Boron–Fluorine Chemistry. III. Silicon–Boron Fluorides

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Abstract: A study has been made of the volatile products of some reactions of the gaseous high-temperature species silicon difluoride, boron monofluoride, silicon atoms, and boron atoms, with silicon and boron fluorides at −196°. Two new silicon–boron fluorides, $F_2Si(BF_2)_2$ and $FSi(BF_2)_3$, have been isolated in small yield and characterized. Other volatile products have mainly been known silicon, boron, and silicon–boron fluorides, but in all cases smaller amounts of volatiles have been formed than intractable, pyrophoric polymers.

The first mixed silicon–boron fluorides to be reported were the thermally stable compounds $Si_2F_5BF_2$, $Si_3F_7BF_2$, and higher homologs.[2] They were made by condensing the high-temperature species silicon difluoride with boron trifluoride on a liquid-nitrogen-cooled surface.

The success of the above method in synthesizing a previously inaccessible group of compounds suggested that other silicon–boron fluorides might be made by related reactions. Accordingly, a study has been made of some of the reactions of four gaseous high-temperature species, silicon difluoride, boron monofluoride,[3] silicon atoms,[4] and boron atoms,[5] with silicon tetrafluoride, boron trifluoride, and diboron tetrafluoride, at −196°. It was hoped that from among such reactions would emerge both ways of making boron-rich silicon–boron fluorides, and of making the simplest silicon–boron fluoride, SiF_3BF_2, which is not formed from silicon difluoride and boron trifluoride.[2]

Experimental Section

Formation and Reaction of the High-Temperature Species. Boron atoms were prepared by electron bombardment evaporation of boron as described by Timms.[5] A diagram of the apparatus is shown elsewhere.[6] In a run, a rate of evaporation of about 1.3 mmoles/min could be maintained for a maximum of 30–40 min.

Silicon atoms were prepared by electron bombardment evaporation of silicon in the same system used for making boron atoms. Evaporation occurred from a molten drop of 99.9% pure silicon at about 1800°, and could be maintained at a rate of about 0.6 mmole/min for up to 60 min. It is believed that at least 99% of the vapor was Si_1, in its ^3P ground electronic state.

Boron monofluoride was prepared from boron and boron trifluoride at 1800–2000° as previously described.[3] During a run, a rate of formation of BF of 2.0 mmoles/min could be maintained for about 40 min.

Silicon difluoride was easily prepared from silicon and silicon tetrafluoride at 1200°.[2] It could be generated for long periods at a rate of about 1.5 mmoles/min.

Reaction of silicon tetrafluoride with boron was carried out in the apparatus used for the preparation of boron monofluoride.[3] Silicon tetrafluoride (Matheson 99.5% pure) was used in place of boron trifluoride and passed over boron at 1800–2000° in a graphite tube, at a rate of 0.5–1.5 mmoles/min. The pressure of gas over the boron was about 1–3 Torr. As with the preparation of boron monofluoride, each run was terminated after about 40 min by partial blocking of the outlet from the graphite tube by deposited boron carbide.

This reaction was used because it conveniently formed BF and SiF_2 simultaneously. The composition of the gas emerging from the hot zone was not measured experimentally. Calculations based on data in the JANAF tables[7] showed that the only species likely to be present were BF, BF_3, SiF_2, and SiF_4, and that BF would predominate at equilibrium. Under the flow conditions used it is unlikely that equilibrium was reached. However, the abundance of the species was probably in the order $BF > SiF_2 > BF_3 > SiF_4$. Variations in the relative amounts of products obtained by condensing the high-temperature species at −196° were observed from run to run. These variations reflected changes in the composition of the mixture of high-temperature species. Changes could be induced by altering the rate of addition of SiF_4 or the temperature, but they also occurred randomly, perhaps caused by subtle variables such as the surface state of the hot boron.

With the exception of silicon difluoride,[2] the high-temperature species were passed directly from the hot zone where they were formed to a surface at −196° with a minimum of intermolecular or wall collisions. Silicon or boron fluorides condensed with them were added in excess to give at least a 3:1 mole ratio on the cold surface.

At the end of a run, the cold surface was allowed to warm to room temperature and liberated volatiles were pumped continuously into a glass vacuum line.

Purification and Characterization of Compounds. Volatile products were handled in vacuum lines employing greaseless O-ring stopcocks, and they were separated either by conventional trap-to-trap fractional condensation, or on a low-temperature fractionation column.[8]

Vapor pressures were measured using a modified Stock apparatus[9] consisting of a small mercury-sealed volume with an external manometer. Data for liquid $F_2Si(BF_2)_2$ and $FSi(BF_2)_3$ are shown in Table I.

Vapor densities were measured on about 10-mg samples in a calibrated constant volume system using a mercury manometer for measuring the pressure.

Mass spectra were taken on either an AEl Model MSlOC2 or a Bendix Model 1400 time-of-flight machine. The spectra of $F_2Si(BF_2)_2$ and $FSi(BF_2)_3$ are summarized in Table II.

^{19}F nmr spectra were run on neat samples of the silicon–boron fluorides on a Varian HA-100 machine at 94.1 MHz, using CCl_3F as reference either externally or in a sealed capillary in the samples.

Infrared spectra were taken on the samples in the vapor phase in a 6-cm gas cell with sodium chloride windows using a Perkin-Elmer Infracord or Model 227 spectrophotometer. The principal absorptions seen in the spectra of $F_2Si(BF_2)_2$ and $FSi(BF_2)_3$ are as follows [frequency, cm^{-1} (intensity)]: $F_2Si(BF_2)_2$, 1443 (w), 1395 (m), 1351 (s), 967 (m), 937 (s), 866 (s), 844 (m); $FSi(BF_2)_3$, 1403 (s), 1370 (vs), 1355 (vs), 1325 (m), 1278 (m), 1254 (m), 1215 (vs), 879 (s).

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(1) Send correspondence to this address.

(2) P. L. Timms, T. C. Ehlert, J. L. Margrave, F. E. Brinckmann, T. C. Farrar, and T. D. Coyle, *J. Amer. Chem. Soc.*, **87**, 3819 (1965).

(3) P. L. Timms, *ibid.*, **89**, 1629 (1967).

(4) P. S. Skell and P. W. Owen, *ibid.*, **89**, 3933 (1967).

(5) P. L. Timms, *Chem. Commun.*, 258 (1968).

(6) P. L. Timms, *Endeavour*, **27**, 133 (1968).

(7) "JANAF Thermochemical Tables," Thermal Research Laboratory, Dow Chemical Co., Midland, Mich., 1965.

(8) For a partial description of this column, see D. Solan and P. L. Timms, *Inorg. Chem.*, **7**, 2157 (1968).

(9) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p 192.

Table I

$F_2Si(BF_2)_2$	T, °C	−21.0	−13.0	0.0	+14.0			(39.0) est
	p_{Torr}	26.4	43.1	100.6	223.7			760
Log p = 9.050 − 1925/T ΔH_{vap} = 8.8 kcal/mole								
Troutons constant = 28.1 eu								
$FSi(BF_2)_3$	T, °C	17.4	25.9	31.9	36.6	40.3	46.8	(67.9) est
	p_{Torr}	62.0	103.0	142.0	180.0	219.0	295.0	760
Log p = 9.194 − 2153/T, ΔH_{vap} = 9.9 kcal/mole								
Troutons constant = 28.7 eu								

Table II. Mass Spectra of $F_2Si(BF_2)_2$ and $FSi(BF_2)_3$ at 70 eV

		Relative intensity[a]	
m/e	Ion	$F_2Si(BF_2)_2$	$FSi(BF_2)_3$
66	SiF_2^+	40	
77	$SiBF_2^+$	Small	16
79	$B_2F_3^+$	38	29
85	SiF_3^+	17	14
96	$SiBF_3^+$	*100*	22
109	$B_3F_4^+$		13
115	$SiBF_4^+$	42	24
126	$SiB_2F_4^+$	Small	*100*
145	$SiB_2F_5^+$	55	23
164	$SiB_2F_6^+$	1	
175	$SiB_3F_6^+$		49
194	$SiB_3F_7^+$		

[a] Corrected to 100% ^{11}B, 100% ^{28}Si.

Results

1. The System BF + SiF_2 + BF_3 + SiF_4. The gaseous mixture resulting from the reaction of silicon tetrafluoride with boron at 1800–2000° gave a brown solid on condensation at −196°. On warming, the condensate liberated the known compounds BF_3, B_2F_4, SiF_4, Si_2F_6, Si_3F_8,[10] and $Si_2F_5BF_2$,[2] which were identified by their infrared and mass spectra. In addition, there was another compound difficult to separate from Si_3F_8 and $Si_2F_5BF_2$ because of its similar volatility.

The infrared spectrum of this other compound showed two regions of absorptions at 800–1000 cm^{-1} corresponding to Si–F stretches and at 1200–1450 cm^{-1} corresponding to B–F stretches. The Si–F stretch region was less complex than in the known silicon–boron fluorides.

The mass spectrum confirmed that the compound contained only silicon, boron, and fluorine. There were no ions in the spectrum of higher *m/e* than a group at 162–166. This group of ions also had the lowest appearance potential of any in the spectrum. The most intense group of ions was at *m/e* 95–98. These groups corresponded respectively in both mass and isotope distribution to $SiB_2F_6^+$ and $SiBF_3^+$. Thus the formula of the compound was indicated as SiB_2F_6, with the ion $SiBF_3^+$ being formed by loss of BF_3 on electron impact, a facile process with many boron–fluorine compounds.[3] The vapor density was measured as 165 ± 2 (required for SiB_2F_6 163.7) confirming the molecular formula.

The ^{19}F nmr spectrum of liquid SiB_2F_6 at −40° showed only two resonances at 48.2 and 146.9 ppm upfield of the reference CCl_3F, with an area ratio of approximately 2:1. The lower field resonance, a singlet, was close to the resonances due to $-BF_2$ groups in $Si_2F_5BF_2$ and $Si_3F_7BF_2$.[1] The higher field resonance, a broad singlet, was in a similar position and of similar width to the $-SiF_2-$ group in $Si_2F_5BF_2$. This strongly suggested a structure $F_2Si(BF_2)_2$ for the compound.

The compound reacted with chlorine gas at −30° to form only SiF_2Cl_2, BF_3, and BCl_3 giving further evidence that the structure was $F_2Si(BF_2)_2$.

Difluorobis(difluoroboro)silane is a pyrophoric compound which slowly decomposes in an inert atmosphere above 30°, liberating boron trifluoride and forming a solid polymer. It melts at −47° and has an estimated boiling point of +39°.

The yield of difluorobis(difluoroboro)silane was poor. Only about 5% of the boron consumed in the reaction with silicon tetrafluoride appeared in the compound. Most of the boron was contained in a brownish white polymer which remained on the surface used for condensation after all the volatiles had been pumped away. This polymer, in common with the polymers formed in each of the reactions below, was pyrophoric and not soluble in inert solvents.

2. The Reaction of Silicon Atoms with Boron Trifluoride. Silicon atoms reacted with boron trifluoride at −196° forming mainly an involatile polymeric material which contained free silicon. Some silicon tetrafluoride was produced, together with very small amounts of B_2F_4 and Si_2F_6. From deposition of 1 g of silicon about 1 mg of B_2F_4 plus Si_2F_6 was obtained. However, the mass spectrum of the mixture of B_2F_4 and Si_2F_6 which had been carefully freed from traces of more or less volatile components, showed an intense group of ions at *m/e* 114–117 in addition to the normal fragments from B_2F_4 and Si_2F_6. This group of ions corresponded in mass and relative abundance to $SiBF_4^+$. A silicon–boron fluoride of very similar volatility to B_2F_4 and Si_2F_6 could have been SiF_3BF_2. On electron impact this would have probably lost F or BF_3, to give $SiBF_4^+$ or SiF_2^+, and no parent molecular ion. The SiF_2^+ peak was present in the spectrum but would have also come from fragmentation of Si_2F_6.

3. The Reaction of Silicon Atoms with Diboron Tetrafluoride. Gaseous silicon was condensed on a cold surface at −196° at the same time as gaseous diboron tetrafluoride. On warming the condensate, excess B_2F_4 was pumped off followed by a trace of $F_2Si(BF_2)_2$ and a small yield of a less volatile new compound. A brown, air-sensitive polymer remained which dissolved smoothly and completely in dilute hydrofluoric acid showing that it contained no elemental silicon.

The mass spectrum of the new volatile compound showed no ions of higher *m/e* than a group at 172–177

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(10) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Amer. Chem. Soc.*, **87**, 2824 (1965).

corresponding to $SiB_3F_6^+$. However, the ions most prominent at low electron voltage were a group at m/e 124–128 corresponding to $SiB_2F_4^+$. As has already been stated, loss of BF_3 on electron impact is a common process with boron–fluorine compounds, and it may occur instead of formation of a parent molecular ion. The mass spectrum thus suggested a molecular formula SiB_3F_7. This was confirmed by the vapor density of the compound measured as 191 ± 2 (required for SiB_3F_7, 193.5).

The ^{19}F nmr spectrum of SiB_3F_7 taken at 20° showed only two features, a large, rather broad doublet at 39.0 ppm on the high-field side of CCl_3F, and a smaller singlet at +234 ppm. The area ratio of the resonances was 6:1. The position of the lower field resonance was similar to that in compounds such as $(BF_2)_3BCO$[3] which contain three $-BF_2$ groups joined to one atom. The doublet structure with a splitting of 160 Hz was typical of a ^{11}B to ^{19}F quartet collapsed by the ^{11}B quadrupole. The higher field resonance was in a position anticipated for a single fluorine atom joined to silicon. This spectrum showed the structure of the compound to be $FSi(BF_2)_3$.

As required for a structure $FSi(BF_2)_3$, the infrared spectrum showed only a single Si–F stretching frequency at 869 cm^{-1}. The shape and positions of the absorptions in the B–F stretching region from 1200 to 1400 cm^{-1} closely resembled those in $(BF_2)_3BCO$.[3]

Fluorotris(difluoroboro)silane is, like the other silicon–boron fluorides, pyrophoric. It melts at 11.5° and has an estimated boiling point of 68°. It decomposes slowly at room temperature into polymers and boron trifluoride.

The yield of fluorotris(difluoroboro)silane was only about 2% of theoretical based on the silicon deposited on the cold surface.

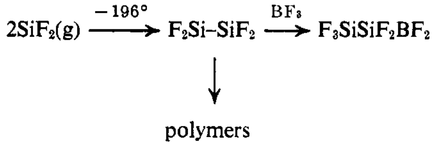
4. The Reaction of Silicon Difluoride with Diboron Tetrafluoride. Cocondensation of silicon difluoride with diboron tetrafluoride at −196° gave a blue solid. On warming, this evolved a small amount of BF_3, excess SiF_4 and B_2F_4, a little Si_2F_6, and a mixture of slightly less volatile compounds containing one extremely unstable component. Wherever this mixture was condensed it deposited a yellow polymer, and a mixture of the relatively stable compounds BF_3, SiF_4, Si_3F_8, $Si_2F_5BF_2$, and $F_2Si(BF_2)_2$ could be pumped away. Unlike other silicon or boron fluorides, the vapor of the unstable part of the fraction caused rapid blackening of Kel-F grease. The unstable part seemed of similar volatility to Si_3F_8, $Si_2F_5BF_2$, and $F_2Si(BF_2)_2$ (see below), and thus it could have been SiF_3BFBF_2. The only known monosubstituted diboron fluoride is F_2BBFBF_2, and this decomposes at −50°.[3] However, it has not yet been possible to get more definite evidence of the nature of the unstable compound.

5. The Reactions of Boron Atoms and Boron Monofluoride with Silicon Tetrafluoride. When boron atoms were condensed with silicon tetrafluoride at −196°, only a very small amount of the silicon tetrafluoride reacted. The products were a little boron trifluoride, and an involatile black, boron-rich solid. Nothing less volatile than silicon tetrafluoride was detected.

Cocondensation of boron monofluoride and silicon tetrafluoride at −196° gave mainly the products formed by condensing boron monofluoride alone.[3] As in the reaction of silicon atoms and boron trifluoride, the diboron tetrafluoride formed contained a tiny amount of a silicon–boron fluoride. The mass spectrum of the fraction showed there was no Si_2F_6 present; thus the ions observed at m/e 66 (SiF_2^+) and 114–117 ($SiBF_4^+$), distinguishable from ions in the spectrum of B_2F_4, could have come from SiF_3BF_2.

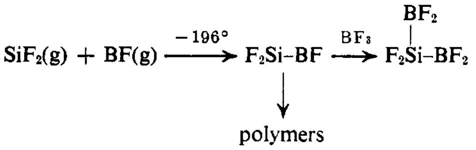
Discussion

The mechanism of the formation of $Si_2F_5BF_2$ from silicon difluoride and boron trifluoride at low temperature has been shown previously[11] to involve the steps



$$\begin{tikzcd} 2SiF_2(g) \arrow[r, "-196°"] & F_2Si\text{–}SiF_2 \arrow[r, "BF_3"] \arrow[d] & F_3SiSiF_2BF_2 \\ & \text{polymers} & \end{tikzcd}$$

The formation of $F_2Si(BF_2)_2$ by condensing a mixture of BF, BF_3, SiF_2, and SiF_4 may take a similar path, *viz.*



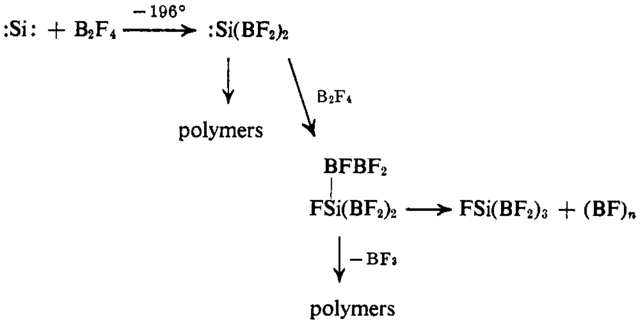
$$\begin{tikzcd} SiF_2(g) + BF(g) \arrow[r, "-196°"] & F_2Si\text{–}BF \arrow[r, "BF_3"] \arrow[d] & F_2\overset{\overset{BF_2}{|}}{Si}\text{–}BF_2 \\ & \text{polymers} & \end{tikzcd}$$

The rate of polymerization of radical intermediates in the above schemes could be much faster at −196° than the rate of addition of boron trifluoride, accounting for the low yields of volatile products.

The mechanism for the formation of $FSi(BF_2)_3$ from silicon atoms and diboron tetrafluoride is less easily rationalized. Tucker[12] has observed that carbon atoms react with diboron tetrafluoride at −196° forming some $C(BF_2)_4$, presumably by a double carbene insertion

$$:C: + B_2F_4 \xrightarrow{-196°} :C(BF_2)_2 \xrightarrow{B_2F_4} C(BF_2)_4$$

However, $Si(BF_2)_4$ was certainly not liberated in the reaction of silicon atoms and diboron tetrafluoride. A plausible scheme for this latter reaction might be



$$\begin{tikzcd} :Si: + B_2F_4 \arrow[r, "-196°"] & :Si(BF_2)_2 \arrow[d] \arrow[dr, "B_2F_4"] & & \\ & \text{polymers} & F\overset{\overset{BFBF_2}{|}}{Si}(BF_2)_2 \arrow[r] \arrow[d, "-BF_3"] & FSi(BF_2)_3 + (BF)_n \\ & & \text{polymers} & \end{tikzcd}$$

There is no reason why SiF_3BF_2 should be less stable than other silicon–boron fluorides. The failure to form this compound in more than trace amounts in any of the reactions which have been tried may arise from two

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(11) J. M. Bassler, P. L. Timms, and J. L. Margrave, *Inorg. Chem.*, 5, 729 (1966).

(12) P. Tucker, Ph.D. Thesis, University of Bristol, 1968.

Table II. Physical Properties of Silicon and Silicon–Boron Fluorides

Compound	Mp, °C	Bp, °C	Trouton's constant, eu
Si_3F_8	-1	$+42$	27.8
Si_4F_{10}	$+66$	$+85$	30.2
$F_3SiSiF_2BF_2$	0	$+42$	29.2
$F_3Si(SiF_2)_2BF_2$	$+11$	$+85$	32.6
$F_2Si(BF_2)_2$	-47	$+39$	28.1
$FSi(BF_2)_3$	$+11$	$+68$	28.7

effects. First, there must be a high activation energy for the direct insertion reaction $SiF_4 + BF \rightarrow SiF_3BF_2$, although the analogous reaction $BF_3 + BF \rightarrow B_2F_4$ goes readily at $-196°$.[3] Second, most other reactions of the high-temperature species probably form a radical intermediate containing at least a two-atom skeleton as the first step which then reacts with a boron fluoride to form a final molecule with at least a three-atom skeleton. The molecule Si_2F_6, which was often a reaction product, may have been formed during the polymerization of radical intermediates[1,10] rather than by a direct process.

Table II shows collected physical data for the silicon–boron and silicon fluorides. The similar volatility of the three perfluorinated compounds containing Si_3, Si_2B, and SiB_2 skeletons indicates little difference in polar character for $-SiF_3$ and $-BF_2$ groups. The properties of $FSi(BF_2)_3$ should only be compared with those of iso-Si_4F_{10} which have not been reported.

Acknowledgments. This work was sponsored in part by the Army Research Office, Durham. One of us (P. L. T.) is grateful to the Trustees of the Ramsay Memorial Fellowships for present support.

Ammonia Exchange in Manganese(II)–Liquid Ammonia Solutions

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Abstract: Kinetic information on the $Mn(NH_3)_6{}^{2+}$–$NH_3(l)$ exchange reaction was obtained. The value for k_1 (25°) from the rate law $R = 6k_1[Mn(II)]$ is $3.6 \pm 0.3 \times 10^7$ sec^{-1}; $\Delta H^* = 8 \pm 0.5$ kcal/mole and $\Delta S^* = 5 \pm 3$ cal mole^{-1} deg^{-1}. The results are very similar to those for the aquo system. Comparisons with related studies are made.

The study reported here is a part of a general nmr program in exchange kinetics of labile species in aqueous and nonaqueous solutions. Comparisons of kinetic parameters among systems of differing metals and solvents may aid in an understanding of the mechanisms of reaction. An understanding of the behavior of solvated species is needed in order to approach more complex processes.

Experimental Section

We have employed ^{14}N nmr techniques as in previous studies.[2] The equipment used has been described.[3] An important modification was that a 24.6-kG Varian magnet was employed. The ^{14}N resonance in ammonia was observed at 7.56 MHz. Sample temperatures were controlled to within ±0.2° using a thermostated ethanol circulation system. Signal enhancement was obtained by using a Fabri-tek 1052 LSH signal averager.

Liquid ammonia and air-free solutions were prepared and handled using standard vacuum-line techniques. Other reagents used were $Mn(ClO_4)_2 \cdot 6H_2O$, *prepared from* $MnCO_3$ *and* $HClO_4$, recrystallized from water, and analyzed; NH_4ClO_4 was prepared from analytical reagent grade NH_4OH and $HClO_4$. Drying the manganese salt by repeated condensation and evaporation of ammonia produced no changes in observed results. All solutions contained 1.63×10^{-2} M NH_4ClO_4 although no effects were noted due to $NHClO_4$, $NaClO_4$, or $NaNO_3$ at that concentration or tenfold higher.

Results

No chemical shifts in the $^{14}NH_3$ nmr line could be observed (>20 ppm). The line-broadening data are given in Table I. The quantity Δ' is the line broadening, in gauss, produced by addition of Mn(II). It is the difference in full line widths, measured at half-maximum intensity in the absorption curve, for the Mn(II) and the reference solutions. The reference was identical in composition with the manganese solution except that $Zn(ClO_4)_2$ was substituted for manganese. The measured line width of the reference (which varied from 0.20 to 0.11 G over the temperature range) was within 0.02 G of that for pure ammonia. The quantity P_MT_{2p} is equal to $2P_M/\gamma\Delta'$, where P_M is the fraction of ^{14}N nuclei bound to manganese (assuming 6 NH_3/Mn) and γ is the magnetogyric ratio for ^{14}N (1934 G^{-1} sec^{-1}).

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[1] To whom inquiries should be addressed. This work supported by U.S.A.E.C. Contract No. AT(45-1)-2040 and is Report No. RLO-2040-13.

[2] H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 1061 (1965).

[3] R. Murray, H. W. Dodgen, and J. P. Hunt, *ibid.*, **3**, 1576 (1964).