The Reaction of Glyoxylatopentaamminecobalt(III) with Chromous Ion. The Rate of Dehydration of the Ligand

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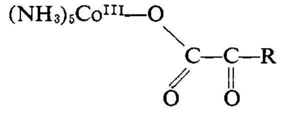
Abstract: The rate at which Cr^{2+} at low concentrations reacts with glyoxylatopentaamminecobalt(III) is first order in each of the reactants, but it becomes almost independent of (Cr^{2+}) when this is high. The kinetic behavior is understood on the basis that the dominant form of the complex contains the hydrated ligand but that the carbonyl form arises from the hydrate and reacts much more rapidly with Cr^{2+} than does the hydrate. The analysis of the kinetic and the nmr data leads to the conclusion that at 25° the specific rate for the reaction of Cr^{2+} with the carbonyl form is $>7 \times 10^3\ M^{-1}\ \text{sec}^{-1}$ and with the hydrate form it is $\sim 1\ M^{-1}\ \text{sec}^{-1}$ and that the rate of dehydration of the complex is given by the law $-d(\text{hydrate})/dt = 0.075\,(\text{hydrate}) + 0.64(H^+)(\text{hydrate})$, where the units of concentration and time are moles per liter and seconds, respectively.

We have been investigating the reaction with reducing agents of complexes of the class



where R is H, CH_3, $C(CH_3)_3$, OH, O^-, or NH_2. For the first three members of the series the degree of hydration of the α-carbonyl group is an important factor affecting the kinetics of the reaction and the interpretation of the results. Among these ligands, glyoxylate occupies an extreme position in its behavior because it exists almost completely in the hydrate form when it is bound to the metal ion. The interpretation of the kinetic data for the reaction of Cr^{2+} with the glyoxylate complex has led to a measure of the rate of dehydration of the ligand. This feature of the system is of interest apart from the other issues which concerned us in our investigation of the general subject area, and we are therefore reporting on it separately here.

Experimental Section

Preparation of the Glyoxylato Complex. About 50 g of aquopentaamminecobalt(III) perchlorate was added to a solution *ca.* 3.6 *M* in glyoxylate ion and 0.4 *M* in the acid (the latter solution was made up using Eastman 40% technical grade glyoxylic acid and adding sodium hydroxide in the requisite amount). The mixture was heated at 40–50° with stirring for about 12 hr. Perchloric acid was added until a precipitate just began to form, and the solution was then cooled. After *ca.* 12 hr the product was collected, washed with cold perchloric acid, and recrystallized, again using perchloric acid to decrease the solubility of the complex. The recrystallized product was washed with cold dilute perchloric acid, ethanol, and ether; it was then dried under vacuum at room temperature.

The analytical results on the complex were as shown in Table I. It should be noted that they agree somewhat better with the "monohydrate" formulation for the complex than with the "anhydrous."

Nmr Measurements. The proton magnetic resonance spectra were obtained at room temperature on a Varian A-60 spectrometer, using D_2O as solvent and H_2O as the reference liquid. Spectra were obtained for solutions of (a) pure glyoxylic acid (K & K Laboratories) and (b) the chloride salt of the glyoxylato complex (the perchlorate salt is too insoluble to give a measurable signal).

Measurements of Stoichiometry. Our concern was to learn whether reduction of the glyoxylato complex to the glycolato takes place in its reaction with Cr^{2+}. The experiments were done using for each concentration level chromous ion at twice the concentration of the cobalt complex and adjusting the reaction time so that the complex was essentially completely consumed, but any glycolato complex, if at all formed, would be only slightly reduced. The specific rate for the reaction of Cr^{2+} with the latter complex has been reported,[1] and for the former was measured in the course of the present work. At low (Cr^{2+}), there is no difficulty in choosing a suitable reaction time because the reduction of the glyoxylato complex is very much more rapid than that of glycolato. However, at the highest (Cr^{2+}) used, 0.05 *M*, significant consumption of any glycolato complex formed would have occurred at the reaction time chosen. The result which is reported makes allowance for possible consumption of the glycolato product.

Table I. Analysis of Glyoxylatopentaamminecobalt(III) Perchlorate

	Calcd for $Co(NH_3)_5$-O_3C_2H-$(ClO_4)_2$, %	Calcd for $Co(NH_3)_5$-O_3C_2H $(ClO_4)_2\cdot H_2O$, %	Obsd, %
Co	14.2	13.6	13.5
C	5.77	5.33	5.39
H	3.88	4.18	4.16
N	16.83	16.14	16.50
ClO_4	47.8	45.8	45.2

In the experiments on stoichiometry, the glyoxylato complex was placed in a small flask stoppered with a serum cap, along with the reagents necessary to make $\mu = 1.00$ at the desired acid concentration. After the air was removed by a stream of deoxygenated nitrogen, a solution containing chromous ion was injected rapidly with stirring and, after the selected time interval, the reaction mixture was quenched using either $Na_2Cr_2O_7$(aq) or $Fe(ClO_4)_3$(aq).[2] The solution was then examined spectrophotometrically for the concentration of Co^{III} left or of Co^{II} produced using the method of Kitson.[3]

Kinetic Measurements. The solution of Cr^{2+} was prepared by standard procedures using zinc amalgam as the reducing agent.

Kinetic measurements were made at an ionic strength of 1.00 and at several concentrations of acid, in the range 0.10–1.00 *M*. The ionic strength was made up to 1.0 with $LiClO_4$, using a solution

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(1) R. D. Butler and H. Taube, *J. Am. Chem. Soc.*, **87**, 5597 (1965).

(2) Blank experiments showed that, although $Cr_2O_7^{2-}$ was a suitable quenching agent at low Cr^{2+} concentration, it was not when (Cr^{2+}) was high. We found that when Cr^{2+} is injected into a solution containing $Cr_2O_7^{2-}$ and the glycolato complex at concentrations so as to constitute a blank for expt 5 of Table II (see below), the cobalt(III)–glycolato complex was almost completely consumed. It is of course possible that if the order of mixing is changed, namely $Cr_2O_7^{2-}$ being added to Cr^{2+}(aq), as is done in the actual experiment, little induced destruction of the cobalt(III) complex occurs. The problem was, however, avoided by using $Fe(ClO_4)_3$ as the quenching agent in this case and measuring the cobalt(III) left at the end of the experiment.

(3) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).

of the salt prepared by dissolving reagent grade Li_2CO_3 in $HClO_4$ (aq). Solutions of Cr^{2+} and of the glyoxylato complex were prepared just before use.

A stopped-flow apparatus was used for the kinetic measurements. The rate was followed spectrophotometrically at wavelengths of 280, 310, or 353 mμ, no difference in the apparent specific rates being noted at the different wavelengths.

Results

Nmr Results. The nmr spectrum of glyoxylic acid showed a large peak at ν 243 cps (corrected to TMS as reference and using a probe frequency of 60 Mc). A very small signal was observed also at ν 248 cps which we attribute to an impurity in the sample. No other signals were observed up to ν 2000 cps. The nmr spectrum of the complex showed only one peak attributable to the glyoxylate ligand, and this appeared at ν 310 cps.

Stoichiometry. Chromous ion reduces glyoxylate fairly rapidly and thus it appeared necessary to investigate whether reduction to the glycolato form occurred in the reaction of Cr^{2+} with the glyoxalato complex. The results of the study of the stoichiometry are described in Table II.

Table II. Reduction of the Glyoxylato to the Glycolato Complex

(H^+), M	Reaction time, sec	$(Cr^{2+}) \times 10^3$, M	$(Co^{III}) \times 10^3$, M	Max prodn of glycolato complex, %
1.0	10	4.4	2.2	12
1.0	7	12	6.3	14
0.50	5	52	27	10
0.10	60	5.1	2.8	3
0.10	26	12	7.8	3

Ligand reduction on the Co^{III} center, if it occurs at all, is so slight as not materially to affect the interpretation of the kinetic data.

Kinetic Results. The plots of optical transmittance *vs.* time obtained by means of the stopped-flow apparatus were used to calculate a second-order rate constant, as defined by the rate law

$$\frac{-\mathrm{d}(Co^{III})}{\mathrm{d}t} = k_{obsd}(Co^{III})(Cr^{2+})$$

Most of the experiments were done under pseudo-first-order conditions with Cr^{2+} in excess. Those that were not were treated using the equation

$$\log\left[\frac{(b/(a-1))(A_0 - A_\infty)}{A_t - A_\infty} + 1\right] = \frac{b-a}{2.303}kt + \log b/a$$

where a and b are the initial concentrations of reactants, b being in excess. A_0 is the measured initial absorbance, A_∞ the final absorbance, and A_t the absorbance at any given time during the course of the reaction. The function on the left side of the equation was plotted against time, and the rate constant k was obtained from the slope of this plot. No kinetic complication was observed for any of the experiments at low (Cr^{2+}) throughout the course of the reaction up to four half-lives. At high (Cr^{2+}), the plots showed curvature toward the end of the reaction. This complication was at first attributed to the production and subsequent reduction of glycolato complex, but the direct investigation of the stoichiometry shows that if the glycolato complex is formed at all, the concentration is too low to account for the behavior.

In Table III is presented a summary of the kinetic data we acquired.

Table III. Results of the Kinetic Measurements[a]

No.	(H^+), M	$(Cr^{2+}) \times 10^3$, M	$(Co^{III}) \times 10^4$, M	k_{obsd},[b] M^{-1} sec^{-1}
1	1.00	0.94	5.1	130
2	1.00	3.81	20.0	81.0[c]
3	1.00	6.9	19.8	62.6
4	1.00	9.6	20.2	56.6
5	1.00	11.5	19.3	44.4[c]
6	0.50	0.96	5.2	111
7	0.50	3.8	5.2	59.7
8	0.50	11.2	5.5	27.8
9	0.50	31	5.8	15.9
10	0.50	50	5.7	7.74
11	0.50	67	5.5	6.83
12	0.50	100	5.7	4.14
13	0.10	0.9	5.2	76.2
14	0.10	3.82	6.0	25.7
15	0.10	7.7	5.7	16.9
16	0.10	11.2	5.3	11.9

[a] Temperature, 25°; $\mu = 1.00$. [b] $k_{obsd} = [\mathrm{d}(Co^{III})/\mathrm{d}t]/[(Co^{III})\cdot(Cr^{2+})$. [c] Average of three runs.

Discussion

It is generally accepted that glyoxylic acid exists in aqueous solution largely as the hydrate;[4] (Strehlow[5] gives for the (hydrate)/(carbonyl) equilibrium constant a value of $\sim 10^2$). Strehlow[5] has also shown that glyoxylic acid dehydrates at a slower rate than does pyruvic acid. This rate is too slow to result in averaging of the nmr peaks for the hydrate and carbonyl forms. The nmr measurements thus show that a single form is dominant and, from the magnitude of the shift, which is much less than is observed for the genuine $-CH(=O)$ structure, we can conclude that this form must be the hydrate. The shift for the complexed glyoxylate is close enough to that of the uncomplexed so that the nmr data alone provide strong evidence for the conclusion that the complexed glyoxylate is also hydrated. Again the equilibrium is too slow for the single peak observed to result from the time averaging of two peaks.[6] Thus the absence of a signal corresponding to the carbonyl structure shows that for the bound ligand (hydrate)/(carbonyl) > 50. The conclusion as to the state of the complexed ligand finds some support in the fact that the solid apparently exists as the monohydrate and the strongest support in the kinetic analysis of the data to be presented, which makes it possible to compare reactivities with those of complexes featuring known α hydroxy or α carbonyl groupings.

Inspection of the data of Table III shows that the rate of the reaction of Cr^{2+} with the complex is not simply first order in each of the reactants, as is the case in most reactions of Cr^{2+} with Co^{III} complexes. At high concentrations of Cr^{2+}, the rate becomes

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(4) M. Becker and H. Strehlow, *Z. Elektrochem.*, **64**, 813 (1960).

(5) H. Strehlow, *ibid.*, **66**, 392 (1962).

(6) We have observed two distinct peaks for the pyruvato complex. Assuming that the dehydration rates for the complexed ligands parallel those of the free acids, one would then expect two peaks for the glycolato complex if two forms were present in appreciable amounts.

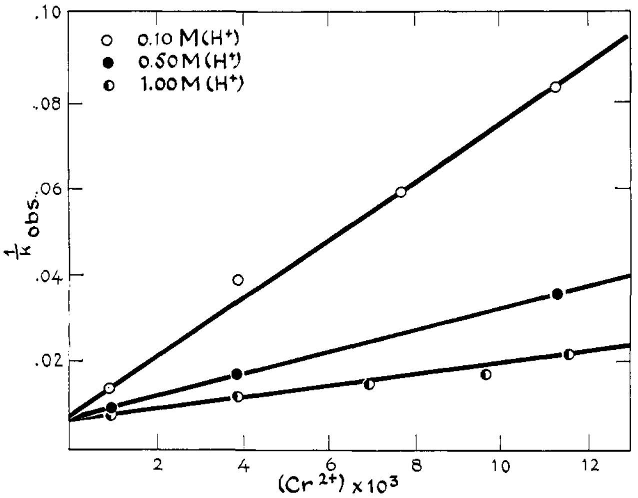


Figure 1. The variation of rate of reaction of $[\mathrm{Co(NH_3)_5O_2CCH(OH)_2}]^{2+}$ with $\mathrm{Cr^{2+}}$ at several concentrations of $\mathrm{H^+}$. Temperature, 25°; $\mu = 1.00$; $k_{\mathrm{obsd}}(M^{-1}\ \mathrm{sec}^{-1}) = [-\mathrm{d(Co^{III})/d}t]/[(\mathrm{Co^{III}})\cdot(\mathrm{Cr^{2+}})]$.

independent of $(\mathrm{Cr^{2+}})$, and dependent only on $(\mathrm{H^+})$ and $(\mathrm{Co^{III}})$. The kinetic results are accounted for by

$$[\mathrm{Co(NH_3)_5O_2CCH(OH)_2}]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Co(NH_3)_5O_2CCHO}]^{2+} + \mathrm{H_2O} \qquad (1)$$

$$[\mathrm{Co(NH_3)_5O_2CCHO}]^{2+} + \mathrm{Cr^{2+}} \xrightarrow{k_2} \mathrm{Co^{2+}} + \mathrm{Cr^{III}} \qquad (2)$$

Since the carbonyl form does not accumulate appreciably, the mechanism leads to the rate law

$$\frac{-\mathrm{d(Co^{III})}}{\mathrm{d}t} = \frac{k_2k_1(\mathrm{Co^{III}})(\mathrm{Cr^{2+}})}{k_{-1} + k_2(\mathrm{Cr^{2+}})}$$

or

$$k_{\mathrm{obsd}} = \frac{k_2k_1}{k_{-1} + k_2(\mathrm{Cr^{2+}})}$$

On this basis, when $1/k_{\mathrm{obsd}}$ is plotted against $(\mathrm{Cr^{2+}})$ a straight line should result with the intercept corresponding to $(\mathrm{Cr^{2+}}) = 0 = k_{-1}/k_1k_2$ and the slope as $1/k_1$. The kinetic data summarized in Table III are shown in Figure 1, plotted according to this prescripition but omitting the data at $(\mathrm{Cr^{2+}}) > 1.2 \times 10^{-2}$ M which were obtained at 0.50 M $(\mathrm{H^+})$. (The data at high $(\mathrm{Cr^{2+}})$ which are omitted will be shown later to provide evidence for a minor additional reaction path.)

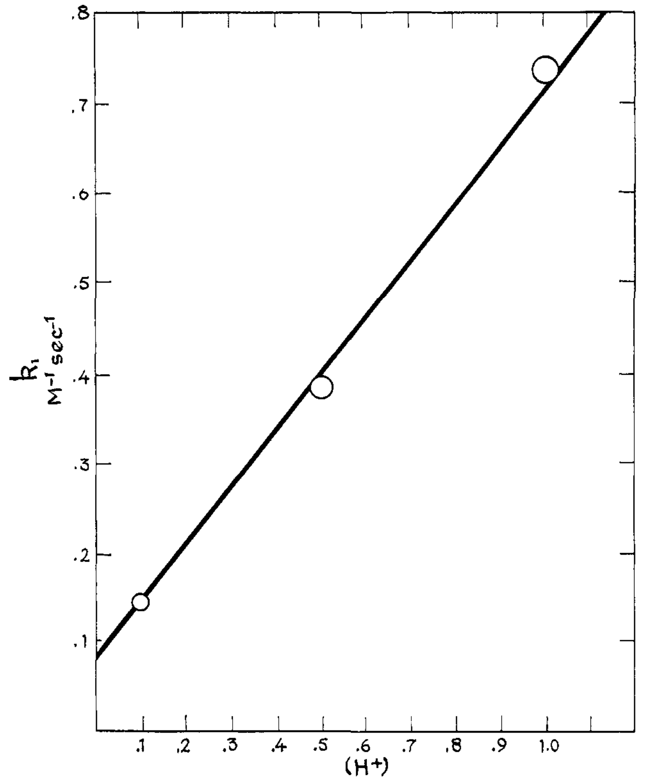
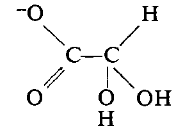


Figure 2. The rate of dehydration of $[\mathrm{Co(NH_3)_5O_2CCH(OH)_2}]^{2+}$ as a function of $(\mathrm{H^+})$. Temperature, 25°; $\mu = 1.00$.

The data at three different concentrations of $\mathrm{H^+}$ conform to the requirements of the mechanism and extrapolate to a common intercept, 0.0070, at $(\mathrm{Cr^{2+}}) = 0$. The ratio k_1/k_{-1} is the equilibrium constant for reaction 1, and this ratio is expected to be independent of $(\mathrm{H^+})$. Thus, because the intercept is independent of $(\mathrm{H^+})$, we conclude that k_2 is independent of $(\mathrm{H^+})$, in accord with our findings with other ligands of this series. The nmr results suggest that not more than 2% of the ligand in solution exists in the carbonyl form; this limit on the equilibrium constant for the hydration reaction when combined with the value of the intercept leads to the conclusion that $k_2 > 7 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$. This conclusion is consistent with the value of $1.2 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$ at 25° which has been measured for the corresponding reaction with pyruvate in the carbonyl form as the ligand.[7] The comparison of the reactivities is the strongest support for the conclusion that the dominant form of the ligand is the relatively unreactive form



The reactivities to $\mathrm{Cr^{2+}}$ of a series of α-hydroxypentaamminecobalt(III) complexes have been measured.[1] Consideration of the trends there suggests that the specific rate for reaction 3 would be less than 3.1 M^{-1}

$$\mathrm{Co(NH_3)_5O_2CCH(OH)_2}^{2+} + \mathrm{Cr^{2+}} \xrightarrow{k_3} \mathrm{Co^{2+}} + \mathrm{Cr^{III}} \qquad (3)$$

sec^{-1}, which is the specific rate for the reaction of $\mathrm{Cr^{2+}}$ with the glycolato complex. Reaction 3 can in principle be exposed by measuring rates at very high concentrations of $\mathrm{Cr^{2+}}$ for, under these conditions, the rate law will become

$$\frac{-\mathrm{d(Co^{III})}}{\mathrm{d}t} = k_1(\mathrm{Co^{III}}) + k_3(\mathrm{Cr^{2+}})(\mathrm{Co^{III}})$$

The experiments (9–12 of Table III) at high $(\mathrm{Cr^{2+}})$ were undertaken to get an estimate of k_3. Using the data at lower $(\mathrm{Cr^{2+}})$ as a guide, the contributions to k_{obsd} in expt 9–12 made by the path consisting of reactions 1 and 2 are 11.6, 7.3, 5.5, and 3.75 $M^{-1}\ \mathrm{sec}^{-1}$, to be compared to the experimental values of 15.9, 7.74, 6.83, and 4.14. Thus k_{obsd} is consistently higher than can be accounted for by the carbonyl path. The differences should be a direct measure of k_3. If the

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(7) H. J. Price and H. Taube, to be published.

result for expt 9 is rejected as deviating too markedly from the others, we find for k_3 a value of approximately 1.0 M^{-1} sec^{-1}. This value, though not accurate, does show that Cr^{2+} reacts very much more rapidly with the Co^{III} complex when the ligand is in the carbonyl form than when it is in the hydrate form.

In Figure 2 the values of k_1, as they are determined by the slopes of the lines in Figure 1, are shown plotted against (H^+). From this graph we find $k_1 = 0.075 + 0.64(H^+)$. The rate of dehydration of pyruvic acid has also been shown to depend on (H^+), and the rate law in this case has the corresponding terms $0.22 + 1.25(H^+)$ where these terms are to be multiplied by (pyruvic acid) to yield the actual rate.[5] The close correspondence between the function we have determined by indirect means and that obtained by Strehlow provides strong support for our interpretation of the data. It should be mentioned also that Strehlow reports that glyoxylic acid dehydrates at about one-half the rate of pyruvic acid.

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Anation, Water Exchange, and Ion-Pair Formation of Aquopentaamminechromium(III) Ion in Acidic Aqueous Solutions Containing Chloride or Thiocyanate Ions[1]

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Contribution from the Hope Chemical Laboratory, Georgetown University, Washington, D. C. 20007. Received July 15, 1966

Abstract: The kinetics of the formation of $Cr(NH_3)_5Cl^{+2}$ and $Cr(NH_3)_5NCS^{+2}$ from $Cr(NH_3)_5H_2O^{+3}$ in dilute acidic aqueous media have been studied. The rate of water exchange of $Cr(NH_3)_5H_2O^{+3}$ and ion-pair formation have also been investigated under similar conditions. NCS^- forms a more stable ion pair and reacts more rapidly than does Cl^-. Both anations are slow with respect to water exchange. The results are interpreted on the basis of a rate-limiting loss of coordinated water followed by collapse of the solvation shell to fill the vacancy created.

The rate of entry of anions into the coordination sphere of dipositive aquo ions of first transition series metals is determined by two factors: the rate of water exchange of the aquo ions and the tendency for ion-pair formation between the cation and the entering anion.[2] The same two factors have been found to dominate substitutions on Co(III) in nonaqueous solvents.[3] The rate of water exchange establishes a limiting rate for substitutions on $Co(CN)_5H_2O^{-2}$ in aqueous solutions, although anions differ in the concentration necessary to approach the limiting rate.[4] There is evidence that ion-pair formation and the rate of water exchange also are important in determining rates of slow substitution on tripositive aquo ions in aqueous media; however, most studies of these systems have been principally concerned with the thermodynamically favored aquation reactions.[5] For most trivalent transition metal ions, one or more of the three relevant quantities (rate of anation, rate of water exchange, ion-pair formation constant) is missing or must be estimated from fragmentary information generated as a by-product in an unrelated investigation. We now report a study of the rate of the reaction by which two anions replace water in $Cr(NH_3)_5H_2O^{+3}$. We have studied the rate of water exchange of the aquo ion and its ion-pair formation with the same anions under closely similar conditions.

Experimental Section

Reagents. Deionized distilled water and analytical reagent grade chemicals were employed. Chromium complexes were prepared from $[Cr(NH_3)_5H_2O](NO_3)_3NH_4NO_3$ by standard methods[6] or modifications of these methods. Analyses were carried out in three to five replicates by standard methods.[7]

Anal. Calcd for $[Cr(NH_3)_5H_2O](ClO_4)_3$: Cr, 11.5; NH_3, 18.8. Found: Cr, 11.4; NH_3, 18.4. Calcd for $[Cr(NH_3)_5Cl](ClO_4)_2$:

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(1) Taken, in part, from a Ph.D. thesis presented at Georgetown University in 1966 by N. V. Duffy.

(2) R. G. Wilkins in "Mechanisms of Inorganic Reactions," R. K. Murmann, Ed. American Chemical Society, Washington, D. C., 1965, p 55.

(3) M. L. Tobe, ref 2, p 7.

(4) A. Haim, R. J. Grassi, and W. K. Wilmarth, ref 2, p 31.

(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

(6) T. Moeller, *Inorg. Syn.*, 5, 132 (1951).

(7) H. F. Walton, "Principles and Methods of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1952, p 348; B. Harrow, E. Borek, A. Mazur, G. C. H. Stone, and H. Wagreich, "Laboratory Manual of Biochemistry," 4th ed, W. B. Saunders Co., Philadelphia, Pa., 1955, p 29.