Contribution No. 2491 from the Institute for Atomic Research and Department of Chemistry,
Iowa State University, Ames, Iowa 50010

Vaporization Reactions of Vanadium Iodides and Evidence for Gaseous Vanadium(IV) Iodide[1]

By K. O. Berry, R. R. Smardzewski, and R. E. McCarley[2]

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Evidence for the presence of VI_4 in the vapor phase has been obtained through a study of the transpiration of $VI_2(s)$ in I_2 vapor. Transpiration data taken as a function of P_{I_2} over the range 495–722°K were treated in terms of the reaction $VI_2(s) + I_2(g) = VI_4(g)$, for which $\log K = -3040T^{-1} + 2.18$, $\Delta H° = 13.9 \pm 0.4$ kcal mol^{-1}, and $\Delta S° = 10.0 \pm 0.6$ eu. Equilibrium dissociation pressures over VI_3–VI_2 mixtures were measured in a glass diaphragm gauge. For the reaction $2VI_3(s) = 2VI_2(s) + I_2(g)$, $\log [P_{I_2}\,(\text{atm})] = -4960T^{-1} + 6.28$, $\Delta H° = 22.70 \pm 0.14$ kcal mol^{-1}, and $\Delta S° = 28.74 \pm 0.20$ eu over the range 671–746°K. At lower temperatures the reaction reached equilibrium too slowly to permit measurements. Reactions between VI_2 and excess liquid iodine at temperatures up to 273° for periods of 5–30 days also failed to provide complete conversion to VI_3. Evidence for solid solution formation between VI_2 and VI_3 was negated. The X-ray powder pattern of VI_3 was indexed on the basis of the hexagonal BiI_3 structure and the refined lattice constants $a = 6.919 \pm 0.002$ Å and $c = 19.91 \pm 0.01$ Å were obtained.

Introduction

Previous investigations of the vaporization processes for several vanadium halide systems in this laboratory have shown the existence of VBr_4[3] and provided evidence for mixed halides $VX_{4-n}Y_n$ (X = Cl, Br; Y = Br, I) formed in reaction of Br_2 or I_2 with VX_2 or VX_3 solid phases at elevated temperature.[4] Because of the relative importance of VBr_4 in the vaporization reactions of VBr_3 it was of interest to investigate the corresponding reactions of VI_2 or VI_3 with the prospect of identifying the unknown VI_4.

At the time this work was started the conditions for synthesis of pure VI_3 were inadequately defined, and the compound was poorly characterized. Although Klemm and Grimm[5] obtained VI_2 by reaction between vanadium metal and iodine at *ca.* 400°, other workers[6–8] have reported formation of VI_3 under different conditions. In particular, we were unable to obtain pure VI_3 by the method of Tolmacheva, *et al.*,[8] which consisted of producing a deposit of vanadium iodide on the surface of vanadium foil during its reaction with liquid iodine at 300°.

Probably the most convenient preparation leading to pure, highly crystalline VI_3 makes use of reaction between V and I_2 in a sealed tube under a temperature gradient such that V is at >400° and I_2 is at about 250–300°. Under these conditions VI_3 is transported to the lower temperature as it is formed and deposited as large micaceous crystals.[9] As shown below this chemical transport is facilitated by the formation of VI_4 *via* (1) or (2) depending on the temperature and I_2 pressure.

$$VI_2(s) + I_2(g) = VI_4(g) \tag{1}$$

$$2VI_3(s) + I_2(g) = 2VI_4(g) \tag{2}$$

Experimental Section

Materials.—The vanadium metal used in this work was high-purity material which had been refined by the iodide-crystal bar process followed by electron-beam melting and was kindly furnished by Professor O. N. Carlson of this laboratory. Before use in the reactions with iodine, the metal was cold-rolled into a thin foil. Iodine was purified by grinding reagent grade crystals with potassium iodide and subliming twice *in vacuo.* Standard drybox procedures were followed during handling of the hygroscopic vanadium iodides.

Vanadium(III) Iodide.—This compound was prepared by the transport reaction between V and I_2 in a sealed Vycor tube which was maintained in a temperature gradient of 549–243° with V at the higher temperature. After 5 days yields of 70% were attained. The VI_3 deposited as large black platelets in a region of the tube at about 350°. Upon removing this product from the reaction tube the crystals were outgassed *in vacuo* to eliminate traces of iodine. *Anal.* Calcd for VI_3: V, 11.8; I, 88.2. Found: V, 11.9 ± 0.1; I, 87.7 ± 0.2 (average of four analyses).

Vanadium(II) Iodide.—Bronze, powdered VI_2 was obtained from thermal decomposition of VI_3 under dynamic vacuum at temperatures in the range 300–500°. *Anal.* Calcd for VI_2: V, 16.7; I, 83.3. Found: V, 16.6; I, 83.4.

Analytical Procedures.—When large samples were available, V was determined by titration of VO^{2+} with standard $KMnO_4$ solution. For small samples the V was determined spectrophotometrically as the intensely colored complex with phosphotungstic acid.[10] Iodide was determined both by titration of I^- with $AgNO_3$ solution and by titration of I_2 with standard $Na_2S_2O_3$ solution.

Transpiration Measurements.—The equilibrium vaporization of VI_2 in I_2 vapor was studied by transpiration using a cell of the type described previously.[3] In these measurements only iodine vapor was used as the carrier gas. The iodine was placed in a flask equipped with a Teflon vacuum stopcock and outgassed thoroughly on the vacuum line. Subsequently the iodine flask was joined directly to the transpiration cell through glass tubing which was maintained at an elevated temperature to prevent condensation of iodine during the experiments. The iodine was held at constant temperature in an oil bath to regulate the pressure of iodine admitted to the transpiration cell. This pressure was measured with a glass diaphragm gauge which was connected to the gas inlet on the cell.

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] Author to whom correspondence should be addressed.

[3] R. E. McCarley and J. W. Roddy, *Inorg. Chem.*, **3**, 54 (1964).

[4] R. E. McCarley, J. W. Roddy, and K. O. Berry, *ibid.*, **3**, 50 (1964).

[5] W. Klemm and L. Grimm, *Z. Anorg. Allgem Chem*, **249**, 198 (1942).

[6] A. Morette, *Compt. Rend.*, **207**, 1218 (1938).

[7] M. Chaigneau, *Bull. Soc. Chim. France*, 886 (1957).

[8] T. A. Tolmacheva, V. M. Tsintsius, and L. V. Andrianova, *Russ. J. Inorg. Chem.*, **8**, 281 (1963); *Zh. Neorgan. Khim.*, **8**, 553 (1963).

[9] H. Schäfer, private communication.

[10] E. R. Wright and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **9**, 251 (1937).

The flow rate of iodine was regulated with the Teflon stopcock on the iodine flask and measured by weighing the quantity of iodine which passed through the cell during each experiment. At 608°K over the range from 14.5 to 54.2 mg min^{-1} the apparent vapor pressure of vanadium iodide was found to be independent of the iodine flow rate. All subsequent measurements were made within this range.

All details of loading, outgassing, and operation of the transpiration cell were as described previously.[3] At the end of each experiment the weight of iodine passed through the cell, the time elapsed, the temperature of the cell, the iodine pressure, and the weight of transported vanadium (as vanadium iodides) were recorded. The latter was determined after opening the cell, removing the deposit of transported vanadium iodide by washing the condenser with water, and determining the total amount of vanadium by analysis. The reaction temperature was measured with a calibrated chromel–alumel thermocouple attached to the cell at a position adjacent to the VI_2 sample.

Calculation of P_{VI_4}, the partial pressure of $VI_4(g)$ present in each experiment, was made in the following way. The mole fraction of vanadium iodide X_V in the collected vapor was given by $X_V = n_V/(n_V + n_{I_2})$, where n_V and n_{I_2} were the total number of moles of V and I_2, respectively. Under the conditions prevailing in these experiments (see under discussion) the total pressure $P_t = P_{VI_4} + P_{I_2}$ can be reduced to $P_t = P_{I_2}$, since $P_{VI_4} \ll P_{I_2}$. The pressure of VI_4 is then obtained from $P_{VI_4} = X_V P_t = X_V P_{I_2}$.

Diaphragm Gauge Measurements.—The equilibrium iodine pressure over VI_3–VI_2 mixtures was measured in a Vycor diaphragm gauge of the type described previously.[3] A 50:50 wt % mixture of VI_3 and VI_2, ground to pass through a 200 mesh screen, was outgassed in the gauge at 250° for 7 hr prior to sealing the sample chamber from the vacuum system. Three chromel–alumel thermocouples were used to measure the temperature at the bottom, middle, and top of the sample chamber. The gauge was positioned in a Marshall furnace so that a small temperature gradient of 1–8° was imposed along the sample chamber, with the higher temperature at the top. In this way the deposition of VI_3 on the diaphragm by chemical transport was avoided. The sample temperature was indicated by the thermocouple at the bottom of the gauge. Temperature control was maintained to within ± 0.5° by control of the power supply to the furnace with a Honeywell electronically proportioning controller. Measurements were made at *ca.* 10° intervals in both ascending and descending steps. Pressures were read visually to within ±0.2 mm on a mercury manometer after balancing the pressure across the diaphragm with argon. The average time to reach equilibrium at each temperature was *ca.* 1 hr, except at the lower end of the range where several hours was required. Measurements below 350° were impractical because approach to equilibrium was too slow (>48 hr).

The observed pressures were corrected for a residual pressure (29.1 mm at 273°K) which resulted from slight hydrolysis after the gauge was sealed. A correction was also applied for dissociation of I_2 into atomic iodine at the higher temperatures of the experiment. The data given by DeVries and Rodebush[11] were employed for this correction.

Equilibrations of VI_2 in Liquid Iodine.—In the early stage of this work some evidence indicated that VI_2 and VI_3 had formed solid solutions. To investigate this more carefully samples of VI_2 were equilibrated at various temperatures with liquid iodine in sealed Pyrex tubes. After a given time (up to 4 weeks) the tube was cooled to room temperature, iodine was removed by sublimation *in vacuo* at 100°, and the vanadium iodide residue was subjected to chemical as well as X-ray powder diffraction analysis.

X-Ray Diffraction Data.—All samples were ground to pass through a 200 mesh screen and sealed in 0.2-mm Lindemann glass capillaries under an argon atmosphere. Ni-filtered Cu Kα radiation was used in conjunction with a 11.46-cm Debye–Scherrer powder camera. The patterns were corrected for film shrinkage and other effects by utilizing the diffraction lines of tungsten as a standard.[12] After indexing the powder pattern, final lattice constants were calculated by the refinement method of Taylor and Sinclair[13] and Nelson and Riley.[14]

Results and Discussion

Transpiration of $VI_2(s)$ in Iodine Vapor.—The data relevant to reaction 1 are summarized in Table I.

TABLE I

EQUILIBRIUM CONSTANTS AND PRESSURES FOR THE REACTION $VI_2(s) + I_2(g) = VI_4(g)$

T, °K	P_{I_2}, Torr	$10^3 P_{VI_4}$, Torr	$10^3 K$(obsd)	$10^3 K$(calcd)[a]
630	21.8	57.3	2.62	2.27
539	21.7	7.40	0.341	0.344
548	21.6	9.33	0.432	0.433
514	21.6	5.12	0.237	0.185
569	21.8	18.2	0.834	0.692
636	21.7	37.6	1.74	2.52
529	21.4	7.78	0.364	0.272
610	21.3	29.6	1.39	1.59
719	20.2	152	7.54	9.02
722	20.4	211	10.3	9.42
713	20.3	134	6.59	8.30
699	20.2	173	8.56	6.82
533	44.8	14.2	0.316	0.303
521	45.0	8.73	0.194	0.222
561	45.2	15.2	0.336	0.585
621	45.4	79.2	1.74	1.94
684	46.6	347	7.43	5.46
712	46.4	407	8.78	8.18
684	30.5	180	5.90	5.46
597	30.8	33.0	1.07	1.56
620	30.7	69.5	2.26	1.91
582	30.8	27.4	0.891	0.908
495	30.5	2.92	0.096	0.110
529	30.4	9.08	0.299	0.270
581	30.8	26.3	0.855	0.889
608	30.6	52.5	1.72	1.52
608	30.8	46.9	1.52	1.52
608	30.3	52.9	1.75	1.52
608	30.4	51.6	1.70	1.52
608	40.5	69.7	1.72	1.52
608	11.4	19.5	1.71	1.52
608	20.7	35.4	1.72	1.52

[a] Calculated from the equation $\log K = -3040T^{-1} + 2.18$.

Over the temperature range of the measurements, 495–722°K, the vapor pressure of VI_2 is estimated to be $\leq 10^{-5}$ Torr, if it is assumed to be comparable to that of VCl_2 or VBr_2.[15] Since the observed pressures were larger by a factor of 10^4, it was apparent that vapor transport by chemical reaction occurred in this system. In addition to (1) other reactions which may be considered to account for the transport of VI_2 are (3) and (4).

$$VI_2(s) + 0.5I_2(g) = VI_3(g) \tag{3}$$

$$2VI_2(s) + I_2(g) = V_2I_6(g) \tag{4}$$

Both (3) and (4) are highly unlikely because the pressure of $VI_3(g)$ or $V_2I_6(g)$ cannot exceed the vapor pressure of $VI_3(s)$. In this temperature range the latter

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[11] T. DeVries and W. H. Rodebush, *J. Am. Chem. Soc.*, **49**, 656 (1927).

[12] M. Straumanis and A. Ievins, *Z. Physik*, **98**, 461 (1936).

[13] A. Taylor and H. Sinclair, *Proc. Phys. Soc.* (London), **57**, 126 (1945).

[14] J. Nelson and D. Riley, *ibid.*, **57**, 160 (1945).

[15] R. E. McCarley and J. W. Roddy, *Inorg. Chem.*, **3**, 60 (1964).

Table II

Equilibrium Constants for the Reaction $2VI_3(s) = 2VI_2(s) + I_2(g)$

T, °K	K(obsd), atm	K(calcd), atm[a]
746.4	0.433	0.431
741.6	0.397	0.390
739.5	0.385	0.373
732.6	0.329	0.323
726.1	0.283	0.281
722.6	0.254	0.260
719.3	0.245	0.242
716.9	0.229	0.230
713.9	0.216	0.215
710.9	0.198	0.200
708.9	0.190	0.192
706.7	0.180	0.182
706.5	0.181	0.181
702.5	0.159	0.165
702.1	0.164	0.163
696.1	0.139	0.142
694.4	0.135	0.137
693.5	0.135	0.134
689.5	0.120	0.122
686.6	0.114	0.114
684.7	0.110	0.108
680.1	0.096	0.097
675.9	0.088	0.087
675.9	0.088	0.087
672.1	0 081	0.079
671.5	0.078	0.078

[a] Calculated from the equation log $[K\text{ (atm)}] = -4960T^{-1} + 6.28$.

Table III

X-Ray Powder Data for VI_3

hkl	d, Å Calcd	d, Å Obsd[a]
003	6.636	6.65 (1)
110	3.460	3.45 (3)
006	3.318	3.31 (4)
113	3.068	3.06 (10)
116	2.395	2.393 (5)
009	2.212	2.212 (0.5)
300	1.997	1.997 (8)
303	1.913	1.911 (0.5)
119	1.864	1.863 (4)
220	1.730	1.729 (0.5)
306	1.711	1.711 (3)
223	1.674	1.674 (4)
0,0,12	1.659	1.658 (1)
226	1.534	1.534 (1)
1,1,12	1.496	1.495 (0.5)
229	1.363	1.363 (2)
413	1.283	1.284 (3)
3,0,12	1.276	1.277 (3)
327	1.238	1.240 (1)
416	1.217	1.217 (2)
2,2,12 500	1.197	1.200 (0.5)
330	1.153	1.154 (1)
419	1.126	1.126 (3)
0,3,15	1.105	1.106 (0.5)
336	1.089	1.089 (1)
1,1,18	1.053	1.054 (2)

[a] All intensities were estimated visually relative to a value of 10 for the most intense line; intensity values are given in parentheses.

is estimated[16] to vary from 10^{-8} to 10^{-2} Torr, which is much too low to support the observed transport. Reaction 3 is eliminated, and (1) is affirmed by data taken at 608°K as a function of P_{I_2}. A plot of P_{VI_4} *vs.* P_{I_2} at this temperature is linear as required by $P_{VI_4} = KP_{I_2}$ for (1) and passes through the origin as required, if vaporization in the absence of I_2 is negligible. Thus the data strongly support VI_4 as the sole vapor species responsible for transport of VI_2 in these experiments.

Least-squares treatment of the data for (1) given in Table I yields the expression log $K = -(3040 \pm 91)T^{-1} + 2.18 \pm 0.15$ over the range 495–722°K. The average values of the enthalpy and entropy of the reaction are $\Delta H° = 13.9 \pm 0.4$ kcal mol^{-1} and $\Delta S° = 0.6$ eu, respectively. Combining $\Delta H°$ for (1) with the estimated $\Delta H_f°(VI_2(s))$ (from V and gaseous iodine) $= -78 \pm 3$ kcal mol^{-1},[8] we get $\Delta H_f°(VI_4(g)) = -64 \pm 3$ kcal mol^{-1}. Since heat capacity data are not available for vanadium iodides, these values are uncorrected for differences in temperature.

Diaphragm Gauge Data.—At temperatures above 300° $VI_3(s)$ undergoes dissociation *via* reaction 5.

$$2VI_3(s) = 2VI_2(s) + I_2(g) \tag{5}$$

This reaction is utilized in the preparation of VI_2 by thermal decomposition of VI_3 *in vacuo* at >300°. Since the pressure of I_2 resulting from (5) is large compared to the pressure of VI_4 (<1 Torr), $VI_3(g)$, or $VI_2(g)$ (both of the latter ≪1 Torr), the total pressure over a VI_3–VI_2 mixture is a measure of the equilibrium constant of (5).

The equilibrium pressure data for (5) are given in Table II. Great care was taken to attain the equilibrium condition at each temperature, because at the lower temperatures the reaction was very slow and up to 48 hr was required. At <330° equilibrium was not attained within a reasonable time. Least-squares treatment of the data provided the expression log P_{I_2}(atm) $= -(4960 \pm 30)T^{-1} + 6.28 \pm 0.04$ over the range 671–746°K. For a standard state of 1 atm the derived thermodynamic quantities are $\Delta H° = 22.70 \pm 0.14$ kcal (mol of I_2)$^{-1}$ and $\Delta S° = 28.74 \pm 0.20$ eu.

After completion of the pressure measurements, X-ray powder patterns of the mixture from the gauge showed that only VI_2 and VI_3 were present, thus eliminating the possibility of solid solution formation. The results of our measurements are in good agreement with those of Tolmacheva, *et al.*,[8] who obtained $\Delta H° = 22 \pm 1$ kcal mol^{-1} and $\Delta S° = 27 \pm 1$ eu over the range 591–804°K.

Addition of reactions 1 and 5 leads to the disproportion reaction (eq 6), for which $\Delta H° = 36.6 \pm 0.5$ kcal

$$2VI_3(s) = VI_2(s) + VI_4(g) \tag{6}$$

mol^{-1} and $\Delta S° = 38.7 \pm 0.8$ eu over the range 495–746°K. These values may be compared with those for the reaction $2VBr_3(g) = VBr_2(s) + VBr_4(g)$, where $\Delta H° = 37.7$ kcal mol^{-1} and $\Delta S° = 34.7$ eu over a comparable temperature range.[3]

Vanadium(III) Iodide.—In early attempts to prepare VI_3 by reaction of V and I_2 in a sealed tube under a temperature gradient of 600–180°, crystalline products having I:V = 2.2–2.3 were obtained. Because initial X-ray powder patterns of these products did not reveal the lines of pure VI_2, solid solution formation between

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[16] Here the assumption is made that the vapor pressure of VI_3 will not be much different from that of VBr_3 as given in ref 15.

VI_2 and VI_3 was suspected. Subsequently a series of equilibration reactions between VI_2 and excess liquid I_2 was performed at various temperatures for times of 5–30 days. The solid products resulting from reactions at 196, 215, and 238° were found to have I:V ratios of 2.33, 2.55, and 2.61, respectively. Thus solid solution formation seemed to be confirmed.

However, when these products were thoroughly ground to pass completely through a 200 mesh screen, lines of VI_2[5] were clearly evident in the X-ray powder patterns along with the original lines noted above. The latter set of lines was subsequently found to match the pattern of pure VI_3, which proved that the "equilibration" reactions had produced only mixtures and not solid solutions. It is quite remarkable that complete conversion of VI_2 to VI_3 in such reactions is not attained after several weeks, even at temperatures up to 273°. Apparently a layer of VI_3 is formed on the crystals of VI_2, and this impedes or nearly halts further conversion to VI_3.

Successful preparation of pure VI_3 may be effected as noted in the Experimental Section. To facilitate the reaction the V metal should be kept at a temperature greater than *ca.* 500° and I_2 should be at 240–300°. Precautions should be taken to prevent damage to equipment or injury to personnel in the event of explosion of the reaction tubes, since the tubes must contain *ca.* 5–10 atm of I_2.

The black micaceous crystals of VI_3 were found to have the hexagonal BiI_3 structure. After assigning indices to all lines in the powder pattern the following lattice constants were obtained from the refinement calculations: $a = 6.919 \pm 0.002$ Å, $c = 19.91 \pm 0.01$ Å, $c/a = 2.876$. The observed and calculated d spacings are given in Table III.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
CORNELL UNIVERSITY, ITHACA, NEW YORK 14850

Isolation and Characterization of Diborazinylamine[1]

BY MAITREYI CHAKRAVORTY AND RICHARD F. PORTER

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The reactions of B-monoaminoborazine with diborane, BF_3, and HBr have been investigated. A slightly volatile product sublimed from the reaction products has been identified mass spectrometrically as $B_6N_7H_{11}$. Evidence from mass, infrared, and boron-11 nmr spectra indicate the compound is diborazinylamine.

Introduction

In the large number of publications in borazine chemistry relatively little work has been reported on the reactions of B-monosubstituted borazine derivatives. Only quite recently have experimental studies with B-monochloroborazine been published.[2] We recently described a photochemical procedure for the preparation of B-monoaminoborazine[3] in quantities adequate for chemical study. Since this compound contains a terminal amino group, it was anticipated that new derivatives could be obtained by its reactions with Lewis acids. In this paper, results of a series of studies of the reactions of aminoborazine with B_2H_6, BF_3, and HBr are discussed.

Experimental Section

Samples of B-monoaminoborazine were prepared by the photolysis of borazine–ammonia mixtures.[3] Aminoborazine was identified by its infrared spectrum.[3] Some experiments were conducted with amino(^{15}N)borazine which was prepared from $^{15}NH_3$ and borazine with the natural isotopic composition. Most experiments were performed with samples weighing between 50 and 20 mg. The reactants were mixed by adding the acid, initially in the gas phase, to the liquid aminoborazine and then freezing the mixture to −196°. The reaction vessel was then warmed to room temperature and the reaction was allowed to proceed for several hours. The unreacted acid was then removed. For quantitative stoichiometry measurements the samples of aminoborazine were weighed in a Pyrex tube containing a break-seal, and the quantity of acid added was determined from initial and final pressure measurements. The borazine used was prepared from NH_4Cl and $LiBH_4$[4] and purified by the addition of ammonia[3] to remove aminodiborane.

B-Monoaminoborazine–B_2H_6 Reaction.—Reaction between aminoborazine and B_2H_6 produced a white polymeric substance that evolved hydrogen at room temperature. After the evolution of hydrogen ceased, the residue was sublimed *in vacuo* at 25° for several hours and a slightly volatile substance was collected in a small Pyrex bulb held at −13° in a glycol slush bath. When this material was resublimed at 50°, needlelike crystals condensed on the cooler walls of the vessel. A mass spectrum of this material is given in Table I. Similar experiments starting with amino(^{15}N)borazine yielded a substance whose mass spectrum is also given in Table I. The infrared spectrum of a solid film of the

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[2] R. Maruca, O. T. Beachley, Jr., and A. W. Laubengayer, *Inorg. Chem.*, **6**, 575 (1967).

[3] G. H. Lee, II and R. F. Porter, *ibid.*, **6**, 648 (1967).

[4] G. W. Schaeffer, R. Schaeffer, and H. J. Schlesinger, *J. Am. Chem. Soc.*, **73**, 1612 (1951).