(*meso*)-2,3-butanediol, were the same as used in this study. In order to be able to compare rate constants between the two systems, it was first necessary to correct the periodate values (which were measured at 0° and at a *p*H value of about 9.1) for the presence of $H_3IO_6^=$ so that they would fit the rate equation

$$\text{Rate} = k_f[IO_4^-][G] - k_r[IO_4G^-]$$

Comparison of the resultant rate constants with the tellurate values (see Table V) shows a remarkable correlation of the constants for the systems with ethylene glycol and propylene glycol but some divergence with (*meso*)-2,3-butanediol. If it is assumed that K_D for the tellurate system is about 0.01 and recalling that $k_{fc} = k_r/K_D$, it turns out that the forward rate constants for the two anions are of the same order of magnitude. This similarity in order of magnitude and the fact that several workers[16,17,20-22] have shown that the periodate oxidation of glycols probably involves the tetrahedral IO_4^- ion, makes it seem logical to assume that a similar species is involved in the formation of the polyol tellurate complexes, namely the isoelectronic $TeO_4^=$. However, it should be emphasized that this correlation between tellurate and periodate data is based on limited information; the agreement that there is could be coincidental. Runs with several other polyols including pinacol and some cyclic diols should be done in both systems before any further conclusions are made.

TABLE V

COMPARISON OF PERIODATE[a] AND TELLURATE[b] RATE AND EQUILIBRIUM CONSTANTS

Constant and system	Eth. gly.	Prop. gly.	*m*-2,3-But.
k_f(periodate)[c]	4300	2100	1300
k_f(tellurate)[c]	24.8	13.8	3.08
k_r(periodate)[d]	23	4.2	19
k_r(tellurate)[d]	2.66	0.676	0.302
Kc_1(periodate)	189	500	68
Kc_1(tellurate)	15.0	33.0	16.5

[a] Periodate rate constants at 0° from ref. 20; see text. [b] Tellurate constants at 25°. [c] k_f in units of M^{-1} sec.$^{-1}$. [d] k_r in units of sec.$^{-1}$.

Acknowledgments.—We are grateful to the Office of Ordnance Research, U. S. Army, for financial aid. H.R.E. is grateful to E. I. du Pont de Nemours and Co. for a Teaching Fellowship.

(21) F. R. Duke, *J. Am. Chem. Soc.*, **69**, 3054 (1957).

(22) V. C. Bulgrin, *J. Phys. Chem.*, **61**, 702 (1957).

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The Preparation of Boron Triisothiocyanate and Some Molecular Addition Compounds

BY D. B. SOWERBY[1]

RECEIVED AUGUST 11, 1961

Boron trichloride reacts with either sodium or potassium thiocyanate in liquid sulfur dioxide to give boron triisothiocyanate. This compound, analogous to the boron trihalides, has Lewis acid characteristics and forms molecular addition compounds with nitrogen donor molecules such as tertiary amines and nitriles. The addition compounds with acetonitrile, benzonitrile and phenylacetonitrile can be prepared from the corresponding boron trichloride adducts and potassium thiocyanate in liquid sulfur dioxide. The infrared spectra of the addition compounds are presented.

Introduction

The boron trihalides and the tendency for these compounds to form molecular addition compounds with electron-pair donor molecules are well known. On the other hand, the pseudo-halogen derivatives of boron are less well characterized and no reactions have been reported which lead to similar Lewis acid-base adducts. The known boron pseudohalides have been listed by Lappert and Pyszora.[2] Although substituted boron isothiocyanates are known, the existence of the parent compound, boron triisothiocyanate is in doubt. The substance was reported to result from treatment of boron tribromide with silver thiocyanate in benzene suspension,[3a] but this could not be confirmed.[3b] The successful use of soluble ionic thiocyanates in acetonitrile or liquid sulfur dioxide as a means of preparing non-metallic isothiocyanates from the corresponding chlorides[4] led to an examination of similar reactions with boron trichloride and some of its molecular addition compounds.

Experimental

Boron triisothiocyanate.—Anhydrous sodium thiocyanate (26 g., 0.32 mole), or an equivalent amount of potassium thiocyanate, was added portionwise to a stirred solution of 13.0 g. (0.11 mole) of boron trichloride in 200 ml. of liquid sulfur dioxide, cooled to −30°. After a few minutes, a white precipitate began to form and the mixture was stirred vigorously for approximately 4 hr. The solution then was cooled to −60° and filtered in the absence of moisture. During removal of the sulfur dioxide from the filtrate under aspirator vacuum, the solution progressively darkened and finally yielded an orange semi-solid mass, which was immediately transferred to a vacuum distillation apparatus. Heating this material gave a pale brown liquid, which on redistillation gave 7.5 g. (38% yield) of a colorless liquid with a boiling point of 92° at 0.1 mm.

Anal. Calcd. for $B(NCS)_3$: C, 19.44; N, 22.69. Found: C, 19.55; N, 22.92.

The compound is miscible with benzene, and on cooling the solution, a white solid, rapidly turning yellow resulted.

Anal. Calcd. for $B(NCS)_3$: NCS^-; 94.17. Found: C, 19.20; N, 22.48; NCS^-, 93.9.

The solid decomposed on heating at ~115°. Although the empirical formula was that of the boron triisothiocyanate, this solid no longer dissolved completely in benzene. Similar solids resulted when the liquid boron isothiocyanate was added to either chloroform or *n*-heptane.

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(2) M. F. Lappert and H. Pyszora, *Proc. Chem. Soc.*, 350 (1960).

(3) (a) H. E. Cocksedge, *J. Chem. Soc.*, **93**, 2177 (1908). (b) E. Pohland, *Z. anorg. u. allgem. Chem.*, **201**, 282 (1931).

(4) D. B. Sowerby, *J. Inorg. & Nuclear Chem.*, in press.

Reactions with Tertiary Amines.—A slight excess of pyridine was added to a solution of 1 g. of boron triisothiocyanate in 10 ml. of benzene. Heat was evolved but no solid separated on cooling. The solvent was removed under vacuum leaving a non-sublimable white solid, which was recrystallized from a warm mixture of benzene and *n*-heptane; m.p. 118–120°.

Anal. Calcd. for $B(NCS)_3 \cdot C_5H_5N$: C, 36.35; H, 1.89; N, 21.10; NCS^-, 66.0. Found: C, 36.43; H, 2.07; N, 21.25; NCS^-, 65.7.

Triethylamine reacted similarly to give the boron triisothiocyanate addition compound melting at 102–104°.

Anal. Calcd. for $B(NCS)_3 \cdot (C_2H_5)_3N$: C, 37.75; H, 5.24. Found: C, 37.89; H, 5.45.

Reactions with Nitriles.—Boron triisothiocyanate is miscible with both acetonitrile and phenylacetonitrile. Evaporation in vacuum of a solution of 2 g. of the isothiocyanate in 20 ml. of acetonitrile gave a pale yellow solid which on sublimation at 0.1 mm. with a bath temperature of 90–100° gave 1.9 g. (79% yield) of the addition compound.

Anal. Calcd. for $B(NCS)_3 \cdot CH_3CN$: C, 26.54; H, 1.33; N, 24.77; NCS^-, 77.1. Found: C, 26.29; H, 1.43; N, 24.76; NCS^-, 77.4.

On heating, a sample darkened at ~115° and melted to a dark liquid at 137°. Similarly a solution of 2 g. of boron isothiocyanate in phenylacetonitrile gave on sublimation 2.5 g. (77% yield) of the nitrile adduct.

Anal. Calcd. for $B(NCS)_3 \cdot C_6H_5CH_2CN$: C, 43.69; H, 2.32. Found: C, 43.84; H, 2.53.

This compound darkens at ~90° and melts with decomposition at 95–96°. The sublimation of this adduct was accompanied by appreciable decomposition, and the product, although originally white, very rapidly turned brown on standing.

Reactions with Boron Trichloride Addition Compounds. (i) **Nitriles.**—To a well-stirred solution containing 7.1 g. (0.045 mole) of resublimed boron trichloride–acetonitrile addition compound in 175 ml. of liquid sulfur dioxide cooled to −25°, there was added portionwise 13.0 g. (0.134 mole) of anhydrous potassium thiocyanate. A white precipitate formed, and after stirring for 2 hr. the solution was cooled and filtered giving 9.3 g. (calcd. 10.0 g.) of potassium chloride. The filtrate was evaporated to dryness and the remaining solid was sublimed in vacuum, giving 6.9 g. (73% yield) of the boron isothiocyanate adduct, identical with that obtained above.

Anal. Found: C, 26.46; H, 1.33.

Similarly, the benzonitrile and phenylacetonitrile-boron isothiocyanate compounds were obtained from the corresponding boron trichloride addition compounds. The benzonitrile compound melted with decomposition at 105–106°.

	Yield (%)	Calcd.	Found
$B(NCS)_3 \cdot C_6H_5CN$	89	C, 41.65; H, 1.74	C, 41.72; H, 1.90
$B(NCS)_3 \cdot C_6H_5CH_2CN$	56	NCS^-, 57.7	NCS^-, 57.5

(ii) **Tertiary Amines.**—No reaction took place within 5 hr. when the boron trichloride addition compounds with pyridine and trimethylamine were treated with three moles of potassium thiocyanate in liquid sulfur dioxide at −25°.

Infrared Spectra.—Infrared spectra were recorded using a Perkin-Elmer, model 21 spectrometer.

Discussion

Complications arise from the use of liquid sulfur dioxide as reaction medium for the preparation of boron triisothiocyanate as described above. Although solutions of boron trichloride in liquid sulfur dioxide are stable, solvolysis takes place in the presence of chloride ion, yielding boric oxide and thionyl chloride as final products.[5] The thionyl chloride so produced then also could react with the ionic thiocyanate giving thionyl thiocyanate, which decomposes on warming to room temperature giving polythiocyanogen and other nonvolatile products.[6,7] However, the rate of solvolysis of boron trichloride under the conditions employed is sufficiently slow to allow this method to be used. The low yield and the insoluble residues remaining after the first distillation indicate that appreciable solvolysis does occur during the preparation. The compound prepared by this method is referred to as an isothiocyanate; the evidence in favor of this is from the infrared spectrum.

Two substances, a liquid and a solid, were obtained, both having the empirical formula of boron triisothiocyanate. The liquid could be redistilled without evidence of crystallization and on cooling to −20° a white solid, liquefying before regaining room temperature, resulted. The mixed halide-pseudohalide, $BBr(NCS)_2$, is also a liquid at room temperature[2] with a boiling point of 80° at 0.15 mm.—a value comparable to that of the triisothiocyanate. The fact that the solid modifications no longer dissolve in benzene may be due to polymerization of the isothiocyanate. Aggregation of this type has been observed with other nonmetallic isocyanates and isothiocyanates.

Boron triisothiocyanate is comparable to the boron trihalides in that the valence shell contains six electrons only, and the compound might be expected to show Lewis acid characteristics. In agreement with this is the isolation of 1:1 molecular addition compounds with electron pair donor molecules such as acetonitrile, benzonitrile, phenylacetonitrile, pyridine and triethylamine. Further reactions with other donor molecules are in progress. As an alternative method for the preparation of such addition compounds, the corresponding boron trichloride addition compounds were used as starting materials. Although the chlorine atoms in three nitrile adducts were readily replaced by thiocyanate groups, similar reactions with the trimethylamine and pyridine compounds were not successful. Boron triisothiocyanate and the nitrile addition compounds are very hygroscopic and treatment with dilute sodium hydroxide solution brings about rapid decomposition to borate and thiocyanate. The tertiary amine adducts are not soluble in water, and warming with alcoholic potassium hydroxide solution was necessary to effect decomposition.

Infrared Spectra. Boron Triisothiocyanate.—The infrared spectrum of boron triisothiocyanate, measured as a capillary film, showed absorption maxima at the following frequencies ($cm.^{-1}$): 760s,[8] 968ms, 1068w, 1115vw, 1310vs.br, 1600w, 1840w, 2010vs.br, 2360w, 2595w, 2780w, 2930w. In benzene solution, the strong band at 1310 $cm.^{-1}$ was resolved into two peaks at 1308s and 1344wm, and a shoulder appeared at 2110 $cm.^{-1}$ in addition to the intense broad band at 2010 $cm.^{-1}$. The bands at 968 and 2010 $cm.^{-1}$ are characteristic of the isothiocyanate group[2,4] (the symmetric and asymmetric NCS stretching vibrations respectively), and thus the compound involves bonding

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[5] A. B. Burg and E. R. Birnbaum, *J. Inorg. & Nuclear Chem.*, **7**, 146 (1958).

[6] G. Jander and D. Ullman, *Z. anorg. u. allgem. Chem.*, **230**, 405 (1937).

[7] P. W. Schenk and H. Blocking, *Chem. Ber.*, **92**, 2333 (1959).

[8] w, weak; m, medium; s, strong; v, very; br, broad; sh, shoulder.

of the thiocyanate groups through nitrogen rather than sulfur. If the nitrogen atoms use sp^2 hybrids, the linear NCS groups will be attached to the boron atom making an angle of 120°. However, there will be a tendency toward coplanarity of the molecule due to back-donation of the nitrogen unshared pair of electrons to the empty boron p orbital. Interaction similar to this is postulated to account for bond shortening in the boron trihalides.

Compounds of the type $B(NR_2)_3$ and $B(NHR)_3$ show strong absorption in the region between 1400 and 1500 cm.$^{-1}$, correlated with the B–N asymmetric stretch.[9] Increasing amounts of $p\pi$–$p\pi$ interaction account for shifts toward higher frequencies. The only strong absorption in this region of the boron isothiocyanate spectrum is at 1308 cm.$^{-1}$, and this is correlated with the B–N asymmetric stretch. Some confirmation of this assignment is the resolution of this maximum in benzene solution to show a weaker absorption on the high frequency side. The separation of the two peaks (36 cm.$^{-1}$) and the relative intensities are close to those expected for the isotopic splitting of the asymmetric stretching vibration.

Boron Triisothiocyanate–Pyridine.—The spectrum of the boron triisothiocyanate–pyridine addition compound was obtained using the potassium bromide disk technique and the major absorptions are listed in Table I. Katritzky[10] and, more recently, Greenwood and Wade[11] have assigned the bands in the spectrum of the corresponding boron trichloride compound. In general, maxima associated with the coördinated pyridine occur at similar frequencies. The asymmetric and symmetric isothiocyanate stretches appear as an intense doublet at 2100 and 2040 cm.$^{-1}$ and a band of medium intensity at 975 cm.$^{-1}$, respectively. Two strong bands at 1080 and 1115 cm.$^{-1}$, with indications of fine structure, appear in the isothiocyanate spectrum, in contrast to a single strong absorption in this region of the spectrum of the boron trichloride compound (1113 cm.$^{-1}$). Greenwood and Wade[11] assigned the latter to the boron–nitrogen stretching vibration but indicate that this is not certain although it is associated with the formation of the boron–nitrogen coördinate bond. The situation with the analogous isothiocyanate compound is more complex, as the change in hybridization at the boron atom will cause the symmetric, as well as the asymmetric boron–nitrogen stretching vibration to be infrared active. It will be difficult under these circumstances to isolate absorption due to the boron–nitrogen (pyridine) stretch. In the free isothiocyanate, the asymmetric boron–nitrogen stretch occurs at 1310 cm.$^{-1}$, but in the pyridine complex, the possibility for $p\pi$–$p\pi$ interaction between the nitrogen and boron atoms is removed, and a lowering of the vibrational frequency would be expected. There may be other effects due to the change in hybridization at the boron atom. It seems likely, therefore, that the complex absorption in the 1100 cm.$^{-1}$ region is due to boron–nitrogen stretching vibrations.

TABLE I

INFRARED SPECTRUM OF $B(NCS)_3 \cdot C_5H_5N$

685m[a,b]
720s
755w[b]
770s[b]
805w
950w[b]
975wm[c]
1015m[b]
1030w
1080vs[d]
1115vs[d]
1123sh[d]
1138sh[d]
1165m[b]
1218m[b]
1265w[b]
1410w[b]
1465s[b]
1494m[b]
1545w[b]
1575w[b]
1625m[b]
1653w
2040vs[c]
2100vs[c]
3040w[b]
3080w[b]

[a] For meaning of abbreviations, see ref. 8. [b] Absorption due to coördinated pyridine. [c] Symmetric and asymmetric NCS stretching vibrations. [d] Absorption due to B–N vibrations.

TABLE II

INFRARED SPECTRA OF TRIETHYLAMINE ADDITION COMPOUNDS

$BF_3 \cdot Et_3N$ capillary film	$BCl_3 \cdot Et_3N$ KBr disk	$B(NCS)_3 \cdot Et_3N$ KBr disk	Et_3N capillary film	
660sh				
665m				B–F
	703s			B–Cl
	725m			B–Cl
760s	750m	740vs	735s	
	765m			B–Cl
		773m		
	784vw			
790w	794w	795w	780w	
805w	815m	812m	800mw	
855w	865m	865s	900w	
900s	895s	900s	920w	
925sh				B–F
		975mw		*sym*-NCS
1020w	1015m	1015w	1000m	
1038w	1038w	1038w	1025w	
1075sh	1077w		1075s	
			1090sh	
		1076s		
		1088sh		B–N
1100s	1100s	1110s		
	1110w			
1150s				B–F
1180s	1170s	1170s	1140s	
1203sh	1190m	1190m	1210s	
1315m	1318w	1310w	1300s	
1350w	1345w	1345w	1352w	
1378wm	1375w	1370w	1365w	
1400sh	1388w			
1410s	1402s	1400s	1390s	
		1410sh		
	1455sh			
1470s	1463s	1458s	1460s	
1490s	1478s	1478s	1480s	
2060w				
		2090vs.br		*asym*-NCS
	2860w	2850w	2830s	
2920sh	2920sh	2920sh	2930sh	
2990s	2980m	2980s	2990s	

Triethylamine Adducts.—The spectra of the boron trifluoride, trichloride and triisothiocyanate addition compounds with triethylamine are summarized in Table II. A capillary film of triethyl-

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[9] D. W. Aubrey, M. F. Lappert and H. Pyszora, *J. Chem. Soc.*, 5239 (1960).

[10] A. R. Katritzky, *ibid.*, 2049 (1959).

[11] N. N. Greenwood and K. Wade, *ibid.*, 1130 (1960).

amine showed the maxima listed in the final column of the table; no analysis of this spectrum has been reported. Bands considered comparable, *i.e.* arising from the presence of coördinated triethylamine, are listed in the same horizontal row of the table. The asymmetric and symmetric B–F stretching vibrations have been assigned[10] respectively to maxima at 1150 and 911 cm.$^{-1}$ [for $BF_3\cdot(CH_3)_3N$] and 1165 and 893 cm.$^{-1}$ [for $BF_3\cdot C_5H_5N$]. However, the pyridine complex also was examined by Luther, Mootz and Radwitz[12] who assigned absorption at 900 and 695 cm.$^{-1}$ to these B–F vibrations. The triethylamine–boron trifluoride spectrum has bands at 1150, 925 and 665 cm.$^{-1}$ which are absent in the spectra of the other complexes and are apparently associated with the BF_3 group. These probably result from the two stretching vibrations and a deformation mode. Corresponding absorptions for the boron trichloride analog appear at 703, 725 and 765 cm.$^{-1}$. The spectrum of the isothiocyanate compound showed the expected bands at 2090 and 975 cm.$^{-1}$ associated with the isothiocyanate stretching vibrations.

The spectrum of the isothiocyanate compound in the 1100 cm.$^{-1}$ region is similar to that found with the pyridine adduct. While the boron trifluoride and trichloride–triethylamine compounds each show a strong, sharp maximum at 1100 cm.$^{-1}$, the isothiocyanate adduct gives two strong bands at 1076 and 1110 cm.$^{-1}$, with evidence of fine structure. This similarity with the pyridine complex would indicate that these maxima also are associated with B–N vibrations. Triethylamine has a strong absorption band at 1075 cm.$^{-1}$, but in the trichloride and trifluoride compounds this appears in a similar position (1077 and 1075 cm.$^{-1}$, respectively) with greatly reduced intensity. It is unlikely then that the strong absorption at this position in the isothiocyanate adduct is due entirely to this band of triethylamine. However, the spectra of boron trihalide–trimethylamine compounds in chloroform solution have been reported,[10] with a band at 1249 cm.$^{-1}$ being assigned to the B–N stretch in the boron trifluoride compound.

Nitrile Adducts.—The nitrile addition compounds show the asymmetric isothiocyanate stretching frequency as a strong doublet at 2130 and 2060 cm.$^{-1}$ for acetonitrile and 2140 and 2050 cm.$^{-1}$ for benzonitrile. Weaker absorption at 2350 and 2305 cm.$^{-1}$, respectively, can be assigned to the $C\equiv N$ stretching vibration of the coördinated nitrile group. As is the case with the boron halide–nitrile addition compounds,[13,14] this absorption occurs at higher frequencies than in the free nitrile.

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[12] H. Luther, D. Mootz and F. Radwitz, *J. prakt. Chem.*, [4], **5**, 242 (1958).

[13] H. J. Coerver and C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958).

[14] W. Gerrard, M. F. Lappert, H. Pyszora and J. W. Wallis, *J. Chem. Soc.*, 2182 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIFORNIA]

The Hybrid Diphosphine $(CH_3)_2PP(CF_3)_2$[1,2]

BY LOUIS R. GRANT, JR., AND ANTON B. BURG

RECEIVED NOVEMBER 21, 1961

The new diphosphine $(CH_3)_2PP(CF_3)_2$ (m.p. −79°; b.p. est. 120°) was made from $(CH_3)_2PH$ and $(CF_3)_2PCl$ at −78°, with or without $(CH_3)_3N$ to remove HCl. Its ultraviolet spectrum is more like that of $P_2(CH_3)_4$ than $P_2(CF_3)_4$. It is far less stable than either of these, apparently because the respective P atoms offer electron donor and acceptor action, as shown by its 1:1 adducts with BH_3 and with $(CH_3)_3N$. Its protolytic cleavage gives high yields of $(CF_3)_2PH$ with the anion going to the $(CH_3)_2P$ group, in accord with thermochemical expectations. Methyl iodide causes it to disproportionate, forming mostly $P_2(CF_3)_4$ and apparently $(CH_3)_2PP(CH_3)_3{}^+I^-$.

The widely different chemical behavior of the diphosphines $P_2(CH_3)_4$[3] and $P_2(CF_3)_4$[4] makes it difficult to predict the properties of the intermediate diphosphines having P-CH_3 and P-CF_3 bonds in the same molecule. Accordingly we have made and explored the chemical character of one such intermediate type, namely, 1,1-dimethyl-2,2-bis-(trifluoromethyl)-diphosphine; and in fact it is found that some of its properties are quite different from the mean between the extremes represented by $P_2(CH_3)_4$ and $P_2(CF_3)_4$. For example, it can be made from $(CH_3)_2PH$ and $(CF_3)_2PCl$ without using an additional base to remove the HCl—whereas $(CF_3)_2PH$ fails to react with $(CF_3)_2PCl$. Also, the $(CH_3)_2P$ group has good base action, whereby it can bond to such an electron acceptor as a BH_3 group; and the $P(CF_3)_2$ group has a tendency toward electron-acceptor bonding, accounting for the formation of a $(CH_3)_3N$ adduct. Then also $(CH_3)_2PP(CF_3)_2$ molecules can attack their own kind in the donor–acceptor manner, causing a far lower thermal stability than observed

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[1] The name "diphosphine" (instead of "biphosphine") for a substitution derivative of P_2H_4 conforms to the most recent IUPAC report on inorganic nomenclature. To avoid confusion, the class of double phosphines having P-(chain)-P connections can be distinguished by the term "bis-phosphines," related to individual names such as 1,2-bis-(dimethylphosphino)-ethane; *cf.* ref. 3.

[2] This research is described in fuller detail in Chapter II of the Ph.D. dissertation by Louis R. Grant, Jr., University of Southern California Libraries, 1961. It was initiated under Office of Naval Research Contract Nonr-228(13) but was supported primarily by the United States Air Force under a subcontract of Prime Contract AF 33(616)-5435, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[3] A. B. Burg, *J. Am. Chem. Soc.*, **83**, 2226 (1961), and other papers there cited.

[4] F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).