CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF BUFFALO, BUFFALO, NEW YORK

Substitution Reactions of Oxalato Complex Ions. III. Kinetics of the Optical Activity Loss, Decomposition, and Oxalate Exchange Reactions of Oxalato-bis-(ethylenediamine)-cobalt(III) Ion in Strongly Basic Aqueous Solution

BY S. SHEEL,[1] D. T. MELOON,[2] AND G. M. HARRIS

Received July 21, 1961

The loss of optical activity, decomposition, and oxalate exchange reactions of oxalato-bis-(ethylenediamine)-cobalt(III) cation in the presence of aqueous alkali all are shown to result from the equilibration: $Coen_2C_2O_4^+ + 2OH^- \rightleftarrows Coen_2(OH)_2^+ + C_2O_4^=$ (1). The three processes have identical second-order kinetics, fitted at 71° by the rate law: $R = k(Coen_2C_2O_4^+)(OH^-)$, where $k = 1.7 \pm 0.3$ l. mole^{-1} min.$^{-1}$. The reactions appear to be controlled by rate-determining de-chelation of the oxalate ligand, *viz.*: $Coen_2C_2O_4^+ + OH^- \rightarrow Coen_2OC_2O_3{\cdot}OH$. Subsequent rapid steps result in the formation of a *cis/trans* equilibrium mixture of the dihydroxy species. The equilibrium constant for reaction 1 is $K_1 = 5000 \pm 1000$ l. mole^{-1} at 71°. Neutral or strongly acidic solutions of $Coen_2C_2O_4^+$ are completely stable for long periods of time at elevated temperatures.

The exchange and racemization reactions of the carbonato-bis-(ethylenediamine)-cobalt(III) ion were studied by Holden and Harris.[3] They showed that the rate of loss of optical activity is much slower than the rate of carbonate exchange, and that the two reactions were in fact quite dissimilar mechanistically. One purpose of the present investigation was to determine the differences in rates and mechanisms of the corresponding reactions for the analogous oxalato–diamine complex. It also was desired to compare the kinetic behavior of this exceedingly stable mono-oxalato compound with that of the tris-oxalato species reported in earlier papers in this series.[4]

Previous studies of the chemistry of the $Coen_2C_2O_4^+$ (en = ethylenediamine) complex ion consist of the preparative work of Werner and coworkers,[5] and the attempted racemization study by Bushra and Johnson.[6] The latter authors showed that long standing of the aqueous solution even in the presence of usually catalytic multivalent cations failed to induce loss of optical activity. Our experiments now have demonstrated that various reactions of this complex are rapid in basic solution, though the complex remains quite unaffected by heating to 90° in the presence of 1 *M* mineral acid. The results of a kinetic investigation of the hydroxide-ion promoted processes are detailed herewith.

Experimental

A. Preparation of Compounds.—*cis*-Dichloro-bis-(ethylenediamine)-cobalt(III) chloride was prepared by a standard procedure[7] and resolved by means of ammonium *d*-α-bromocamphor-π-sulfonate to give the *levo* isomer. Optically active *d*-$(Coen_2C_2O_4)_2C_2O_4$ was obtained from the *l*-$Coen_2Cl_2Cl$ by a modification of a previous procedure,[8] as follows: the *l*-dichloro salt and C.P. silver oxalate were ground together in an ice-cold mortar with an insufficient quantity of ice water to allow complete solution of the complex. The slurry was allowed to warm slowly to room temperature, and after 6 hr. standing the resultant *d*-oxalato-oxalate was dissolved in a minimum quantity of water and separated from the insoluble silver salt residues by filtration. The active oxalato compound then was precipitated from the filtrate by addition of a 1:1 alcohol–ether mixture.[9] Racemic $Coen_2C_2O_4Cl$ was prepared by

---

[1] Deceased December 1958. Work done as part of the Ph.D. requirements of the University of Buffalo.

[2] Work done as part of the M.A. requirements of the University of Buffalo, 1960.

[3] J. S. Holden and G. M. Harris, *J. Am. Chem. Soc.*, **77**, 1934 (1955).

[4] (a) F. D. Graziano and G. M. Harris, *J. Phys. Chem.*, **63**, 330 (1959); (b) K. V. Krishnamurty and G. M. Harris, *ibid.*, **64**, 346 (1960).

[5] (a) A. Werner and A. Vilmos, *Z. anorg. Chem.*, **21**, 145 (1899); (b) A. Werner and McCutcheon, *Ber.*, **45**, 3281 (1912); (c) A. Werner, *Ann.*, **386**, 77 (1912); (d) A. Werner, *Ber.*, **47**, 2171 (1914).

[6] (a) E. Bushra and C. H. Johnson, *J. Chem. Soc.*, 1937 (1939); (b) A new synthetic procedure has been reported recently by F. P. Dwyer, I. K. Reid, and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 1285 (1961).

[7] W. C. Fernelius, Ed., "Inorganic Syntheses," Vol. II, McGraw-Hill Book Company, Inc., New York, N. Y., 1946, p. 223.

[8] J. C. Bailar, Jr., and R. Auten, *J. Am. Chem. Soc.*, **56**, 774 (1934).

[9] Specific rotation of this preparation $[\alpha]^{20}D$, was 570°, measured on a 0.1% solution. Werner and McCutcheon[5b] initially obtained a product with a specific rotation of 200°, but Werner[5d] later reported this was increased to a maximum of about 800° by repeated recrystallization. Dwyer, *et al.*,[6b] got a product of similar activity to Werner's maximum. Bailar and Auten[8] give no quantitative rotation data for this complex.

the method of Werner and Vilmos,[5a] using C.P. reagents. The purity of the complex compound preparations was confirmed by analyses for cobalt (as Co_3O_4 by direct ignition), for oxalate (by potassium permanganate titration), and for chloride (by silver nitrate titration).

B. Optical Rotation Experiments.—All measurements were made on a Rudolph Model 80 research-type polarimeter, capable of ±0.001° precision. In the present work, the high absorbancy of the oxalato complex ion at the sodium-D line reduced the precision to not much better than ±0.01°. Kinetic runs were commenced by pipetting pre-determined volumes of standardized NaOH solution and distilled water into a 25-ml. volumetric flask thermostated at 71.0 ± 0.05°. The required weighed quantity of anhydrous *d*-complex then was added, with vigorous stirring. The reaction solution was transferred quickly to a thermostated polarimeter tube and rotation measurements were made at appropriate intervals.

C. Spectrophotometric Experiments.—A Beckman DU spectrophotometer was employed. Solutions were prepared as described in (B) above, except that racemic $Coen_2C_2O_4Cl$ salt was used. In the equilibrium constant determinations, it was necessary to add excess sodium oxalate for reasons obvious later. Reaction samples were "frozen" by quickly cooling the spectrophotometer cells in which they were contained to ice temperature before making the spectral measurements at 360 and 500 mμ, the absorption peaks of the oxalato complex. In a few experiments, the spectrophotometer cell compartment was itself thermostated at 71°, enabling observation of the spectral changes at much more frequent intervals than by the "freezing" technique. Concentrations of the $Coen_2C_2O_4^+$ ion and of the *cis–trans* equilibrium mixture of $Coen_2(OH)_2^+$ ion were obtained by use of the known molar extinction coefficient data.[10,11]

D. Oxalate Exchange Experiments.—The technique used in previous oxalate exchange work in this Laboratory[4] was but little modified in the present study. Reaction mixtures always were equilibrated chemically at the chosen temperature for one day prior to "seeding" with a small portion of highly active sodium oxalate-C-14. Standard solid sample counting procedure was employed on the precipitated, dried, and weighed calcium oxalate monohydrate samples. The data were obtained in terms of exchange half-times from the usual linear McKay plots. The precision of the data was not of a high order, due to the reaction complications mentioned below, but a series of repetitive experiments indicated a standard deviation of not greater than ±10% in the half-time values.

Results and Discussion

It was obvious from preliminary stoichiometry experiments[12] that the over-all chemical reaction between alkali hydroxide and the complex cation is represented by the equilibrium

$$Coen_2C_2O_4^+ + 2OH^- = Coen_2(OH)_2^+ + C_2O_4^= \quad (1)$$

The dihydroxy species is considered to be in *cis–trans* equilibrium, since this equilibration occurs very rapidly at the temperature of the present experiments.[11,13] The *cis* to *trans* reaction also provides a path for loss of optical activity; no such loss occurs, in fact, unless the hydroxyl ion concentration is appreciable.[14] Polarimetric runs were carried out in which the complex ion concentration was varied from 2.4×10^{-3} to 9.7×10^{-3} *M*, and that of the base from 2×10^{-3} to 24×10^{-3} *M*. A coherent set of rate constants could be obtained only by treating the optical activity loss not as a racemization in the true sense but as a direct result of chemical reaction, as suggested by reaction 1, with a rate law of the form

$$R_r = k_r(Coen_2C_2O_4^+)(OH^-) \quad (2)$$

The rate constants were computed in the usual manner from the slope of the standard integrated form of the appropriate second-order equation

$$\ln \frac{a(c-2x)}{c(a-x)} = k_r(c-2a)t \quad (3)$$

In this, *a* and *c* represent the known initial concentrations of complex and of hydroxide, respectively, and *x* is readily calculated from the rotation angles measured initially and at time *t*. The polarimetric rate constant data are collected in Table I. The only inconsistent results (experiments 9 and 10) are those from runs in which

TABLE I

RATE OF OPTICAL ACTIVITY LOSS AT 71°

Expt. no.	Initial Concentrations ($M \times 10^3$) (Complex cation)	(Hydroxide)	Rate const. k_r l. mole^{-1} min.$^{-1}$
1	4.89	8.0	1.7
2	4.91	8.0	1.9
3	4.90	16.0	2.0
4	4.92	24.0	2.0
5	2.47	24.0	1.6
6	2.46	24.0	1.8
7	2.47	16.0	2.1
8	2.44	8.0	1.5
9	9.73	8.0	0.6[a]
10	4.87	2.0	0.5[a]

k_r, mean and average deviation, expt. 1–8, 1.8 ± 0.2

[a] k_r values obtained from apparent initial slope of nonlinear plot.

---

(10) Data obtained in the present study showed that Beer's law holds for $Coen_2C_2O_4^+$ in the range 0.003 to 0.01 *M*, and that the conventional molar extinction coefficient, $\epsilon_\lambda = (1/cl) \log I_0/I$, had the values 138 and 113 at 360 and 500 mμ, respectively.

(11) The molar extinction coefficients of $Coen_2(OH)_2^+$ are 70.2 and 65.5 at 360 and 500 mμ, respectively; J. Bjerrum and S. Rasmussen, *Acta Chem. Scand.*, **6**, 1277 (1952); *ibid.*, **9**, 735 (1955).

(12) Based on spectrophotometric observations and on the increase in amount of "free" oxalate determined by precipitation.

(13) J. Y. Tong and P. E. Yankwich, *J. Am. Chem. Soc.*, **80**, 2664 (1958).

(14) A "neutral" solution of *d*-$(Coen_2C_2O_4)_2C_2O_4$ underwent no measurable decrease in optical activity during 32 hr. at 71° or in 38 days at room temperature.

TABLE II

SPECTROPHOTOMETRIC RATE AND EQUILIBRIUM DATA AT 71.0°

Expt. no.	Initial Concentrations ($M \times 10^3$) (Complex)	(OH⁻)	Free oxalate	Rate const. k_s, l. mole^{-1} min.$^{-1}$	Equil. const. K_1, l. mole^{-1} $\times 10^{-3}$
11	5.0	8.0	...	1.5	...
12	5.0	16.0	...	1.7	...
13	10.0	15.0	...	1.9	...
14	20.0	20.0	...	1.4	...
15	5.0	7.5	31.0	(1.0)[a]	4.8
16	5.0	12.0	150.6	(0.7)[a]	5.3
17	10.1	15.0	98.9	(1.1)[a]	6.4
18	10.0	15.0	149.8	...	3.5
k_s, mean and average dev., expt. 11–14,				1.6 ± 0.2	
K_1, mean and average dev., expt. 15–18,					$(5.0 \pm 1.0) \times 10^3$

[a] k_s value obtained from apparent initial slope of non-linear plot.

the (OH⁻) is considerably less than the stoichiometry requirement of equation 1. In these cases, the unidirectional reaction assumption inherent in equation 3 is no doubt invalid.[15] An alternative possibility, that the low k_r values of these runs result from ionic strength effects, is not tenable since the μ values for experiments 9 and 10 bracket those of several of the other experiments. In fact, the random scatter of k_r in experiments 1 through 8, in which μ varies from about 0.01 to 0.03, establishes the non-sensitivity of the reaction to change in ionic strength within the limits specified.

The spectrophotometric data also were analyzed in terms of the simple second-order kinetics concept used above. The concentrations of reactants and products could be followed by use of the known initial concentrations of complex and of hydroxyl, and of the optical density measurements at 360 and 500 mμ. It also was possible to obtain the magnitude of the equilibrium constant, K_1, of reaction 1 provided excess "free" oxalate was added initially in order to prevent the reaction from going essentially to completion. These runs, however, gave non-linear rate plots and low k_s values, undoubtedly for the same reason that the rotation runs at low hydroxyl ion concentration were unsatisfactory.[15] The spectrophotometric results are presented in Table II. The scatter in the values of the equilibrium constant seems large, but is unavoidable due to the great sensitivity of the determination to the final value of (OH⁻), which must be determined by difference and therefore is subject to considerable error.

It was found satisfactory to treat the oxalate exchange rate data in terms of the same second-order rate-determining process as before. The exchange rate law applicable to the chemically equilibrated reaction mixtures may be written

$$\frac{0.693}{t_{1/2}} = \frac{R(a+b)}{(a-x)(b+x)} = k_e \frac{(c-2x)(a+b)}{(b+x)} \qquad (4)$$

where a and c are as already defined and b is the known initial[16] concentration of "free" oxalate. Utilizing the known value of K_1 to calculate x from the expression

$$K_1 = \frac{x(b+x)}{(a-x)(c-2x)^2} \qquad (5)$$

the k_e's were computed from the observed exchange half-times of the various runs, with the results given in Table III.[17]

It is seen that, within experimental error, $k_r = k_s = k_e$, which must be true if the three processes have identical rate-determining steps, as has been assumed. A mechanism which is consistent with this point of view is

$$\mathrm{Coen_2C_2O_4^+ + OH^- \rightleftarrows \mathit{cis}\text{-}Coen_2{\cdot}OC_2O_3{\cdot}OH} \quad \text{(slow)} \quad (6)$$

$$\mathrm{Coen_2{\cdot}OC_2O_3{\cdot}OH + OH^- \rightleftarrows \mathit{cis}\text{-}Coen_2(OH)_2^+ + C_2O_4^=} \quad \text{(fast)} \quad (7)$$

$$\mathrm{\mathit{cis}\text{-}Coen_2(OH)_2^+ \rightleftarrows \mathit{trans}\text{-}Coen_2(OH)_2^+} \quad \text{(fast)} \quad (8)$$

The assumption that reaction 6 is rate-determining leads to the observed kinetic behavior. Reactions 6 and 7 may or may not take place with complete retention of configuration, since the rapid equilibration according to (8) results in any case in loss of optical activity. However, inversion

---

(15) The assumption only holds if the equilibrium constant of reaction 1 is rather large (as is shown later to be the case here), the (OH⁻) not too low, and the "free" oxalate concentration not too high.

(16) All these initial values refer to the state of affairs prior to chemical equilibration at the reaction temperature. Establishment of this equilibrium requires modification of the standard McKay equation as shown in (4).

(17) Columns 5 and 6 are included in the Table since the excellent agreement between these two sets of figures provides a gravimetric confirmation of the spectrophotometrically determined magnitude of K_1.

TABLE III

OXALATE EXCHANGE RATE DATA AT 71°

Expt. no.	(Complex)[a] $(a - x)$ $(M \times 10^3)$	(OH^-)[a] $(c - 2x)$ $(M \times 10^4)$	Free[a] [Oxalate] $(b + x)$ $(M \times 10^3)$	$(b + x)/(a + b)$		Rate const. k_e, l. mole^{-1} min.$^{-1}$
				Obsd.[b]	Calcd.[a]	
19	16.5	10.0	23.5	0.58	0.59	1.9
20	26.4	8.0	23.6	0.48	0.47	1.8[c]
21	26.5	9.4	33.5	0.56	0.56	1.8
22	36.3	6.8	23.7	0.39	0.40	1.9
23	36.4	8.2	33.6	0.48	0.49	1.8
24	36.5	9.2	43.5	0.55	0.54	1.8
25	37.3	5.8	22.7	0.37	0.38	2.1[c]
26	38.2	4.4	21.8	0.37	0.36	1.7[c]
27	56.3	5.6	23.7	0.29	0.30	1.7[c]
28	16.5	10.0	23.5	0.59	0.59	0.7[c,d]
29	36.3	6.8	23.7	0.39	0.40	0.6[c,d]
k_e, mean and average deviation, expt. 19–27, at 71°						1.8 ± 0.2

[a] "x" calculated from the known values of a, b, c, and K_1. [b] x determined from increase in weight of precipitated "free oxalate" over that expected from known "b" value. [c] Single experiment only. Other results averaged from two or more duplicate runs. [d] Runs made at 64°. K_1 assumed to have same value as at 71°.

of configuration in either (6) or (7) is ruled out, since this would require that $k_r = 2k_e = 2k_s$ for the mechanism as proposed. The assumption that the initial dihydroxy product is in fact the *cis* form is based on the following evidence. The isosbestic wave lengths for $Coen_2C_2O_4^+$ and the *cis–trans* $Coen_2(OH)_2^+$ equilibrium mixture are at 384 and 536 mμ, with absorption coefficients of 72 and 67, respectively. It was noted in some runs done with the thermostated spectrophotometer cell that, during the first few minutes of reaction, the absorption at these wave lengths increased slightly to a maximum, then fell off to the true equilibrium values. This is the expected behavior if *cis*-$Coen_2(OH)_2^+$ is the first dihydroxy product, since it has absorption coefficients of 94 and 87 at the quoted isosbestic wave lengths.

One notes the contrast in the oxalate exchange behavior of this mono-oxalato complex, where de-chelation of the oxalate group appears to be rate-determining, with that of the tris-oxalato type of complex, where de-chelation probably occurs during a very rapid proton pre-equilibration.[4] A possible explanation is the one of hydrogen bonding stabilization, previously invoked in studies of the carbonato diamine cobaltic complexes[18] and recently supported by deuterium exchange experiments.[19] It is obvious that strong internal hydrogen bonding can exist in the mono-oxalato diamine ion, but not in tris-oxalato ions. The higher negative charge of the latter species also is probably of significance. The role of the OH^- ion in promoting the de-chelation of the mono-oxalato group may be conceived as one of a partial de-protonation equilibration followed by a rate-determining attack by water molecules on the imido intermediate. Reaction 6 then would be replaced by

$$Coen_2C_2O_4^+ + OH^- \rightleftarrows CoenNH_2(CH_2)_2NHC_2O_4 + H_2O \quad \text{(fast)} \quad (6a)$$

$$CoenNH_2(CH_2)_2NHC_2O_4 + H_2O \rightarrow Coen_2OC_2O_3{\cdot}OH \quad \text{(slow)} \quad (6b)$$

This SN1CB concept of the mechanism, of course, leads to the same kinetics as the SN2 assumption inherent in the previous proposal, but there is no evidence in the present study on which to base a choice between the two.

It is of interest that the displacement of en from $Coen_3^{+++}$ by OH^- appears to have the same second-order kinetics as the mono-oxalato ion reaction. The former has been interpreted in terms of rate-determining de-chelation of one of the ethylenediamine ligands.[20] The process is, however, only about 2×10^{-3} times as rapid as the oxalate substitution at 70°. For the $Coen_3^{+++}$ ion, the rate constant is given as $k_{en} = 6.5 \times 10^{19} \exp(-38{,}000/RT)$ l. mole^{-1} sec.$^{-1}$. The limited data on the temperature dependence of the oxalate substitution reaction (Table III above) suggest an activation energy for the process of 34,000 cal./mole, leading to the Arrhenius rate expression $k_{ox} = 9 \times 10^{19} \exp(-34{,}000/RT)$ l. mole^{-1} sec.$^{-1}$. It is seen that the difference in velocity of the two reactions is almost en-

---

[18] J. E. Boyle and G. M. Harris, *J. Am. Chem. Soc.*, **80**, 782 (1958).

[19] G. Lapidus and G. M. Harris, manuscript in preparation.

[20] J. A. Friend and E. K. Nunn, *J. Chem. Soc.*, 1567 (1958).

tirely ascribable to the activation energy difference. This near-identity of the frequency factors (and thus entropies of activation) offers support for the assumption of identical mechanisms.

Finally, one must note the differences in the reactions of $\mathrm{Coen_2CO_3^+}$ ion[3] and $\mathrm{Coen_2C_2O_4^+}$. The sensitivity of the carbonato species to acid decomposition must arise from a major difference in mechanism. It has been suggested by experiments using $\mathrm{H_2O^{18}}$ that the initial process in the acid decomposition of $\mathrm{Co(NH_3)_4CO_3^+}$ is probably C–O bond cleavage,[21] and one would expect $\mathrm{Coen_2CO_3^+}$ to show similar behavior. Unfortunately, no comparable data are available for the $\mathrm{Coen_2C_2O_4^+}$–$\mathrm{OH^-}$ reaction. However, the possibility exists that in the mono-oxalato decomposition, the initial step is metal–oxygen bond fission; such a mechanism would provide a basis for the contrast in behavior observed with the two carbonato species.

Financial support of this work has been generously provided by the U. S. Atomic Energy Commission through Contract No. AT(30-1)-1578 with the University of Buffalo.

[21] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **75**, 4099 (1953); J. P. Hunt, A. C. Rutenberg, and H. Taube, *ibid.*, **74**, 268 (1952).

CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Some Metal Chelates of Ethylenediaminetetraacetic Acid, Diethylenetriaminepentaacetic Acid, and Triethylenetetraminehexaacetic Acid[1,2]

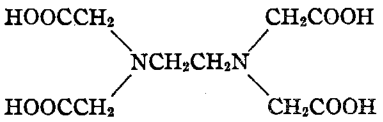
BY ROBERT E. SIEVERS AND JOHN C. BAILAR, JR.

Received September 18, 1961

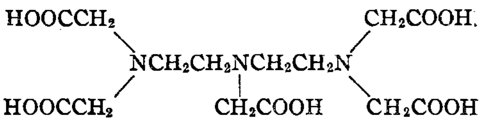
The properties and structural characteristics of some metal chelates of ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, and triethylenetetraminehexaacetic acid are reported. For chelates of 33 different metal ions, a correlation is observed between the charge/size ratio of the metal ion and the degree of covalency in the metal–oxygen bond. The infrared spectra of chelates of metal ions having charge/size ratios larger than 3.6 exhibit carbonyl absorption maxima in the 1625 to 1650 cm.$^{-1}$ region, but in complexes where the ratio is below 3.6 the maxima occur between 1590 and 1615 cm.$^{-1}$. A Th(IV) complex, in which diethylenetriaminepentaacetic acid apparently functions as an octodentate ligand, was isolated. Syntheses of binuclear Mo(V) complexes of diethylenetriaminepentaacetic acid and triethylenetetraminehexaacetic acids are reported.

Introduction

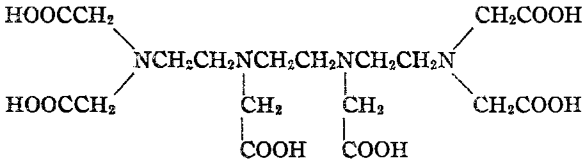
This study is concerned with some of the properties and structural characteristics of metal chelates of the polyaminocarboxylic acids shown in I–III.



(I) $\mathrm{H_4EDTA}$



(II) $\mathrm{H_5DTPA}$



(III) $\mathrm{H_6TTHA}$

Earlier studies[3-9] of the infrared spectra of metal complexes of EDTA have revealed some very interesting phenomena. It was learned that the asymmetric stretching frequency of the carbonyl group varies considerably in structure IV

---

[1] Based upon a portion of a dissertation submitted by Robert E. Sievers in August, 1960 in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

[2] This research was supported in part by the Socony-Mobil Corporation, whose assistance is gratefully acknowledged.

[3] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 4574 (1953).

[4] D. H. Busch and J. C. Bailar, Jr., *ibid.*, **78**, 716 (1956).

[5] T. Moeller, F. A. J. Moss, and R. H. Marshall, *ibid.*, **77**, 3182 (1955).

[6] M. L. Morris and D. H. Busch, *ibid.*, **78**, 5178 (1956).

[7] S. Kirschner, *ibid.*, **78**, 2372 (1956).

[8] D. T. Sawyer and P. J. Paulsen, *ibid.*, **80**, 1597 (1958).

[9] D. T. Sawyer and P. J. Paulsen, *ibid.*, **81**, 816 (1959).