

blue deposit. On warming this to room temperature excess silicon tetrafluoride was pumped away and a number of other volatile liquid fractions were obtained, together with a residue of a white spontaneously inflammable polymer. Mass spectrometric investigation of the liquid fractions showed that extensive exchange of fluorine and chlorine between the silicon and boron had occurred. No ion containing boron was observed except BF_2^+ . However the predominance at low electron voltages of ions of the type $\text{Si}_n\text{F}_{2n-z}\text{Cl}_z^+$ suggests that compounds of the type $\text{Si}_n\text{F}_{2n+1-z}\text{Cl}_z\text{BF}_{2-x}\text{Cl}_x$ (where $x = 2$ to 0 and z was observed to be 3 to 0) were present in

the mixture, as both Si_2BF_7 and Si_3BF_9 readily give Si_2F_4^+ and Si_3F_6^+ , respectively, on electron impact.

Acknowledgments. We gratefully acknowledge the support of this work at Rice University by the Advanced Research Projects Agency, under a contract administered by the Army Research Office at Durham. We thank Dr. S. Slaymaker of the Shell Refinery, Houston, Texas, for helping initiate the n.m.r. studies of the compounds, Dr. K. Sathianandan for helpful comments on the infrared spectra, and Mr. Dechard Stump for assistance in preparing and purifying many of the samples studied.

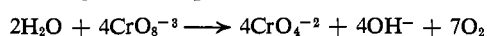
Kinetics of the Decomposition of Tetraperoxychromate(V) Ion in Basic Solution

Denis Quane and Joseph E. Earley

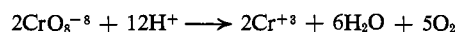
Contribution from the Department of Chemistry, Georgetown University, Washington, D. C. Received April 15, 1965

The rate of decomposition of tetraperoxychromate ion in basic 3 M NaClO₄ follows the rate law $R = k_1[H^+][\text{CrO}_8^{3-}]_{\text{total}}/[H^+] + k''$, where $k_1 = 1.04 \text{ min.}^{-1}$ and $k'' = 6.9 \times 10^{-8} \text{ M}$ at 30°; at 40° $k_1 = 1.4 \text{ min.}^{-1}$, $k'' = 4.0 \times 10^{-8} \text{ M}$; at 50° $k_1 = 1.9 \text{ min.}^{-1}$, $k'' = 2.5 \times 10^{-8} \text{ M}$. The presence of NH_4^+ , CO_3^{2-} , EDTA, O_2 , or H_2O_2 causes little or no change in the rate. A mechanism involving unimolecular decomposition of a protonated peroxychromate(V) ion is proposed.

Hydrogen peroxide reacts with chromates in basic solution to give brown crystals of tetraperoxides, M_3CrO_8 . These compounds decompose in basic solution according to the equation¹



The structure of the tetraperoxychromate(V) ion has been well established and the presence of chromium in the +5 oxidation state confirmed.² The kinetics of the decomposition is not as well known. Bogdanov³ has studied the kinetics of this reaction by following the rate of oxygen evolution. In basic solution the rate is first order in $[\text{CrO}_8^{3-}]$. The reaction in acid solution is said to be more complex, there being two modes of decomposition: by means of the equation above, and also by the equation



The mechanism of the first-order decomposition in basic solution has not been established. The reaction lends itself readily to study spectrophotometrically and titrimetrically (using a pH-Stat); these methods should yield results of greater accuracy than can be obtained from oxygen evolution.

(1) E. H. Riesenfeld, H. E. Wohlers, and W. A. Kutsch, *Ber. deut. chem. Ges.*, **38**, 1885 (1905).

(2) J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, **6**, 301 (1964).

(3) G. A. Bogdanov, *Zh. Fiz. Khim.*, **25**, 61 (1951); *Chem. Abstr.*, **45**, 6028f (1951); *Tech. Trans.*, **11**, 1176 (1964), OTS 63-23208.

Experimental

Potassium peroxychromate(V) was prepared by the reaction of hydrogen peroxide with chromium trioxide⁴ in the presence of KOH. Samples were analyzed for potassium by ion exchange and for chromate spectrophotometrically at 370 μ after decomposition. *Anal.* Calcd. for K_3CrO_8 : K, 39.46; Cr, 17.49. Found: K, 38.49; Cr, 17.82. All other reagents were prepared and purified by standard methods.

Reactions were followed on a Sargent pH-Stat, a Cary Model 14 spectrophotometer at 370 μ , and a Warburg apparatus. On the pH-Stat, solid K_3CrO_8 was dissolved in water having a concentration of NaClO_4 calculated to bring the total, nominal ionic strength to 3 M and sufficient NaOH to give the desired pH. The rate of decomposition of the sample was followed from the point at which dissolution was complete. For reactions followed on the Cary spectrophotometer and the Warburg apparatus, aliquots of a stock solution of K_3CrO_8 in 0.1 M NaOH were mixed with solutions containing sufficient NaClO_4 and buffer to make the final solutions 0.1 M in buffer with 3 M total, nominal ionic strength. pH measurements of reactions followed using the pH-Stat were made on the instrument itself. The pH of all other solutions was measured using a Beckman Model G pH meter. Reaction mixtures were thermostated to $\pm 0.1^\circ$.

First-order rate constants were calculated using an IBM 1620 computer, programed to find the values of D_∞ and k giving the best straight-line fit to the equation

$$\ln(D_\infty - D) = \ln(D_\infty - D_0) + kt$$

by least-squares analysis where D represents volume of acid added to maintain pH for reactions followed on the pH-Stat. When points taken over two half-times were used, values of D_∞ so computed agreed well with

(4) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Vol. 2, Georg Thieme Verlag, Stuttgart, 1962, p. 1216.

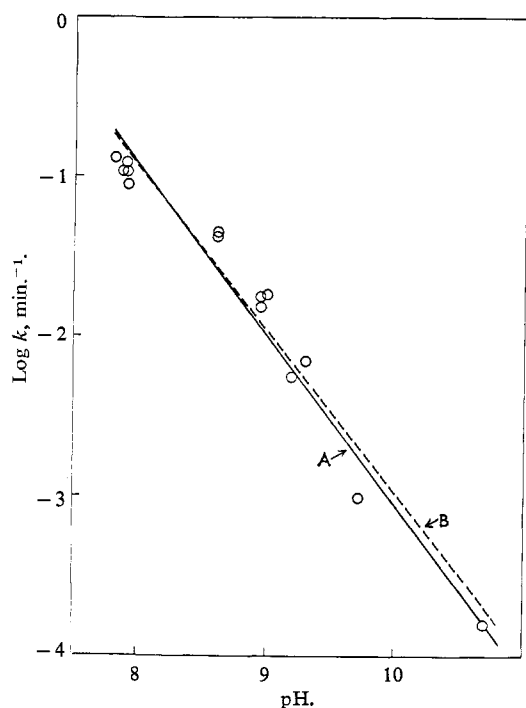


Figure 1. Decomposition of peroxychromate(V) ion in solutions with carbonate buffers at 30.0°. Effect of pH on rate (all solutions 0.1 *M* in carbonate, 3.0 *M* total nominal ionic strength): A, least-squares fit; B, $k = k'[\text{H}^+]$, $k' = 1.1 \times 10^8$.

measured D_∞ values. This procedure allows more efficient use of the pH-Stat and results in a considerable time saving.

Results

Reactions followed on the pH-Stat show that one (within 5%) hydrogen ion is added for each peroxychromate ion decomposed. Runs on the Warburg apparatus gave 1.75 moles (within 10%) of oxygen evolved per mole of peroxychromate. This confirms the stoichiometry of the basic decomposition established by earlier workers.^{1,3} All reactions go to completion under the conditions studied. Rates of reactions in unbuffered solutions were followed on the pH-Stat. These reactions show first-order kinetics for at least five half-times. The pH dependence was studied over the range 8.5–9.9. An approximate rate law is $k = k'[\text{H}^+]$ where $k' = 1.25 \times 10^8$ (Table I). A least-

Table I. Rate of Decomposition of Peroxychromate(V) Ion at 30.0° in 3 *M* NaClO₄

pH	$[\text{CrO}_8^{3-}]_{\text{total}}$, <i>M</i> × 10 ³	<i>k</i> , min. ⁻¹	$k' \times 10^{-8}$, ^a <i>M</i> ⁻¹ min. ⁻¹
8.49	2.61	0.332	1.03
8.50 ^b	1.06	0.346	1.07
8.70	2.56	0.187	0.94
8.70 ^b	1.10	0.229	1.14
8.90	2.31	0.179	1.42
8.90 ^b	1.32	0.174	1.38
9.10	2.29	0.1165	1.47
9.30	1.42	0.0780	1.56
9.50	2.08	0.0410	1.30
9.70	2.65	0.0237	1.19
9.90	2.39	0.0278	2.21 ^c
			Average 1.25

^a $k' = k/[\text{H}^+]$. ^b Nitrogen atmosphere. ^c Omitted from average.

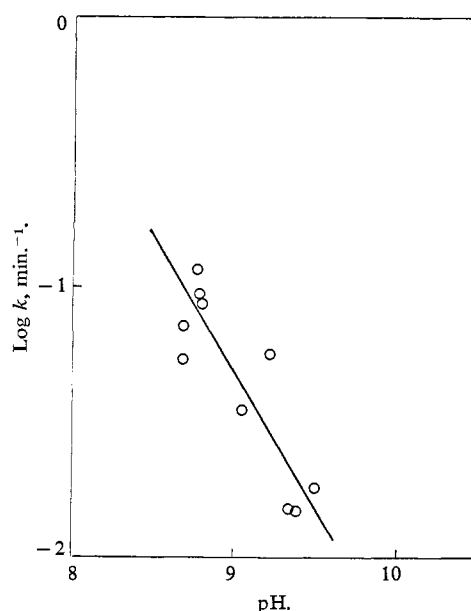


Figure 2. Decomposition of peroxychromate(V) ion at 30.0° in solutions with aqueous ammonia buffers. Effect of pH on rate (all solutions 0.1 *M* in aqueous ammonia, 3.0 *M* in total nominal ionic strength): line represents $k = k'[\text{H}^+]$, $k' = 5.0 \times 10^7$.

squares fit of pH vs. log rate gives a line whose slope deviates slightly from unity. The trend in the values of k' as the pH is increased suggests that a more complex rate law may be required (see below). No difference in rate was observed when reactions were run under nitrogen atmosphere to exclude O₂.

Three basic reagents were tested for their effect on the rate of decomposition. Experiments involving added aqueous NH₃ and carbonate ions were followed spectrophotometrically at 370 mμ. At this wave length the appearance of the chromate ion is followed. These reactions also show first-order kinetics. No evidence of absorbing species other than CrO₈³⁻ and CrO₄²⁻ was encountered at any wave length. The pH dependence of the rate of decomposition in solutions buffered with ammonium perchlorate or with sodium carbonate is similar to that found for unbuffered solutions (Figures 1 and 2). No increase in the rate of decomposition results from the presence of either reagent. The rate is slightly slower ($k' = 1.1 \times 10^8$) in the solutions with added carbonate than in solutions with no added base and even slower ($k' = 5.0 \times 10^7$) for solutions with added ammonia. The difference is not large in view of the fact that the added species are in large excess and could be due to medium effects. The rate of decomposition of solutions with added chloride ion was followed on the pH-Stat. No significant change in rate is evident. No appreciable change in rate was noted on the addition of excess chromate ion. The results of these experiments are included in Table II.

The rate of decomposition of unbuffered solutions to which hydrogen peroxide was added was followed on the pH-Stat. Figure 3 shows the rates as a function of hydrogen peroxide concentration. There is a change in the rate at the point where the concentration of the added peroxide is equal to the concentration of the peroxychromate. At higher concentrations the rate is slower but does not change with increasing peroxide

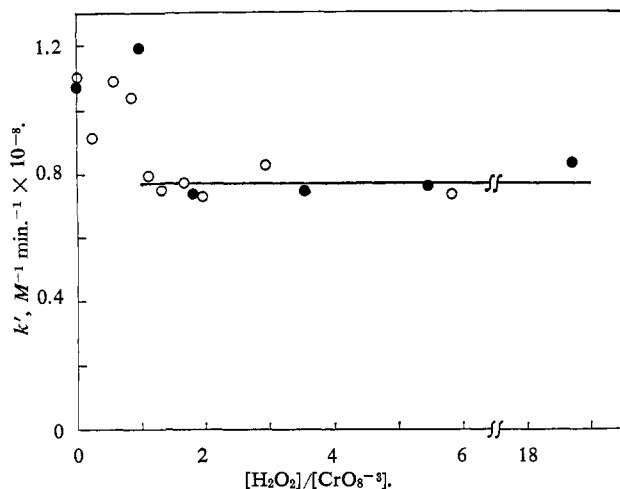


Figure 3. Decomposition of peroxychromate(V) ion in solutions with added hydrogen peroxide. Rate (k') as a function of mole ratio $\text{H}_2\text{O}_2/\text{CrO}_8^{3-}$ (all solutions 3.0 M in NaClO_4): ●, pH 8.50; ○, pH 8.67.

concentration. The stoichiometry of the reaction is unchanged.

Peroxide decomposition catalyzed by trace metal ions is inhibited by the addition of EDTA, which complexes such metal ions, inhibiting their catalytic effect.⁵ Experiments in which 10^{-3} M EDTA was added (Table II) resulted in no change in the rate of peroxychromate decomposition.

Table II. Rate of Decomposition of Peroxychromate(V) Ion at 30.0° in Unbuffered Solutions with Added Reagents^a

pH	$[\text{CrO}_8^{3-}]_{\text{total}}$, $M \times 10^3$	Added reagent	k , min^{-1}	$k',^b M^{-1}$ $\text{min}^{-1} \times 10^8$
8.50	1.09	0.1 M NaCl	0.387	1.23
8.70	1.17	0.1 M NaCl	0.307	1.54
8.50	0.869	2.03×10^{-3} M Na_2CrO_4	0.350	1.11
8.90	1.14	2.63×10^{-3} M Na_2CrO_4	0.134	1.07
8.86	1.67	0.966×10^{-3} M EDTA	0.172	1.25

^a Total ionic strength 3.0 M. ^b $k' = k/[\text{H}^+]$.

Rates of reactions in unbuffered solutions at 40.0 and 50.0° followed on the pH-Stat are shown in Table III. The trend in the value of k' with increasing pH at 50° indicates that a more complex rate law is required.

Table III. Rate of Decomposition of Peroxychromate(V) Ion at 40.0 and 50.0° in 3 M NaClO_4

Temp., °C.	pH	k , min^{-1}	$k' \times 10^{-8}$, $\text{min}^{-1} M^{-1}$ ^a
40	8.90	0.343	2.76
	9.10	0.213	2.68
	9.30	0.148	2.95
50	9.10	0.456	5.74
	9.30	0.343	6.85
	9.70	0.143	7.17
	9.90	0.100	7.94

^a $k' = k/[\text{H}^+]$.

(5) E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun, and J. O. Edwards, *J. Am. Chem. Soc.*, **85**, 2263 (1963).

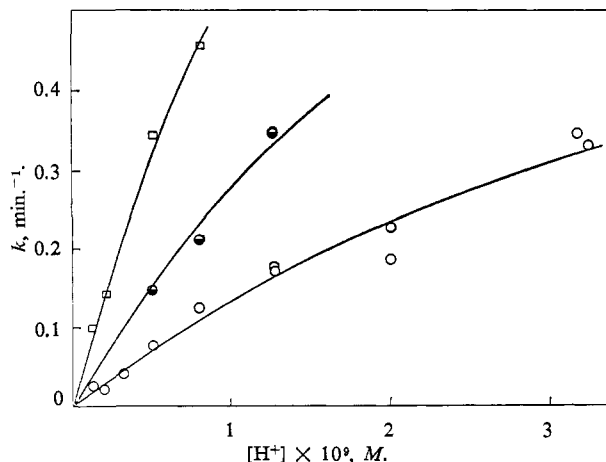


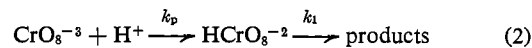
Figure 4. Rate of decomposition of tetraperoxychromate(V) ion. Experimental data fitted to $k = k_1[\text{H}^+]/[\text{H}^+] + K_a$, where $k_1 = 1.04 \text{ min}^{-1}$, $K_a = 6.9 \times 10^{-8} M$, $\Delta H_a = -10 \text{ kcal./mole}$, and $\Delta H_1^* = 5.7 \text{ kcal./mole}$: ○, 30.0°; ●, 40.0°; □, 50.0°.

A rate law with an acid-independent term was considered. In order to account for the data, this term should give a half-time of about 30 min. at 30.0°. It would be expected that this would be the limiting half-time in basic solution. Stock solutions of K_2CrO_8 in 0.1 M NaOH were kept for periods of several weeks with only partial decomposition (about 50%).

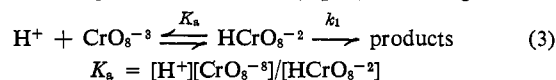
Another possible rate law (eq. 1) accounts for the

$$k = \frac{k_1[\text{H}^+]}{[\text{H}^+] + k''} \quad (1)$$

variation of rate with $[\text{H}^+]$ between pH 8 and 10 at all temperatures and also agrees with the stability of CrO_8^{3-} in more concentrated base. A rate law of this form would be obtained from either of two mechanisms. A rate-determining protonation of CrO_8^{3-} followed by decomposition of the conjugate acid (eq. 2) would give



rise to this rate law if $k_p = k_1/k''$. Formation of HCrO_8^{3-} in a rapid prior equilibrium with subsequent rate-determining decomposition (eq. 3) would give rise



to this rate law where k'' was equal to K_a , the acidity constant of HCrO_8^{2-} .

The data at 30° were fitted to eq. 1 using a nonlinear least-squares program and the IBM 1620.⁶ From this, $k'' = 6.9 \times 10^{-9} M$ and $k_1 = 1.04 \text{ min}^{-1}$. Using these values and trial values ranging from -12 to +10 kcal./mole for the ΔH associated with each parameter, curves were constructed to fit the data at 40 and 50°. The best fit was obtained with $\Delta H_1 = 5.7 \text{ kcal./mole}$ ($\Delta S_1 = -48 \text{ kcal./mole}$) and an enthalpy of -10 kcal./mole for the k'' term. Curves generated using these parameters are shown in Figure 4.

Discussion

The lack of effect of EDTA indicates that trace metal catalysis is not an important factor in this reaction. That the rate of decomposition is not increased by basic reagents shows that the system is not markedly

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sensitive to nucleophilic attack. The small effect of H_2O_2 appears to indicate that peroxide equilibria are not dominant but does not rule out such reactions completely. Since exclusion of O_2 does not affect the rate, it may be inferred that free radicals are not important in or prior to the rate-determining step.

The structure of CrO_8^{3-} in the solid states consists of four O_2^{2-} groups located tetrahedrally about the Cr(V) ion. One oxygen of each peroxide is 1.85 Å. from the Cr(V), the other 1.94 Å. Formation of $HCrO_8^{2-}$ might be expected to involve a considerable distortion of this structure. For this reason it does not seem possible to rule out a slow protonation step in this reaction. The alternative rapid protonation and rate-determining decomposition is also in accord with the data. The value 6.9×10^{-9} is not unreasonable for the acidity constant of $HCrO_8^{2-}$, which would be expected to be more acidic than HPO_4^{2-} ($K_a \approx 10^{-12}$). However, negative enthalpy is not usual for simple acid dissociation.

Whether or not protonation of CrO_8^{3-} is rapid, the rate constant k_1 corresponds to decomposition of $HCrO_8^{2-}$.

Several studies of the decomposition of peroxides have obtained evidence that decomposition results from the nucleophilic attack of a peroxy anion on a protonated peroxy molecule. Mechanisms of this type have been proposed for the decomposition of Caro's acid (H_2SO_5)^{7,8} and several organic and inorganic peroxy acids.^{5,9} In these cases the kinetics are second order. In the case of the peroxychromate(V) ion, first-order kinetics would result if interaction occurs between two peroxide groups on the same ion. The mechanism of decomposition of $HCrO_8^{2-}$ is likely to involve interaction of adjacent protonated and unprotonated peroxide groups.

Acknowledgment. This work was supported by the U. S. Atomic Energy Commission under contract AT-40-1-2842. We are grateful to Professors J. O. Edwards, G. Gordon, and E. Koubek for helpful discussion.

(7) E. Koubek, G. Levey, and J. O. Edwards, *Inorg. Chem.*, **3**, 1331 (1964).

(8) D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1125 (1956).

(9) J. F. Goodman, P. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962).

The Reduction of Various *cis*- and *trans*-Chlorobis-(ethylenediamine)cobalt(III) Complexes by Iron(II)¹

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Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania. 16802. Received April 10, 1965

*The kinetics of reductions of *cis*- and *trans*-substituted $Co(en)_2XCl^{+n}$ by $Fe(II)$ have been studied at 25° and $\Sigma[ClO_4^-] = 1.0 M$. For the *trans* complexes, the second-order rate constants corresponding to the rate law $k[Co(III)][Fe(II)]$ are $2.4 \pm 0.2 \times 10^{-1}$, $3.6 \pm 0.3 \times 10^{-2}$, $3.2 \pm 0.4 \times 10^{-2}$, 1.3×10^{-4} , $6.6 \pm 0.3 \times 10^{-5}$, and $6.2 \pm 0.4 \times 10^{-2} M^{-1} sec^{-1}$ for $X = H_2O$, Br^- , Cl^- , SCN^- , NH_3 , and N_3^- , respectively. For the *cis* isomers the second-order rate constants are $1.6 \pm 0.4 \times 10^{-3}$, $4.6 \pm 0.3 \times 10^{-4}$, 1.7×10^{-4} , and $1.8 \pm 0.1 \times 10^{-5} M^{-1} sec^{-1}$ for $X = Cl^-$, H_2O , SCN^- , and NH_3 , respectively. It is suggested that, except for *trans*- $Co(en)_2N_3Cl^+$, the reactions proceed by an activated complex that makes use of a Cl^- bridge, and the observed nonbridging ligand effects are discussed on the basis of a model which involves stretching of the bridge and of the group *trans* to it away from the $Co(III)$ center and the transfer of an electron from Fe^{+2} to the d_{z^2} orbital of cobalt.*

Introduction

Kinetic and stoichiometric studies of the reduction of cobalt(III) ammine complexes have yielded important information regarding the mechanism of "electron-transfer" reactions.² Most of the work in this area

has dealt with complexes of the pentaammine class, the emphasis being placed on the dependence of reaction rates upon the nature of the sixth ligand. Taube^{2a,3,4} has called attention repeatedly to the fact that, for inner-sphere mechanisms involving a single bridging ligand, there are ten coordinating positions in addition to the bridge, and that variations in the nature of the groups in these positions give rise to nonbridging ligand effects. With regard to cobalt(III) complexes, such effects have been recently documented. Fraser has studied the effect of chelation by nonbridging ligands on the reductions of aquo-, sulfato-, acetato-, and chlorocobalt(III) complexes by chromium(II) or vanadium(II).^{5,6} Kopple and Miller have examined the kinetics of reduction of carboxylatotetraamminecobalt(III) complexes by chromium(II).^{7,8} Schendel has examined the effect of successive substitution of ammonia in $Co(NH_3)_5Cl^{+2}$ by one or two water ligands on the rate of reaction with iron(II).⁹ We have demonstrated previously that the rates of

(2) (a) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959); (b) J. Halpern, *Quart. Rev. (London)*, **15**, 207 (1961); (c) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).

(3) H. Taube, *Can. J. Chem.*, **37**, 129 (1959).

(4) H. Taube, *Brookhaven Symp. Biol.*, **15**, 1 (1962).

(5) R. T. M. Fraser, *Proc. Chem. Soc.*, 262 (1963).

(6) R. T. M. Fraser, *Inorg. Chem.*, **2**, 954 (1963).

(7) K. D. Kopple and R. R. Miller, *Proc. Chem. Soc.*, 306 (1962).

(8) K. D. Kopple and R. R. Miller, *Inorg. Chem.*, **2**, 1204 (1963).

(9) D. Schendel, M.S. Thesis, The Pennsylvania State University, Sept. 1964.

(1) This work was supported by Grant GP-2001 from the National Science Foundation.