attempts were made to observe the two-halide transition when the absorbance was not due mainly to the parent complex,
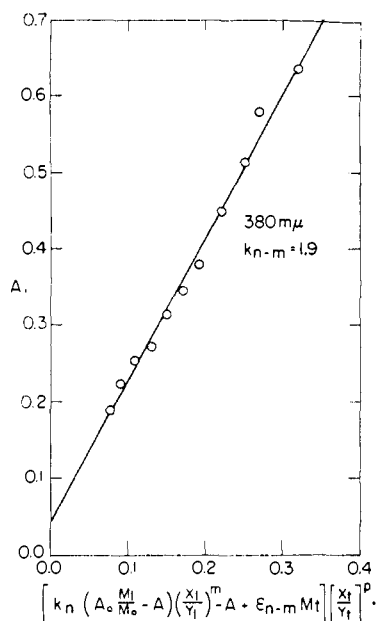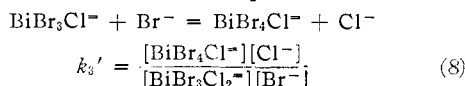
Fig. 6.—Determination of equilibrium constant for the reaction $BiBr_4Cl^- + 2Cl^- \rightarrow BiBr_2Cl_3^- + 2Br^-$ at 380 mμ where all three of the species present absorb.

a stepwise transition was observed and the following equilibrium was found to take place

$$BiBr_3Cl^- + Br^- = BiBr_4Cl^- + Cl^-$$

$$k_3' = \frac{[BiBr_4Cl^-][Cl^-]}{[BiBr_3Cl_2^-][Br^-]} \qquad (8)$$

The constant, k_2', could only be approximated as equal to 0.3 ± 0.2. The weakness of this complex certainly accounts for the fact that, unless the extinct on coefficient of $BiBr_3Cl_2^-$ is large in comparison to the other species, its presence cannot be detected.

It is then possible to calculate for

$$BiBr_2Cl_3^- + Br^- = BiBr_3Cl_2^- + Cl^-$$

$$k_3' = \frac{[BiBr_3Cl_2^-][Cl^-]}{[BiBr_2Cl_3^-][Br^-]}$$
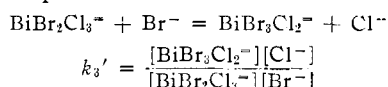
with a value of 10 ± 5. The value of 3.3 ± 0.5 observed at 390 mμ was taken as the best estimate for the constant $k_2'k_3'$ since it was obtained when the absorbance due to $BiBr_3Cl_2^-$ was at a minimum.

Replacement of Chloride by Bromide.—In order to determine the formation constants for the replacement of chloride by bromide, the data for high chloride-to-bromide ratios were utilized. Since at 4 M sodium chloride there was still some ionization of $BiCl_5^-$ the A_0 values were taken from the calculated curve for $BiCl_5^-$ (Fig. 9, ref. 4). In order to neglect the equilibrium between $BiCl_5^-$ and $BiCl_4^-$, it was assumed that as soon as any sodium bromide was added, the $BiCl_4^-$ would be completely complexed by the bromide. This assumption may not have been valid when the chloride-to-bromide ratio was very high. However, the results of the application of eq. B12 at four wave lengths given in Fig. 7 show that no appreciable error was introduced. It should be remembered, that since the parent complex is $BiCl_5^-$, X_t now refers to chloride and Y_t to bromide.
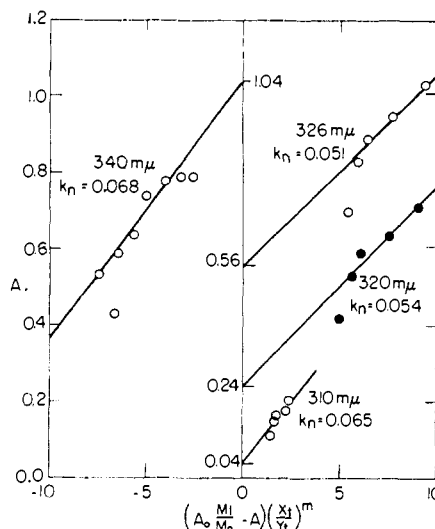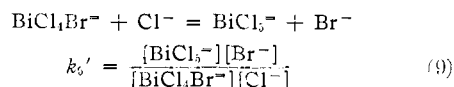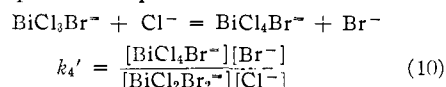

Fig. 7.—Determination of equilibrium constant for the reaction $BiCl_4Br^- + Cl^- \rightarrow BiCl_5^- + Br^-$ where one of the two species absorbs.

From the slopes of the lines in Fig. 7, the equilibrium

$$BiCl_4Br^- + Cl^- = BiCl_5^- + Br^-$$

$$k_5' = \frac{[BiCl_5^-][Br^-]}{[BiCl_4Br^-][Cl^-]} \qquad (9)$$

was found to have a $k_n = k_5'$ of 0.060 ± 0.005 where the intercepts are the absorbance of 7.17×10^{-5} M of $BiCl_4Br^-$. The value of the formation constant was independent of whether the $BiCl_4Br^-$ complex was the principal species contributing to the absorbance or whether it was the $BiCl_5^-$.

When the absorbance of samples having lower chloride to bromide ratios was taken and the data applied to eq. B9 the equilibrium was found to be

$$BiCl_3Br^- + Cl^- = BiCl_4Br^- + Br^-$$

$$k_4' = \frac{[BiCl_4Br^-][Br^-]}{[BiCl_2Br_2^-][Cl^-]} \qquad (10)$$

From the slope of the curve plotted in Fig. 8, the value of the formation constant $k_{n-m} = k_4'$ was determined at 320 mμ as 0.17 ± 0.03. The inter-
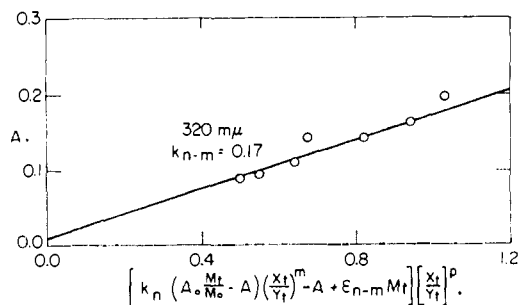

Fig. 8.—Determination of equilibrium constant for the reaction $BiCl_3Br_2^- + Cl^- \rightarrow BiCl_4Br^- + Br^-$ when all three species present absorb.

cept of 0.01 is the absorbance of 7.17×10^{-5} M of $BiCl_3Br_2^-$ at 320 mμ. The product of all the stepwise formation constants in the series $BiCl_5^-$ to

$BiBr_5^-$ gives an estimate, 180, for the ratio of the formation constants of the two ions. This value at $\mu = 5.00$ is in good qualitative agreement with the value derived from potentiometric measurements on the chloride and bromide series made by Dr. Sten Åhrland at $\mu = 2.00$ and kindly made available to us prior to publication.

Continuous Variations.—It has been shown that when chloride and bromide were added in varying ratios to a bismuth solution containing 1 M perchloric acid, three mixed ligand complexes, $BiBr_4Cl^-$, $BiBr_2Cl_3^-$, $BiBrCl_4^-$ with a small amount of $BiBr_3Cl_2^-$ were formed in equilibrium with the parent complexes $BiBr_5^-$ and $BiCl_5^-$. Since the total halide concentration was maintained at 4 M and the bismuth concentration at 15 p.p.m., the data plotted in Fig. 1 might be used for a continuous variations plot. The simplifying assumption was made that the parent complexes would react to form a single mixed ligand complex.

As Katzin and Gebert[6] and Woldbye[7] have concluded that the method of continuous variations should not be strictly valid under conditions like these where more than one complex is present and absorbing, it was of interest to see what application of the method would indicate. Application of the method of continuous variations at a number of wave lengths showed several maxima and minima, of which the most definite corresponded to formation of the species $BiBrCl_4^-$. The results as a whole, however, did not tend to inspire confidence and it was concluded that as predicted,[6,7] the method was not properly applicable to such a complicated system.

Acknowledgment.—This work was supported in part by the United States Atomic Energy Commission.

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CAMBRIDGE, MASS.

The Ethylenediamineplatinum Trihalides[1]

BY GEORGE W. WATT AND ROBERT E. MCCARLEY

The mode of formation of $Pt(en)X_3$, where $X = Cl$, Br or I, together with a variety of chemical and physical properties, are interpreted as indicating that these compounds do not involve the 3^+ oxidation state of platinum. Partly by analogy with other platinum and palladium compounds, it is concluded that these compounds contain alternating Pt^{2+} and Pt^{4+} in polymeric species in which the essential units $[Pt(en)Br_2]$ and $[Pt(en)Br_4]$ are bridged through halogen. Accordingly, the bromide, for example, should be formulated as ethylenediaminedibromoplatinum(II) tetrabromoethylenediamineplatinum (IV), $[Pt(en)Br_2][Pt(en)Br_4]$. Evidence bearing upon some unusual color changes exhibited by these compounds is presented and discussed.

As a part of a program of studies on the lower oxidation states of platinum, we have carried out an extensive investigation of the synthesis and properties of compounds of the type $Pt(en)X_3$, in which platinum exhibits the *apparent* but still controversial 3^+ oxidation state. That platinum should form compounds corresponding to the 3^+ state is reasonable by analogy to complexes of the type represented by bis-(triethylphosphine)-tribromonickel(III)[2-6] and the monomeric[7] palladium(III) fluoride.[8,9] Levy[10] has reported the preparation of $H[Pt(CN)_4]$ and $Pt(CN)_3$, but whether these species involve Pt^{3+} remains in doubt. There are several other cases that involve the apparent 3^+ oxidation state of platinum but in which it seems more likely that halogen bridging between alternating Pt^{2+} and Pt^{4+} is involved,[11-18] and

much the same conclusions have been reached with respect to closely related palladium compounds.[19] In addition, Hall and Plowman[20] interpret an inflection in the current–potential curve for the reduction of $[Pt(en)_3]^{4+}$ at the dropping mercury electrode as indicative of the transient intermediation of Pt^{3+}. Finally, Rich and Taube[21] postulate Pt^{3+} as an intermediate involved in the exchange of Cl^- with $(PtCl_6)^{2-}$ and of Cl between $(PtCl_6)^{2-}$ and $(PtCl_4)^{2-}$.

Although originally concerned largely with the question of the oxidation states of platinum, some of the work described in this paper was stimulated by the unusual color characteristics of (particularly) $Pt(en)Br_3$.

Experimental

Unless otherwise indicated, all materials used were reagent grade chemicals. Reactions in liquid ammonia were carried out under strictly anhydrous conditions.[22]

(1) This work was supported in part by the Atomic Energy Commission, Contract AT-(40-1)-1639.

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