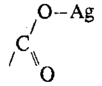
Gerstein et al.[35] have derived expressions for the magnetic susceptibility for a linear chain ($N = 2$, $S = 1/2$) with intermediate anisotropies, as indicated by the value for γ in eq 1. The equations are

$$\chi_{\parallel} = \frac{Ng_{\parallel}^2\beta^2}{kT} \frac{1}{1 + \exp(-J/kT)\cosh(J\gamma/kT)} \quad (5)$$

$$\chi_{\perp} = \frac{Ng_{\perp}^2\beta^2}{J(\gamma-1)} \frac{\exp(J\gamma/kT) - \exp(J/kT)}{\exp(J/kT) + \cosh(J\gamma/kT)} \quad (6)$$

The best mathematical fit of the data for $Ag(nic)_2$ to these equations was obtained with a value of γ outside the range $0.0 \leq \gamma \leq 1.0$ and thus was discarded. Calculations using reasonable values of J, $g_{\parallel}$, $g_{\perp}$, and γ did not yield good agreement.

Infrared spectra of solid KBr pellet specimens of uncomplexed nicotinic acid and of bis(nicotinato)silver(II) obtained here are in agreement with earlier results;[15] the broad absorption due to the asymmetric carbonyl stretch of the free acid at ~1700 cm^{-1} is shifted to 1630 cm^{-1} in the complex, which is characteristic of silver–carboxylate bonding in the manner[36]



Far-infrared spectra have confirmed the presence of silver–nitrogen bonds,[10] and roughly square-planar coordination about the silver(II) ions of $Ag(nic)_2$ has been postulated on the basis of visible spectroscopy.[10,22]

A structure for $Ag(nic)_2$, incorporating the specific inventory of structural clues listed above and capable of providing a pathway for the observed linear-chain type antiferromagnetic exchange in the complex is difficult to construct. Although Kleinstein and Webb[10] preferred a square-planar coordination for $Ag(nic)_2$, the six-coordinate structure that they proposed, in general, provides a chainlike pathway for magnetic exchange.

Magnetic exchange in complexes of silver(II) is probably not confined to the complex $Ag(nic)_2$. It has been established that magnetic interaction across pyrazine and quinoxaline bridges occurs in the compounds $Cu(pyr)(NO_3)_2$ and $Cu(quinox)(NO_3)_2$.[30,31] Since nitrogen-donor ligands stabilize the Ag(II) oxidation state, it ought to be possible to synthesize stable pyrazine (and pyrazine derivatives)-bridged silver(II) polymers exhibiting magnetic interaction such as that found for bis(nicotinato)silver(II).

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Registry No. $Ag(nic)_2$, 32068-84-1.

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Notes

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Structural Study of Phosphoryl Bromide by Means of Nuclear Quadrupole Resonance

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The crystal structure of phosphoryl bromide ($POBr_3$) was determined recently by Olie, *et al.*,[1] as orthorhombic, space group $Pn2_1a$. Later, the Templetons[2] reexamined the crystal structure on the basis of the data obtained by Olie, *et al.*, and concluded that there was no reason to reject *Pnma* as the correct space group because their calculations reduced the discrepancy index R below 11.3% in both space groups. Therefore, we investigated this compound by means of nuclear quadrupole resonance (nqr) in order to clarify its crystal structure and to examine the P–Br bond character.

Experimental Section

Phosphoryl bromide was purchased from Katayama Chemical Industries Co., Ltd. The single crystal was prepared by the Bridgman–Stockbarger method. The nqr spectrometer was a superregenerative oscillator with frequency modulation. The magnetic field used for the Zeeman study was provided by a Helmholtz coil with a field strength of about 200 G. The temperature of the sample was set at the desired value by controlling the flow rate of nitrogen gas over the sample.

Results and Discussion

Phosphoryl bromide shows two ^{81}Br resonance lines as seen in Table I. The intensity ratio of the lower line (ν_1) to the

Table I. Nuclear Quadrupole Resonance Frequencies, ν, Asymmetry Parameters, η, and Quadrupole Coupling Constants, e^2Qq, in Phosphoryl Bromide at Room Temperature

Resonance line	ν, MHz	η, %	e^2Qq, MHz
ν_1	197.48	2.7 ± 0.7	394.92
ν_2	198.34	3.0 ± 0.6	396.62

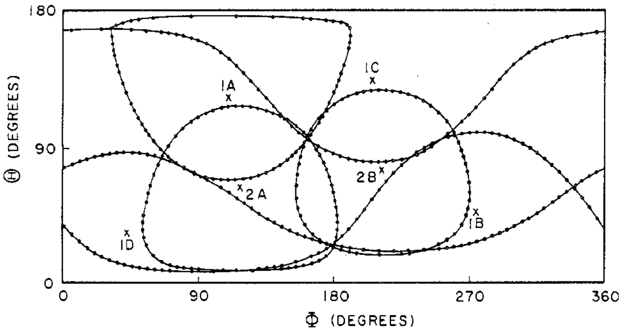

Figure 1. Zero-splitting patterns of ^{81}Br Zeeman lines in POBr$_3$.

higher line (ν_2) is about 2:1. The spectrum is similar to that of phosphoryl chloride[3] in which, however, the relative intensity is reversed.

The patterns of zero-splitting loci were obtained by measuring the Zeeman effect on each resonance line as shown in Figure 1. Four and two zero-splitting patterns were obtained for ν_1 and ν_2, respectively. When the orientations of the z axes were plotted on a globe, three mutually perpendicular twofold axes and a plane of symmetry were found. This finding suggests that the crystal is orthorhombic. However, it is impossible to distinguish between *Pn*2$_1$*a* and *Pnma* because the Zeeman analysis always introduces a center of symmetry to the crystal.[4] However, the number of resonance lines may discriminate between these space groups. In the case of space group *Pn*2$_1$*a*, three ^{81}Br resonance lines should be observed in accordance with the number of nonequivalent bromine atoms in the crystal. On the other hand, two resonance lines should be observed in *Pnma*. The temperature dependences of the resonance lines in phosphoryl bromide are shown in Figure 2. Only two resonance lines were observed in the range from +42 to −196°. Therefore, it is concluded that phosphoryl bromide forms orthorhombic crystal with a space group *Pnma* and that ν_1 and ν_2 are due to the bromine atoms (Br$_1$) situated out of a mirror plane and those (Br$_2$) in a mirror plane, respectively.

The angles between two P–Br bonds can be calculated by assuming that the z axis of the field gradient of bromine is parallel to that of the P–Br bond. The results thus obtained are shown in Table II along with the results of the X-ray analysis by the Templetons. The bond angles Br–P–Br obtained from the Zeeman analysis are 107.7, 107.7, and 107.6°. These values are larger by about 2° than those from the X-ray analysis.

The values for the asymmetry parameter of the electric field gradient are determined from the distortion of the zero-splitting loci. Once the asymmetry parameter is obtained, the quadrupole coupling constant can be calculated from the observed resonance frequency. The results are given in Table I.

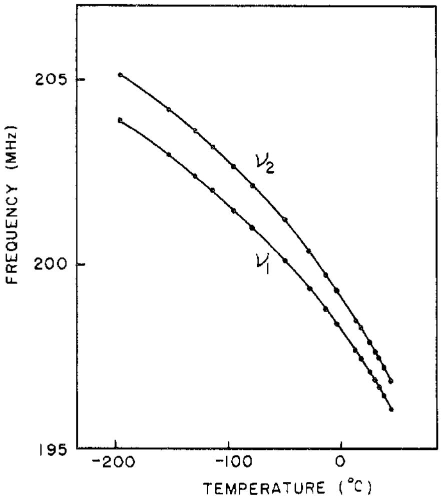

Figure 2. Temperature dependences of ^{81}Br nqr frequencies in POBr$_3$.

Table II. Angles between P–Br Bonds in Phosphoryl Bromide[a]

	Br$_{1A}$	Br$_{1B}$	Br$_{1C}$	Br$_{1D}$	Br$_{2A}$
Br$_{1B}$	165.2 (161.6)[b]				
Br$_{1C}$	70.2 (74.2)	107.7 (105.8)			
Br$_{1D}$	107.7 (105.8)	70.4 (74.2)	165.4 (161.6)		
Br$_{2A}$	60.7 (59.6)	107.7 (105.3)	107.4 (105.3)	60.9 (59.6)	
Br$_{2B}$	107.7 (105.3)	60.5 (59.6)	60.9 (59.6)	107.7 (105.3)	86.8 (83.0)

[a] The experimental error is about ±1°. [b] The value in parentheses is the angle calculated from ref 2.

According to the X-ray analysis, the P–Br bond lengths are 2.131 and 2.147 Å. These are somewhat shorter than the covalent single-bond length corrected for partial ionic character. The double-bond character estimated from the bond length by using the Pauling method[5] is about 10%, whereas that obtained from nqr data is so small as to be neglected. If the value of the covalent single-bond length estimated by Pauling and Huggins[6] is reliable, the P–Br bond must contain a dπ–pπ bond or a dπ–dπ bond in order to account for its shorter bond length. The participation of a dπ–pπ bond generally leads to a characteristic small negative or positive temperature coefficient. However, ν_1 and ν_2 show large negative temperature coefficients as reproduced in Figure 2. On the other hand, a dπ–dπ bond makes only negligible contributions to quadrupole coupling constant and asymmetry parameter of bromine. Therefore, it is concluded that there is little evidence for the π bonding between phosphorus and bromine from nqr data.

The X-ray analysis has revealed that the intermolecular distance between oxygen and bromine in the mirror plane is 3.07 Å which is considerably shorter than the sum of van der Waals radii. Consequently, the intermolecular bond will be formed by the charge transfer from oxygen to bromine. The charge from oxygen will enter the bonding orbital of bromine, and the quadrupole coupling constant of Br$_2$ will be lower than that of Br$_1$. This is in conflict with the results listed in Table I. This discrepancy may be attributed to the influence of the external charges, and so we calculated the electric field gradient due to external charges, using a point charge model. The z axis was chosen along the P–Br bond, while the x and y axes were taken in an arbitrary direction perpendicular to the z axis. The net charges were cited from the values of Wagner,[7] *i.e.*, $\rho_{Br} = -0.056$ e, $\rho_O = -0.596$ e, and $\rho_P = 0.766$ e. Calculations were performed for all external atoms in a sphere, which has its center at the resonant nucleus and a radius of 40 Å. The increments of the quadrupole coupling constants due to the external charges at the bromine atom are $-48(1-\gamma)$ kHz for ν_1 and $273(1-\gamma)$ kHz for ν_2. Here γ is the Sternheimer antishielding factor and its value is negative for the bromine ion.[8] This result indicates that the external charges decrease the quadrupole coupling constant of Br$_1$, while they increase that of Br$_2$, and this is the case. Unfortunately, it is difficult to evaluate the absolute values of the changes in the quadrupole coupling constants because the value of γ is still unknown for covalently bonded bromine.

Registry No. $\mathrm{POBr_3}$, 7789-59-5.

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Germanium Atoms in Synthesis

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The low-temperature cocondensation technique, originally developed for synthetic purposes by Skell,[1] has been extended to many elements and other short-lived molecular species,[2] and this, combined with the advances in matrix-isolation spectroscopy,[3] has opened new vistas to the chemist. Although carbon has been extensively studied,[4] few forays have been made into the chemistry of the remaining group IV elemental species.[5] We now wish to report on some reactions of germanium atoms whereby halides of carbon and silicon are converted, in modest yields, into trihalogermyl derivatives

$$\mathrm{Ge} + 3\mathrm{MX}_n \rightarrow \mathrm{MX}_{n-1}\mathrm{GeX}_3 + (\mathrm{MX}_{n-1})_2$$

Experimental Section

Atomic germanium vapor, produced in an evacuated apparatus described elsewhere,[2c,6] was codeposited at −196° with the appropriate group IV halide, the excess unreacted substrate was removed at −78°, and the less volatile products were fractionally sublimed *in vacuo*. The products were identified mass spectrometrically. The mass spectra of compounds containing both chlorine and germanium are complicated by the relationship $2 \times {}^{35}\mathrm{Cl} \equiv 1 \times {}^{70}\mathrm{Ge}$ ($=m/e$ 70). To avoid fallacious assignments the previously tabulated[7] isotopic contributions of various combinations of $\mathrm{Ge}_x\mathrm{Cl}_y$ were used.

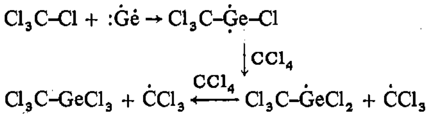
Trichloromethyltrichlorogermane was identified by comparison of its mass spectrum and melting point (106°) with published data.[7,8] $\mathrm{CCl_3GeCl_3}$ sublimes as colorless leaf-shaped crystals. Dichloromethyltrichlorogermane is a high-boiling liquid[9] showing $\nu_{\max}$(C–H) at 2975 cm^{-1}. The mass spectrum shows major peaks attributable to $\mathrm{CGeCl_5^+}$, $\mathrm{CGeCl_4^+}$, $\mathrm{CGeCl_3^+}$, $\mathrm{GeCl_3^+}$, $\mathrm{GeCl_2^+}$, $\mathrm{CCl_3^+}$, and $\mathrm{CHCl_2^+}$. Trichlorosilyltrichlorogermane is an involatile liquid showing major peaks assignable to $\mathrm{SiGeCl_6^+}$, $\mathrm{SiGeCl_5^+}$, $\mathrm{GeCl_4^+}$, $\mathrm{SiCl_4^+}$, $\mathrm{GeCl_3^+}$, and $\mathrm{SiCl_3^+}$. Mass spectra were recorded on a CEC 21-110-B spectrometer operating at 70 eV with an inlet temperature of 150°.

Results and Discussion

Reaction of Ge atoms with $\mathrm{CCl_4}$ yields $\mathrm{CCl_3GeCl_3}$ (20%) and $\mathrm{C_2Cl_6}$. The fact that $\mathrm{(GeCl_3)_2CCl_2}$ is readily isolable[7] from the reaction of carbon atoms with $\mathrm{GeCl_4}$ precludes the possibility that $\mathrm{(CCl_3)_2GeCl_2}$ was produced but not isolated in the present reaction; the latter compound would be expected to be even more volatile and hence more easily pumped out of the reaction system. $\mathrm{SiCl_4}$ reacts similarly to produce $\mathrm{GeCl_3SiCl_3}$ (10%); this compound had previously been postulated as an intermediate in the reaction of $\mathrm{GeCl_2}$ with $\mathrm{SiCl_4}$ but was claimed to be unstable.[10] A tentative claim has also been made by Urry[11] that $\mathrm{GeCl_3SiCl_3}$ is formed upon heating $\mathrm{Cl_3Si{-}Hg{-}GeCl_3}$. The physical similarities of that compound and of the one produced in the present study indicate that Urry's tentative assignment was probably correct. When $\mathrm{CHCl_3}$ was used as the substrate, the only germane formed was $\mathrm{CHCl_2GeCl_3}$ (8%) indicating that no C–H insertion or abstraction occurred; presumably this is a reflection of the relative C–H and C–Cl bond strengths (96 and 72 kcal/mol, respectively).[12]

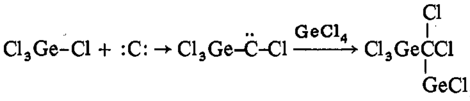
It is interesting to note that ethyl chloride fails to react under cocondensation conditions, perhaps indicating that the well-known direct synthesis of alkylgermanium halides[13] does not involve germanium insertion to give intermediate germenes but is rather a radical-initiated process. Moreover, these industrial processes are catalyzed by copper which Timms[14] has shown to be an excellent dehalogenating agent.

Germanium atoms possess a ^{3}P ground state and at the temperature of vaporization (~1250°) less than 0.1% would be expected to be in the ^{1}D or ^{1}S excited states.[15] Thus, unlike carbon[4] and silicon[5c] atoms which are best generated using an arc or electron gun, respectively, the chemistry should be essentially that of ground-state germanium. The data are rationalizable on the basis of an intermediate triplet germene which then abstracts halogens in a stepwise manner characteristic of radicals



$$\begin{array}{l} \mathrm{Cl_3C{-}Cl} + :\dot{\mathrm{G}}\mathrm{e} \rightarrow \mathrm{Cl_3C{-}\dot{G}e{-}Cl} \\ \qquad\qquad\qquad\qquad\qquad \downarrow \mathrm{CCl_4} \\ \mathrm{Cl_3C{-}GeCl_3} + \dot{\mathrm{C}}\mathrm{Cl_3} \xleftarrow{\mathrm{CCl_4}} \mathrm{Cl_3C{-}\dot{G}eCl_2} + \dot{\mathrm{C}}\mathrm{Cl_3} \end{array}$$

Such a scheme is analogous to the reactions of ^{3}P carbon atoms with alkyl halides to produce trihalomethyl derivatives[4] and contrasts with the behavior of ^{1}D or ^{1}S carbon atoms which undergo double insertions characteristic of successive singlet carbene reactions[7]



$$\mathrm{Cl_3Ge{-}Cl} + :\mathrm{C}: \rightarrow \mathrm{Cl_3Ge{-}\ddot{C}{-}Cl} \xrightarrow{\mathrm{GeCl_4}} \mathrm{Cl_3Ge}\overset{\mathrm{Cl}}{\underset{\mathrm{GeCl_3}}{\mathrm{C}}}\mathrm{Cl}$$

Mechanistic analogies may also be found in the elegant studies of the chemistry of $\mathrm{SiF_2}$ and $\mathrm{GeF_2}$ by Margrave and his coworkers.[16,17]

Thus, the cocondensation procedure provides another viable synthetic route to organogermanium compounds; it is also more selective in its mode of attack than "hot" Ge atoms produced by nuclear recoil methods.[5d]

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Registry No. Ge, 7440-56-4.

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