plex if it were not dissociated at all. The difference between this extrapolated curve and the actual measured curve at a mole fraction of 0.5 should represent the uncomplexed uranium(VI). From Beer's law

$$[(UO_2)(GH_4)(OH)_2^-] = kA \qquad (8)$$

$$[(UO_2)(OH^+)] = k(A_{ext} - A) \qquad (9)$$

where k is a proportionality constant, A is the measured absorbance, and A_{ext} is the extrapolated absorbance. Substitution of eq. 8 and 9 into eq. 7 and insertion of the values for A and A_{ext} from Fig. 2 at a mole fraction of 0.5 gives a value for K equal to 1×10^6. However, it should be emphasized that this type of measurement is quite inaccurate; the calculated value can be considered only an order of magnitude estimate. At the low concentrations represented in Fig. 2 hydrolysis reactions may compete with reaction 6. Also, Fig. 2 indicates that under the conditions of measurement a higher complex involving a uranium(VI)-to-gluconate ratio equal to 3 is apparently formed. This would interfere further with an accurate evaluation of K.

Table II summarizes the values for K determined both polarographically and spectrophotometrically; the average value for K equals 1.8×10^6.

TABLE II

SUMMARY OF VALUES DETERMINED FOR THE FORMATION CONSTANT OF THE URANIUM(VI)–GLUCONATE COMPLEX

Variable Used for Evaluation	K
Polarography: (OH⁻)	3.5×10^6
(GH⁻)	1.7×10^6
(UO₂⁺⁺)	1.0×10^6
Spectrophotometry	$1. \times 10^6$
Av. of 4 evaluations	1.8×10^6

The Effect of Coördination on the Reactivity of Aromatic Ligands. II. Bromination of Some Complexes of Palladium(II) Bromide with Aromatic Amines[1]

BY ROBERT L. JETTON AND MARK M. JONES[2]

A series of palladium(II) bromide complexes with aromatic amines of the type [Pd(A)₂Br₂] has been brominated using small and large mole ratios of bromine to complex. The brominated complexes have been analyzed and the ligands subsequently recovered and characterized. In each case the orientation of the bromination was *ortho* or *para* to the amino group. These results are discussed in terms of theoretical models of the coördinate bond.

Previous work in this Laboratory[1] has indicated that, contrary to the predictions which might be made on the basis of a simple picture of the coordinate bond *and* the resonance theory of the preferred positions for attack of aniline by electrophilic reagents,[3] coördination *does not* exert a

great effect upon the reactivity of aniline toward bromination *nor upon the orientation of substitution*. Because of the profound implications of these results, the studies have been extended to a series of complexes where it is possible to isolate and characterize the brominated complexes, *viz.*, the complexes of palladium(II) bromide with aniline and with the *ortho-*, *meta-*, and *para*-toluidines.

Because the lone pair of electrons on the nitrogen atom, which is not involved in bonding in the

(1) Previous paper in this series: J. C. Taft and M. M. Jones, *J. Am. Chem. Soc.*, **82**, 4196 (1960).

(2) To whom correspondence concerning this paper should be addressed.

(3) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, third edition, 1960, pp. 207–208.

free amine, is used to explain both the regions of high electron density (preferred positions for attack by electrophilic reagents) and the formation of the coördinate linkage

H—N—H H—N—H H—N—H
  M

H—N—H   H—N—H   H—N—H
  +   +   +
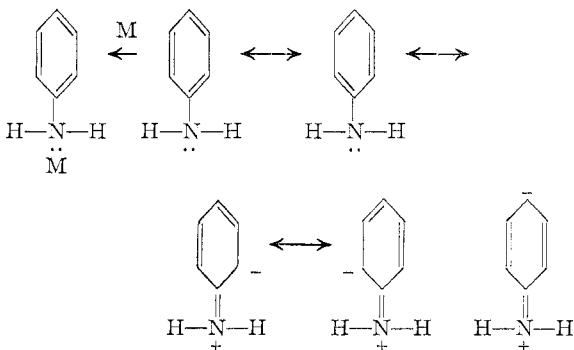
the reactivity of the amine should undergo a considerable change upon coördination. The reactions of the free and the complexed amine then can be examined under strictly comparable conditions to determine the extent of such changes. Obviously, if the reaction of the ligand with electrophilic reagents produces substituted amines with the same type orientation as are obtained by reaction of the free amine, then it is highly probable that the resonance explanation of one of these processes is incorrect. It has been suggested[3] that, but for this special type of resonance, aromatic amino groups would not be *ortho–para* directing. The fact that the quaternization of the nitrogen in an aromatic amine leads to a *meta* directing influence by the resultant positive group insofar as electrophilic attack is concerned is well established and generally is dated from the work of Vorlander.[4] That protonation of an aromatic amine also could lead to a change from *ortho–para* to *meta* substitution had been demonstrated much earlier for the case of *para*-toluidine by Hafner.[5] Hafner also demonstrated quite conclusively that the protonation of aniline has a very pronounced deactivating effect insofar as reactions with chlorine or bromine are concerned.

The present study was concerned with the bromination of palladium(II) complexes of the type $[Pd(A)_2Br_2]$, where A represents an aromatic amine: aniline, *o*-toluidine, *m*-toluidine, or *p*-toluidine. The use of palladium was dictated by the desire to study reasonably inert complexes. Since the amine complexes used are prepared from

a strongly acid solution, the complications due to partial dissociation are absent. A previous report of the chlorination of the copper(II) sulfate complex with *meta*-toluidine, $[Cu(H_2NC_6H_4–CH_3)_2]-SO_4$, indicated that the initial attack resulted in a chloro substituent *para* to the amino group, *i.e.*, 6-chloro-3-amino-toluene, though the complex with the substituted ligand was not isolated.[6]

Experimental

Preparation of Complexes.—Palladium(II) bromide was prepared by the method of von Bonsdorff.[7] *Anal.* Calcd. for $PdBr_2$: Br, 59.97. Found: Br, 59.65. The complexes were prepared by the method used by Hardin[8] to make dichlorodianiline palladium(II). The analyses on the starting materials were (a) dibromodianilinepalladium(II), Calcd. for $[Pd(C_6H_7N)_2Br_2]$: C, 31.88; H, 3.09; N, 6.18; Br, 35.3; Pd, 25.8. Found: C, 32.02; H, 3.27; N, 6.02; Br, 35.5; Pd, 25.3. (b) Dibromodi-(*ortho*-toluidine)-palladium(II), Calcd. for $[Pd(C_7H_9N)_2Br_2]$: C, 34.97; H, 3.75; N, 5.83; Br, 33.35; Pd, 22.16. Found: C, 35.29; H, 3.85; N, 5.73; Br, 33.29; Pd, 23.10. (c) Dibromodi-(*para*-toluidine)-palladium(II), Calcd. for $[Pd(C_7H_9N)_2-Br_2]$: C, 34.97; H, 3.75; N, 5.83; Br, 33.35. Found: C, 35.29; H, 3.98; N, 5.78; Br, 33.14. (d) Dibromodi-(*meta*-toluidine)-palladium(II), Calcd. for $[Pd(C_7H_9N)_2-Br_2]$: C, 34.97; H, 3.75; N, 5.83; Br, 33.35; Pd, 22.16. Found: C, 35.07; H, 3.71; N, 6.25; Br, 33.54; Pd, 22.9.

Bromination Reactions.—It was found that dimethylformamide was one of the very few solvents in which these palladium complexes could be dissolved to any extent, and this solvent accordingly was used for the bromination studies on both the free ligands and the coördinated ligands. The brominations were carried out under two sets of conditions. In the first, the bromine was not present in sufficient amount to allow the bromination to proceed to the point of complete replacement of all active aromatic hydrogens (usually one mole of bromine per mole of aromatic amine). In the second, an amount of bromine slightly in excess of twice this amount was added. In a typical bromination, 10 g. of the dry starting complex was dissolved in 100 g. of N,N-dimethylformamide and the solution was placed, with a stirring magnet, in a 500-ml. round bottom flask with two standard taper openings. A dropping funnel containing a chloroform solution of bromine was placed in one of the openings and an air condenser in the other. The flask was placed in a constant temperature bath to maintain the reaction at 25° and stirred from below by a magnetic stirrer. The bromine solution was added dropwise over a period of 20 min. Stirring was continued for 1 hr. after addition of the bromine was completed. The reaction mixture then was diluted with cold distilled water and the bright yellow precipitate which formed was collected on a Büchner funnel and washed with small portions of chloroform until the washings were clear. The yellow solid next was washed with several portions of a cold dilute solution of sodium sulfite, then

(4) D. Vorlander, *Ber.*, **52**, 263 (1919); D. Vorlander and E. Siebert, *ibid.*, **52**, 286 (1919); for a more recent and detailed interpretation see J. D. Roberts, R. A. Clement, and J. A. Drysdale, *J. Am. Chem. Soc.*, **73**, 2181 (1951).

(5) R. Hafner, *Ber.*, **22**, 2524, 2902 (1889).

(6) M. Gentschev, I. Pojarliev, and D. Kolev, *Compt. rend. acad. bulgare sci.*, **12**, 307 (1959) (in German).

(7) P. A. von Bonsdorff, *Annalen von Physik und Chemie*, **19**, 377 (1830).

(8) W. L. Hardin, *J. Am. Chem. Soc.*, **21**, 944 (1899).

TABLE I

ANALYSES OF THE BROMINATED COMPLEXES

Complex Brominated		Insufficient Bromine[a]				Excess Bromine[b]			
		C	H	N	Br	C	H	N	Br
[Pd(aniline)₂Br₂]	Calcd.	23.60	1.97	4.58	52.40	18.80	1.31	3.65	62.58
	Found	23.20	1.95	4.31	52.37	18.47	1.54	3.92	62.32
[Pd(o-toluidine)₂Br₂]	Calcd.	26.53	2.51	4.38	50.13	21.09	1.76	3.52	60.27
	Found	26.49	2.65	4.48	49.90	...	...	...	60.09
[Pd(p-toluidine)₂Br₂]	Calcd.	26.35	2.51	4.38	50.13	21.09	1.76	3.52	60.27
	Found	27.01	2.77	4.37	48.75	...	...	...	60.39
[Pd(m-toluidine)₂Br₂]	Calcd.	26.35	2.51	4.38	50.13	21.09	1.76	3.52	60.27
	Found	26.33	2.51	4.42	49.87	...	...	...	60.38

[a] Calculated values for monobromination of ligand. [b] Calculated values for dibromination of ligand.

with distilled water, and drying was carried out in air.

The free ligands were brominated under conditions as similar to those used for the complexes as their different solubilities allowed. The brominated amines were purified by a recrystallization from 60% ethanol.

The analyses on the brominated complexes obtained using insufficient bromine and an excess of bromine are collected in Table I. As can be seen these results are in rather good accord with the expectation that each coordinated amine will pick up one bromine with insufficient bromine and two (or) more when there is more bromine. It still is necessary, however, to determine the position of the substituent bromines and for this purpose the complexes were decomposed and the ligands isolated and characterized by their physical properties. The yields of the brominated complexes are given in Table II.

TABLE II

YIELDS OF BROMINATED COMPLEXES (%)[a]

Complex Brominated	Insufficient Br₂	Excess Br₂
[Pd(aniline)₂Br₂]	69.5	30.0
[Pd(p-toluidine)₂Br₂]	83.2	75.2
[Pd(o-toluidine)₂Br₂]	39.7	64.8
[Pd(m-toluidine)₂Br₂]	84.5	55.7

[a] Calculated on the basis of the products given in Table III.

Decomposition of the Brominated Complexes.—It is well known that many palladium(II) complexes are thermally unstable and initial attempts were made to recover the ligands by sublimation from the complexes at elevated temperatures. Although such treatment successfully brought about decomposition of the complex it also was found to cause further reaction. Thus, heating [Pd-(*para*-bromoaniline)₂Br₂] *in vacuo* resulted in the formation of elemental palladium and 2,4,6-tribromoaniline. It subsequently was found that H₂S was a suitable agent for the decomposition of these materials at room temperature and also provided an environment in which further bromination was impossible.

The brominated complex (0.005 mole) was slurried with 75 ml. of distilled water and H₂S gas then was passed into the slurry while it was stirred with a magnetic stirrer. The pressure was released at 10-min. intervals over a period of 30 min., after which time the decomposition reaction was essentially complete. The reaction mixture then was filtered and washed well with 5% hydrochloric

acid. The filtrate then was rendered basic by the addition of aqueous ammonia, and the brominated amine which precipitated was collected on a Hirsch funnel and washed several times with cold distilled water. The white crystalline product was air dried and then recrystallized from 60% ethanol. (The product obtained from the bromination of the complex with *para*-toluidine with insufficient bromine was an oil at room temperature. The mixture of the oil and the basic solution was placed in a small separatory funnel for separation. The oil then was washed several times with distilled water and dried.) The recovered products together with their melting points (the boiling point was used to identify 2-bromo-4-methylaniline) are given in Table III. The literature values for these constants were obtained from Heilbron's compilation.[9]

Exchange of Ligands.—Some simple experiments were carried out to determine whether the aromatic amines in the complexes were easily replaced. A sample of the aniline complex was allowed to stand in contact with its saturated solution in dimethylformamide for several days. The solid then was recovered and analyzed. *Anal.* Calcd. for [Pb(C₆H₇N)₂Cl₂]: C, 39.64; H, 3.85. Found: C, 39.57; H, 3.94. This shows that there is no rapid exchange of ligand with the solvent used. A second experiment was carried out to determine the possibility of the amine coming off in the solvent, undergoing bromination, and recoördinating. For this, a saturated solution of the aniline complex in dimethylformamide (100 ml.) which contained 10 g. of *s*-tribromoaniline was stirred vigorously for over 24 hr. At the end of this time the complex was recovered, washed with acetone to remove excess dimethylformamide, and analyzed. *Anal.* Calcd. for [Pd(C₆H₇N)₂Cl₂]: C, 39.64; H, 3.85. Found: C, 39.60; H, 4.06. This indicates that the exchange of aromatic amine is unlikely under these conditions.

Discussion

The most striking result of these studies is that there is no change in the orientation of the entering bromine induced by coördination. The differences in the degree of bromination encountered in some cases are no more than the differences known to arise from changes in the solvent.[10] It follows

(9) I. Heilbron and H. M. Bunbury, ed., "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953, four vols.

(10) P. B. D. DeLaMare, "Aromatic Substitution," Butterworths Scientific Publ., London, 1959.

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TABLE III

PRODUCTS OF BROMINATIONS IN N,N-DIMETHYLFORMAMIDE

| | Free Ligand | | Recovered Ligand | |
Species	Insufficient Bromine	Excess Bromine	Insufficient Bromine	Excess Bromine
Aniline	2,4,6-tribromoaniline, m.p. 119–120°; lit. 122°	2,4,6-tribromoaniline, m.p. 119–120°; lit. 122°	4-bromoaniline, m.p. 66°; lit. 66°	2,4-dibromoaniline, m.p. 78–80°; lit. 79–80°
p-Toluidine	2,6-dibromo-4-methylaniline, m.p. 79–79.5°; lit. 79°	2,6-dibromo-4-methylaniline, m.p. 78–79°; lit. 79°	2-bromo-4-methylaniline, b.p. 240°; lit. 240°	2,6-dibromo-4-methylaniline, m.p. 77–79°; lit. 79°
o-Toluidine	2,4-dibromo-6-methylaniline, m.p. 48–50°; lit. 50°	2,4-dibromo-6-methylaniline, m.p. 48–50°; lit. 50°	4-bromo-2-methylaniline, m.p. 57–59°; lit. 59°	2,4-dibromo-6-methylaniline, m.p. 48–50°; lit. 50°
m-Toluidine	4-bromo-3-methylaniline, m.p. 78–81°; lit. 81°	2,4,6-tribromo-4-methylaniline, m.p. 100–101°; lit. 101°	4-bromo-3-methylaniline, m.p. 79–80°; lit. 81°	2,4,6-tribromo-3-methylaniline, m.p. 99–101°; lit. 101°

then that the strict valence bond treatment of these reactions is inconsistent. So far as these results are concerned, the conclusion drawn by Fries[11] from his extensive study of the bromination of the toluidines holds also for coördinated toluidine. This is the fact that the amino group is the dominant factor in determining the active positions for substitution by bromine. It also appears that the initial point of attack, *para to the amino group*, is unchanged by coördination. In all the cases observed here only *ortho* and *para* substitution was observed. It should be noted that the coördination process involves the pair of electrons on the nitrogen in some manner fundamentally different from that found for either quaternary aromatic amines or ammonium ion formation. This difference is related to the fact that coördination does not necessarily put a positive charge on the nitrogen, while both of these other processes do.

The few differences in the degree of bromination observed may be attributed to (a) removal of the complex from the reaction by precipitation prior to complete bromination (the solid product obtained in the bromination of [Pd-(*meta*-toluidine)₂-Br₂] is probably [Pd-(4-bromo-3-methylaniline)-(2,4,6-tribromo-3-methylaniline)Br₂]), (b) a difference in the solvent effects for free ligand and complex, and (c) a possible very slight deactivation resulting from coördination. From the work of Fuchs[12] it is possible to estimate that such a deactivation must be considerably *less* than that produced by acetylation of the amino group.

A factor of prime importance which must be incorporated into any electronic theory of the

reactions of coördinated aromatic ligands is the somewhat smaller than expected transfer of charge which occurs when a coördinate bond forms. It now is widely accepted that the valence bond theory gives an estimate of charge transfer which is misleadingly greater than is found by any experimental probe.[13] A reasonable model of the coördinate bond is provided by ligand field theory. This model provides an adequate opportunity for the polarization of the ligand,[14] without building up large formal charges. In principle, the molecular orbital theory would provide the most satisfactory model of charge distributions in such complexes. Unfortunately, the calculations of such charge distributions are extremely difficult to carry out in detail.

There are other examples of the same general sort as are presented above. One may be seen in the work of Heldt[15] on reactions of coördinated isonitriles. In this case also, the inadequacy of the strict valence bond approach arises from the unrealistic formal charge distribution which it demands. The change in orientation of the coördinated isonitriles which was predicted did not occur. A similar change in the reactive positions

(13) As an example, B. R. McGarvey, *J. Phys. Chem.*, **60**, 71 (1956) found that the paramagnetic resonance of single crystals of copper(II) acetylacetonate is explicable on the basis of weak sigma and strong pi bonds between the metal and the ligand. Since the pi bonds of this model involve back-donation of electrons from the metal to the ligand, it is obvious that the electron donation cannot be taken too literally.

(14) The effects arising from this are comprehensively surveyed by G. Hesse in G. M. Schwab, "Handbuch der Katalysis," Springer Verlag, Vienna, 1943, Vol. VI, part 2, pp. 68–105. A detailed discussion of the various theoretical models of the coördinate bond and their descriptions of the charge distribution has been given by R. W. Parry and R. N. Keller in J. C. Bailar, Jr., "Chemistry of the Coördination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956, Ch. 3 and 4.

(15) W. Z. Heldt in "Advances in the Chemistry of Coördination Compounds," ed. by S. Kirschner, the Macmillan Co., New York, N. Y., 1961, page 321.

(11) K. Fries, *Ann.*, **346**, 128 (1906).
(12) W. Fuchs, *Monatsh.*, **38**, 311 (1917).

of pyridine which was reported[16] has since been shown[17] to be in error.

(16) H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **75**, 3865 (1953).

(17) N. Muller and W. J. Wallace, *J. Org. Chem.*, **24**, 1151 (1959).

Bromide Complexes of Thallium(I)[1]

BY ALLEN B. SCOTT, ROLAND G. DARTAU, AND SURANG SAPSOONTHORN

The solubility of TlBr in KBr solutions, and the absorption spectra of solutions containing both TlBr and KBr, have been analyzed. The data are consistent with the assumed existence of the complexes TlBr, $TlBr_2^-$, and $TlBr_4^{---}$, whose dissociation constants and molar absorptivities are given.

Introduction

Thallium(I) has been found to form chloride complexes having the formulas TlCl and $TlCl_2^-$, and some evidence has been reported for the existence of higher complexes in aqueous solutions of high chloride concentration.[2-4] Nilsson[4] also reported experiments which show that thallium(I) forms complexes of the type $TlX_q^{-(q-1)}$ with bromide and iodide, q ranging from one through four, and determined formation constants (expressed in concentration units) at an ionic strength of 4 M, in NaBr–NaClO$_4$ mixed solutions. However, even though the ionic strength was kept constant, activity coefficients in such solutions may be expected to vary widely as the NaBr/NaClO$_4$ ratio varies. Robinson[5] reported for 4 m NaBr, $\gamma = 0.939$; Jones[6] reported for 4 m NaClO$_4$, $\gamma = 0.627$. Constants such as Nilsson's $k_3 = [TlBr_4^{-3}]/[Br^-]^3$, where [ ] represents concentration, may vary by a factor of two or more over the range of compositions used. It is of course uncertain what activity coefficients should be used for multiply charged ions in this case. We conclude that the formulas

of complexes reported by Nilsson are not established.

We have determined the solubility of TlBr in solutions of varying KBr concentration and have calculated dissociation constants for the complexes as was done for the chloride complexes by Hu and Scott.[2] The use of KBr solutions, whose activity coefficients are known, rather than a mixture of two salts, makes it possible to determine dissociation constants for TlBr and $TlBr_2^-$ involving activities rather than concentrations. Further, since the mean ionic activity coefficient of KBr is fairly constant in the range 1–4 m, lying in the range 0.589–0.612, it is likely that concentration constants for higher complexes will remain fairly constant with varying KBr concentration. This is not true of NaBr, for γ varies[6] from 0.690 at 1 m to 0.939 at 4 m. We then have utilized these constants in the analysis of the absorption spectra of solutions of TlBr in KBr, as a means both of testing the dissociation constants and determining the molar absorptivities of the several species, using the method of Scott and Hu.[3]

Experimental

Solutions of KBr were saturated with TlBr at 25°; the solutions were analyzed for thallium(I) polarographically by reduction at the dropping mercury cathode.[7] At each concentration of KBr not less than four analyses were performed: one of a solution brought to equilibrium from oversaturation by three days agitation, one of a solution

(1) Presented before the Northwest Regional Meeting, the American Chemical Society, Richland, Washington, June 16, 1960. Taken from the M.S. theses of Roland G. Dartau (1958) and Surang Sapsoonthorn (1960), Oregon State College. Research Paper No. 419, O.S.C. Monographs.

(2) K. H. Hu and A. B. Scott, *J. Am. Chem. Soc.*, **77**, 1380 (1955).

(3) A. B. Scott and K. H. Hu, *J. Chem. Phys.*, **23**, 1830 (1955). In this paper, Table II, column headings should read $\epsilon_{w,x,y} \times 10^{-3}$.

(4) R. O. Nilsson, *Arkiv Kemi*, **10**, 363 (1957).

(5) R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1217 (1939).

(6) J. H. Jones, *J. Phys. Chem.*, **51**, 516 (1947).

(7) Y. Terui, *Bull. Inst. Phys. Chem. Research* (Tokyo), **17**, 595 (1938).