The X-ray diffraction data of $H_2AlOSi(CH_3)_3$ are shown in Table I.

TABLE I
X-RAY POWDER DIFFRACTION DATA
OF DIHYDROTRIMETHYLSILOXYALUMINUM

d, Å	I/I_1	d, Å	I/I_1	d, Å	I/I_1
9.5	30	3.42	8	2.25	10
7.3	100	3.16	5	2.21	3
5.65	50	3.08	15	2.17	4
4.95	6	3.02	15	2.13	12
4.70	75	2.90	6	2.09	4
4.20	20	2.81	6	2.04	4
4.00	5	2.60	5	2.00	4
3.90	5	2.53	5	1.98	4
3.77	20	2.42	8	1.94	5
3.51	8	2.35	10	1.90	8

Discussion

A new nonsolvated aluminum dihydride, $H_2AlOSi(CH_3)_3$, has been synthesized by the reaction between etherated aluminum hydride and trimethylsilanol. Nmr and molecular weight data indicate that it is a dimer of the structure
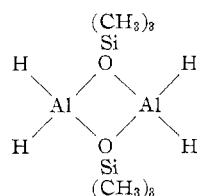
This structure is similar to those of the analagous dihalogen compounds characterized by Ercolani, *et al.*, and $(CH_3)_2AlOC(C_6H_5)_2CH_3$ prepared by Ashby, Laemmle, and Parris.[6] It is a white crystalline compound, soluble in diethyl ether and benzene. Upon standing at room temperature, a benzene solution of $H_2AlOSi(CH_3)_3$ forms a gel, accompanied by the release of a gas identified as trimethylsilane by gas–liquid chromatography and nmr. The formation of the gel may be due to the formation of Al–O–Al bonds, which occurs simultaneously with the release of $(CH_3)_3SiH$.

The neat crystalline material slowly decomposes at room temperature. When a tightly sealed bottle containing the compound was kept in a drybox for 10 days, a clear viscous liquid appeared. Upon opening the bottle the sample foamed up, leaving a dry, white solid which was soluble in ether. It is presumed that the same process was occurring as in benzene, except that in this case the $(CH_3)_3SiH$, unable to escape, remained as a liquid. On releasing the pressure it quickly volatilized, leaving a partially polymerized solid.

Dihydrotrimethylsiloxyaluminum is readily oxidized and reacts violently with water. It can be polymerized by the controlled addition of either oxygen or water, forming a clear compound with a molecular weight between 1600 and 3000. This material is film forming but hydrolyzes slowly when exposed to air.

(6) E. C. Ashby, J. Laemmle, and G. E. Parris, *J. Organometal. Chem.*, 19, 24 (1969).

Substitution Reactions of Metallic Complexes of β,β′,β″-Triaminotriethylamine. IV. Kinetics of Aquation of cis-Bromoaquo(triaminotriethylamine)cobalt(III) Ion

By WARREN V. MILLER[1] AND STANLEY K. MADAN[2]

A considerable amount of kinetic data has been reported for the acid hydrolyses of complex ions of the type $MA_4X_2{}^+$ where M is either Co(III) or Cr(III), A represents a nonreplaceable monodentate or polydentate amine, and X represents either Cl or Br. In all of the complexes of this type which have been studied, the aquation was found to occur in two separate steps

$$MA_4X_2{}^+ + H_2O \xrightarrow{k_1} MA_4H_2OX^{2+} + X^- \qquad (1)$$

$$MA_4H_2OX^{2+} + H_2O \xrightarrow{k_2} MA_4(H_2O)_2{}^{3+} + X^- \qquad (2)$$
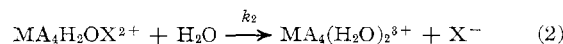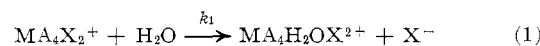
In the case of Cr(III) both aquation steps have been studied for several *cis* and *trans* complexes.[3,4] However, in the case of cobalt, while the primary aquation step for many *cis*- and *trans*-dihaloaminecobalt(III) complexes has been studied extensively, very little is known about the secondary aquation step of the corresponding haloaquo species. In fact, the only data available in the literature for the aquation of complexes of this type are the aquation constants for *cis*- and *trans*-Co(en)$_2$H$_2$OCl^{2+} at 25° in the pH range 2–3 reported by Chan.[5]

The lack of kinetic studies on such complexes may be due in part to the difficulty in obtaining accurate data because of the complicating isomerization reactions of the haloaquo species.

Since octahedral Co^{III}–tren complexes (tren = β,β′,β″-triaminotriethylamine) have been previously shown to form only the *cis* isomer,[6,7] the haloaquotriaminotriethylaminecobalt(III) complexes should be ideal systems for studying the aquation reactions of species of this type.

(1) NDEA Predoctoral Fellow, 1969–1970.
(2) Author to whom inquiries should be addressed.
(3) T. J. Williams and C. S. Garner, *Inorg. Chem.*, 9, 52 (1970), and references therein.
(4) L. P. Quin and C. S. Garner, *J. Chem. Soc.*, 1348 (1964).
(5) S. C. Chan, *ibid.*, 5137 (1963).
(6) (a) S. K. Madan and J. Peone, Jr., *Inorg. Chem.*, 6, 463 (1967); (b) S. K. Madan and J. Peone, Jr., *ibid.*, 7, 824 (1968).
(7) S. K. Madan, W. M. Reiff, and J. C. Bailar, Jr., *ibid.*, 4, 1366 (1965).

Furthermore, from two previous studies of the primary aquation of $Co(tren)Br_2^+$ [6a] and $Co(tren)Cl_2^+$ [7] it was found that the rate constant, k_1, was much larger than that for the corresponding cis-dihalobis(ethylenediamine) complexes of both Co(III) and Cr(III) despite the increased degree of chelation in the tren complexes. The increased rate of aquation of the tren species has been attributed to a distortion of the complex by the tren ligand, which results in a labilizing of the halide ligands. However, since no data are available for the second aquation step, it is not known whether the distortion affects both or only one of the halide ligands. With these facts in mind, we have now investigated the kinetics of aquation of $Co(tren)H_2OBr^{2+}$ ion under various conditions of temperature, ionic strength, and acid concentration.

Experimental Section

Synthesis of Compounds.—$[Co(tren)Br_2]Br$ was prepared as described in an earlier publication.[6a]

$[Co(tren)H_2OBr]ClO_4Br$.—Addition of 5 ml of 48% HBr to a solution of $[Co(tren)CO_3]ClO_4 \cdot H_2O$[8] in 5 ml of H_2O immediately gave a deep purple solution. After slight warming to expel all of the CO_2 gas, the addition of anhydrous $NaClO_4$ gave a bright purple precipitate when cooled to $0°$. The precipitate was filtered, washed with ethanol, and dried *in vacuo*. The yield was 79%. *Anal.* Calcd for $[Co(tren)H_2OBr]ClO_4Br$: C, 14.94; H, 4.15; N, 11.62. Found: C, 15.14; H, 4.22; N, 11.79. Recrystallization from a $NaClO_4$ solution replaced only a small amount of the bromide anion by perchlorate.

Electronic Absorption Spectra.—The visible spectra of all species were obtained with a Cary Model 14M recording spectrophotometer. The spectra were obtained with 5 mM solutions in aqueous perchloric acid using matched cells of 1-cm path length.

Kinetic Measurements. Spectrophotometric Method.—The bromoaquo species used in this study was prepared by dissolving $[Co(tren)Br_2]Br$ in water and allowing it to undergo the primary aquation step at room temperature (10 min). Since the second aquation step is very slow at $26°$, the major part of the kinetic data was obtained at $65°$. A scan of the visible spectrum of the solution at the end of the first aquation step showed that the species was identical with that of $Co(tren)H_2OBr^{2+}$ whose spectrum has been reported earlier.[6a] A series of scans of the spectrum during the second aquation step at $55°$, and pH 0, is shown in Figure 1. The scans showed two sharp isosbestic points at 438 and 513 mμ, which did not change during the course of the reaction. The final spectrum was identical with that of $Co(tren)(H_2O)_2^{3+}$ and indicated that, under our experimental conditions, no appreciable amount of bromoaquo species was present at the end of the reaction. A series of scans at pH 2.3 gave similar results. The wavelength chosen for this kinetic study was 560 mμ, where the molar absorptivity of the bromoaquo species is 153 M^{-1} cm^{-1} and that of the diaquo species is only 65 M^{-1} cm^{-1}. All kinetic measurements were made after withdrawing samples from a temperature bath controlled to within $\pm 0.05°$ by using a Cary Model 16 spectrophotometer with matched cells of 1-cm path length and 1 mM solutions. The pseudo-first-order rate constants were obtained from the slope of a plot of log $(A_\infty - A_t)$ vs. t where A_∞ is final absorbance reading and A_t is the absorbance at time t. The plots all gave straight lines for at least 3 half-lives, and consecutive runs usually agreed to within 2%.

Results and Discussion

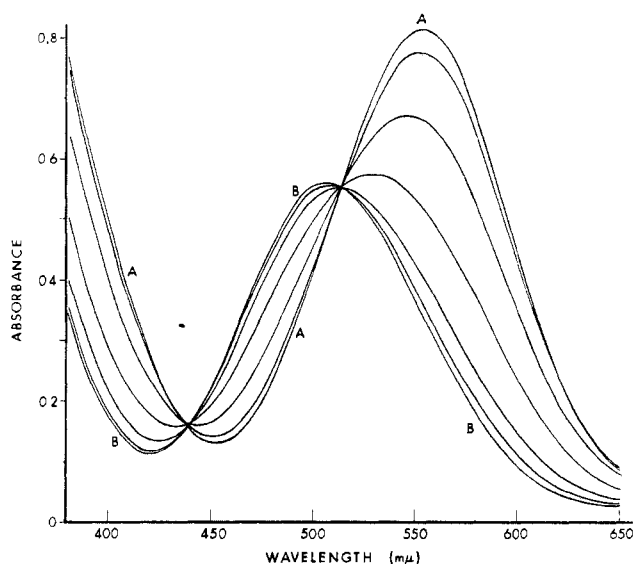The aquation rate for the secondary aquation of $[Co(tren)Br_2]Br$ was determined in 1 M $HClO_4$ at

(8) H. A. Scheidegger, Doctoral Thesis, E.T.H., Zurich, 1966.

Figure 1.—Spectral changes during the aquation of $Co(tren)$-H_2OBr^{2+}: (A) initial trace, $Co(tren)H_2OBr^{2+}$, 5.28×10^{-3} M; (B) final trace, $Co(tren)(H_2O)_2^{3+}$.

$65°$ at three different wavelengths. The values obtained for the aquation rate constant, k_2, at 560, 480, and 390 mμ were 5.04×10^{-4}, 5.06×10^{-4}, and 5.12×10^{-4} sec^{-1}, respectively. All three values were in good agreement with the value obtained by aquating $[Co(tren)H_2OBr]ClO_4Br$, which gave a value of 4.93×10^{-4} sec^{-1}.

The aquation of the bromoaquo ion was studied in 1 M $HClO_4$ under various conditions of temperature and ionic strength, and the values of k_2 which were obtained are shown in Table I. The Arrhenius plot

TABLE I
RATES OF AQUATION OF $Co(tren)H_2OBr^{2+}$ UNDER VARIOUS
CONDITIONS IN 1 M $HClO_4$

Temp, °C	Added electrolyte	Ionic strength	k_2, sec^{-1}
25.0	None	1.00	3.29×10^{-6}
35.0	None	1.00	1.44×10^{-5}
45.0	None	1.00	4.89×10^{-5}
55.0	None	1.00	1.69×10^{-4}
65.0	None	1.00	5.04×10^{-4}
65.0	1.50 M NaClO$_4$	2.50	5.03×10^{-4}
65.0	1.00 M NaClO$_4$	2.00	5.13×10^{-4}
65.0	0.50 M NaClO$_4$	1.50	5.04×10^{-4}
65.0	0.050 M NaBr	1.05	5.05×10^{-4}
65.0	0.10 M Na$_2$SO$_4$	1.30	7.11×10^{-4}
65.0	0.050 M Na$_2$SO$_4$	1.15	6.11×10^{-4}

for the data in Table I in the range of $25.0–65.0°$ was refined by using a computerized least-squares program and gave a straight line with a standard deviation of only 1.1%. The plot gave an activation enthalpy, $\Delta H^{\ddagger}$, of 24.4 kcal mol^{-1}. The values of $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ were found to be 24.9 kcal mol^{-1} and -1.7 cal mol^{-1} deg^{-1}, respectively. The activation enthalpy for the aquation of $Co(tren)H_2OBr^{2+}$ is considerably higher than that reported for the primary aquation of $Co(tren)Br_2^+$ (15.1 kcal mol^{-1}).[6a] The increased activation enthalpy is most likely a result of the higher

charge of the bromoaquo species, which makes charge separation in the transition state more difficult. The value of $\Delta H^{\ddagger}$ for the aquation of $Co(tren)H_2OBr^{2+}$ is nearly identical with that for the aquation of $Co(NH_3)_5Br^{2+}$ (24 kcal mol^{-1}) which is also a dipositive ion.[9] A comparison of $\Delta S^{\ddagger}$ for the primary and secondary aquation steps of $Co(tren)Br_2^+$ ion shows that the value for the aquation of the bromoaquo ion (-1.7 cal mol^{-1} deg^{-1}) is considerably less negative than that for aquation of the dibromo ion (-14.8 cal mol^{-1} deg^{-1}).[6a] The less negative $\Delta S^{\ddagger}$ for the secondary aquation step may be due to an increase in SN1 character in the second aquation step relative to the first; however, solvation effects may also be responsible.

The data in Table I show that in highly acidic solution the aquation rate of $Co(tren)H_2OBr^{2+}$ ion is ionic strength independent when an "inert" electrolyte such as $NaClO_4$ is present. This behavior is similar to that of the primary aquation of the dibromo species and is expected, since water, one of the reactants, has no charge. The addition of an excess of bromide ions also did not affect the rate. This further substantiates the spectral scans, which showed that any equilibrium present between $Co(tren)H_2OBr^{2+}$ and $Co(tren)(H_2O)_2^{3+}$ lies far toward the latter species. However, the addition of Na_2SO_4 was found to accelerate the aquation rate, presumably through an ion-pair mechanism, as in the case of the aquation of the dibromo ion.

A study of the aquation of $Co(tren)H_2OBr^{2+}$ was also performed at higher pH values, and the rate of aquation was found to be inversely proportional to the hydrogen ion concentration. The data for the aquation of 1 mM $Co(tren)H_2OBr^{2+}$ at 65° are summarized in Table II.

TABLE II
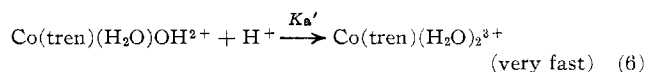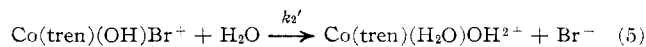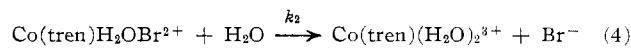RATES OF AQUATION OF $Co(tren)H_2OBr^{2+}$ BETWEEN pH 1.0 AND pH 3.0 WITH ADDED $NaClO_4$ AT 65°

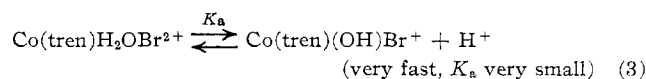| [H$^+$], mM	Ionic strength[a]	$10^4 k_{obsd}$, sec^{-1}	[H$^+$], mM	Ionic strength[a]	$10^4 k_{obsd}$, sec^{-1}
5.00	0.025	8.75	4.00	1.00	7.99
6.00	0.025	7.94	5.00	1.00	7.39
7.50	0.025	7.55	6.07	1.00	7.13
10.0	0.025	6.81	10.0	1.00	6.39
15.0	0.025	6.10	15.0	1.00	6.03
17.5	0.025	6.00	40.0	1.00	5.45
100.0	0.100	5.10			

[a] $NaClO_4$ was used as the inert electrolyte.

From the data in Table II it is clear that the aquation of $Co(tren)H_2OBr^{2+}$ is acid inhibited. Similar behavior has been observed in the aquation kinetics of *cis*- and *trans*-$Co(en)H_2OCl^{2+}$,[5] $Cr(en)NH_3(H_2O)_2Br^{2+}$,[10] $Cr(en)(H_2O)_3Br^{2+}$,[11] and $CrNH_3(H_2O)_4Cl^{2+}$.[3]

The acid inhibition in these aquo complexes has been attributed to an equilibrium between the haloaquo complex and the much faster aquating halohydroxo

complex. In the case of $Co(tren)H_2OBr^{2+}$, this equilibrium would lead to the reaction scheme

$$Co(tren)H_2OBr^{2+} \underset{}{\overset{K_a}{\rightleftharpoons}} Co(tren)(OH)Br^+ + H^+ \quad (3)$$
(very fast, K_a very small)

$$Co(tren)H_2OBr^{2+} + H_2O \xrightarrow{k_2} Co(tren)(H_2O)_2^{3+} + Br^- \quad (4)$$

$$Co(tren)(OH)Br^+ + H_2O \xrightarrow{k_2'} Co(tren)(H_2O)OH^{2+} + Br^- \quad (5)$$

$$Co(tren)(H_2O)OH^{2+} + H^+ \xrightarrow{K_a'} Co(tren)(H_2O)_2^{3+} \quad (6)$$
(very fast)

The observed rate of aquation is then simply a combination of the rates for reactions 4 and 5, and the observed rate constant for the overall reaction, k_{obsd}, is given by

$$k_{obsd} = k_2 + k_2'K_a/[H^+] \quad (7)$$

A plot of k_{obsd} *vs.* $1/[H^+]$ would then give a straight line with a slope equal to the product of $k_2'K_a$ and an intercept equal to k_2. At $\mu = 1.0$ a plot of k_{obsd} *vs.* $1/[H^+]$ for the data in Table II gave a straight line. From the slope and intercept was obtained

$$k_{obsd} = 5.2 \times 10^{-4} \text{ sec}^{-1} + 1.1 \times 10^{-6} \text{ sec}^{-1}/[H^+] \quad (8)$$

At ionic strength 0.025 the expression was found to be

$$k_{obsd} = 4.9 \times 10^{-4} \text{ sec}^{-1} + 1.9 \times 10^{-6} \text{ sec}^{-}/[H^+] \quad (9)$$

The values of k_2 obtained from eq 8 and 9 are very close to the experimental value of 5.04×10^{-4} sec^{-1}, which was obtained in 1 M $HClO_4$, and show that the value of k_2 is not ionic strength dependent. However, it is clear from the second terms in eq 8 and 9 that the $k_2'K_a$ product does show a dependence on the ionic strength of the solution. The decrease in the $k_2'K_a$ product with increasing ionic strength is most likely due to changes in the activity coefficients of the three species present, since as the ionic strength increases, K_a decreases. A similar but opposite effect has been observed in the acid-catalyzed aquation studies of $Cr(H_2O)_5OAc^{2+}$,[12] *cis*-$Cr(H_2O)_4(CN)_2^+$,[13] and $Cr(H_2O)_5CN^{2+}$,[14] in which the K_a term appears in the denominator rather than the numerator of the rate expression.

In order to substantiate further the fact that the acid inhibition is due to an acid dissociation of the bromoaquo species, the second aquation step of $Co(tren)Br_2^+$ was measured at pH 0 and 2.0 in deuterium oxide and compared with that in water under identical conditions.

At pH 0, where k_{obsd} is equal to k_2, the observed rate constant in D_2O is 3.49×10^{-4} sec^{-1} at 65° and is 31% less than the corresponding value in H_2O. Decreases of nearly the same order of magnitude have previously been reported by Adamson and Basolo when H_2O is replaced by D_2O in the aquation of $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$.[9] The slower rate in D_2O

(9) A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955).
(10) T. J. Williams and C. S. Garner, *Inorg. Chem.*, **8**, 1639 (1969).
(11) R. G. Hughes and C. S. Garner, *ibid.*, **7**, 1988 (1968).

(12) E. Deutsch and H. Taube, *ibid.*, **7**, 1532 (1968).
(13) D. K. Wakefield and W. B. Schaap, *ibid.*, **8**, 811 (1969).
(14) D. K. Wakefield and W. B. Schaap, *ibid.*, **8**, 513 (1969).

has been attributed to a smaller degree of solvent-aided dissociation of the halide group in the transition state. In H_2O at 65° and at pH 2, the value of k_{obsd} is 27% higher than at pH 0 because of the acid dissociation of the bromoaquo species. In D_2O, however, the increase in k_{obsd} in going from pH 0 to pH 2 is is only 17%. This observation is consistent with an acid–base equilibrium in which the acidic species aquates slower, since it has been established previously that weak acids are less dissociated in D_2O than in H_2O.[15]

The opposite effect has been observed in the acid-catalyzed aquation of *trans*-Co(en)$_2$F$_2^+$ since, in this case, the protonated species reacts faster.[16]

A final point of interest in this study is a comparison of the primary and secondary aquation constants for Co(tren)Br$_2^+$ with those of similar complexes. As stated previously, the value of k_1 for the aquation of Co(tren)Br$_2^+$ is 27 times larger than that for *cis*-Co(en)$_2$Br$_2^+$ at 25° and is 10 times larger than that of *cis*-Cr(en)$_2$Br$_2^+$.[4] This increased aquation rate in the tren complex has been attributed to a distortion of the complex by the tren ligand, which causes both a strain in the complex and an increased exposure of the bromide ligands to the solvent.[6a] The effect of this distortion would then be to labilize the bromide groups in either an S_N1 or an S_N2 mechanism. A similar comparison of the second aquation steps of these complexes, however, shows that the value of k_2 for the aquation of the tren complex at 25° is almost $^1/_{58}$th as fast as that for *cis*-Cr(en)$_2$H$_2$OBr^{2+}.[4] Furthermore, although no data are available for the aquation of *cis*-Co(en)$_2$H$_2$OBr^{2+}, a comparison of the value of k_2 for the aquation of *cis*-Co(en)$_2$H$_2$OCl^{2+}[5] with that of Co(tren)H$_2$OBr^{2+} at 25° shows that the tren complex aquates only twice as fast, while Co(tren)Br$_2^+$ aquates over 100 times faster than *cis*-Co(en)$_2$Cl$_2^+$ at the same temperature.

The marked decrease in labilization of the second bromide ion relative to that of the first can only be explained by a reduction in the distortion of the complex after the loss of the first bromide ion. This is not unreasonable, since the replacement of a bulky *cis* bromide group by water, combined with the increased positive charge of the complex, would allow the second bromide group to be pulled in closer to the cobalt and hence decrease its vulnerability to solvent attack by an S_N2 mechanism. The increase in $\Delta S^{\pm}$ of the second aquation step relative to that of the first is consistent with a decrease in S_N2 character for the aquation of the bromoaquo species, although the mechanism is undoubtedly of mixed S_N1 and S_N2 character.

(15) V. K. LaMer, *Chem. Rev.,* **19,** 363 (1936).

(16) F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Amer. Chem. Soc.,* **78,** 4883 (1956).

Electron Paramagnetic Resonance Identification of a Nickel(III) Compound Produced by Electrochemical Oxidation of Nickel(II) Tetraphenylporphyrin

By Alexander Wolberg and Joost Manassen[1]

In complexes with certain large organic chelating ligands it is difficult to assign the true valency state of the metal ion.[2] Therefore, there has been a controversy over the identification of Ni(III) and NI(IV) species in solution.[3–7] The critics[6,8] of the Ni(III) assignment base their arguments on the expected difference between a free-radical type and a 3d^7 type epr signal. Magnetic susceptibility is not sensitive enough to distinguish between the two. More recently additional claims of Ni(III) species in solution were made;[9–11] however, attempts to observe the epr signal either failed[9] or were not reported.[10,11] During our studies of the physical properties in solution of the iron through zinc tetraphenylporphyrins[12] we have found evidence for the existence of a nickel(III) tetraphenylporphyrin cation.

Experimental Section

Nickel tetraphenylporphyrin, Ni^{II}TPP, was synthesized according to ref 13. A 10^{-3} M solution of Ni^{II}TPP in 0.1 M (C$_4$H$_9$)$_4$NClO$_4$-benzonitrile was prepared. The solvent was purified by passing it over a column of alumina adsorbent just prior to its use, to ensure anhydrous conditions.

The electrochemical oxidation was studied by cyclic voltammetry and controlled-potential coulometry, using a Wenking 66TS10 potentiostat in conjunction with a Hewlett-Packard 3300A function generator, using a saturated aqueous calomel electrode as reference. Oxidation products obtained by controlled-potential electrolysis were transferred into a flat cell or sealed quartz ampoule and were studied on an X-band Varian Associates 4502 epr spectrometer, equipped with a Hewlett-Packard X530A frequency meter and using peroxylaminedisulfonate ion as a standard. Optical spectra were measured on a Coleman Hitachi 124 double-beam spectrometer.

Results

Figure 1 displays a cyclic voltammogram taken at

(1) On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel, 1968–1969.

(2) G. N. Schrauzer, *Accounts Chem. Res.,* **2,** 72 (1969).

(3) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Amer. Chem. Soc.,* **85,** 2029 (1963).

(4) J. C. Goan, E. Berg, and M. E. Podall, *J. Org. Chem.,* **29,** 975 (1964).

(5) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.,* **86,** 4580 (1964).

(6) E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *ibid.,* **87,** 3016 (1965).

(7) A. H. Maki, T. E. Berry, A. Davison, R. H. Holm, and A. L. Balch, *ibid.,* **88,** 1080 (1966).

(8) P. Kreisman, R. Marsh, J. R. Preer, and H. B. Gray, *ibid.,* **90,** 1067 (1968).

(9) D. W. Meek, E. C. Alyea, J. K. Stalick, and J. Ibers, *ibid.,* **91,** 4920 (1969).

(10) R. J. Wilson, L. F. Warren, Jr., and M. F. Hawthorne, *ibid.,* **91,** 758 (1969).

(11) D. C. Olson and J. Vasilevskis, *Inorg. Chem.,* **8,** 1611 (1969).

(12) A. Wolberg and J. Manassen, *J. Amer. Chem. Soc.,* **92,** 2982 (1970).

(13) J. T. Horeczy, B. N. Hill, A. E. Walters, H. G. Schutze, and W. H. Bonner, *Anal. Chem.,* **27,** 1899 (1955).