[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions in Complex Ions. IV. Kinetics of the Reactions of *cis*- and *trans*-Chloronitro-bis-(ethylenediamine)-cobalt(III) and Aquonitro-bis-(ethylenediamine)-cobalt(III) Ions with Various Reagents in Aqueous Solutions[1,2]

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The kinetics of the reactions between *cis*- and *trans*-chloronitrobis-(ethylenediamine)-cobalt(III) ions and azide, nitrite and thiocyanate ions have been studied. In each case the mechanism is shown to be an aquation followed by the coördination of the anion. The reactions of the intermediate aquonitro complexes were studied at high anion concentrations. Under these conditions, ion-pair formation prevents any definite conclusions as to the mechanism in the case of reactions with thiocyanate or azide ions. Formation of the nitritonitro complex complicates the nitrite ion reaction.

Numerous studies have been made of substitution reactions in cobalt(III) complexes,[5] but none of these has furnished definitive information as to the molecularity of the reactions involved. Recent studies[6] indicate a duality of mechanism in that some of these reactions apparently proceed by way of a dissociation mechanism and others by direct displacement of one ligand by another. This paper reports a detailed kinetic study of the reactions of *cis*- and *trans*-$[\mathrm{Coen_2NO_2Cl}]^+$ and $[\mathrm{Coen_2NO_2H_2O}]^{+2}$ ions in aqueous solutions with azide, nitrite and thiocyanate ions.

Experimental

Preparation of Compounds.—The *cis*-chloronitro-bis-(ethylenediamine)-cobalt(III) chloride and *trans*-chloronitro-bis-(ethylenediamine)-cobalt(III) nitrate were prepared according to the procedure of Werner.[7] The starting material in these syntheses, *trans*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride, was prepared as described by Bailar.[8]

Anal. Calcd. for *cis*-$[\mathrm{Coen_2NO_2Cl}]\mathrm{Cl}$:[9] Cl, 23.95. Found: Cl, 24.20. Calcd. for *trans*-$[\mathrm{Coen_2NO_2Cl}]\mathrm{NO_3}$: Cl, 10.88. Found: Cl, 10.95.

The *cis*- and *trans*-aquonitro-bis-(ethylenediamine)-cobalt(III) complexes could not be isolated but were obtained in solution by allowing the corresponding chloronitro complexes to aquate overnight. It has been shown previously[1b] that aquation occurs with essentially retention of configuration.

Kinetic Methods.—Four different methods were used for the determination of the kinetic data. The method used to study a particular reaction depended upon the characteristics of the reaction and the specific information desired. In all the kinetic studies made, the reacting anion was in large excess with respect to the complex. Consequently, the rate constants were all calculated as pseudo-first-order constants.

1. **Spectrophotometric.**—The change in optical density was followed with time. The wave length chosen to follow a particular reaction was the one at which a maximum absorption difference occurred between the reactant and product. For example, this maximum difference between the dinitro complexes and the aquonitro complexes occurs at 440 mμ. This was therefore the wave length used to determine the rate of conversion of aquonitro to dinitro cations. On the other hand, the rate of aquation of the *cis*-chloronitro complex was followed at 460 mμ, while the reactions resulting in the formation of the "*cis*"-azidonitro was studied at 490 mμ. The reaction producing the *cis*-thiocyanatonitro complex was studied at 490 mμ and at 290 mμ. Measurements were made on a Beckman Model DU spectrophotometer using quartz cells of 1 cm. path length. The temperature was controlled to within ±0.1° by circulating thermostated water through the compartment surrounding the cells. The concentration of the complex in these runs was approximately 0.003 *M*. Rate constants were obtained from typical first-order plots of log $(D_\infty - D_0/D_\infty - D)$ *vs.* time.

2. **Determination of Chloride Ion.**—The following techniques were used to obtain rate data:

a. **Titration with Mercury(II) Nitrate.**—The rate of production of chloride ion in the presence of nitrite ion was determined by titration with standard mercury(II) nitrate[10] in dilute nitric acid using sodium nitroprusside as the turbidity indicator. The technique consisted of pipetting aliquots of the reaction mixture, which was immersed in a thermostat, onto crushed ice to quench the reaction. Since nitrite ion interferred with the end-point, it had to be destroyed with sulfamic acid before the titration. This caused a small reproducible error for which correction factors were determined on blank solutions. The concentration of the complex on these runs was approximately 0.005 *M*.

Thiocyanate ion also interfered in the titration but it could not be destroyed at conditions which would not interfere with the kinetics of the reaction under investigation. Hence, it was not possible to follow the rate of chloride ion formation in the presence of thiocyanate ion.

b. **Potentiometric Titration.**—The mercury(II) nitrate titration could not be used in the presence of azide ion due to the concurrent precipitation of mercury(II) azide. A potentiometric method, using a Beckman *p*H meter, proved quite satisfactory. A glass electrode served as a reference electrode, since the *p*H of the solution remained constant, and a Ag–AgCl indicator electrode was utilized. Aliquots of the thermostated reaction mixture were discharged into an iced solution consisting of two parts acetone to three parts of methanol to which was added a little nitric acid. The methanol–acetone mixture sharpened the end-point considerably and the presence of dilute nitric acid rendered the silver azide soluble. This procedure was adapted from reference six.

The solution was rapidly titrated with 0.01 *M* silver nitrate using a microburet, directly graduated to 0.01 ml. The concentration of complex in these runs was approximately 0.003 *M*. Rate constants were calculated from plots of log $(V_\infty - V_T)$ *vs.* time.

3. **Conductometric.**—Because of the rapidity of the aquation reaction of the *trans*-chloronitro complex, this reaction was followed conductometrically. For these measurements, a Jones conductance bridge equipped with a 1000 cycle signal and a cathode-ray oscillograph as the null detector was used. The conductance cell, of the standard

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(1) Previous papers in this series: (a) F. Basolo, J. G. Bergmann and R. G. Pearson, *J. Phys. Chem.*, **56**, 22 (1952); (b) F. Basolo, B. D. Stone and R. G. Pearson, THIS JOURNAL, **75**, 819 (1953); (c) R. G. Pearson, C. R. Boston and F. Basolo, *ibid.*, **75**, 3089 (1953).

(2) This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT (11-1)-89-Project No. 2.

(3) Atomic Energy Commission Predoctoral Fellow, 1950–1952.

(4) Taken in part from theses submitted by B. D. Stone (1952) and J. G. Bergmann (1954) in partial fulfillment of the requirements for the Ph.D. degree.

(5) F. Basolo, *Chem. Revs.*, **51**, 459 (1953).

(6) D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2680 (1953); reference 1b,c.

(7) A. Werner, *Ann.*, **386**, 252 (1912).

(8) J. C. Bailar, Jr., "Inorganic Syntheses," Vol. II, 1946, p. 223.

(9) Ethylenediamine is designated as *en*.

(10) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Interscience Publishers, Inc., New York, N. Y., 1947, Vol. II, p. 331.

type, was immersed in a thermostat during the course of the reaction. The concentration of the complex was approximately 0.005 *M*. The data collected were plotted as log $(R/(R - R_\infty))$ *vs.* time.

Results

Rate of Chloride Ion Formation.—The effect of nitrite ion on the rate of formation of chloride ion from *cis*- and *trans*-$[Coen_2NO_2Cl]^+$ and also the effect of azide ion on the rate of chloride formation from the *cis* complex has been determined in aqueous nitric acid solutions. These rates at the various reaction conditions are presented in Table I. The ionic strength was not kept constant as the rate of reaction was found to be virtually independent of ionic strength for additions of up to 1 *M* sodium nitrate. These results show that the rate of chloride formation is independent of the concentration of nitrite ion or of azide ion and therefore the formation of $[Coen_2(NO_2)_2]^+$ and $[Coen_2NO_2N_3]^+$ must occur by an intermediate equation step.

TABLE I

EFFECT OF NITRITE AND AZIDE IONS ON THE RATE OF CHLORIDE ION FORMATION IN AQUEOUS SOLUTIONS AT 25°

Reaction conditions	0.005 *M* *cis*-$[Coen_2NO_2Cl]Cl$ $k \times 10^3$ (min.$^{-1}$)	0.005 *M* *trans*-$[Coen_2NO_2Cl]NO_3$ $k \times 10^3$ (min.$^{-1}$)
Mercury(II) nitrate titration		
0.05 *M* HNO_3, no $NaNO_2$	6.4^a	66
.05 *M* HNO_3, 0.1 *M* $NaNO_2$	6.4	68^a
.05 *M* HNO_3, 0.2 *M* $NaNO_2$	5.9	
.05 *M* HNO_3, 1.0 *M* $NaNO_2$		68^a
Potentiometric titration with silver nitrate		
0.05 *M* HNO_3, no NaN_3	7.0^a	
.05 *M* HNO_3, 0.1 *M* NaN_3	6.7	
.05 *M* HNO_3, 0.5 *M* NaN_3	6.7	

[a] Indicates reactions where duplicate runs were made. In such runs rate constants agreed to about 5%.

Spectral Changes.—When the reaction of a chloronitro complex with excess thiocyanate ion was followed spectrophotometrically and a plot made for a first-order reaction, a straight line was not obtained. However, an expression was derived to account for the spectral changes based on the following two-step reaction path

$$\underset{A}{[Coen_2NO_2Cl]^+} + H_2O \xrightarrow{k_1} \underset{B}{[Coen_2NO_2H_2O]^{+2}} + Cl^- \quad (1)$$

$$\underset{B}{[Coen_2NO_2H_2O]^{+2}} + CNS^- \xrightarrow{k_2} \underset{C}{[Coen_2NO_2CNS]^+} + H_2O \quad (2)$$

where both 1 and 2 are first order kinetically. Using the known equations for each concentration as a function of time, and the known extinction coefficients for each component, one can derive the equation for the optical density at any time

$$D = E_aA_0e^{-k_1t} + E_bA_0\frac{k_1}{k_2 - k_1}(e^{-k_1t} - e^{-k_2t}) + E_cA_0\left[1 - e^{-k_1t} - \frac{k_1}{k_2 - k_1}(e^{-k_1t} - e^{-k_2t})\right] \quad (3)$$

The needed values of k_1 and k_2 for this expression were determined by independent runs on reactions 1 and 2 under the same conditions as the experimental run to be compared. Using equation 3, *D* values at various times were calculated for a given set of initial concentrations. These *D* values were then used to calculate the expression, log $(D_\infty - D_0/D_\infty - D)$. Plots of this function *vs.* time were made and good agreement was obtained with the experimental value of the same function. A typical example of this comparison is shown in Fig. 1.

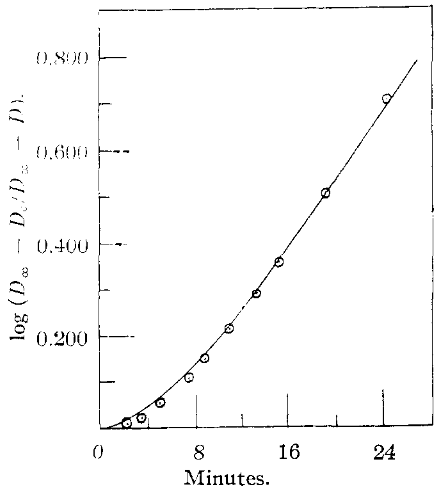

Fig. 1.—Rate of change of optical density at 470 mμ for the reaction of 0.003 *M* *trans*-$[Coen_2NO_2Cl]^+$ with 0.2 *M* NaCNS at *p*H 2.9 and 35°: ——, calculated; ⊙ ⊙ ⊙, experimental.

Rates of Reaction of the Aquonitro Complexes with Various Ions.—The effect of the concentration of the reacting ion on the rates of these reactions was determined spectrophotometrically at a *p*H of 5.4. The acid dissociation constants for the *cis*- and *trans*-aquonitro complexes were determined by titration with a standard solution of sodium hydroxide and the *p*K_a's were found to be 6.34 and 6.44, respectively. Therefore, to ensure that the complex is predominantly present in the aquo form, a *p*H of 5.4 was chosen at which to run the reactions. Since sodium nitrite and sodium azide are salts of weak acids, it was necessary to add acid in order to keep the solutions buffered at a *p*H of 5.4. In order to maintain this *p*H throughout the series of reactions involving different concentrations of nitrite and azide ions, a constant ratio of perchloric acid to sodium nitrite or sodium azide was used. Since thiocyanic acid is a fairly strong acid, sodium thiocyanate does not hydrolyze in aqueous solution and the described procedure was not necessary in this case.

There is reason to be somewhat concerned about the decomposition of nitrous acid since its concentration was 0.02 *M* at the highest value used. Certainly there was some decomposition but the amount was small since reactions were run in a closed system with but little build-up of pressure. The decomposition is known to be a reversible reaction. It is of interest to report that formation of dinitro complex occurred readily at a *p*H of 0.85 (at a rate about a tenth of that at a *p*H of 5.4). Since the ionization constant of nitrous acid is 6×10^{-4}, the concentration of nitrite ion is negligible at this *p*H. It must therefore be concluded that molecular nitrous acid (or possibly N_2O_3) can react.

Although it was observed that the salt effect is relatively small, an attempt was made to keep the ionic strength constant by the addition of sodium perchlorate. Unfortunately this is not entirely satisfactory because at high concentrations different anions at the same ionic strength will have a different effect on activity coefficients. A good discussion of the principle of a "constant ionic medium" at high concentrations is given by Biederman and Sillen.[11] The conclusion of these authors is that in a reaction such as we have here between two ions of opposite sign, the maintenance of a constant ionic medium is of little value. If the reactants are of the same charge, or uncharged, and if the concentration of the inert ion of opposite charge is constant, the procedure may be quite useful.

The reactions with either azide or nitrite ions go essentially to completion as shown by the fact that a constant value of D_∞, optical density at infinite time, is reached in each case no matter what concentration of azide or nitrite ions is used. For thiocyanate ion, the reactions were incomplete since D_∞ increased with increasing thiocyanate concentration. From the variation of D_∞ with concentration, a value of the equilibrium constant was estimated and the observed first-order rate constant was corrected for the rate of the reverse reaction using the usual expression for a reversible first-order process. The reverse rate constant is, of course, only pseudo-first-order and was recalculated for each ionic concentration. The estimated equilibrium constant for the reaction with thiocyanate ion is 1.7.

The pseudo-first-order rate constants for these reactions are summarized in Table II. The changes in rate with concentration are shown graphically in Fig. 2.

TABLE II

RATES OF REACTION OF THE AQUONITRO COMPLEXES WITH VARIOUS IONS AT A *p*H OF 5.4 AT 35°

0.003 *M* $[Coen_2NO_2H_2O]^{+2} + X^- \rightarrow [Coen_2NO_2X]^+ + H_2O$

$[X^-]$, mole/l.	$X^- = NO_2^-$ *cis*	*trans*	$X^- = SCN^-$ *cis*	$X^- = N_3^-$ *cis*
	$k \times 10^3$ (min.$^{-1}$)			
0.1	7.7	42	1.5	
.25			5.2	
.4	36.9	202		7.5
.5			7.7	
.6	45.8	267		
.8	49.1	295		14.4
1.0	50.2	357	9.1	
1.5	46.6	510	12.8	
1.6				22.8
1.7		550		
2.0	51.6	550	17.5	
2.4				31.4
3.2				42.2

Duplicate runs were made in about half the above cases. Reproducibility was 10%.

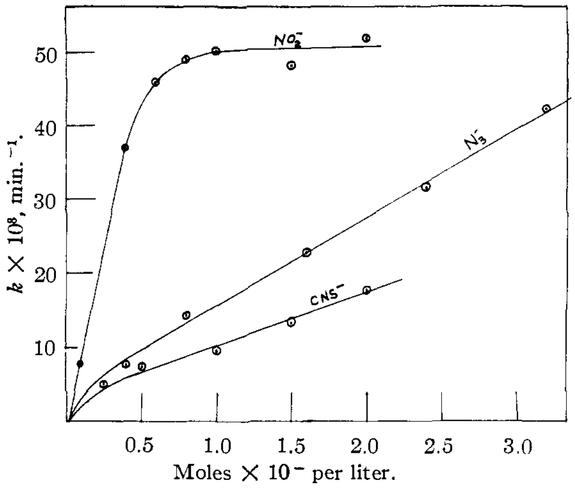

Fig. 2.—Rates of reaction of 0.003 *M* *cis*-$[Coen_2NO_2H_2O]^{+2}$ with increasing concentrations of azide, nitrite and thiocyanate ions at a *p*H 5.4 and 35°.

Discussion

The over-all reaction $[Coen_2NO_2Cl]^+ + X^- \xrightarrow{H_2O} [Coen_2NO_2X]^+ + Cl^-$, where X^- is azide, nitrite or thiocyanate ion, proceeds by a two-step process as described by equations 1 and 2. Proof of this two-step process is afforded by the fact that the rate of formation of chloride ion is independent of the concentrations of the reacting species and also the experimental rate of spectral change for the reactions with excess thiocyanate ions is in good agreement with the spectral change calculated on the basis of the two reactions.

That reactions of this type in aqueous solution take place through the intermediate aquo complex had been suggested previously. Bailar and Peppard[12] observed that the conversion of *l*-$[Coen_2Cl_2]^+$ into the optically active $[Coen_2CO_3]^+$ yielded a dextrorotatory product when done in water but a *l*-carbonato complex if performed in the absence of water. It was therefore suggested that the reaction carried out in aqueous solution involved the intermediate formation of *d*-$[Coen_2H_2OCl]^{+2}$. A second example was given by Ettle and Johnson,[13] who reported no direct exchange of radiochloride ion and the chloro groups of $[Coen_2Cl_2^+]$ in aqueous solution. It has recently been demonstrated that direct displacement does occur with certain reagents for reactions in absolute methanol.[6]

In regard to the reaction of the aquonitro complex with nitrite ion, the disappearance of first-order dependence on nitrite ion at high concentrations of nitrite ion was originally interpreted to be indicative of a dissociative process involving a pentacovalent intermediate.[5] Thus, a limiting rate constant would be reached which would be equal to the rate of dissociation of a water molecule from the complex ion. Evidence for such a mechanism would consist of (a) finding that several ligands gave the same limiting rate, (b) measuring the rate of water exchange and finding it equal to the limiting rate.

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[11] G. Biederman and L. G. Sillen, *Arkiv fur Kemi*, **5**, No. 40, 425 (1953).

[12] J. C. Bailar, Jr., and D. F. Peppard, THIS JOURNAL, **62**, 820 (1940).

[13] G. W. Ettle and C. H. Johnson, *J. Chem. Soc.*, 1490 (1940).

However, nitrito complexes have been isolated[14] and we have observed recently the rapid formation of the nitritonitro complex ($[Coen_2NO_2(ONO)]^+$) under our experimental conditions.[15] The kinetics of the rearrangement of nitrito complexes to the corresponding nitro compounds were the subject of extensive investigation by Adell.[16] The zero order dependence on nitrite ion at high concentrations of nitrite ion (Fig. 2) results from the very rapid formation of the nitritonitro complex and thus the observed change in optical density is due to the rearrangement of the nitritonitro compound to the dinitro complex. At the wave length used (440 mμ) the extinction coefficient of the nitritonitro complex is close to that of the aquonitro compound. The fact that the unstable nitrito intermediate is formed rapidly suggests the cobalt–oxygen bond is not broken.[15] Instead the attack occurs on the coördinated oxygen which thus accounts for the formation of the nitrito isomer (Co–ONO) rather than the more stable nitro form ($Co–NO_2$).

There is no sign of reaching a limiting rate in the reactions with thiocyanate or azide ions (Fig. 2). Unfortunately these reactions are complicated by ion-pair formation. The occurrence of ion-pair formation can be observed by a shift of the ultraviolet spectra toward longer wave lengths immediately upon addition of thiocyanate or azide ions.[17]

In the case of thiocyanate ion, apparently there is ion-pair formation occurring, since considerable spectral shifts are observed, but there is no indication of its being complete at 2.0 *M* thiocyanate. At this concentration, the highest used, the optical density at zero time increased from 0.322 to 0.475 at 275 mμ upon addition of 2.0 *M* thiocyanate ion to a 8.1×10^{-6} *M* solution of the *cis*-aquo complex. This observation is in agreement with the continued rate dependence on thiocyanate ion as shown in Fig. 2.

With azide ion, there is a much smaller change in the spectrum of the *cis*-aquonitro complex but here again one is limited by the absorption of the azide ion. Thus, it is not possible to say whether ion-pair formation occurs only slightly, or that it occurs extensively but with only small spectral changes. However, the general character of all the rate constant–concentration curves, shown in Fig. 2, indicates ion-pair formation. Thus, the data for azide ion and thiocyanate ion are approximately linear but do not extrapolate to zero rate at zero concentration.

In view of the possibility of stepwise formation of higher ion-pairs at high concentrations, and because each ion-pair and the free complex ion would have its own rate of reaction, it does not seem possible to resolve the rate data of Fig. 2 any further. Hence, no conclusions can be drawn concerning the molecularity of these reactions.

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[14] A. Werner, *Ber.*, **40**, 285, 783 (1907).

[15] R. G. Pearson, P. Henry, J. G. Bergmann and F. Basolo, forthcoming publication.

[16] B. Adell, *Svensk. Kem. Tid.*, **56**, 318 (1944); **57**, 260 (1945); *Z. anorg. Chem.*, **252**, 272 (1944); **271**, 49 (1952); *Acta. Chem. Scand.*, **1**, 624, 659 (1947); **4**, 1 (1950); **5**, 54, 941 (1951).

[17] M. Linhard, *Z. Electrochem.*, **50**, 224 (1944); H. Taube and F. Posey, THIS JOURNAL, **75**, 1463 (1953).

EVANSTON, ILLINOIS

NOTES

The Iron–2,2′,2″-Terpyridine System[1]

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The bis-2,2′,2″-terpyridine-ferrous ion has been utilized considerably in analytical procedures.[2] However, the system itself has received little study even though it is closely related to the iron–2,2′-bipyridine and iron–1,10-phenanthroline systems which have received considerable attention. This investigation was undertaken to provide some of the fundamental information concerning the terpyridine molecule and its complexes with iron.

Experimental

Reagents.—Ferrous ammonium sulfate was used in the preparation of the ferrous solutions. A small amount of hydroxylamine was added to the stock solutions to prevent air oxidation. The solution of perchloric acid in glacial acetic acid was standardized with diphenylguanidine, which had been recrystallized from toluene according to the method of Carlton.[3] The 2,2′,2″-terpyridine was obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio.

Determination of the Oxidation Potential.—The oxidation–reduction potential of the bis-2,2′-2″-terpyridine-iron(II) complex was determined by potentiometric titration with cerium(IV) in 0.1 *F* sulfuric acid. The reactants were weighed directly into 0.1 *F* sulfuric acid in ratios varying from 2.0–2.4 moles of 2,2′,2″-terpyridine to 1.0 mole of iron(II). The graphically determined value of the formal potential[4] was 1.10 ± 0.01 volt.

The oxidation of bis-2,2′-2″-terpyridine-iron(II) to bis-2,2′,2″-terpyridine-iron(III) in 0.1 *F* sulfuric acid is accompanied by a vivid color change from deep wine red to a light green. The green solution changes very rapidly to a bright yellow upon standing a minute or two. In 1.0 *F* sulfuric acid the deep wine red changed directly to the yellow. No green form was observed. This phenomenon did not alter the potentiometric results.

Determination of the Acid Equivalency.—The reaction of the bis-terpyridine-iron(II) ion with hydrogen ion may be represented as

$$\mathrm{FeTerpy_2{}^{++}} + 2n\mathrm{H^+} \longrightarrow \mathrm{Fe^{++}} + 2\mathrm{TerpyH}_n{}^{n+} \quad (1)$$

The value of *n* in this equation was evaluated by potentio-

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[1] Presented before the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 3, 1953. Abstracted from a thesis submitted by Jack P. Wright to the Graduate School of Purdue University, 1952, in partial fulfillment of the requirements for the degree of Master of Science.

[2] G. F. Smith and F. R. Richter, "Phenanthroline and Substituted Phenanthroline Indicators," The G. Frederick Smith Chemical Company, Columbus, Ohio, 1944.

[3] C. A. Carlton, THIS JOURNAL, **44**, 1469 (1922).

[4] E. H. Swift, "Introductory Quantitative Analysis," Prentice–Hall, New York, N. Y., 1950, p. 109.