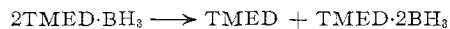


sure⁷ to be TMED). The clear melt produced TMED and TMED·2BH₃ in the ratio 1.06:1, in good agreement with the values required by the equation



Proton magnetic resonance measurements support the view that the solution prepared by dissolving solid TMED·2BH₃ in liquid TMED at elevated temperatures contains only the monoadduct. The proton n.m.r. spectrum of such a solution showed four peaks at +2.24, +2.61, +2.73, and +2.78 p.p.m. relative to tetramethylsilane as the external reference. While the proximity of the solvent peak at +2.22 p.p.m. rendered impractical measurement of the relative area of the first resonance, the remaining three had relative areas of 3:1:1, respectively.

Protons attached to boron atoms were not observable with the techniques employed; in consequence, these do not appear in the assignment of the resonances reported above. Both TMED and TMED·2BH₃, being symmetrical molecules, exhibit only two resonances of relative areas 3:1. The monoadduct TMED·BH₃ is quite unsymmetrical and, therefore, should show four proton resonances in the ratio 3:3:1:1. On the assumption that the methyl groups most distant from the boron atom in TMED·BH₃ do not differ greatly from those in TMED itself, and that the methyl groups closest to the boron atom do not differ greatly from those in TMED·2BH₃, the assignments in Table I appear reasonable. (All protons on carbons adjacent to B-N bonds are referred to as α protons, all protons on other carbons as β protons.) The expected quartet was observed in the B¹¹ spectrum of TMED·BH₃. This was located at +26.3 p.p.m. relative to trimethoxyborane as an external reference. Relative areas were approximately 1:3:3:1 with $J = 96$ c.p.s. For TMED·2BH₃ the shift was +28.4 p.p.m. with $J = 96$ c.p.s.

TABLE I
ASSIGNMENT OF PROTON SHIFTS^a IN TMED, TMED·2BH₃,
AND TMED·BH₃^b

	α - Methyl	β - Methyl	α - Methylene	β - Methylene
TMED		+2.22 (2.8)		+2.37 (1)
TMED·2BH ₃	+2.59 (3.0)		+3.12 (1)	
TMED·BH ₃	+2.61 (3.2)	+2.24 (c)	+2.78 (1)	+2.73 (1)

^a Relative to tetramethylsilane as an external reference.

^b Observed relative areas indicated in parentheses. ^c Masked by solvent.

The monoadduct TMED·BH₃ can be stored below its melting point at least 24 hr. without decomposition. Above its melting point, however, it quickly decomposes in the absence of excess TMED.

Extension of the above studies to boron halide adducts is currently in progress.

Experimental Section

Preparations and purifications were carried out in conventional Stock-type vacuum apparatus. TMED·2BH₃ was made by the

direct reaction of TMED with excess B₂H₆ at -45° and was purified by sublimation at 110°.

Proton n.m.r. spectra were determined with a Varian A60 spectrometer and B¹¹ n.m.r. spectra with a Varian 4300-2 12-Mc. spectrometer. Chloroform was employed as a solvent for both TMED and TMED·2BH₃.

Infrared spectra were run on mineral oil and perchlorobutadiene mulls using a Beckman IR 5A spectrophotometer.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CASE INSTITUTE OF TECHNOLOGY, CLEVELAND, OHIO 44106

Pseudohalo Silicon and Germanium Phthalocyanines¹

By A. J. STARSHAK, R. D. JOYNER, AND M. E. KENNEY

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For the pseudohalo compounds of silicon and germanium there is always at least a possibility that the groups are nitrogen-bonded to the metal. This possibility has led, in the course of a search for silicon and germanium phthalocyanines having the central metal octahedrally coordinated by nitrogen, to the study of the pseudohalo phthalocyanino derivatives of these two metals.

Experimental Section

Bis(socyanato(phthalocyanino)silicon, PcSi(NCO)₂.—A mixture of 0.61 g. of PcSiCl₂,² 1.50 g. of silver cyanate (*caution*),³ and 25 ml. of 1,2-dichlorobenzene was refluxed for 30 min. The product was cooled, filtered off, washed with ethanol, 7.4 *M* aqueous ammonium thiocyanate, and water, and dried; yield 566 mg. (91%). Recrystallization gave purple reflecting crystals.

Anal. Calcd. for C₃₄H₁₆N₁₀O₂Si: C, 65.37; H, 2.58; Si, 4.50. Found: C, 65.18; H, 2.74; Si, 4.72.

Bis(isothiocyanato(phthalocyanino)silicon, PcSi(NCS)₂.—A slurry of 1.22 g. of PcSiCl₂ and 3.32 g. of silver thiocyanate in 50 ml. of 1,2-dichlorobenzene was refluxed for 30 min. The product was cooled, filtered off, washed with ethanol, aqueous ammonium thiocyanate, and water, and dried; yield 1.19 g. (91%). Recrystallization gave purple reflecting crystals.

Anal. Calcd. for C₃₄H₁₆N₁₀S₂Si: C, 62.10; H, 2.56; S, 9.77; Si, 4.28. Found: C, 62.23; H, 2.50; S, 9.77; Si, 4.08.

Bis(selenocyanato(phthalocyanino)silicon, PcSi(NCSe)₂.—A mixture of 215 mg. of recrystallized PcSiCl₂, 795 mg. of silver selenocyanate, and 49 ml. of chlorobenzene was refluxed under nitrogen for 30 min. and cooled. The product, after being washed with ethanol, aqueous ammonium thiocyanate, water, and acetone and dried, weighed 331 mg. (87%). Attempted purifications of this green product failed because of its thermal and chemical instability. The similarity of its infrared spectrum to that of its sulfur analog was taken as evidence of its nature.

Bis(socyanato(phthalocyanino)germanium, PcGe(NCO)₂.—A mixture of 1.30 g. of PcGeCl₂ and 2.91 g. of silver cyanate in 50 ml. of 1,2-dichlorobenzene was refluxed for 30 min. and cooled. The product, after being washed with acetone, aqueous ammonium thiocyanate, and water and dried, weighed 1.22 g.

(1) This work was supported first by the Air Force Office of Scientific Research under Contract AF 49(638)-773 and later by the Office of Naval Research under Contract Nonr-1141(18).

(2) M. K. Lowery, A. J. Starshak, J. N. Esposito, P. C. Krueger, and M. E. Kenney, *Inorg. Chem.*, **4**, 128 (1965).

(3) The reactivity of the silver pseudohalides should be kept in mind. See B. L. Evans and A. D. Yoffe, *Proc. Roy. Soc. (London)*, **A238**, 568 (1957).

(7) The vapor pressure of the liquid recovered (18 mm. at 21.7°) was identical with that of the TMED originally employed.

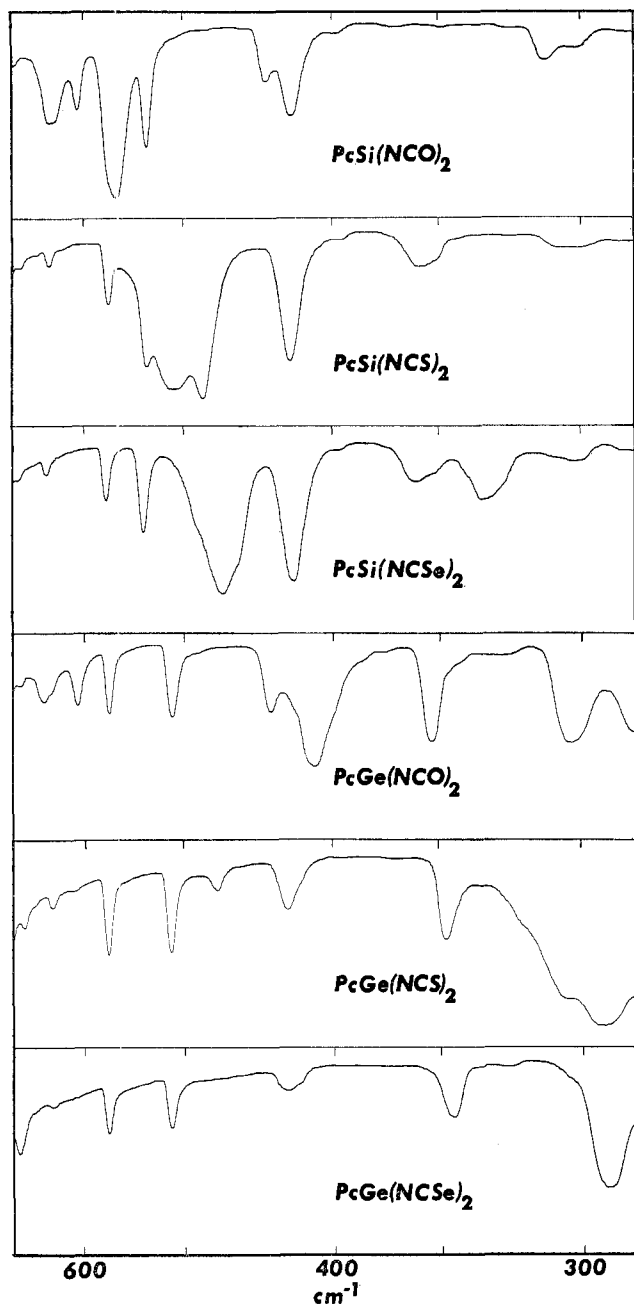


Figure 1.—Infrared spectra.

(92%). A 1.20-g. portion of this was recrystallized twice from diphenyl ether, yielding 124 mg. of purple reflecting crystals.

Anal. Calcd. for $C_{34}H_{18}N_{10}O_2Ge$: C, 61.02; H, 2.41; Ge, 10.85. Found: C, 61.19; H, 2.58; Ge, 10.56.

Bisthiocyanato(phthalocyanino)germanium, $PcGe(NCS)_2$.—A slurry of 1.40 g. of $PcGeCl_2$ and 3.45 g. of silver thiocyanate in 50 ml. of 1,2-dichlorobenzene was refluxed for 30 min. The product was cooled, washed with ethanol, aqueous ammonium thiocyanate, and water and dried; yield 1.42 g. (96%). Recrystallization of 687 mg. of it from 59 ml. of 1-chloronaphthalene gave 307 mg. of purple reflecting crystals.

Anal. Calcd. for $C_{34}H_{18}N_{10}S_2Ge$: C, 53.31; H, 2.30; S, 9.14; Ge, 10.35. Found: C, 53.36; H, 2.39; S, 9.15; Ge, 10.17.

Bisselenocyanato(phthalocyanino)germanium, $PcGe(NCSe)_2$.—A slurry of 75 mg. of recrystallized $PcGeBr_2$,⁴ 201 mg. of silver selenocyanate, and 15 ml. of chlorobenzene was refluxed for 30

min. under nitrogen and cooled. After being washed with ethanol, aqueous ammonium thiocyanate, and water and dried, the dark product weighed 70 mg. (88%). No method of purifying it was found.

Infrared Spectra.—The Nujol mull spectra of these compounds were obtained with Beckman IR5A NaCl and CsBr instruments. Each of the spectra showed the typical phthalocyanino bands in addition to those attributable to the pseudohalo group. The frequencies in cm^{-1} of the strong bands probably associated with the pseudohalo groups are: $PcSi(NCO)_2$, 2245 and 567; $PcSi(NCS)_2$, 2075, 511, and 487; $PcSi(NCSe)_2$, 2060 and 471; $PcGe(NCO)_2$, 2205 and 413; $PcGe(NCS)_2$, 2060 and 297 (?); and $PcGe(NCSe)_2$, 2045. In all cases the $\sim 2100\text{ cm}^{-1}$ bands are very strong.

Discussion

Microwave work on H_3SiNCS has shown that the pseudohalo group in this compound is nitrogen-bonded to the silicon.⁵ Spectral work on $Si(NCO)_4$ and $Si(NCS)_4$ has indicated that the pseudohalo groups in these compounds also are bonded to the silicon through the nitrogen.⁶⁻⁸ On the basis of these findings it is reasonable to expect the pseudohalo phthalocyanino derivatives of silicon to be of the "iso" type. Bond energy arguments analogous to those used for the tetrahedral pseudohalo compounds of silicon lead⁹ to this same expectation for the NCS and NCSe derivatives; however, they may favor a "normal" structure for the NCO derivative. Chemical considerations appear to favor an "iso" arrangement for the NCSe and probably the NCS derivative as well.

Some experimental data with regard to this point are provided by the spectra of these compounds. They all show, in addition to the anticipated phthalocyanino absorptions and a strong absorption at $\sim 2100\text{ cm}^{-1}$ (attributable to what loosely can be described as a pseudoasymmetric pseudohalo vibration), one or two strong bands in the 460 to 580 cm^{-1} region. Since octahedral pseudohalo silicon-nitrogen bonds reasonably can be expected to give rise to absorptions in this region while silicon-oxygen, -sulfur, and -selenium bonds can be expected to give absorptions occurring over a wider range, these spectra appear to favor "iso" structures for the three compounds.

The case for the germanium derivatives is less clear-cut. However, for $PcGe(NCO)_2$ the postulate of an "iso" structure seems reasonable, both because of the similarity of the phthalocyanino bands in its spectrum to those in the spectrum of $PcSi(NCO)_2$ (even to the accentuation of the 613 cm^{-1} band) and because of the occurrence of a strong band in the region where octahedral pseudohalo germanium-nitrogen bands reasonably can be expected. Supporting this postulate are the results of spectral work on $Ge(NCO)_4$,^{6,7} and H_3GeNCO ,¹⁰ indicating that these compounds have an "iso" structure.

(5) D. R. Jenkins, R. Kewley, and T. M. Sugden, *Proc. Chem. Soc.*, 220 (1960).

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(8) G. L. Carlson, *Spectrochim. Acta*, **18**, 1529 (1963).

(9) E. A. V. Ebsworth, "Volatile Silicon Compounds," The Macmillan Co., New York, N. Y., 1963, p. 152.

(10) T. N. Srivastava, J. E. Griffiths, and M. Onyschuk, *Can. J. Chem.*, **40**, 739 (1962).

(4) $PcGeCl_2$ did not react.

The germanium-sulfur and -selenium compounds may be of the "iso" type too, but since their spectra show no strong absorptions attributable to bonds between the pseudohalo groups and the germanium above $\sim 300 \text{ cm.}^{-1}$ a definite conclusion cannot be drawn.

The vibrations of the pseudohalo groups which can be referred to as pseudosymmetric do not give strong enough absorptions to have been detected in the spectra of any of the six compounds and, accordingly, structure arguments based on the positions of these absorptions cannot be applied.

If, as seems probable, the silicon compounds are of the iso type, the sizes of the Si-N-C bond angles are of interest in view of the fact they may point to the presence or absence of $d_{\pi}-p_{\pi}$ bonding between the sp^3d^2 hybridized silicon and the nitrogen.¹¹

(11) J. W. Linnett, *Nature*, **199**, 168 (1963).

CONTRIBUTION FROM MONSANTO COMPANY,
CENTRAL RESEARCH DEPARTMENT,
ST. LOUIS, MISSOURI

K-Edge X-Ray Absorption of Arsenic Compounds

BY RICHARD M. LEVY, JOHN R. VAN WAZER, AND JAMES SIMPSON

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Since we have recently been investigating certain areas of arsenic chemistry¹ as well as the use of K-edge X-ray absorption in characterizing compounds of transition metals,² it seemed desirable to look at the K-edge absorption spectra of a number of arsenic compounds. Outside of AsCl_3 and a number of interstitial metal arsenides,³ we have been able to find no literature on K-edge absorption spectra of arsenic compounds. The samples were run on a General Electric XRD-5 single-crystal monochromator employing a scintillation counter moved at a continuous rate of $0.04^\circ (2\theta)/100 \text{ sec.}$ Under these conditions, the diffractometer clearly and cleanly resolves the low-energy spike in the permanganate spectrum.

All of the compounds investigated in this study (listed in Table I) exhibited similar spectra, as typified by Figure 1. Within an experimental error of several electron volts, the position of point A in Figure 1 was found to be the same for all of the compounds investigated. Although the distance from A to B varied somewhat from compound to compound, this variation

(1) *E.g.*, J. R. Van Wazer, K. Moedritzer, and D. Matula, *J. Am. Chem. Soc.*, **86**, 807 (1964); M. D. Rausch, J. R. Van Wazer, and K. Moedritzer, *ibid.*, **86**, 814 (1964); and K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 139 (1964).

(2) R. M. Levy, *J. Chem. Phys.*, **43**, 1846 (1965); R. M. Levy and J. R. Van Wazer, *Advan. Anal. Chem. Instrumentation*, in press.

(3) D. Coster and G. H. Klamer, *Physica*, **1**, 889 (1934); W. Eberbeck, *Z. Physik*, **149**, 412 (1957).

TABLE I
MEASURED PARAMETERS IN X-RAY ABSORPTION
MEASUREMENTS OF ARSENIC COMPOUNDS

Compound	Replicate runs	Escape potential, e.v. ^a	Estd. av bond length, Å.
As_2O_3^c	5	93	1.85
		95	1.83
		93	1.85
		96	1.87
		94	1.85
As_2S_5	3	83	2.45
$(\text{NH}_2\text{C}_6\text{H}_5)_2\text{AsO}(\text{OH})_2$	2	100	1.95
$(\text{C}_6\text{H}_5)_2\text{AsO}$	3	98	1.81
$(\text{C}_6\text{H}_5)_2\text{AsCH}_3 + \text{Cl}^-$	2	82	1.89
Na_3AsO_4	2	99	1.71
$\text{Na}_2(\text{CH}_3)\text{AsO}_4$	2	101	1.63
$\text{H}_4\text{As}_2\text{O}_7$	2	95	1.88
AsI_3	2	40	2.38
AsCl_3	3	73	2.20
AsF_3	2	90	1.90
$(\text{C}_6\text{H}_5)_3\text{As}$	2	77	1.93
$\text{As}(\text{OCH}_3)_3$	4	86	1.78
$\text{As}(\text{OC}_2\text{H}_5)_3$	1	87	1.70
As_2O_3	2	90	1.80
$\text{As}_2(\text{NCH}_3)_3$	2	87	1.69
$\text{As}[\text{N}(\text{CH}_3)_2]_3$	1	92	1.90
AsS (amorphous)	2	84	2.02
AsS (crystalline)	2	91	1.87

^a Difference from A to C (see Figure 1). ^b $r_1 = (151/\Delta E)^{1/2}$ (see Figure 1). ^c The reproducibility of the data is typified by these five independent runs on arsenic pentoxide.

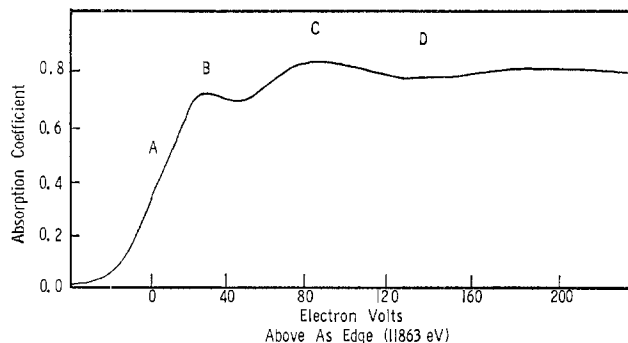


Figure 1.—K-edge X-ray absorption spectrum of As_2O_3 . The labeled features are discussed in the text. A is the half-maximum of the adsorption edge.

was not as great as the change in the distance between B and C. According to the treatment² which seems to be generally applicable to the transition metals, the maximum, labeled B in Figure 1, should correspond to a transition from the 1s to a vacant p level, and that labeled C to a kind of ionization or "escape" energy for the 1s electron. Furthermore, the distance, ΔE , from the maximum at C to the minimum at D should be a measure of the radius of the first coordination sphere around the arsenic through the Bragg relation, $r_1 = (151/\Delta E)^{1/2}$.

In a purely electrostatic model, as successfully applied to third-row transition metal complexes,² the energy of C varies almost exactly as the conventional ionization potential of the equivalently charged gaseous ions. Such correspondence is not observed in the arsenic compounds where, for example, the difference