summarized in Table IV. The heats of formation of (CH$_3$)$_2$SiF$_2$ and (CH$_3$)$_3$SiF were estimated from the known heats of formation of gaseous SiF$_4$,[12] CH$_3$SiF$_3$,[13] and (CH$_3$)$_4$Si.[12] From the available thermochemical data the replacement of a methyl group by a fluorine atom was estimated to lower the heat of formation by 79.1 kcal/mol. The heats of formation of other species are collected in the table. There are no available data with which to compare the calculated ionic heats of formation. The values reported in Table IV represent upper limits to the heats of formation since excess energy has not been measured or included in the calculations.

Acknowledgments. The support of this work by the National Science Foundation under Grant GP-20608X is gratefully acknowledged. Thanks are also expressed to Mr. Rick Pauls, who prepared the sample of SiH$_4$.

Registry No. CH$_3$SiF$_3$, 373-74-0; (CH$_3$)$_2$SiF$_2$, 353-66-2; (CH$_3$)$_3$SiF, 420-56-4; (CH$_3$)$_4$Si, 75-76-3; SiH$_4$, 7803-62-5; SF$_6^-$, 25031-39-4; (CH$_3$)SiF$_4^-$, 44244-53-3; (CH$_3$)$_2$SiF$_3^-$, 51108-60-2; (CH$_3$)$_3$SiF$_2^-$, 51202-29-0; (CH$_3$)$_4$SiF$^-$, 51108-61-3.

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Spectra and Structure of Organogermanes. XVI.[1] Microwave Spectrum of Trimethylcyanogermane

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The rotational spectrum of trimethylcyanogermane has been recorded from 26.5 to 40.0 GHz. The ground-state rotational constants have been determined for 12 different isotopic species and r_s values of 1.155 ± 0.002 and 1.947 ± 0.006 Å have been determined for the CN and Ge$\overline{CN}$ distances, respectively. With these values and an assumed structure for the methyl group, the following two structural parameters were obtained: r(GeC) = 1.930 ± 0.006 Å and $\angle$CGe$\overline{CN}$ = 106.2 ± 0.1°. The determined structural parameters are compared to the corresponding ones for other methyl-substituted germanes. The infrared spectrum in the 2100-cm^{-1} region indicates the presence of approximately 5% of the isocyanide in the sample.

Introduction

A systematic elongation of the C-X bond in (CH$_3$)$_3$CX compounds in which X = H,[2a] Cl,[2b] C≡CH,[3] and C≡N,[3] in contrast to the similar bond in CH$_3$X, has been found. A similar situation is also found as one compares the SiBr bond distance (2.24 ± 0.02 Å) in trimethylbromosilane,[4] (CH$_3$)$_3$SiBr, with the similar distance in silyl bromide (2.209 ± 0.001 Å).[5] The GeCl bond distance (2.170 ± 0.001 Å) in trimethylchlorogermane,[6] (CH$_3$)$_3$GeCl, was determined to be 0.022 Å longer than the corresponding distance in germyl chloride[7] (2.148 ± 0.003 Å). Recently, we completed microwave studies of trimethylgermane[8] and trimethylbromogermane[9] and found additional examples of the general elongation effect in the trimethylgermyl compounds. As a continuation of our studies on the spectra and structure of organogermanes,[6,8,9] we have carried out a microwave investigation of trimethylcyanogermane. Isotopic species studied included (CH$_3$)$_3$Ge^{12}C^{14}N, (CH$_3$)$_3$Ge^{13}C^{14}N, and (CH$_3$)$_3$Ge^{12}C^{15}N along with four of the naturally abundant isotopic species of the germanium atom. This experimental information should allow the determination of the r_s structure of Ge-C≡N and the r_0 structure of the trimethylgermyl moiety which, in turn, could be compared with corresponding distances in germyl cyanide.[10] We were also interested in the possibility of the presence of isocyanide in the sample of trimethylcyanogermane as a comparison to the case of trimethylsilyl cyanide in which some of the isocyanide has been found to coexist.[11]

Experimental Section

The (CH$_3$)$_3$Ge^{12}C^{14}N, (CH$_3$)$_3$Ge^{13}C^{14}N, and (CH$_3$)$_3$^{12}C^{15}N molecules were prepared by the addition of AgCN containing the desired isotopes of carbon and nitrogen to (CH$_3$)$_3$GeCl.[12] The ^{13}C and ^{15}N isotopes were obtained from the British Oxygen Co. in the form of KCN. The (CH$_3$)$_3$GeCl was purchased from Ventron Inorganics.

A 1-g KCN sample was treated with an equimolar quantity of AgNO$_3$, filtered, and dried in a vacuum desiccator for 24 hr in the dark. The resulting AgCN was suspended in benzene and allowed to react with (GH$_3$)$_3$GeCl; the mixture was refluxed for 24 hr. The AgCl was then removed by filtration and the benzene was removed by distillation at atmospheric pressure to concentrate the product. When the volume of the solution approached 5 ml, it was transferred to a ministill and the remaining benzene removed under vacuum. The remaining material was a slightly discolored product. This product was then vacuum distilled and collected in a receiver cooled with Dry Ice. The resulting white crystals were stable if not exposed to the air or elevated temperatures.

The microwave spectrum of trimethylcyanogermane was investigated in the R-band frequency range (26.5–40.0 GHz) by the use of a Hewlett-Packard Model 8460A MRR spectrometer. The Stark cell

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was modulated with a square wave of 33.33-kHz frequency. Since the Dry Ice temperature was too cold to give sufficient sample vapor pressure for the microwave studies, frequency measurements were made while the cell was only partially packed with Dry Ice. Both cool and room temperatures were used to search for lines of the isocyanide molecules.

Results

In the molecule of trimethylcyanogermane, the germanium atom is located closer to the center of mass than any other atom. There are five naturally occurring isotopes of germanium with a relative abundance of 7, 36, 7, 27, and 20% for ^{76}Ge, ^{74}Ge, ^{73}Ge, ^{72}Ge, and ^{70}Ge, respectively. Thus, for a given rotational transition, the relative position of the lines arising from the different germanium isotopes will depend on the distance of the Ge atom from the center of mass.

The microwave spectra were typically those for a symmetric-top rotor. Each band consisted of many lines due to different isotopic species of the germanium atom in both the ground and excited vibrational states (see Figure 1). The ground-state lines were assigned and measured based on their relative intensity with the temperature study. Most of the measured lines were very broad which is probably caused by the unresolved quadrupole pattern from the quadrupole moment of ^{14}N, the unresolved fine structure from the centrifugal distortion effect, and the interference from some excited vibrational lines. The frequency accuracy is, therefore, not expected to be better than 0.1 MHz.

In Table I are listed the measured rotational transitions of trimethylcyanogermane. The broadening effect arising from the quadrupole moment of the ^{73}Ge atom prevented us from measuring the rotational transitions of $(CH_3)_3{}^{73}GeCN$. In Table II are listed the rotational constants and the moments of inertia. In those cases where all three transitions (8 ← 7, 9 ← 8, and 10 ← 9) were measured, the mean values of the rotational constants from all three transitions are given.

Structure

Our present study has provided sufficient information for calculating the coordinates of the Ge, C (in the CN group), and N atoms along the molecular symmetry axis by Kraitchman's method.[13] The substituted GeC and CN distances could, therefore, be obtained. In fact, there are many combinations which can be used for obtaining these distances depending on which isotopic species is chosen as the "parent" molecule in the calculation. Summarized in Table III are the results of the calculation in which the isotopic species $(CH_3)_3{}^{76}Ge^{12}C^{14}N$, $(CH_3)_3{}^{74}Ge^{12}C^{14}N$, $(CH_3)_3{}^{72}Ge^{12}C^{14}N$, and $(CH_3)_3{}^{70}Ge^{12}C^{14}N$ are taken as the "parent" molecules, respectively. A different series of calculations gives consistent results within a reasonable range of error. Thus, we obtain $\bar{r}_s$(GeC) = 1.947 ± 0.006 Å and $\bar{r}_s$(CN) = 1.155 ± 0.002 Å.

In our previous studies of trimethylgermane[8] and trimethylbromogermane,[9] it was found that the skeletal structure was insensitive to the locations of the hydrogen atoms in the methyl groups. Although our available data failed to give a good methyl group structure, it should be possible to obtain the heavy-atom structure (GeC bond and CGeC angle) by the least-squares fitting to the observed rotational constants under the assumption of the methyl group structures concurrent with the resulting r_s distances. Given in Table IV are the structural parameters of trimethylcyanogermane; these parameters give rotational constants which agree with the experimental values within experimental error.

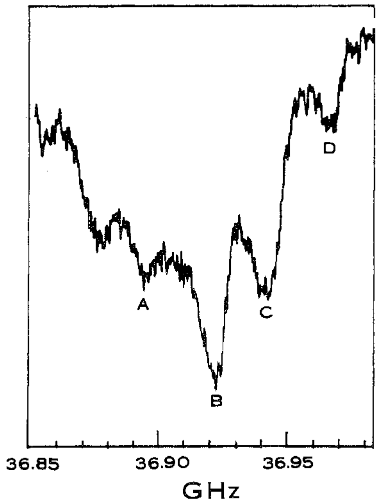

Figure 1. The microwave spectrum of the 10 ← 9 transition of cyanotrimethylgermane at a Stark field of 2400 V/cm. The gound-state transitions are indicated as follows: A, $(CH_3)_3{}^{76}Ge^{12}C^{14}N$; B, $(CH_3)_3{}^{74}Ge^{12}C^{14}N$; C, $(CH_3)_3{}^{72}Ge^{12}C^{14}N$; D, $(CH_3)_3{}^{70}Ge^{12}C^{14}N$.

Discussion

In the present study, attempts have been made to observe transitions assignable to the isocyanide molecule. Our failure to observe the spectrum of this isomer suggests that if there is any of it present, its abundance should be less than 6%. It should be emphasized that our results do not exclude the presence in low concentration of the isocyanide. In the case of trimethylsilyl cyanide, it was suggested that the presence of the isocyanide may depend on the solvent used for the reaction between $(CH_3)_3SiCl$ and AgCN.[14] Presumably, this may also be the case for trimethylgermyl cyanide; thus, our conclusion applies only to the sample prepared by the method as given in the Experimental Section.

We have scanned the infrared spectrum of a chloroform solution of trimethylcyanogermane and observed a strong line at 2182 cm^{-1} and a weak one at 2090 cm^{-1}. The strong one is assignable to the C≡N stretching motion while the weak one may be due to the N=C stretching of the isocyanide molecule. A similar solution for $(CH_3)_3Ge^{13}CN$ (~60% isotopic abundance) has also been studied in the same frequency region, and a strong band at 2136 cm^{-1} and a weak one at 2055 cm^{-1} were observed in addition to those two lines found in $(CH_3)_3GeCN$. Both the relative intensity and the isotopic shifts seem to certify the correct C≡N and N=C stretching assignments. For the sake of comparison with a closely similar molecule, we have also investigated the gaseous infrared spectrum of trimethylsilyl cyanide in the corresponding C≡N and N=C stretching region and found a strong line at 2198 cm^{-1} and a weak line at 2094 cm^{-1}. These two lines have been assigned from the isotopic shifts and the relative intensity study to the C≡N stretch in $(CH_3)_3SiCN$ and the N=C stretch in $(CH_3)_3SiNC$.[15] The intensity of the 2095-cm^{-1} line relative to the 2198-cm^{-1} line is observed to be similar to the corresponding relative intensity as observed in the case of the trimethylgermyl cyanide sample. It is assumed that the extinction coefficients of the stretchings in the trimethylsilyl cyanide are transferable to the case in the trimethylgermyl cyanide. From the abundance of $(CH_3)_3$-

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Table I. Rotational Transitions (MHz) of Trimethylcyanogermane[a]

Isotopic molecule	8 ← 7		9 ← 8		10 ← 9	
	ν_{obsd}	$\nu_{\mathrm{obsd}} - \nu_{\mathrm{calcd}}$[b]	ν_{obsd}	$\nu_{\mathrm{obsd}} - \nu_{\mathrm{calcd}}$[b]	ν_{obsd}	$\nu_{\mathrm{obsd}} - \nu_{\mathrm{calcd}}$[b]
$(CH_3)_3{}^{76}Ge^{12}C^{14}N$					36,899.1	−0.1
$(CH_3)_3{}^{74}Ge^{12}C^{14}N$	29,537.4	0.4	33,228.9	−0.2	36,920.8	−0.4
$(CH_3)_3{}^{72}Ge^{12}C^{14}N$	29,555.1	0.4	33,248.9	−0.2	36,943.1	−0.3
$(CH_3)_3{}^{70}Ge^{12}C^{14}N$	29,573.1	0.3	33,269.3	−0.1	36,965.9	−0.1
$(CH_3)_3{}^{76}Ge^{13}C^{14}N$	29,223.8	0.7	32,875.0	−0.9	36,528.6	−0.2
$(CH_3)_3{}^{74}Ge^{13}C^{14}N$	29,244.0	1.0	32,897.4	−1.0	36,553.6	−0.2
$(CH_3)_3{}^{72}Ge^{13}C^{14}N$	29,262.5	0.1	32,920.2	0.0	36,578.1	0.1
$(CH_3)_3{}^{70}Ge^{13}C^{14}N$	29,282.7	0.1	32,943.0	0.1	36,602.9	−0.3
$(CH_3)_3{}^{76}Ge^{12}C^{15}N$					35,866.5	−0.1
$(CH_3)_3{}^{74}Ge^{12}C^{15}N$					35,890.3	−0.1
$(CH_3)_3{}^{72}Ge^{12}C^{15}N$					35,916.2	0.0
$(CH_3)_3{}^{70}Ge^{12}C^{15}N$					35,941.6	0.0

[a] Frequency accuracy is around 0.2 MHz. [b] ν_{calcd} is obtained from the rotational constant listed in Table II.

Table II. Rotational Constants (MHz) and Moments of Inertia (amu Å^2)[a] of Trimethylcyanogermane

Isotopic molecule	B	I
$(CH_3)_3{}^{76}Ge^{12}C^{14}N$	1844.96 ± 0.02	273.923 ± 0.003
$(CH_3)_3{}^{74}Ge^{12}C^{14}N$	1846.06 ± 0.03	273.760 ± 0.005
$(CH_3)_3{}^{72}Ge^{12}C^{14}N$	1847.17 ± 0.02	273.595 ± 0.003
$(CH_3)_3{}^{70}Ge^{12}C^{14}N$	1848.30 ± 0.02	273.427 ± 0.003
$(CH_3)_3{}^{76}Ge^{13}C^{14}N$	1826.44 ± 0.04	276.701 ± 0.006
$(CH_3)_3{}^{74}Ge^{13}C^{14}N$	1827.69 ± 0.04	276.511 ± 0.006
$(CH_3)_3{}^{72}Ge^{13}C^{14}N$	1828.90 ± 0.01	276.327 ± 0.002
$(CH_3)_3{}^{70}Ge^{13}C^{14}N$	1830.16 ± 0.02	276.138 ± 0.003
$(CH_3)_3{}^{76}Ge^{12}C^{15}N$	1793.33 ± 0.02	281.810 ± 0.003
$(CH_3)_3{}^{74}Ge^{12}C^{15}N$	1794.52 ± 0.02	281.626 ± 0.003
$(CH_3)_3{}^{72}Ge^{12}C^{15}N$	1795.81 ± 0.02	281.420 ± 0.003
$(CH_3)_3{}^{70}Ge^{12}C^{15}N$	1797.08 ± 0.02	281.221 ± 0.003

[a] Conversion factor: 505377 MHz amu Å^2.

Table III. Calculation of the r_s(Ge–CN) and r_s(C≡N) Distances from Different Isotopic Species[a]

Substituted molecule	Original molecule			
	$(CH_3)_3$-$^{76}Ge^{12}C$-^{14}N	$(CH_3)_3$-$^{74}Ge^{12}C$-^{14}N	$(CH_3)_3$-$^{72}Ge^{12}C$-^{14}N	$(CH_3)_3$-$^{70}Ge^{12}C$-^{14}N
(A)	Calculation of $\|Z\|$(Ge)			
$(CH_3)_3{}^{76}Ge^{12}C^{14}N$		0.288	0.291	0.293
$(CH_3)_3{}^{74}Ge^{12}C^{14}N$	0.284		0.289	0.294
$(CH_3)_3{}^{72}Ge^{12}C^{14}N$	0.283	0.285		0.292
$(CH_3)_3{}^{70}Ge^{12}C^{14}N$	0.282	0.285	0.288	
$\|Z\|(Ge)_{av}$	0.283	0.286	0.289	0.293
(B)	Calculation of $\|Z\|$(C)			
$(CH_3)_3{}^{76}Ge^{13}C^{14}N$	1.669			
$(CH_3)_3{}^{74}Ge^{13}C^{14}N$		1.662		
$(CH_3)_3{}^{72}Ge^{13}C^{14}N$			1.656	
$(CH_3)_3{}^{70}Ge^{13}C^{14}N$				1.650
r_s(GeC)[b]	1.952	1.948	1.945	1.943
(C)	Calculation of $\|Z\|$(N)			
$(CH_3)_3{}^{76}Ge^{12}C^{15}N$	2.822			
$(CH_3)_3{}^{74}Ge^{12}C^{15}N$		2.818		
$(CH_3)_3{}^{72}Ge^{12}C^{15}N$			2.811	
$(CH_3)_3{}^{70}Ge^{12}C^{15}N$				2.806
r_s(CN)[c]	1.153	1.157	1.155	1.156

[a] All the coordinates and the distances are in units of angstroms. [b] $r_s(GeC) = |Z|(Ge)_{av} + |Z|(C)$. [c] $r_s(CN) = |Z|(N) - |Z|(C)$.

SiNC found in the microwave study,[11] a comparison of their relative intensities gives an estimation of approximately 5% for the isocyanide in $(CH_3)_3GeCN$.

The rotational line assignments were based on the relative intensity and the temperature study, as well as the expected line position from the preliminary prediction. A consistent result obtained from different combinations of isotopic data has given further confirmation of our assignment.

Table IV. Structural Parameters of Trimethylcyanogermane

r(CH)[a]	1.095 Å	r(CN)[b]	1.155 ± 0.002 Å
∠GeCH[a]	111.0°	$r(\mathrm{Ge\underline{C}})$	1.930 ± 0.006 Å
$r(\mathrm{Ge\overline{CN}})$[b]	1.947 ± 0.006 Å	$\angle\mathrm{CGe\overline{CN}}$	106.2 ± 0.1°

[a] Assumed parameter. [b] Substituted parameter calculated in Table III.

Since the rotational constants of $(CH_3)_3GeCN$ were obtained from the high-J transitions, one might be concerned about the possible centrifugal distortion effect. Based on a similar argument given in the microwave work of trimethylbromogermane,[9] there should be little effect in the resulting structure caused by the centrifugal distortion effect.

The structure of the trimethylgermyl moiety obtained in the present study is similar to those of trimethylchlorogermane[6] and trimethylbromogermane.[9] Furthermore, it is worth noting that the CGeC angle in the trimethylgermyl moiety opens up appreciably and the GeC distance decreases when one substitutes the hydrogen in the trimethylgermane with a chlorine, bromine, or cyano group. One of the most interesting results in this study is the fact that the Ge–CN distance is consistently longer than the corresponding distance (1.919 Å) in germyl cyanide[10] although the C≡N triple bond distances are essentially identical in both molecules. The Ge–CN bond distance in trimethylcyanogermane is essentially the same as the Ge–C bond length in CH_3-GeH_3[16] and may be taken as the normal Ge–C bond length. Perhaps, therefore, it would be more appropriate to consider the shortening of the Ge–C bond length in germyl cyanide rather than an elongation effect in trimethylcyanogermane. The shortening effect can be explained by the hyperconjugation which causes the Ge–C bond in the GeH_3-CN to take on a partial double-bond character.

The crystal structure of trimethylcyanogermane has been reported[17] to have r(Ge–CH$_3$) = 1.98 ± 0.04 Å, r(Ge–CN) = 1.98 ± 0.06 Å, r(C≡N) = 1.15 ± 0.13 Å, and ∠(CH$_3$)Ge(CH$_3$) = 114.8 ± 1.4°. It was pointed out that the large uncertainty involved in the parameters could be attributed to the presence of some isocyanide and the intermolecular effect. Within the error limits our C–N and Ge–CN distances (see Table IV) are in agreement with those reported. However, the Ge-CH$_3$ distance and the (CH$_3$)-Ge-(CH$_3$) angle are smaller than the corresponding values in the solid state. Using the crystal structure, we have obtained the predicted moments of inertia which are at least 4.5 amu Å^2 larger than our experimental values. The larger predicted moment of inertia indicates that the spreading of the CH$_3$-Ge-CH$_3$ angle is not

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enough to compensate for the longer Ge–CH_3 distance as found in the crystal.

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Registry No. $Me_3{}^{76}Ge^{12}C^{14}N$, 51015-78-2; $Me_3{}^{74}Ge^{12}C^{14}N$, 51015-79-3; $Me_3{}^{72}Ge^{12}C^{14}N$, 51015-80-6; $Me_3{}^{70}Ge^{12}C^{14}N$, 51065-33-9; $Me_3{}^{76}Ge^{13}C^{14}N$, 51015-81-7; $Me_3{}^{74}Ge^{13}C^{14}N$, 51015-82-8; $Me_3{}^{72}Ge^{13}C^{14}N$, 51015-83-9; $Me_3{}^{70}Ge^{13}C^{14}N$, 51015-84-0; $Me_3{}^{76}Ge^{12}C^{15}N$, 51015-85-1; $Me_3{}^{74}Ge^{12}C^{15}N$, 51015-86-2; $Me_3{}^{72}Ge^{12}C^{15}N$, 51015-87-3; $Me_3{}^{70}Ge^{12}C^{15}N$, 51015-88-4; trimethylcyanogermane, 7293-42-7.

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Preparation and Characterization of Some CoXY Compounds Where X = P, As, Sb and Y = S, Se[1]

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The lattice parameters for the CoXY series of compounds where X = P, As, Sb and Y = S, Se were determined. CoPS is tetragonal, CoAsS is cubic, CoSbS and CoPSe are orthorhombic, and CoAsSe and CoSbSe are "anomalous" marcasites. Partial ordering of As–S pairs was found for ground single crystals of CoAsS. Magnetic measurements made on the CoXY type compounds showed weak, temperature-independent paramagnetism except for CoSbS, which was diamagnetic. Electrical data indicate that the specific anion appears to affect the nature of the electrical properties.

Introduction

A number of recent studies have described the preparation and properties of anion-substituted cobalt chalcogenides.[2-5] Some of these studies have been concerned with the electrical, magnetic, and crystallographic characterization of the CoXY materials (Table I), where X is a pnictide and Y is the chalcogenide.[6-11] However, the more general problem of the properties of these materials as a class has not been considered.

CoPS was first reported by Hulliger[6] to be cubic with a cell edge $a = 5.422$ Å. However, close examination of CoPS diffractometer patterns[5] revealed a splitting of all peaks requiring an indexing on the basis of a tetragonal unit cell.

CoAsS has been observed to crystallize in both a high- and low-temperature form.[7] The high-temperature pyrite phase is indicative of a random distribution of the anions throughout the structure. The low-temperature form shows additional reflections not allowed in the pyrite space group *Pa*3. The additional reflections are believed to be due to anion ordering. Two models have been proposed for this low-temperature form. Onerato[8] has suggested a monoclinic crystal structure (space group $P2_1/b$) characterized by an ordered anion substitution of alternating As–As, S–S pairs in a series of lattice planes perpendicular to the *a* crystallographic axis (Figure 1). Giese and Kerr[7] have studied mineral samples of CoAsS (cobaltite) and reported a high-temperature pyrite form in the 800–850° range. They also reported that some CoAsS samples showed anion ordering consistent with the orthorhombic $Pca2_1$ space group. Such an ordered structure would have a spatial arrangement containing As–S pairs in a series of lattice planes as shown in Figure 2.

Both synthetic and naturally occurring CoSbS (paracostibite) are orthorhombic and give a set of reflections similar to those of α-$NiAs_2$ (pararammelsbergite). Hence, CoSbS may have a structure similar to that of α-$NiAs_2$ [12,13] which is intermediate between that of pyrite and marcasite. In the pyrite structure all the corners of each cation octahedron share corners with two neighboring octahedra. This results in a total sharing of each octahedron with 12 neighboring octahedra (Figure 3). In the marcasite structure each octahedron shares two parallel and opposite edges with two neighboring octahedra and corners with an additional eight neighboring octahedra (Figure 4). The combination of both the pyrite and marcasite stacking sequence of the octahedra results in the α-$NiAs_2$ structure. In this structure each octahedron shares an edge with one neighboring octahedron and corners with ten additional neighboring octahedra.

CoAsSe has been reported by Hulliger[6] to crystallize as a cubic pyrite (space group *Pa*3) with a cell edge of $a = 5.76$ Å. There have been no previous X-ray studies reported for either CoPSe or CoSbSe.

In order to correlate the effects of anion substitution on the transport and magnetic properties of CoS_2 and $CoSe_2$, a systematic study of CoXY type compounds (X = P, As, Sb and Y = S, Se) was initiated..

Experimental Section

Polycrystalline samples of all compositions were prepared directly from the elements in evacuated silica tubes. (Spectroscopic grade Co, P, As, Se, and S were obtained from Atomergic Chemical Co., Division of Gallard-Schlesinger Chemical Corp., New York, N. Y.) Samples were given three heat treatments (800–850°) and two intermediate grindings under a dry nitrogen atmosphere. The

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