species upon titration of the HEDTA complex with base may be evidence for having two coordinated water molecules on the complex.

Of the three complexes studied the $Mn^{III}CyDTA^-$ potassium salt was by far the most stable in the solid state. This fact is probably due to kinetic factors as is shown by the decomposition rates of the compounds in solution. The potassium salt of $Mn^{III}CyDTA^-$ was so stable that a sample of it was kept at room temperature for several months in the dark with no experimentally observable change in its assay as an oxidizing agent.

Because of the very slow rate of decomposition of the $Mn^{III}CyDTA^-$ complex it can be used as a moderately strong one-electron oxidizing agent for studies of the kinetics of oxidation of various species. It can be used over a very wide range of pH for oxidation–reduction studies.[9] Almost all previous studies of oxidation of compounds by means of manganese(III) complexes have been in very acid solution because of the instability of the complexes (sulfate and pyrophosphate) as the pH increases.[10]

The ratio of the formation constants of the Mn(III) complex to those of the Mn(II) complex remains quite constant for the three complexes investigated. One might expect this constant ratio for CyDTA and EDTA, as they are very similar ligands. The HEDTA ligand is not greatly different.

Acknowledgment.—The authors wish to express their thanks to the Research Committee of Washington State University and to the National Science Foundation for the funds which made this investigation possible.

[9] M. A. Suwyn and R. E. Hamm, *Inorg. Chem.*, **6**, 142 (1967).

[10] W. A. Waters and J. S. Littler, "Oxidations in Organic Chemistry," K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, part A, pp 213, 214.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Mechanism of Oxidation of Oxalate with *trans*-1,2-Diaminocyclohexanetetraacetatomanganate(III) in Aqueous Solution

BY MARK A. SUWYN AND RANDALL E. HAMM

Received June 15, 1966

The oxidation of oxalate with the 1,2-diaminocyclohexanetetraacetatomanganate(III) ion can be fitted by the rate equation $d[Mn^{III}CyDTA^-]/dt = -2k_1[Mn^{III}CyDTA^-][HC_2O_4^-] - 2k_2[Mn^{III}CyDTA][C_2O_4^{2-}]$, over the pH range 3.0–7.0. At 20° the specific rate constants were determined to be $k_1 = 5.4 \times 10^{-3}$ sec^{-1} M^{-1} and $k_2 = 7.08 \times 10^{-3}$ sec^{-1} M^{-1}. Experiments over a range of temperatures from 15 to 35° gave $\Delta H_1^{\ddagger} = 20.9$ kcal mole^{-1}, $\Delta S_1^{\ddagger} = 3.5$ cal deg^{-1} mole^{-1}, $\Delta H_2^{\ddagger} = 16.0$ kcal mole^{-1}, and $\Delta S_2^{\ddagger} = -13.0$ cal deg^{-1} mole^{-1}.

The oxidation of various compounds with permanganate ion in acid solution has been considered to involve the rapid formation of manganese(III) complexes which then decompose unimolecularly to the manganese(II) ion and oxidation products. The reaction of permanganate ion with oxalic acid has been extensively investigated.[1–3] Taube[3] has studied the kinetics of decomposition of the oxalate complexes of manganese(III) and has found that the rates could be accounted for by the simple mechanism in which each of the ions $MnC_2O_4^+$, $Mn(C_2O_4)_2^-$, and $Mn(C_2O_4)_3^{3-}$ undergoes decomposition. These species are known to be in equilibrium with one another according to

$$MnC_2O_4^+ \underset{}{\overset{+C_2O_4^{2-}}{\rightleftharpoons}} Mn(C_2O_4)_2^- \underset{}{\overset{+C_2O_4^{2-}}{\rightleftharpoons}} Mn(C_2O_4)_3^{3-}$$

Owing to the equilibria involved between the different species of the oxalatomanganese(III) complexes and between the three forms of oxalic acid, it is kinetically impossible to distinguish between the reactions

$$Mn(C_2O_4)_2^- + HC_2O_4^- \xrightarrow{\text{fast}} H^+ + Mn(C_2O_4)_2^{3-} \xrightarrow{\text{slow}} Mn(C_2O_4)^{2-} + C_2O_4^- \quad (1)$$

$$Mn(C_2O_4)_2^- + HC_2O_4^- \xrightarrow{\text{slow}} Mn(C_2O_4)_2^{2-} + H^+ + C_2O_4^- \quad (2)$$

It is possible that a part of the reaction involves a reaction of the second type as well as the first.

The *trans*-1,2-diaminocyclohexanetetraacetic acid (CyDTA) complex of manganese(III) has been found to be a very stable solid compound that decomposes only slowly in aqueous solution.[4] It undergoes a unimolecular decomposition with a specific rate constant of 6.8×10^{-6} sec^{-1} at 25° and an ionic strength of 0.20. The composition of the complex is expressed as $Mn(CyDTA)H_2O^-$ where either the CyDTA ligand is acting as a pentadentate ligand or it is a hexadentate ligand with the manganese(III) having a water molecule in a seventh coordination position. The idea of manganese being seven coordinated is not completely unreasonable as indicated by the crystal structure investigation of the $Mn^{II}EDTA$ complex which shows it

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[1] S. J. Adler and R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2036 (1955).

[2] H. F. Launer, *ibid.*, **54**, 2597 (1932).

[3] H. Taube, *ibid.*, **70**, 1216 (1948).

[4] R. E. Hamm and M. A. Suwyn, *Inorg. Chem.*, **6**, 139 (1967).

to be seven coordinated.[5] $Mn^{III}CyDTA$ would be expected to react with oxalate by a reaction similar to (2) above, because it is extremely unlikely that the chelation of the oxalate is required before the electron transfer takes place.

Experimental Section

The potassium salt of *trans*-1,2-diaminocyclohexanetetraacetatomanganate(III) was prepared as previously described.[4] Reagent grade sodium oxalate was used to prepare stock solutions of oxalate at varying hydrogen ion concentrations. The pH was adjusted with perchloric acid and carbonate-free sodium hydroxide solution. The ionic strength was maintained at 0.20 with sodium perchlorate prepared by neutralizing perchloric acid with carbonate-free sodium hydroxide.

The reaction rate was determined by observing the change in absorption at the absorption maximum of $Mn^{III}CyDTA^-$ (510 mμ) with a Beckman Model DU spectrophotometer which was fitted with a constant-temperature cell block. Solutions containing the oxalate ion at a given pH and ionic strength were prepared by adding the proper amount of stock solution and the proper amount of sodium perchlorate to bring the ionic strength to 0.20 and then by diluting to volume with deionized water. A 50-ml volume of the prepared solution was placed in each of the reaction flasks which were placed in a constant-temperature bath. The bath was maintained within ±0.02° of the desired temperature. After the solutions had come to the temperature of the bath, weighed amounts of $KMn^{III}CyDTA$ complex were introduced into the flasks and stirred by means of a Teflon-coated stirring bar. No experimental difference could be detected for parallel samples run in the presence and absence of dissolved oxygen.

Absorbance readings were taken over several half-lives. The pseudo-first-order rate constant was obtained from the slope of a plot of $-\log A$ against time.

Ionic strengths were calculated assuming a -1 charge for the $Mn^{III}CyDTA^-$ complex. The concentrations of the oxalate species were calculated using dissociation constants for oxalic acid of $K_1 = 5.90 \times 10^{-2}$ and $K_2 = 6.40 \times 10^{-5}$.[6]

The reaction was studied in the pH range 3.0–7.0. All pH readings were taken with a Beckman research pH meter equipped with a calomel electrode filled with 4 M sodium chloride to prevent precipitation of potassium perchlorate.

No photochemical reaction was found to result from ordinary room light or when the sample was left in the path of the light beam in the spectrophotometer between readings. The products of the reaction were found to be carbon dioxide, $Mn^{II}CyDTA^{2-}$, and hydrogen peroxide. The hydrogen peroxide was determined by addition of potassium iodide to a completely reacted sample with subsequent titration of the liberated iodine. The carbon dioxide was determined by a manometric gas analysis method and by an Ascarite absorption method.

Results and Discussion

When samples were prepared such that the concentrations of $Mn^{III}CyDTA^-$ and the total oxalate were constant, a plot of pH *vs.* the observed pseudo-first-order rate constant has the appearance shown in Figure 1. This curve is best understood by noting that, at a pH greater than 5.5, the oxalate ion ($C_2O_4^{2-}$) is essentially the only oxalate species in solution. If one assumes that the $HC_2O_4^-$ ion reacts more slowly with $Mn^{III}CyDTA^-$ than the $C_2O_4^{2-}$ ion, the curve can be fitted.

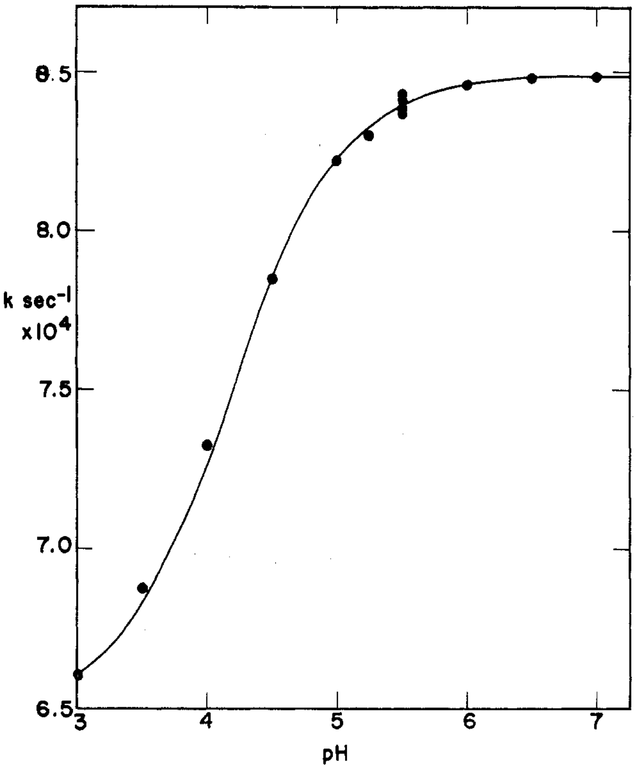

Figure 1.—Observed rate constant as a function of pH at 20°.

When the concentration of the $Mn^{III}CyDTA^-$ complex was held constant and the total concentration of the oxalate species was increased at constant pH and constant ionic strength, the reaction was found to be first order in total oxalate concentration as shown in Figure 2. Since the log (absorbancy) plots were straight, the reaction was also first order in Mn^{III}-$CyDTA^-$ complex.

The data presented above can be interpreted by the mechanism: for the $HC_2O_4^-$ ion

$$Mn(CyDTA)^- + HC_2O_4^- \xrightarrow{k_1} Mn(CyDTA)^{2-} + H^+ + C_2O_4^- \quad (3)$$

$$Mn(CyDTA)^- + C_2O_4^- \xrightarrow{k_R} Mn(CyDTA)^{2-} + 2CO_2 \quad (4)$$

and for the $C_2O_4^{2-}$ ion

$$Mn(CyDTA)^- + C_2O_4^{2-} \xrightarrow{k_2} Mn(CyDTA)^{2-} + C_2O_4^- \quad (5)$$

followed by reaction 4. The rate-determining steps are reactions 3 and 5. Reaction 4 which is the second step in each case is a free-radical reaction and will be expected to be much faster than reactions 3 or 5. The over-all stoichiometry of the reactions is given in

$$2Mn^{III}CyDTA + C_2O_4^{2-} \longrightarrow 2CO_2 + 2Mn^{II}CyDTA \quad (6)$$

$$2Mn^{III}CyDTA + HC_2O_4^- \longrightarrow 2CO_2 + 2Mn^{II}CyDTA + 2H^+ \quad (7)$$

The rate law for this mechanism is given by

$$-\frac{d[Mn(CyDTA)^-]}{dt} = 2k_1[Mn(CyDTA)^-][HC_2O_4^-] + 2k_2[Mn(CyDTA)^-][C_2O_4^{2-}]$$

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[5] S Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964).

[6] These values, taken from the "Handbook of Chemistry and Physics," 44th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, are reasonably in agreement with H. S. Harned and L. D. Fallen, *J. Am. Chem. Soc.*, **61**, 3111 (1939); L. S. Darken, *ibid.*, **63**, 1007 (1941); and H. W. Dawson and C. R. Hoskins, *J. Chem. Soc.*, 1884 (1929), none of whom give data for the exact ionic strength and temperature desired in this investigation.

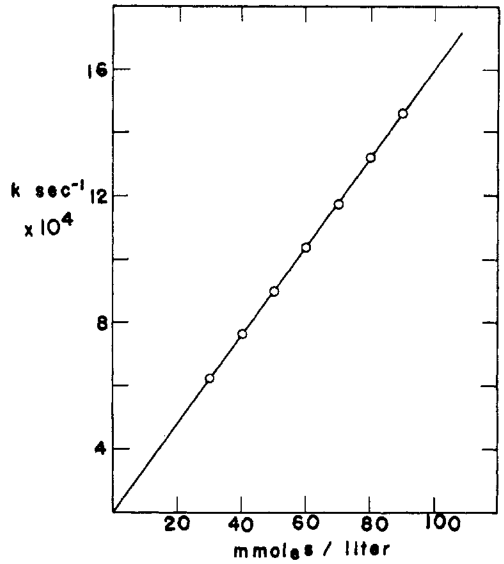

Figure 2.—Observed rate constant at pH 6.0 and at 20° as a function of total oxalate concentration.

The factor 2 is introduced since two $\mathrm{Mn^{III}(CyDTA)^-}$ ions are reduced for each oxalate ion which is oxidized. The pseudo-first-order rate constant, k_{obsd}, will be given by

$$k_{\mathrm{obsd}} = 2k_1[\mathrm{HC_2O_4^-}] + 2k_2[\mathrm{C_2O_4^{2-}}]$$

Experiments were run at pH above 6.00 to evaluate k_2. A value of 7.08×10^{-3} sec^{-1} M^{-1} was obtained at 20°. Once k_2 was known, runs carried out at lower pH values permitted k_1 to be evaluated at 5.40×10^{-3} sec^{-1} M^{-1} at 20°. Using these rate constants the expected value of the pseudo-first-order rate constant can be calculated at any pH by use of

$$k_{\mathrm{obsd}} = \frac{2C_{\mathrm{ox}}}{[\mathrm{H^+}] + K_2}([\mathrm{H^+}]k_1 + K_2k_2)$$

where C_{ox} is the total oxalate concentration, K_2 is the second ionization constant of oxalic acid, and k_1 and k_2 are the second-order rate constants. Table I contains some of the data determined on typical rate experiments. Some features of the data require special emphasis. Special care had to be taken to remove the last traces of dissolved oxygen from the solutions.

Launer[7] has shown in the $\mathrm{Mn^{III}(C_2O_4)}_x$ system that the reducing intermediate formed reacts with oxygen and thereby induces the reaction

$$\mathrm{H_2C_2O_4 + O_2 = H_2O_2 + 2CO_2}$$

When oxygen was present and the pH was 4.5 or less, $\mathrm{H_2O_2}$ was found to be present at the end of the reaction. The pseudo-first-order rate plots also tended to curve somewhat toward slower rates after 1 or 2 half-lives. When the solution was completely free of oxygen, linear plots were obtained over several half-lives.

In solutions where the pH was 4.5 or greater, no $\mathrm{H_2O_2}$ was found when oxygen was present in the solution. When $\mathrm{H_2O_2}$ was added to a solution of $\mathrm{Mn^{III}CyDTA^-}$ at varying pH values, it was found that the peroxide will reduce the $\mathrm{Mn^{III}CyDTA^-}$ rapidly at pH values greater than 5. The reaction of $\mathrm{H_2O_2}$ with $\mathrm{Mn^{III}CyDTA^-}$ is quite slow at a pH of 4 and becomes slower as the pH gets smaller. This explains why no $\mathrm{H_2O_2}$ was found in solutions of higher pH when oxygen was present.

TABLE I

KINETICS OF OXIDATION OF OXALATE AT 20° AND IONIC STRENGTH 0.20[a]

C_{ox}	[Mn(CyDTA)$^-$]	pH	10^4k_{obsd}, sec^{-1} Exptl	10^4k_{obsd}, sec^{-1} Calcd
60.0	1.12	6.00	8.46	8.45
60.0	1.14	6.50	8.48	8.48
60.0	1.15	7.00	8.48	8.48
60.0	1.12	3.00	6.60	6.60
60.0	1.14	3.50	6.88	6.83
60.0	1.14	4.00	7.33	7.26
60.0	1.11	4.50	7.85	7.84
60.0	1.15	5.00	8.22	8.23
60.0	1.14	5.25	8.30	8.32
60.0	1.14	5.50	8.37	8.40
60.0	0.70	5.50	8.42	8.40
60.0	1.29	5.50	8.39	8.40
60.0	1.53	5.50	8.44	8.40
40.0	1.14	3.50	4.53	4.54
29.5	1.14	3.00	3.29	3.25
50.0	1.14	4.50	6.56	6.53
49.2	1.15	3.00	5.40	5.42
20.0	1.14	4.00	3.57	3.62

[a] Starting concentrations expressed in millimoles per liter.

The rate constants were determined at other temperatures by the same procedure. First k_2 was determined at each temperature and then a second series of experiments was made in more acid solutions to determine k_1 at each temperature. The data are given in Table II. The slopes and intercepts of these data plotted according to the method of absolute reaction rates were determined by means of the method of least squares. Values of k_1 and k_2 were used in evaluating the activation parameters. The following activation parameters and standard deviations were calculated: for k_1, $\Delta H_1^{\ddagger} = 20.9 \pm 0.2$ kcal and $\Delta S_1^{\ddagger} = +3.5 \pm 0.7$ eu; for k_2, $\Delta H_2^{\ddagger} = 16.0 \pm 0.4$ kcal and $\Delta S_2^{\ddagger} = -13.0 \pm 1.3$ eu.

TABLE II

C_{ox}, mM	Temp, °C	pH	10^3k_1, sec^{-1} M^{-1}	10^3k_2, sec^{-1} M^{-1}
60.0	15	6.0		4.18
60.0	20	6.0		7.08
60.0	25	6.0		11.4
60.0	30	6.0		18.0
60.0	35	6.0		26.6
53.8	15	3.8	2.88	
53.8	20	3.8	5.40	
53.8	25	3.8	10.4	
53.8	30	3.8	18.4	
53.8	35	3.8	33.4	

The rates were found to increase as the ionic strength increased which is consistent with the effect predicted for a reaction of two similarly charged ions.

If the formation of a relatively stable $\mathrm{Mn^{III}CyDTA(C_2O_4)^{3-}}$ was required which then unimolecularly decomposed, one might suspect that the absorption spectrum should change upon the addition of oxalate.

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[7] H. F. Launer, *J. Am. Chem. Soc.*, **55**, 865 (1933).

No such change in the spectrum was found so the slow step is looked at as the interaction of the two species.

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Coordination Complexes of Diphenyl(*o*-diphenylarsinophenyl)phosphine Sulfide and Diphenyl(*o*-diphenylarsinophenyl)phosphine[1,2]

BY PHILIP NICPON[3] AND DEVON W. MEEK

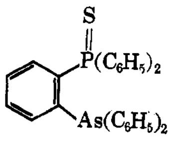
Received July 8, 1966

Diphenyl(*o*-diphenylarsinophenyl)phosphine sulfide (I) forms stable complexes with palladium(II), platinum(II), gold(I), and copper(I). Ligand I forms a chelate by coordinating both the thiophosphoryl and arsino groups to palladium(II), platinum(II), and copper(I), whereas it is bonded only through the arsenic atom in the gold(I) chloride complex. Electronic absorption spectra of the palladium(II) complexes indicate that the phosphine sulfide, I, exerts a weaker ligand field than the corresponding phosphine, II. The yellow palladium thiocyanate complex of diphenyl(*o*-diphenylarsinophenyl)phosphine, $[Pd(C_{30}H_{24}AsP)(NCS)(SCN)]$, is an example of an unusual type of thiocyanate complex because it contains one N-bonded and also one S-bonded thiocyanate ion in the same molecular complex.

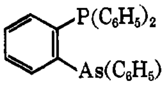
Introduction

In contrast to numerous metal complexes of phosphine oxides[4] and arsine oxides,[5] few phosphine sulfide complexes had been reported before 1965.[6,7] Recently, we[8] have been investigating the coordination properties of tertiary phosphine sulfides toward transition metal ions. In spite of the limited results of previous investigators,[6,7] our results indicate that tertiary phosphine sulfides form numerous stable complexes with metals which normally bond to easily polarized donor atoms, *e.g.*, "class b" or "soft" metals, using the designations of Ahrland, Chatt, and Davies[9] and Pearson,[10] respectively.

The ligand diphenyl(*o*-diphenylarsinophenyl)phosphine sulfide (I), which potentially could function as a chelating ligand, was synthesized to ascertain if introduction of the P═S group into a chelate ring would materially increase the coordination tendency of the thiophosphoryl group and facilitate isolation of "class a" metal complexes. Also, by comparing the electronic absorption spectra of palladium(II) complexes of ligand I with analogous complexes of diphenyl(*o*-diphenylarsinophenyl)phosphine (II), one can determine the position of the P═S group in the spectrochemical series, relative to the parent phosphine.



I



II

Experimental Section

Materials.—Sodium tetrachloroaurate(III) (Alfa), sodium tetrachloroplatinate(II) (Platinum Chemicals Co.), palladium nitrate (Alfa), sodium tetrachloropalladate(II) (Engelhard), and 1-butyllithium (Foote Mineral) were reagent grade chemicals and were used without further purification. Diphenylchlorophosphine was fractionated before use, bp 170–172° (10 mm). Dimethylformamide (DMF) was dried for 2 days over anhydrous barium oxide and then distilled, bp 55° (20 mm), from fresh BaO. Diphenylthiophosphoryl chloride, $(C_6H_5)_2P(S)Cl$, bp 183–184° (3 mm), was prepared in 96% yield from diphenylchlorophosphine (93.9 g, 0.425 mole) and elemental sulfur (13.6 g, 0.425 g-atom) in 100 ml of refluxing toluene.

Preparation of Diphenyl(*o*-diphenylarsinophenyl)phosphine Sulfide.—To a stirred solution (0–5°) of diphenyl(*o*-bromophenyl)arsine[11] (24.8 g, 0.0644 mole) in 200 ml of anhydrous diethyl ether was added 0.064 mole of 1-butyllithium over a period of 1.5 hr. The mixture was stirred for 1 hr more at 0–5° and then diphenylthiophosphoryl chloride, $(C_6H_5)_2P(S)Cl$ (16.2 g, 0.064 mole), in 50 ml of ether was added over a period of 45 min. The mixture was stirred for 2 hr at room temperature and then hydrolyzed with 0.2 N HCl. The insoluble material was collected by filtration and washed successively with water, ethanol, and ether. The crude product (19.2 g, mp 186–190°) was recrystallized from 375 ml of hot 1-butanol; yield 15.3 g

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[1] The authors gratefully acknowledge the financial support of the U. S. Public Health Service (Grant No. ES00170) and the National Science Foundation (Grant No. GP-5729).

[2] Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965; Abstracts, p O-13.

[3] Public Health Service Predoctoral Fellow (No. 5-Fl-GM-25), 1965–1966.

[4] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961); E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1878, 2276 (1960).

[5] D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961); D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 2298, 3735 (1961).

[6] E. Bannister and F. A. Cotton, *ibid.*, 1959 (1960).

[7] J. Philip and C. Curran, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 28L.

[8] D. W. Meek and P. Nicpon, *J. Am. Chem. Soc.*, **87**, 4951 (1965).

[9] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

[10] R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

[11] W. Cochran, R. A. Hart, and F. G. Mann, *J. Chem. Soc.*, 2816 (1957).