contain the magnetic electrons and are directed toward the centers of the 12 edges of the octahedron formed by the $Cr(H_2O)_6^{+3}$ complex.

Acknowledgment.—The author wishes to express his appreciation to Drs. J. A. Jackson, W. B. Lewis, and J. F. Lemons, all of whom have contributed significantly to this work through their continued interest and helpful suggestions. He is indebted to Dr. B. B. McInteer and Mr. R. M. Potter of this laboratory for supplying the enriched oxygen-17.

CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY,
MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN

Niobium(IV) Compounds Containing Ethoxide: $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ and $Nb(OC_2H_5)_4$

BY R. A. D. WENTWORTH AND C. H. BRUBAKER, JR.[1]

Received June 14, 1963

Further investigations of niobium(IV) solutions in ethyl alcohol have led to the preparation of two diamagnetic compounds, $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ and $Nb(OC_2H_5)_4$. The former is prepared by the addition of pyridine to niobium(IV) chloride solutions in ethyl alcohol. The structure of the dimer is thought to involve chloride bridging on the basis of its chemical properties. $Nb(OC_2H_5)_4$ is prepared by the reaction of $NaOC_2H_5$ with $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$. Both compounds are readily converted to $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$.

Recently, we described[2,3] the preparation and characterization of a series of compounds containing the pentachloroalkoxoniobate(IV) anion. The successful preparation of these compounds has led to a more complete investigation of niobium(IV) solutions in ethyl alcohol and the isolation of two new compounds, dichlorohexaethoxobis(pyridine)diniobium(IV), $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$, and tetraethoxoniobium(IV).

Thomas[4] has previously attempted the preparation of the tetraalkoxide by the alcoholysis of tetrakis(diethylamido)niobium(IV), but the product was always $Nb(OR)_5$. Bradley[5] has suggested the cause for the instability of the tetraalkoxide in the presence of alcohol, that is

$$2Nb(OR)_4 + 2ROH \longrightarrow 2Nb(OR)_5 + H_2$$

Experimental

Materials.—The source and purification of niobium pentachloride, pyridine, hydrogen chloride, and nitrogen were described previously.[3]

Anhydrous ethyl alcohol was obtained by azeotropic distillation with benzene. Anhydrous benzene was obtained by azeotropic distillation with ethyl alcohol.

Magnetic Susceptibility Measurements.—The measurements were accomplished using the techniques and apparatus previously described.[3]

Spectroscopic Measurements.—The infrared spectra were obtained with Nujol mulls and the use of a Perkin-Elmer Model 21 spectrophotometer. The mulls were prepared under a purified nitrogen atmosphere.

The visible and near-infrared spectra were obtained by the use of a Beckman Model DK-2 spectrophotometer and capped, 1-cm. silica cells which had been dried at 100° for several hours.

Analytical Methods.—Niobium and chloride analyses were performed as with the pentachloroalkoxoniobates.[3] Ethoxide was determined by the method of Bradley.[6]

Pyridine was determined spectrophotometrically at 255 $m\mu$ in 0.05 N H_2SO_4. Samples were digested in aqueous solutions of H_2SO_4 of known concentration, filtered, and the solutions made up to 1 l. with sufficient H_2SO_4 and water so that the final H_2SO_4 concentration was 0.05 N.

Molecular Weight Measurement.—The molecular weight of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ was determined ebullioscopically in $CHCl_3$ by Huffman Microanalytical Laboratories, Wheatridge, Colorado. Due to the sensitivity of this compound to oxidation, the measurement was performed in dry nitrogen atmosphere with a precision of ±10%.

Preparation, Properties, and Reaction of Compounds. $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$.—$NbCl_5$ (6.20 g., 0.0229 mole) in 25 ml. of ethyl alcohol saturated with HCl was reduced electrolytically,[3] and the solution was evaporated to dryness. The tacky, dark substance which remained was dissolved in 20 ml. of ethyl alcohol and 5 ml. of pyridine was added. The color of the solution changed from deep purple to an equally deep yellow-red. Crystallization began within 1 hr. and was seemingly complete after another 9 hr. The red compound was collected on a filter under a nitrogen atmosphere and was washed with three 10-ml. portions of cold ethyl alcohol; yield 5.04 g. (64% based on $NbCl_5$). Concentration of the mother liquor produced only a small additional amount of the compound.

Anal. Calcd. for $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$: C_5H_5N, 23.1; Cl, 10.4; Nb, 27.1; molecular weight of dimer, 686. Found: C_5H_5N, 23.2; Cl, 10.3; Nb, 27.1; molecular weight, 674; molecular complexity, 1.97. The infrared spectrum showed that ethoxide was present.

The dimer is very soluble in $CHCl_3$ and slightly soluble in ethyl and isopropyl alcohols at room temperature, but it is insoluble in benzene, ethers, ketones, other halogenated hydrocarbons, dimethylformamide, dimethyl sulfoxide, and glacial acetic acid.

The visible and near-infrared spectrum of the dimer in $CHCl_3$ and ethyl alcohol is simple, consisting only of a shoulder at 365

---

[1] To whom correspondence should be directed.

[2] R. A. D. Wentworth and C. H. Brubaker, Jr., *Inorg. Chem.*, **1**, 971 (1962).

[3] R. A. D. Wentworth and C. H. Brubaker, Jr., *ibid.*, **2**, 551 (1963).

[4] I. M. Thomas, *Can. J. Chem.*, **39**, 1386 (1961).

[5] D. C. Bradley, R. N. Kapoor, and B. C. Smith, *J. Inorg. Nucl. Chem.*, **24**, 864 (1962).

[6] D. C. Bradley, F. M. Abd-el Halim, and W. Wardlaw. *J. Chem. Soc.*, 3453 (1950).

Fig. 1.—Infrared spectra: ———, $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$; ---------, $Nb(OC_2H_5)_4$.

mμ adjacent to a high intensity band in the ultraviolet. Attempts to obtain reproducible values for the molar extinction coefficient were not successful, probably due to oxidation.

A powdered sample of the dimer was found to have a corrected susceptibility of -1150×10^{-6} c.g.s. unit.

When heated in a sealed, evacuated tube, this compound turns brown at about 100° and liquefies with gas evolution (pyridine?) at about 155°.

Reaction of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ with Pyridinium Ion in Alcoholic HCl.—To 5 ml. of ethyl alcohol saturated with HCl, 0.20 g. of the dimer was added. After gentle heating to accelerate the solution process, 0.2 ml. of pyridine was added, and the solution held at $-10°$ for 24 hr. The small, orange crystals were collected on a filter under nitrogen, washed with two 10-ml. portions of $CHCl_3$, and dried by continuous pumping for 12 hr.; yield 0.12 g. (43% based on the dimer) of $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$. The infrared spectrum was identical with that of a sample of $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$.[3] *Anal.* Calcd. for $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$: Cl, 37.3. Found: Cl, 36.9.

Attempted Displacement of Chloride Ion from $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$.—About 0.1 g. of the dimer was heated to 150° with isopropyl alcohol in a sealed, evacuated tube for 24 hr. The solvent was distilled away to give a brown, tacky substance. Large amounts of pyridine were found in the distillate. Analysis of the residue indicated that no solvolytic replacement of chloride ion had occurred, and that the nature of the residue was uncertain, but it may be crude $NbCl(OC_2H_5)_3(C_3H_7OH)$.

Anal. Calcd. for $NbCl(OC_2H_5)_3(C_3H_7OH)$: Cl, 11.0; Nb, 29.5. Calcd. for $NbCl(OC_3H_7)_3$: Cl, 11.5; Nb, 30.1. Found: Cl, 11.7; Nb, 28.7; Cl/Nb, 1.07.

A small amount of the dimer was dissolved in about 3 ml. of ethyl alcohol with heating, and several ml. of a saturated alcoholic KI solution was added. No precipitation occurred even after heating for several minutes. If a labile chloride ion had been present, a precipitate of KCl would have been expected.

$Nb(OC_2H_5)_4$.—$[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ (4.97 g., 0.00724 mole) was added to an ethyl alcohol solution containing 0.01448 mole of $NaOC_2H_5$. The bright blue precipitate which formed initially slowly disappeared with the formation of a red-brown solution. Evaporation to dryness, addition of benzene, and filtration ensured the removal of NaCl. The filtrate was then evaporated to dryness at 65° to yield a red-brown oil.

Anal. Calcd. for $Nb(OC_2H_5)_4$: Nb, 34.1; Cl, 0.00. Found: Nb, 35.9; Cl, 0.34; in a subsequent preparation, Nb, 33.0; Cl, 0.47.

When this compound was exposed to the so-called dry atmosphere of a nitrogen-filled drybox, the color changed to brown and the niobium content increased, which is indicative of hydrolysis.

Sublimation at 0.002 mm. and a bath temperature of 160° yielded the tacky, red-brown $Nb(OC_2H_5)_4$ in relatively pure form.

Anal. Calcd. for $Nb(OC_2H_5)_4$: Nb, 34.1; OC_2H_5, 65.9; Cl, 0.00. Found: Nb, 34.5; OC_2H_5, 64.9; Cl, 0.00; OC_2H_5/Nb, 3.90.

The compound had a corrected susceptibility of -100×10^{-6} c.g.s. unit in benzene. The visible and near-infrared spectrum of $Nb(OC_2H_5)_4$ in ethyl alcohol is similar to that of the dimer with only a shoulder at 380 mμ (ε 20 l. mole^{-1} cm.$^{-1}$).

Reaction of $Nb(OC_2H_5)_4$ with Pyridinium Ion in Alcoholic HCl.—This reaction was carried out analogously to that with $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ and resulted in an 87% yield of $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$. *Anal.* Calcd. for $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$: Cl, 37.3. Found: Cl, 37.2.

Results and Discussion

The dimeric $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ possesses so many nonequivalent ligands that a structural determination based on chemical and physical properties alone is virtually impossible. We calculate 123 possible isomers, based on the following assumptions. (1) Each niobium ion is octahedrally surrounded by ligands. (2) Each niobium ion is maintained in the tetravalent state, *i.e.*, a Nb(III)–Nb(V) combination is not allowed. (3) Pyridine cannot act as a bridging ligand, but any other combination of bridging ligands is possible.

The infrared spectrum, Fig. 1, makes it clear that ligand pyridine is present since the strong absorption characteristic of pyridinium ion at 1630 cm.$^{-1}$ is absent.[7] The region of the spectrum in which the characteristic C–O absorption occurs (*ca.* 1100 cm.$^{-1}$)[8] is considerably more complex than those of the pentachloroethoxoniobates[3] and those of the tetraethoxides which will be discussed later. Exact frequencies are 1010 (m), 1040 (s), 1080 (s), 1120 (s) (shoulder), and 1140 (m) cm.$^{-1}$. The observed complexity may constitute evidence for nonequivalent ethoxide groups and could be interpreted as evidence for bridging and terminal alkoxide groups.

The inability to replace chloride ion by solvolysis and precipitation as KCl, however, points to the inertness of this ligand. In the kinetically stable [Co-

---

[7] N. S. Gill, R. H. Nuttal, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen & Co. Ltd., London, p. 95.

$(NH_3)_5Cl]^{+2}$ and $[Pt(NH_3)_3Cl]^+$ ions, the chloride ions are fairly readily replaced. It is only in certain polynuclear palladium and platinum complexes which involve chloride bridging that kinetic inertness of the chloride ion is encountered.

For example, when $PdCl_2$ reacts with amines under special conditions, only partial bridge-breaking occurs to form $[(am)_2PdCl]_2$.[9] However, Chatt has shown that the reaction $[L_2PdCl]_2 + 2am = 2L_2(am)PdCl$ lies mainly on the side of the mononuclear complex, except where the amine is weakly basic.[10] In the present system, isopropyl alcohol or iodide ion would function as weak Lewis bases.

It seems logical, then, to assume that in the dimeric niobium compound the chloride ions are bridging groups. With this assumption, the number of isomers is reduced to five (Fig. 2).

If chloride bridges are present, one must consider the complexity of the infrared spectrum between 1000 and 1150 cm.$^{-1}$. In the structures shown in Fig. 2, all of the ethoxide groups are not really equivalent since some are *trans* to pyridine or chloride, while others are *trans* to ethoxide. Such a complex molecule could have more than one C–O stretching frequency due to the overall symmetry, rather than to a chemical distinction.

The diamagnetic NbI_4 has been shown[11] to consist of infinite linear chains of NbI_6 octahedra sharing opposite edges. The niobium ions are shifted toward one another in pairs to give a resulting metal–metal distance of 3.3 Å. The diamagnetism is explained[12] in terms of metal–metal bonding resulting from overlap of the adjacent metal d_{xy}-orbitals.

We have estimated the metal–metal distance in $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ to be about 3.5 Å., based on the assumptions that the Nb–Cl–Nb angle is 90°, that the bridging chloride ion has a somewhat larger radius (by 10%) than the covalent radius of 0.99 Å.,[13] and that the radius of the niobium ion is 1.3 Å.[13] The closeness to the metal–metal distance in NbI_4 seems to be sufficient to postulate that the diamagnetism results from direct metal–metal bonding. If the niobium ions are shifted from the centers of their octahedra toward each other, as is observed in NbI_4, then overlap would be even more favorable.

The reaction of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ with sodium ethoxide proceeds rapidly with the formation of tetraethoxoniobium(IV). The successful preparation of this compound makes it clear that it is stable in the presence of alcohol, at least for short periods of time $Nb(OC_2H_5)_4$ is, however, extremely easily hydrolyzed and oxidized, and attempts to prepare stable solutions of the $Nb(OC_2H_5)_4$ alone were unsuccessful.

Polymerization among the tetraalkoxides is common,[14] and the diamagnetism of the niobium compound suggests that it is also polymeric. Such a molecule would, no doubt, involve bridging and terminal ethoxide groups. The infrared spectrum, Fig. 1, in the region between 1000 and 1150 cm.$^{-1}$ is relatively simple with bands at 1030 (m) (shoulder), 1040 (s) (shoulder, almost masked), 1100 (s), and 1140 (m) (shoulder) cm.$^{-1}$. The spectrum is in accord with those of other polymeric metal ethoxides[15] and is surprisingly similar to that of the pentachloroethoxoniobate(IV) anion,[3] which is thought to be monomeric. All of these possess two major bands in the 1000–1150 cm.$^{-1}$ region. In the case of the tetraethoxides the bands have been assigned[15] to bridging and terminal ethoxide groups.

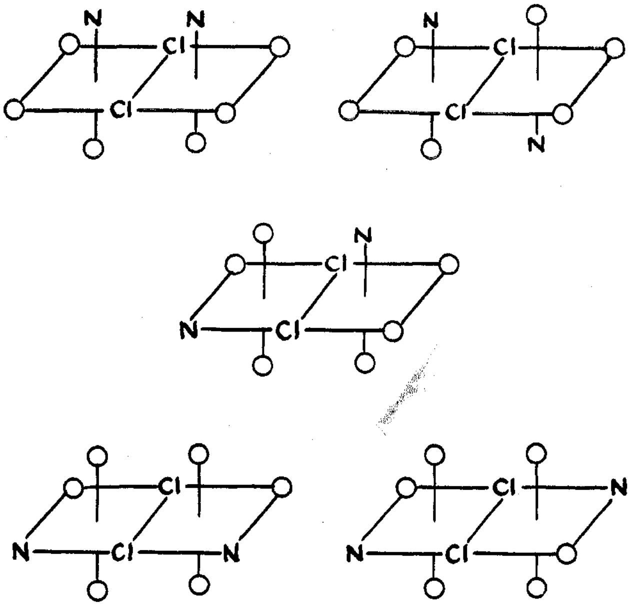


Fig. 2.—Isomers of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ with chloride bridging: O is oxygen in ethoxide; N is nitrogen in pyridine.

If the bands are due to bridging and terminal groups, then the pentachloroalkoxoniobate(IV) anion cannot be octahedral. The assignment of these bands to bridging and terminal groups does not seem probable when the spectra of ethyl alcohol and sodium ethoxide are considered.[16] In the spectra of the alcohol and the ethoxide are seen two bands between 1000 and 1150 cm.$^{-1}$, and in neither case would one expect bridging and terminal C–O groups. Further assurance is had from the simplicity of the spectra of the pentachloromethoxoniobates,[8] which exhibit a single maximum at about 1100 cm.$^{-1}$. Methyl alcohol and sodium methoxide behave similarly.[16] Thus, it seems likely that the two bands present in the tetraethoxides are due to vibrations of terminal ethoxide groups, analogous to those of $NaOC_2H_5$ and $[Nb(OC_2H_5)Cl_5]^{-2}$. One must then assume that absorptions due to bridging groups are masked by the strong absorptions of the terminal groups.

Both $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ and $Nb(OC_2H_5)_4$ are labile to substitution by chloride ion in solutions of high acidity. An interesting cycle of reactions is observed.

---

(9) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1962, p. 850.

(10) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 3858 (1955).

(11) L. F. Dahl and D. L. Wampler, *Acta Cryst.*, **15**, 903 (1962).

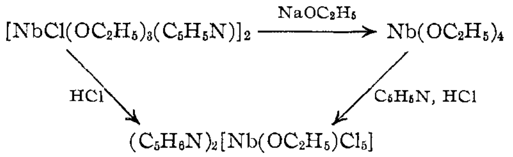
(12) L. F. Dahl and D. L. Wampler, *J. Am. Chem. Soc.*, **81**, 3150 (1959).

(13) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1958, p. 135.

(14) See, for example, D. C. Bradley, *Progr. Inorg. Chem.*, **2**, 337 (1960).

(15) C. G. Barraclough, D. C. Bradley, J. Lewis, and I. M. Thomas, *J. Chem. Soc.*, 2601 (1961).

(16) F. H. Seubold, *J. Org. Chem.*, **21**, 156 (1956).



This cycle demonstrates the equivalence of the oxidation state of niobium in each compound and thus proves the tetravalent state in $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ and $Nb(OC_2H_5)_4$ since the pentachloroethoxoniobate anion is known to contain niobium(IV).

Acknowledgment.—R. A. D. W. wishes to thank the National Science Foundation for fellowship aid in 1962–1963.

Contribution from the Institute for Atomic Research and
Department of Chemistry, Iowa State University, Ames, Iowa

Transport Reactions of Some Vanadium(III) Halides. Mixed Halide Formation[1a]

By ROBERT E. McCARLEY, JAMES W. RODDY,[1b] and KEITH O. BERRY

Received September 8, 1962

The reactions of VCl_2, VCl_3, and VCl_3–VBr_3 mixtures with bromine vapor at 350 to 450° led to vaporization of the halides and deposition of mixed halides of vanadium(III) at lower temperatures. A study of solid solution formation in the system VCl_3–VBr_3 showed that the two components were miscible in the solid state, and that the mixed halide VCl_2Br should be regarded as such a solid solution. The pure compounds VCl_3 and VBr_3, the mixed halides VCl_2Br and VBr_2I, and solutions of all compositions in the system VCl_3–VBr_3 were hexagonal solids with the BiI_3 layer structure; lattice constants for all of the compounds are given. Vaporization of VBr_2 in iodine vapor at 350 to 400° resulted in the transport and deposition of VBr_2I, but the analogous reaction between VCl_2 and iodine yielded only a deposit of VCl_2. Vanadium(IV) mixed halides containing iodine were postulated to account for the vaporization at these temperatures.

Introduction

Sublimation of the vanadium(III) halides VX_3 (where X = Cl, Br, I) as a means of purification is not practical because of the stability relationships to the respective lower and higher halides. For example, it has been shown[2] that VCl_3 is unstable at high temperature with respect to reaction 1

$$2VCl_3(s) = VCl_2(s) + VCl_4(g) \qquad (1)$$

whereas VBr_3 is decomposed[3a] *via* reactions 2 and 3

$$VBr_3(s) = VBr_2(s) + {}^1/_2Br_2(g) \qquad (2)$$

$$2VBr_3(s) = VBr_2(s) + VBr_4(g) \qquad (3)$$

Simple vaporization of the trihalides is not feasible because at the temperatures required for sublimation of the solids the decomposition pressures are comparable in magnitude to the vapor pressures.

However, vaporization and deposition of compounds which are unstable in this manner frequently may be performed by means of chemical reactions. In this connection, a volatile species containing the metallic element must be formed in a reversible reaction of the type

$$A(s) + B(g) = C(g)$$

The conditions necessary for the transport of a crystalline phase through a temperature gradient T_1 to T_2 have been outlined and demonstrated by Schäfer, *et al.*[4] Reactions of this type will be referred to as transport reactions in this work.

Based on these considerations some transport reactions of the crystalline vanadium halides have been studied, and the decreased stability of the higher-valent vanadium bromides and iodides has been utilized. For example, reactions of types 4 and 5 have been performed where X = Cl or Br and X′ = Br or I.

$$VX_3(s) + {}^1/_2X_2'(g) = VX_3X'(g) \qquad (4)$$

$$VX_2(s) + n/2X_2'(g) = VX_2X_n' \qquad (5)$$

In the case of (4), equilibrium studies previously have been completed where X = X′ = Cl[5] or Br.[3a] As a result of the work reported here some new, mixed halide compounds of vanadium(III) were prepared and characterized, while indirect evidence was obtained for the formation of some mixed halides of vanadium(IV) in the vapor phase.

Experimental

Materials.—Commercial chlorine was taken from the cylinder and purified by passing the gas through a potassium permanganate solution to remove hydrogen chloride and then through sulfuric acid and over phosphorus(V) oxide to remove moisture. Reagent grade bromine was vacuum distilled from phosphorus (V)

---

(1) (a) Contribution No. 1215. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission; (b) this paper was taken in part from a thesis submitted by J. W. Roddy to the Iowa State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) (a) O. Ruff and H. Lickfett, *Ber.*, **44**, 506 (1911); (b) V. Funk and C. Muller, *Z. anorg. allgem. Chem.*, **244**, 94 (1940); (c) W. Blitz, *ibid.*, **109**, 132 (1919); (d) M. Oranskaya, Y. Lebedev, and I. Perfilova, *Zh. Neorgan. Khim.*, **6**, 259 (1961).

(3) (a) R. E. McCarley and J. W. Roddy, *Inorg. Chem.*, **3**, 54 (1964); (b) R. E. McCarley and J. W. Roddy, *ibid.*, **3**, 60 (1964).

(4) (a) H. Schäfer, H. Jacob, and K. Etzel, *Z. anorg. allgem. Chem.*, **286**, 42 (1956); (b) *ibid.*, **286**, 27 (1956); (c) H. Schäfer, E. Weiss, and F. Wartenpfull, *ibid.*, **295**, 268 (1958); H. Schäfer, E. Weiss, and F. Wartenpfull, *Angew. Chem.*, **69**, 479 (1957).

(5) J. Simons and M. Powell, *J. Am. Chem. Soc.*, **67**, 75 (1945).