The Effect of Coordination on the Reactivity of Aromatic Ligands. XII. Reactions of Coordinated Aniline[1]

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Abstract. The rate of bromination of coordinated aniline in $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$ has been determined and found to be less than that for free aniline by a factor of about 10^{10}. The coordinated aniline, in turn, reacts more rapidly than the anilinium ion by a large factor (about 10^6). The ion $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$ was prepared by the aquation of $[Co(en)_2(NH_2C_6H_5)(Cl)]^{2+}$. The rate of this aquation reaction over the temperature range 25 to 40° can be described by the first-order rate constant $k_1 = 1.1 \times 10^{15} \exp(26{,}800/RT)$. The ion $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$ also reacts with water at a very slow rate to split off aniline and form $[Co(en)_2(H_2O)_2]^{3+}$. This reaction has a first-order rate constant $k_1 = 3.2 \times 10^{15} \exp(30{,}100/RT)$ over the same temperature range. The rate constant for the bromination of $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$ over the temperature range 10–25° is given by $k_2 = 4.6 \times 10^6 \exp(10{,}200/RT)$. Studies on the rate of iodination of $[Pd(NH_2C_6H_5)_4]^{2+}$ were unsuccessful because of the rapid replacement of coordinated aniline by iodide.

Although studies in this series have examined a variety of aromatic ligands, few of these lend themselves to such direct demonstrations of effects as the simplest aromatic ligand which coordinates without loss of a proton: aniline. It is with this ligand that the most unambiguous data can be obtained, but it is also unfortunately true that the water-soluble complexes of aniline are neither numerous nor well characterized. A further complication arises from the fact that aniline is not a notably good donor species, and in many circumstances seems unable to compete for coordination positions with the anions present in the reaction mixture (*e.g.*, with Pt(II) or Pd(II) complexes in bromide or iodide solutions). The present studies were carried out largely on *trans*-$[Co(en)_2(NH_2C_6H_5)(Cl)]Cl_2 \cdot H_2O$, because it proved to furnish one of the most direct routes for obtaining coordinated aniline in an aqueous environment. A further advantage, which this compound possessed over others which were considered, was that its only reaction with bromine was aromatic halogenation.

Experimental Section

Preparation of *trans*-$[Co(en)_2(NH_2C_6H_5)(Cl)]Cl_2 \cdot H_2O$. This compound was prepared by the method of Meisenheimer and Kiderlen.[2] *Anal.* Calcd for $[Co(en)_2(NH_2C_6H_5)Cl]Cl_2 \cdot H_2O$: Co, 14.87; C, 30.27; H, 6.31; N, 17.66; $NH_2C_6H_5$, 23.46. Found: Co, 14.77; C, 30.25; H, 6.16; N, 17.71; $NH_2C_6H_5$, 23.23.

Preparation of $[Pd(NH_2C_6H_5)_4]Br_2 \cdot 3H_2O$. $[Pd(NH_2C_6H_5)_2Br_2]$[3] (10.42 g, 0.023 mole) was mixed with aniline (75 ml) in a 200-ml flask fitted with an air condenser. This mixture was kept on a steam bath for 28 hr after which the resultant slurry was filtered. The residue was washed with several portions of water, and these washings were combined with the filtrate and agitated. The water layer was separated and evaporated to obtain a residue which was then recrystallized from 95% ethanol. The yield of the light buff solid complex was 4.2 g (26%). *Anal.* Calcd for $[Pd(NH_2C_6H_5)_4]Br_2 \cdot 3H_2O$: C, 41.61; H, 4.91. Found: C, 41.73; H, 4.71.

Rate of Aniline Loss from $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$. While free aniline reacts at an extremely rapid rate with bromine in aqueous solution, the reaction of the coordinated aniline is extraordinarily slow. As a result, it is possible to use an amperometric–coulometric titration to distinguish the two. Solutions of the complex were aged in a constant-temperature bath, and at the appropriate times aliquots were taken and put into a solution 0.25 *M* in potassium bromide and 0.05 *M* in hydrochloric acid. Bromine was generated using a coulometer, and the concentration of free bromine in solution was monitored with a platinum–calomel electrode system and a polarograph.[4] The current was measured at a constant voltage on the diffusion current plateau and was linearly related to the bromine concentration in all calibration runs. Aniline itself was found to undergo nearly instantaneous tribromination, and the presence of free aniline prevented free bromine from accumulating in the system. After the free aniline had been converted completely to the tribromide, the bromine concentration increased at a rate corresponding to the current setting of the coulometer. From the time required to reach this point, the amount of aniline which had been hydrolyzed from $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$ could be determined. Since the rate of release of aniline from this complex was extremely slow in comparison to the rate of bromination of free aniline, no correction had to be applied for the amount of hydrolysis which occurred during the course of the analysis.

Rate of Chloride Loss of *trans*-$[Co(en)_2(NH_2C_6H_5)(Cl)]^{2+}$. The rate of chloride loss from *trans*-$[Co(en)_2(NH_2C_6H_5)(Cl)]^{2+}$ was determined conductometrically over the concentration range 0.88×10^{-3} to 4.4×10^{-3} *M*, and the data were reduced by standard techniques.[5]

Rate of Bromination of Coordinated Aniline. The bromination of coordinated aniline was examined with both $[Co(en)_2(NH_2C_6H_5)(Cl)]^{2+}$ and $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$ as substrates. The rate of decrease of bromine concentration in solutions containing these complex ions was determined using the potentiometric method of Bell and Robinson[6] and a Beckman Research Model pH meter. The same procedure was used to establish the rate of vaporization of bromine in blank runs and to search for evidence for the reaction of bromine with $[Co(en)_2(Cl)_2]^+$ and its hydrolysis products. These solutions were all 0.05 *M* in HCl and 0.25 *M* in KBr.

For bromination of $[Co(en)_2(NH_2C_6H_5)(Cl)]^{2+}$ a solution containing potassium bromide and hydrochloric acid was allowed to reach the desired temperature in a jacketed vessel through which water from a constant-temperature bath was pumped. A weighed sample of the chloro complex was added and the timer started. Millivolt readings were then taken at various times using the platinum–glass electrode system. Even though some of the chloro complex is hydrolyzed to the aquo complex during the time required for bromination, linear plots were obtained because the two species are brominated at the same rate (*vide infra*).

For bromination of $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$, a weighed sample of $[Co(en)_2(NH_2C_6H_5)(Cl)]Cl_2 \cdot H_2O$ was dissolved in 0.25 *M*

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[1] This work was supported by a grant from the Army Research Office, Durham. We wish to thank Professor D. L. Tuleen for his helpful comments on this work.

[2] J. Meisenheimer and E. Kiderlen, *Ann.*, **438**, 242 (1924).

[3] R. L. Jetton and M. M. Jones, *Inorg. Chem.*, **1**, 309 (1962).

[4] G. S. Kozak and Q. Fernando, *Anal. Chim. Acta*, **26**, 541 (1962); *J. Phys. Chem.*, **67**, 811 (1963).

[5] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1962, p 28 ff.

[6] R. P. Bell and R. R. Robinson, *Proc. Roy. Soc.* (London), **A270**, 411 (1962).

potassium bromide and 0.05 *M* hydrochloric acid and kept at 40° for at least 10 hr (11 half-lives for the replacement of the chloride ion by water) to prepare the aquo complex, during which time some aniline also hydrolyzed to give some diaquo species. The solution was transferred to the jacketed vessel and allowed to attain the desired temperature. Bromine was then generated coulometrically until all the free aniline had been consumed and free bromine was being generated, as shown by the linear increase of the current with time; the concentration of free aniline was computed from the intersection of the two lines. After a convenient amount of bromine had been generated, the coulometer was switched off at the same moment the timer was started. The coulometer electrodes were replaced by the platinum-glass electrode system and millivolt readings were taken at various times. The initial concentration of aquo complex at the start of the bromination is the concentration of chloro complex taken minus the concentration of free aniline determined coulometrically at the beginning of the experiment.

In these systems bromine is consumed in three processes: (1) reaction of $[Co(en)_2(NH_2C_6H_5)(Cl)]^{2+}$ or $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$ with bromine, assumed to be monobromination, (2) reaction of 3 moles of bromine with each mole of free aniline released by the concurrent hydrolysis of the complex, (3) a blank at least partly due to bromine evaporation. Since the concentration of complex was much greater than the concentration of bromine, the rate constant for the bromination of the complexes was computed in the following way. The millivolt reading taken at time t was converted to bromine concentration (A_t) using a linear calibration curve of log (Br_2) *vs.* millivolts. The concentration of free aniline at time t, Δx, was computed from the equation $\Delta x = k_h C_0 \Delta t$, where k_h is the measured rate constant for aniline release (Table II), C_0 is the initial concentration of complex, and Δt is the time elapsed since the timer was started. Multiplication of Δx by 3 gave the concentration of bromine used in reaction with free aniline (B_t). Then $C_t = A_t + B_t$, where C_t is the concentration of bromine used by reaction with the complex and by the blank.

The rate constant for these two processes (k_1') was found by multiplying the slope of a plot of log C_t *vs.* time by 2.303; from k_1' was subtracted the rate constant determined separately for the blank to give the first-order rate constant (k_1) for bromination of the complex. The second-order rate constant (k_2) was computed by dividing k_1 by the initial concentration of complex.

No correction was made to accommodate any bromination by tribromide, which has recently been reported[7] to be effective in the second step of the bromination of 8-hydroxyquinoline. The fact that rate constants for bromination with tribromide are about 1-2% of those with bromine means that in our case no less than 92% of the reaction proceeds *via* bromine.

Rate of Iodination of Aniline and of $[Pd(NH_2C_6H_5)_4]Br_4 \cdot 3H_2O$. These were determined by both the coulometric-amperometric technique and spectrophotometrically. A 0.1 *M* phosphate buffer at pH 7 which was also 0.05 *M* in potassium iodide was used as the reaction medium.

Search for Spectral Evidence for Molecular Complexes of Bromine and Coordinated Aniline. The visible spectra of solutions containing bromine and $[Co(en)_2(NH_2C_6H_5)(Cl)]^{2+}$ were examined over the region 300 to 600 mμ with a Bausch and Lomb 502 spectrophotometer to determine if molecular complexes of the sort postulated by Bell and Ramsden[8] were present.

Results

The complex ion *trans*-$[Co(en)_2(NH_2C_6H_5)(Cl)]^{2+}$ undergoes aquation with the loss of chloride at a moderate rate. A much slower second aquation reaction, in which the coordinated aniline is replaced by water, also occurs. As a consequence, the bromination rate for coordinated aniline was also determined with the ion $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$, which was generated *in situ*.

Rate of Chloride Release by *trans*-$[Co(en)_2(NH_2C_6H_5)(Cl)]^{2+}$. As expected the replacement of chloride by water was found to be first order in the *trans*-$[Co(en)_2(NH_2C_6H_5)(Cl)]^{2+}$ ion. First-order rate constants for this reaction at 25, 35, and 40° and for a variety of initial concentrations are given in Table I. The reactions were followed from one to four half-lives, and the estimated error is 5%. The use of the Arrhenius equation gives an activation energy of 26.8 kcal mole^{-1} and a frequency factor of 1.1 × 10^{15} for this reaction.

Table I. First-Order Rate Constants for the Aquation of *trans*-$[Co(en)_2(NH_2C_6H_5)(Cl)]^{2+}$ (Loss of Chloride)

	40°					
$[Complex]_{t=0}$, $M \times 10^3$	0.88	1.76	2.20	2.37	2.47	4.40
k_1, $sec^{-1} \times 10^4$	2.07	2.23	2.22	2.10	2.18	2.04
	35°			25°		
$[Complex]_{t=0}$, $M \times 10^3$	1.76	2.39		1.76	1.76	3.47
k_1, $sec^{-1} \times 10^4$	1.10	1.18		0.231	0.256	0.241

Rate of Aniline Release by $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$. The replacement of aniline by water occurs at a much slower rate than that at which chloride is replaced by water. The rate of aniline release was obtained using solutions in which the chloride replacement had been allowed to run essentially to completion during a 10-hr incubation period at 40° (approximately 11 half-lives). The rate of loss of aniline was found to be first order in complex. The results of these studies are summarized in Table II. These rate constants have an estimated error of 7%. For this reaction the activation energy is found to be 30.1 kcal mole^{-1} and the frequency factor is 3.2 × 10^{15} sec^{-1}.

Table II. Rates of Aniline Release from $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$

Initial complex concn, $M \times 10^3$	Temp, °C	k_1, sec^{-1}
1.62	25	2.86×10^{-7}
1.76	25	3.19×10^{-7}
4.05	30	7.86×10^{-7}
1.76	35	1.62×10^{-6}
1.62	35	1.52×10^{-6}
1.76	40	3.11×10^{-6}
8.73	40	3.58×10^{-6}

Rates of Bromination of Free and Coordinated Aniline. Even with aniline concentrations as low as 10^{-6} *M*, the rate of bromination in a solution 0.05 *M* in HCl and 0.25 *M* in KBr is extremely rapid; its rate is at the limit which can be estimated by the amperometric-coulometric apparatus used in this work. At 25°, the second-order rate constants can be estimated to be about 3 × 10^{10} l. mole^{-1} sec^{-1}. The bromination of the coordinated aniline in $[Co(en)_2(NH_2C_6H_5)(H_2O)]^3]$ is too slow to be measured by the same technique. The limited solubility of the complex and the volatility of bromine prevented adjustment of the reactant concentrations to obtain the large increases in rate which would have been necessary for the use of this method. The potentiometric method was used to measure bromine consumption in separate solutions of $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$ and $[Co(en)_2(NH_2C_6H_5)(Cl)]^{2+}$ and in a blank as well as a solution of $[Co(en)_2(H_2O)_2]^{3+}$. In the case of the blank, it was found that the rate of loss of bromine by evaporation from the solution could be allowed for by using an experimentally determined first-order rate constant for the process.

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(7) G. O'Dom and Q. Fernando, *Anal. Chem.*, **38**, 844 (1966).
(8) R. P. Bell and E. S. Ramsden, *J. Chem. Soc.*, 161 (1958).

In a series of experiments, the rate of volatilization of bromine was determined for solutions which also contained buffer, hydrochloric acid, and potassium chloride of identical concentration to that used in the bromination studies. The first-order rate constants were found to be

Temp, °C	25	30	35	40
k, sec^{-1} × 10^4	0.82	1.00	1.53	2.07

Allowance was made also for the bromine taken up by the released aniline during the bromination of the complex. These were used to correct the second-order rate constants for bromination for the concurrent loss of bromine by evaporation. The rates of bromination of complexed aniline are for reactions of the type

$$[Co(en)_2(NH_2C_6H_5)(OH_2)]^{3+} \xrightarrow{Br_2} [Co(en)_2(NH_2C_6H_4Br)(H_2O)]^{3+} + H^+ + Br^-$$

A typical run is given in Table III, and the rate constants are summarized in Table IV.

Table III. Bromination of $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$ at 25° [a]

t, sec	A_t, M × 10^5	B_t, M × 10^5	C_t, M × 10^5	k_1', sec^{-1} × 10^4 [b]
432	6.30	0.06	6.36	3.07
684	5.80	0.09	5.89	3.07
936	5.40	0.13	5.53	2.92
1188	5.00	0.16	5.16	2.87
1422	4.62	0.19	4.81	2.90
1632	4.30	0.22	4.52	2.90
1848	4.00	0.25	4.25	2.90
2058	3.70	0.28	3.98	2.92
2262	3.42	0.30	3.72	2.95
2442	3.18	0.33	3.51	2.98
2622	2.94	0.35	3.29	3.02
2778	2.72	0.37	3.09	3.07
2952	2.55	0.40	2.95	3.04

[a] 1.49 × 10^{-3} M complex; 7.26 × 10^{-5} M Br_2; 0.05 M HCl; 0.25 M KBr. [b] Average $k_1' = 2.97 \times 10^{-4}$ sec^{-1}; $k_1 = (2.97 - 0.82) \times 10^{-4} = 2.15 \times 10^{-4}$ sec^{-1}; $k_2 = 1.44 \times 10^{-1}$ M^{-1} sec^{-1}.

Table IV. Rate of Bromination of $[Co(en)_2(NH_2C_6H_5)(X)]^{3+}$

X	[Complex]$_0$, M × 10^3	[Br_2]$_0$, M × 10^5	Temp, °C	$10k_2$, M^{-1} sec^{-1}
H_2O	1.40	7.06	25	1.45
	1.49	7.26	25	1.44
Cl^-	3.87	4.55	25	1.48
	2.27	11.0	15	0.85
	2.00	9.05	10	0.59

The possibility that the coordinated ethylenediamine was undergoing a reaction with bromine was ruled out by the determination of the rate of bromine loss of a blank solution containing *trans*-$[Co(en)_2(H_2O)_2]^{3+}$. In such a system the rate of loss of bromine is identical with that found when the complex was absent. The rate constants for the bromination of the coordinated aniline have an estimated uncertainty of 10% or less. The rate of bromination of the coordinated aniline is considerably more rapid than the loss of aniline from the complex. The relative reaction rates found thus completely exclude any alternative reaction scheme involving only bromination of released aniline. From these data, the activation energy is found to be 10.2 kcal/mole and frequency factor is 4.6 × 10^6 sec^{-1}.

Spectral Evidence for Molecular Complexes. The spectra of solutions which contained both bromine and $[Co(en)_2(NH_2C_6H_5)(Cl)]Cl_2 \cdot H_2O$ had absorbances which were simply the sums of the absorbances due to the individual components; hence no evidence for molecular complexes was found.

Iodination Rates for $[Pd(C_6H_5NH_2)_4]Br_2 \cdot 3H_2O$. The apparent second-order rate constants for the iodination of the coordinated aniline in this complex are 2.0 × 10^3 (20°), 2.82 × 10^3 (25°), 5.9 × 10^3 (35°), and 17.4 × 10^3 (40°) (all l. mole^{-1} min^{-1}). These rates were found to be very nearly *four* times the rate of iodination of aniline itself under identical conditions. These ratios were 4.07 (25°), 4.19 (35°), and 4.01 (50°). The conclusion that the iodide in the solution displaced the aniline from the complex in a rather rapid reaction is almost inescapable. This conclusion is supported by spectral evidence which shows that aniline is rapidly released from the complex in the phosphate buffer system used in the iodination experiments. Attempts to examine this reaction in solutions in which the iodide was replaced by bromide or chloride, and the iodine added as the element, were unsuccessful because the resulting solutions are much more effective iodinating agents than I_3^-, and comparable data could not be obtained with the required degree of precision.

Discussion

The results with $[Pd(NH_2C_6H_5)_4]^{2+}$ illustrate the problems which arise when the substitution reactions of the central metal are facile in the reaction medium. In this case, the rate of iodination of the aniline is the same as in the free state because it is all replaced in the complex by iodide. This type of reaction makes the use of palladium complexes less attractive than they might seem otherwise.

The very drastic reduction in the rate of bromination of aniline when it is coordinated to cobalt(III) in $[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}$ is in accord with the expectation that coordination will deactivate the aniline toward electrophilic substitution. This effect, however, is not as great as that which occurs upon protonation. From the data of Suthers, Riggins, and Pearson,[9] it is possible to estimate an *upper limit* for the second-order rate constant for the bromination of the anilinium ion as 3 × 10^{-7} l. mole^{-1} sec^{-1}, and this may be too high by several orders of magnitude. The sequence of rate constants at 25° is thus $k_{NH_2Ph} = 3 \times 10^{10}$ l. mole^{-1} sec^{-1} $\gg k_{[Co(en)_2(NH_2C_6H_5)(H_2O)]^{3+}} = 1.5 \times 10^{-1}$ l. mole^{-1} sec^{-1} $\gg k_{^+NH_3Ph} = 3 \times 10^{-7}$ l. mole^{-1} sec^{-1}. This fits into the sequence proposed previously,[10] *i.e.*, $k_{NH_2Ar} > k_{M-NH_2Ar} > k_{^+NH_3-Ar}$. One implication of these results, which is of considerable importance, is that the net charge on the complex is so diffusely distributed that the effective charge adjacent to or on the nitrogen is less than +1, even though it is adjacent to a metal ion with an ostensible charge of +3. The attainment of the transition state for aromatic bromination is thus somewhat more difficult to achieve in the complex than in the free ligand. The basis for this may be seen in the comparison of the data obtained on

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(9) B. R. Suthers, P. H. Riggins, and D. E. Pearson, *J. Org. Chem.*, 27, 447 (1962).

(10) N. K. Chawla and M. M. Jones, *Inorg. Chem.*, 3, 1549 (1964).

methylbenzenes[11] with that presented here on aniline and its derivatives. In each case, this basis is the manner in which the substituents affect the ability of the system to accommodate the positive charge of the transition state *via* structures of the type $^{+}R{=}C{<}$, where R = $-NH_2$, $-NH_2Co(en)_2(H_2O)^{3+}$, and $-{}^{+}NH_3$, for the sequence aniline, cobalt complex, anilinium ion. On the basis of the order of the rate constants, we may postulate that coordination to cobalt(III) decreases the relative importance of such a structure but not so much as protonation does.

The spectra of mixtures of bromine and the aniline complexes indicate, by the absence of any deviation from additivity of absorbances, that molecular complex formation between these two is not apparent under the conditions used in this study.

The activation energy (10.2 kcal) and frequency factor (4.6×10^6 sec^{-1}) for the reaction of the coordinated aniline reveal that both steric and electronic factors are involved in the decrease of the rate upon coordination. For the bromination of aniline and other aromatic amines, the rates are close to those expected for a diffusion-controlled reaction. The low frequency factor for the coordinated aniline shows that the steric aspects of its reaction with bromine are not so favorable as is found with aniline itself. This is consistent with the rather great sensitivity of bromination to unfavorable steric features, which has been found with many other aromatic systems. The over-all results are in close agreement with previous work on complexed ligands which has shown that coordination generally leads to a considerable decrease in the preexponential factor of the Arrhenius equation.[10,12,13]

The results obtained here also allow the clarification of some problems which have arisen with ligands of more complicated structure. The first of these is the confusion between the quantitative change in rates which is generally found as a result of coordination,[12,14] and drastic changes in relative reactivity of ligand sites which have been claimed more frequently than substantiated.[15] These changes are directly determined by the degree to which reaction rates are changed by minor changes in substituents; with aromatic electrophilic substitution it is known that such sensitivity to substituents varies enormously from reaction to reaction. With reference to such a reaction in which the substrate is coordinated to a metal, it can be confidently anticipated that the change in rate constant will increase as the Hammett ρ value for the reaction increases in absolute magnitude[11] (or becomes more negative for typical electrophilic substitutions). It should be noted that one reason for the enormous range of rate constants in the present case is the great sensitivity of bromination rates to substituent variations ($\rho \approx -12$).

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(11) R. Breslow, "Organic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1965, p 155 ff.

(12) K. D. Maguire and M. M. Jones, *J. Am. Chem. Soc.*, **85**, 154 (1963).

(13) J. B. Breinig and M. M. Jones, *J. Org. Chem.*, **28**, 852 (1963).

(14) A. F. Richards, J. H. Ridd, and M. L. Tobe, *Chem. Ind.* (London), 1, 1727 (1963).

(15) C. Bostic, Q. Fernando, and H. Freiser, *Inorg. Chem.*, **2**, 232 (1963); **4**, 602 (1965).