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Reactions of Fluoroxypentafluoroselenium

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Fluoroxypentafluoroselenium, SeF_5OF, is produced in good yield by the action of fluorine upon the solid formed by combining seleninyl fluoride, $SeOF_2$, with potassium fluoride. Reactions of SeF_5OF with c-C_5F_8, CO, SF_4, N_2F_4, C_2H_4, C_2F_4, and C_3F_6 have been studied, and the following new compounds have been identified: $SeF_5OC_5F_9$, SeF_5OCFO, SeF_5OSF_5. Evidence strongly suggesting the existence of SeF_5OSeF_5 has also been obtained

Introduction

Fluoroxypentafluorosulfur, SF_5OF, was first reported in 1956.[1] Since that time its reactions have been studied by a number of workers.[2-10] The selenium analog, SeF_5OF, was reported in 1959 by Mitra and Cady,[11] who prepared the compound by the reaction of either selenium dioxide or seleninyl chloride, $SeOCl_2$, with fluorine in the presence of a silver difluoride catalyst. The yield of SeF_5OF was rather low and the product was difficult to purify because of contamination by relatively large amounts of SeF_6.

The success of the cesium fluoride catalyzed reaction of thionyl fluoride with fluorine[12] for the preparation of SF_5OF suggested that the analogous reaction in the selenium system might be a good method for preparing SeF_5OF.

Experimental Section

Preparation of SeF_5OF.—Seleninyl fluoride, $SeOF_2$, was prepared by the reaction of SeF_4 with SeO_2 in a Pyrex flask, as described by Peacock.[13] SeF_4 was prepared by the fluorination of Se at 0° as described by Aynsley, *et al.*[14]

In a typical preparation of SeF_5OF, 3.7 mmol of $SeOF_2$ was transferred to a Hoke 4HS30 sampling cylinder containing 2 g of dry potassium fluoride. The reactor was fitted with a brass valve having a stainless steel needle. The reactor was allowed to warm to room temperature, during which time it seems probable that the salt, $KSeOF_3$, was formed as described by Paetzold and Aurich.[15] The vessel was then cooled to $-196°$ and 10 mmol of fluorine was added. The bomb was then allowed to warm slowly to room temperature and remain there for 12 hr. Following this the vessel was chilled to $-183°$ and noncondensed gases, mostly F_2, were pumped away. That part of the remaining material which was volatile at 25° was separated into its components by fractional codistillation or gas chromatography. For the latter process a 3.6-m column packed with 40–60 mesh Chromosorb W loaded with perfluorotributylamine was used. The gaseous product was found to consist of 1.5 mmol of SeF_5OF and 0.4 mmol of SeF_6. By using this type of procedure, up to as much as 15 mmol of SeF_5OF was obtained in a single run. At no time during this work was SeF_5OF observed to decompose spontaneously at room temperature. Caution was used at all times, however, in handling the compound, because Mitra and Cady[11] had experienced explosions in their work.

SeF_5OF was identified by its molecular weight (observed: 209.1, 209.7; theoretical: 209.0), infrared spectrum, and nmr spectrum. The infrared spectrum showed strong sharp absorption bands at 750 and 422 cm^{-1}. Mitra and Cady reported a rather broad absorption at 758 cm^{-1} but the instrument used by them did not operate at 422 cm^{-1}. The ^{19}F nmr spectrum for the SeF_5 group was of the AB_4 type and was very much like the spectrum for the SF_5 group in SF_5OF.[16] It was centered at -55.7 ppm relative to trichlorofluoromethane used as an internal standard.

The fluorine atom bonded to oxygen gave a complex pattern at -177.5 ppm relative to $CFCl_3$, which was similar to that reported for SF_5OF. The spin–spin coupling constant of ^{77}Se with fluorine atoms bonded to selenium was found to be 1410 Hz. This can be compared with the constants found for other selenium(VI) fluorides by Birchall, *et al.*,[17] who reported $J(^{77}Se{-}F)$ in Hz to be 1445 for $HSeO_3F$, 1432 for SeF_6, and 1577 for SeO_2F_2.

Reaction with Perfluorocyclopentene, C_5F_8.—Two millimoles of C_5F_8 and 2.1 mmol of SeF_5OF were condensed into a 300-ml Pyrex glass flask fitted with a Fischer-Porter Lab Crest valve. Two millimoles of dry nitrogen also was added. The flask was then allowed to warm slowly from $-183°$ and to stand at room temperature for 2 days. It was then cooled to $-183°$ and nitrogen was pumped away. The flask was then warmed to room temperature and the contained gas was slowly passed through a trap at $-45°$ and a second at $-183°$. Subsequent tests showed the first trap to contain substantially pure $SeF_5OC_5F_9$ (formed in high yield) and the second to contain SeF_5OF and a small amount of SeF_6.

The sample of $SeF_5OC_5F_9$ was a white solid which melted to a colorless liquid over the range -74 to $-71°$. It had a vapor pressure of about 20 mm at room temperature and did not attack glass, water, or mercury at room temperature. Vapor densities of the gas from two determinations gave experimental molecular weights of 428 and 432 (theoretical value for $C_5F_{14}OSe$ is 421).

Chemical analysis was performed by allowing a weighed sample to react with excess potassium at elevated temperatures. The product was then taken up in water. Free carbon was filtered off and weighed, after oxidizing the selenium with fuming nitric acid. Fluoride was determined potentiometrically using an Orion fluoride-sensitive electrode and titrating with 0.2 N $La(NO_3)_3$. Selenium was determined gravimetrically as the element, after reduction with hydroxylamine hydrochloride. *Anal.* Calcd for $C_5F_{14}OSe$: C, 14.3; F, 63.2; Se, 18.8. Found: C, 13.3; F, 63.7; Se, 18.4.

The infrared spectrum of $SeF_5OC_5F_9$ is shown in Figure 1. Absorptions occur at 1317 (m), 1222 (br, s), 1160 (m), 984 (s),

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(1) F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *J. Am. Chem. Soc.*, **78**, 1553 (1956).

(2) S. M. Williamson and G. H. Cady, *Inorg. Chem.*, **1**, 673 (1962).

(3) S. M. Williamson, *ibid.*, **2**, 421 (1963).

(4) G. Pass and H. L. Roberts, *ibid.*, **2**, 1016 (1963).

(5) J. R. Case and G. Pass, *J. Chem. Soc.*, 946 (1964).

(6) W. H. Hale, Jr., and S. M. Williamson, *Inorg. Chem.*, **4**, 1342 (1965).

(7) J. K. Ruff, *ibid.*, **4**, 1788 (1965).

(8) W. H. Hale, Jr., *Dissertation Abstr.*, *B*, **27**, 3834 (1967).

(9) B. W. Tattershall and G. H. Cady, *J. Inorg. Nucl. Chem.*, **29**, 3003 (1967).

(10) R. Czerepinski and G. H. Cady, *J. Am. Chem. Soc.*, **90**, 3954 (1968).

(11) G. Mitra and G. H. Cady, *ibid.*, **81**, 2646 (1959).

(12) J. Ruff and M. Lustig, *Inorg. Chem.*, **3**, 1422 (1964).

(13) R. D. Peacock, *J. Chem. Soc.*, 3617 (1953).

(14) E. E. Aynsley, R. D. Peacock, and P. L. Robinson, *ibid.*, 1231 (1952).

(15) R. Paetzold and K. Aurich, *Z. Anorg. Allgem. Chem.*, **348**, 94 (1966).

(16) C. I. Merrill and G. H. Cady, *J. Am. Chem. Soc.*, **84**, 2260 (1962).

(17) T. Birchall, R. J. Gillespie, and S. L. Vekris, *Can. J. Chem.*, **43**, 1672 (1965).

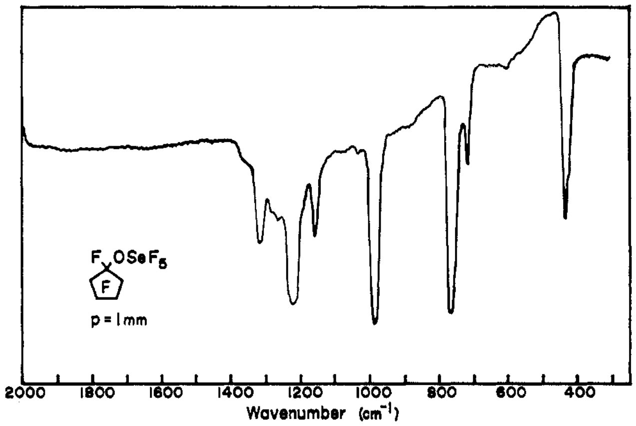

Figure 1.—Infrared spectrum of $SeF_5OC_5F_9$.

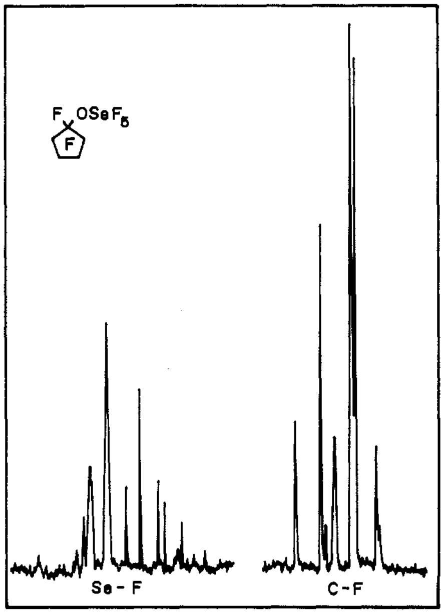

Figure 2.—Fluorine-19 nmr spectrum of $SeF_5OC_5F_9$.

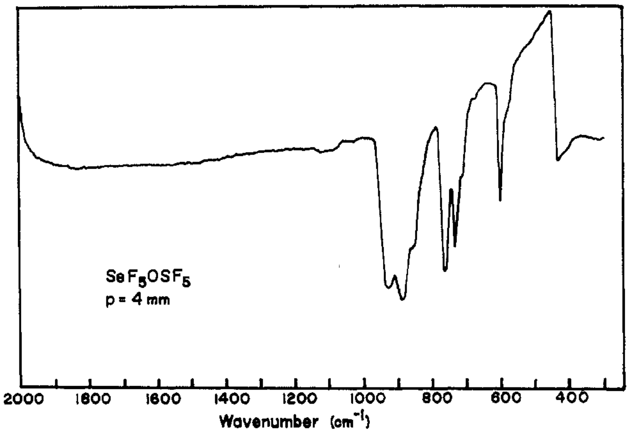

Figure 3.—Infrared spectrum of SeF_5OSF_5.

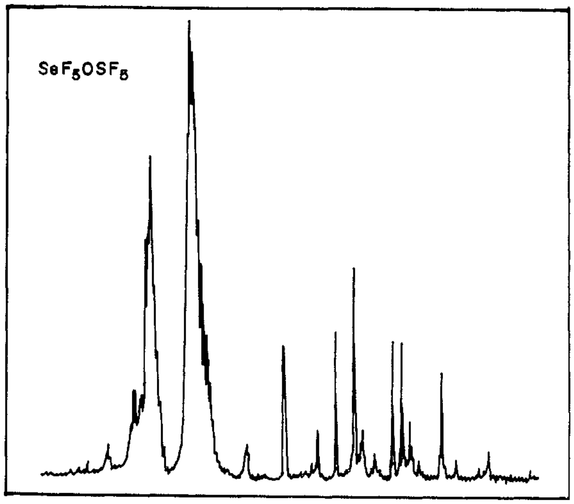

Figure 4.—Fluorine-19 nmr spectrum of SeF_5OSF_5.

767 (s), 718 (m), and 434 cm^{-1} (s). The ^{19}F nmr spectrum shown in Figure 2 contains an AB_4-type pattern centered at -73.0 ppm relative to $CFCl_3$ as an internal standard. This part of the spectrum is that of the SeF_5 group. A ^{77}Se–F spin–spin coupling constant of 1436 Hz was found. The complex pattern caused by fluorine attached to carbon centers close to $+131$ ppm relative to $CFCl_3$.

Reaction with Sulfur Tetrafluoride.—SeF_5OF (1.38 mmol) and 1.62 mmol of SF_4 were mixed and allowed to stand in a 30-ml stainless steel bomb at room temperature for 10 days. The product was codistilled and found to consist of SO_2F_2 and SOF_2 plus a little SiF_4 (total 0.34 mmol), SeF_6 plus a little SOF_2 and SOF_4 (total 0.86 mmol), and two additional substances (0.22 and 0.23 mmol) of such low volatility that they distilled only after the column had warmed to almost room temperature. The less volatile of the two was not identified. The other was again codistilled and was found to be a single compound, later identified as SeF_5OSF_5. The average vapor density from five determinations gave an experimental molecular weight of 325 (theoretical value for SeF_5OSF_5 is 317). Chemical analysis was accomplished in a manner similar to that described for $SeF_5OC_5F_9$ except that bromine was used as the oxidizing agent rather than nitric acid. Sulfur was determined as $BaSO_4$. *Anal.* Calcd for SeF_5OSF_5: F, 60.0; S, 10.1; Se, 24.9. Found: F, 60.3; S, 9.4; Se, 23.8.

The infrared spectrum of SeF_5OSF_5 is shown in Figure 3. The absorptions occur at 927 (s), 886 (s), 855 (m, sh), 763 (s), 730 (m), 600 (m), and 429 cm^{-1} (m). The absorptions at 927 and 886 cm^{-1} are in the same region as those observed for other SF_5O compounds.

The ^{19}F nmr spectrum of SeF_5OSF_5 shown in Figure 4 is interpreted to consist of two AB_4 patterns superimposed upon one another. Merrill, *et al.*,[18] have found that the chemical shift of the four fluorine atoms in the plane may be found by measuring the shift from about the midpoint between the two large peaks found in the spectrum. When this is done for SeF_5OSF_5, the chemical shift of the four fluorine atoms in the plane is found to be -72.7 ppm relative to $CFCl_3$. The peaks to the right of the two large ones result from the apical fluorine atoms and are more numerous than for a compound containing only an SF_5 group. This is considered to be due to presence of lines from both SF_5 and SeF_5 groups.

The mass spectrum was run at 40 eV, and the fragments observed are shown in Table I. Ions containing selenium are

Table I

Peak	*m/e*	Rel[a] abund	Peak	*m/e*	Rel[a] abund
S^+	32	27	SOF_3^+	105	100
SO^+	48	12	$^{80}SeOF^+$	115	9
SF^+	51	4	SOF_4^+	124	6
SOF^+	67	46	SF_5^+	127	23
SF_2^+	70	9	$^{80}SeOF_2^+$	134	12
SOF_2^+	86	68	$^{80}SeF_5^+$	175	4
SF_3^+	89	20	$^{80}SeOSF_9^+$	299	<1

[a] Relative to SOF_3^+.

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(18) C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, *Inorg. Chem.*, **1**, 215 (1962).

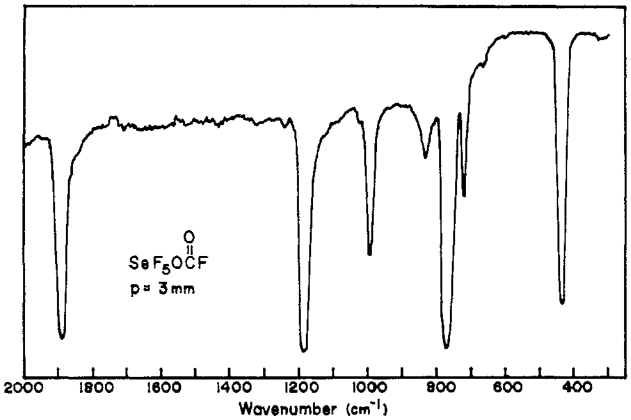

Figure 5.—Infrared spectrum of SeF_5OCFO.

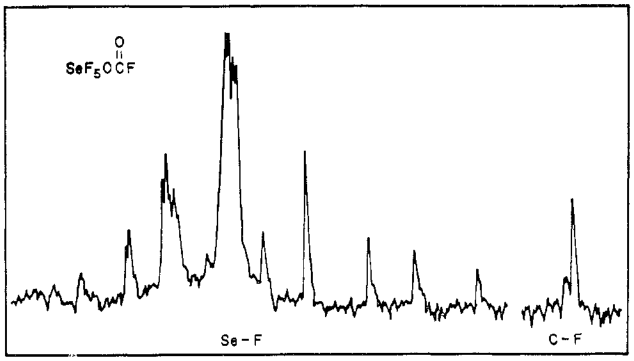

Figure 6.—Fluorine-19 nmr spectrum of SeF_5OCFO.

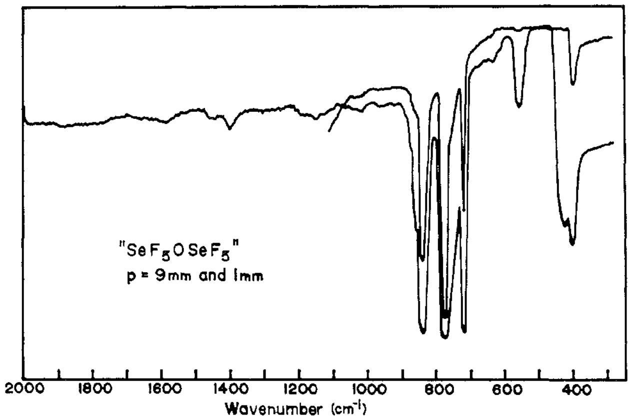

Figure 7.—Infrared spectrum of the compound which is probably SeF_5OSeF_5.

tabulated as the fragment containing only ^{80}Se. In all cases lines for the other isotopes of selenium and sulfur were present in the correct relative amounts. The presence of the $SeOSF_9^+$ peak is strong evidence that the compound was SeF_5OSF_5. Many fluorides give the parent peak minus one fluorine atom and fail to give the parent peak.

Reaction with Carbon Monoxide.—The reaction of CO with SeF_5OF was found to proceed very slowly if at all at room temperature. At temperatures near 65° the reaction proceeded to completion in about 12 hr to give the new compound SeF_5OCFO and probably SeF_5OSeF_5. In a typical run 1.15 mmol of SeF_5OF and 0.46 mmol of CO were condensed into a 30-ml stainless steel reactor which was held at 65° for 12 hr. The product was then fractionally codistilled and found to consist of the following compounds in the amounts indicated (per cent by volume of the total gas in the system): COF_2 + some SeF_6 + CO_2 (38.2), SeF_6 (13.6), SeF_5OF (34.6), SeF_5OCFO (8.2), and the compound thought to be SeF_5OSeF_5 (5.4). This reaction was studied over the temperature range 45–100°, and with varying quantities of reactants; the maximum yield of SeF_5OCFO was found under the conditions described.

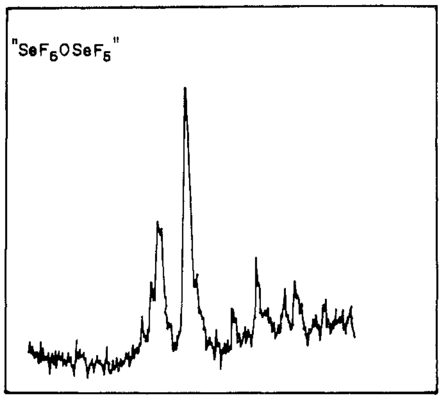

Figure 8.—Fluorine-19 nmr spectrum of the compound which is probably SeF_5OSeF_5.

Vapor densities of SeF_5OCFO from three determinations corresponded to experimental molecular weight values of 232, 236, and 235 (theoretical value for SeF_5OCFO is 237).

The chemical analysis was performed by allowing a known amount of the gas to react with excess sodium hydroxide, after which the fluoride ion was determined using an Orion fluoride-sensitive electrode, and the selenium was weighed as elemental selenium after reduction with hydroxylamine hydrochloride. *Anal.* Calcd for SeF_5OCFO: Se, 33.3; F, 48.1. Found: Se, 31.9; F, 48.0.

The infrared spectrum of SeF_5OCFO is shown in Figure 5. Absorptions occur at 1890 (s), 1185 (s), 996 (m), 831 (m), 770 (s), 720 (m), and 434 cm^{-1} (s). The absorption at 1890 cm^{-1} corresponds to C=O stretch, that at 1185 cm^{-1} to CF stretch, and that at 996 cm^{-1} to the CO stretch. Absorptions at 770 and 434 cm^{-1} are close to those observed in SeF_6.

The ^{19}F nmr spectrum is shown in Figure 6. The SeF_5 group gives an AB_4 pattern centered at −47.0 ppm relative to $CFCl_3$. The nmr spectrum was run on such a small sample that the ^{77}Se–F spin–spin splitting was not observed.

The mass spectrum of SeF_5OCFO was run at 70 eV and was found to consist of the following fragments in order of their decreasing abundances: COF^+, SeF_5^+, $SeOF_2^+$, $SeOF^+$, SeF_3^+, and CF^+.

Another compound produced in the reaction of SeF_5OF with CO probably was bis(pentafluoroselenium) oxide, SeF_5OSeF_5. The vapor density gave molecular weights of 368 and 373 for two determinations (theoretical value for SeF_5OSeF_5 is 366). The sample which was prepared was not adequate for a chemical analysis so none was attempted.

The infrared spectrum is shown in Figure 7. The following absorptions were observed: 1400 (w), 860 (w, sh), 842 (m), 779 (s), 722 (m), 557 (m), 425 (w, sh), and 405 cm^{-1} (m). The peroxide, SeF_5OOSeF_5, has been reported and its infrared spectrum can be compared with that of the monoxide. Mitra and Cady reported the following absorptions for SeF_5OOSeF_5: 1405 (w), 1295 (w), 858 (m), 842 (s), 775 (vs), 762 (vs), 737 (vs), and 722 cm^{-1} (s).

The ^{19}F nmr spectrum of the compound considered to be SeF_5OSeF_5 is shown in Figure 8. The chemical shift is −32.2 ppm relative to the solvent $CFCl_3$. Merrill, *et al.*,[18] have published the ^{19}F nmr spectra of SF_5OSF_5 and SF_5OOSF_5, and it can be seen that the oxide has a wide range of absorption of the order of 700 Hz whereas the peroxide has a range of the order of 30 Hz. In this regard the oxide, SeF_5OSeF_5, is similar to the sulfur system in that it also shows a broad range of absorption of the order of 500 Hz. The sample was too small to observe the ^{77}Se–F coupling.

TABLE II

MASS SPECTRUM OF "SeF_5OSeF_5"

Fragment	m/e	Rel[a] abund	Fragment	m/e	Rel[a] abund
$^{80}Se^+$	80	10	$^{80}SeOF_2^+$	134	99
$^{80}SeO^+$	96	19	$^{80}SeF_3^+$	137	92
$^{80}SeF^+$	99	12	$^{80}SeOF_3^+$	153	28
$^{80}SeOF^+$	115	100	$^{80}SeF_5^+$	175	50
$^{80}SeF_2^+$	118	26	$^{80}SeF_5O^{80}SeF_4^+$	347	<1

[a] Relative to $^{80}SeOF^+$.

The mass spectrum was obtained at an accelerating voltage of 40 eV and the fragments identified are shown in Table II. The elenium isotope ratios for all ions corresponded to those expected. There was no evidence for an ion containing two atoms of oxygen.

Other Reactions of SeF_5OF.—Several unsuccessful attempts were made to prepare compounds containing the SeF_5O group by reactions analogous to some used successfully with SF_5OF. For the following reactants, when contacted with SeF_5OF, no products containing the SeF_5O group were identified: N_2F_4, SO_2, C_2H_4, C_2F_4, C_3F_6. Explosions occurred with C_2H_4. In all other cases much of the SeF_5OF was converted to SeF_6. For the latter two reactants there was some evidence for low yields of products containing the SeF_5O group.

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The Nuclear Magnetic Resonance Spectra and the Electronic Spectra of Some Silicon and Germanium Phthalocyanines[1,2]

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The nmr spectra of the phthalocyanines $PcSi(OSi(C_6H_5)_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$, $PcSi(CH_3)(OSi(C_3H_7)_3)$, $PcSi(OSi(C_3H_7)_3)_2$, $PcSi(C_3H_7)(OSi(CH_3)(OSi(CH_3)_3)_2)$, $PcSi(CH_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$, and $PcSi(CH_3)(OSi(CH_3)_2OSi(CH_3)(OSi(CH_3)_3)_2)$ have been examined. For the first four compounds particular attention has been given to the simplification of the spectra of the side groups caused by the ring current of the phthalocyanine ring. For the last two compounds attention has been given to a determination of the ^{29}Si–C–H coupling constants of the side groups. Also examined have been the electronic spectra of the first four members of the series of compounds $(((CH_3)_3SiO)_2(CH_3)SiO)(PcSiO)_n(Si(CH_3)(OSi(CH_3)_3)_2)$ and the first two members of the analogous series of germanium compounds.

Introduction

In previous papers on the nmr spectra of the group IV phthalocyanines, the spectra of various groups attached to the *trans* positions of the central metal atom have been studied.[3–7] The present paper describes additional work of this same type. Here attention is given to an examination of the spectra of the triphenylsiloxy, tripropylsiloxy, propyl, and $-OSi(CH_3)_2OSi(CH_3)(OSi(CH_3)_3)_2$ groups and to a reexamination of the spectra of the methyl and $-OSi(CH_3)(OSi(CH_3)_3)_2$ groups. For the phenyl and propyl groups the main emphasis is on the simplification of the spectra caused by the ring current of the phthalocyanine ring, while for the methyl and methylsiloxy groups the emphasis is on the ^{29}Si–C–H coupling constants.

In addition to these nmr studies, work on the electronic spectra of the oligomers $(((CH_3)_3SiO)_2(CH_3)SiO)(PcSiO)_{1-4}(Si(CH_3)(OSi(CH_3)_3)_2)$ and $(((CH_3)_3SiO)_2(CH_3)SiO)(PcGeO)_{1-2}(Si(CH_3)(OSi(CH_3)_3)_2)$ is presented. The nmr spectra of these compounds have been described and analyzed in detail earlier[3] but their electronic spectra, although of interest because of their unusual ring-upon-ring structures, have not been taken up before.

Experimental Section

$PcSi(OSi(C_6H_5)_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$.—A mixture of $PcSi(OH)(OSi(CH_3)(OSi(CH_3)_3)_2$ (0.39 g),[7] triphenylsilanol (0.55 g), and chlorobenzene (25 ml) was refluxed for 1.5 hr and evaporated to dryness. The product was chromatographed on Woelm alumina (activity II–III). This gave red-reflecting, blue-transmitting crystals (0.12 g). These were crushed and vacuum dried at 100°. *Anal.* Calcd for $C_{57}H_{52}N_8O_4Si_5$: C, 64.98; H, 4.98; Si, 13.33. Found: C, 64.77; H, 4.91; Si, 13.63.

$PcSi(CH_3)(OSi(C_3H_7)_3)$.—A mixture of $PcSi(CH_3)(OH)$ (0.57 g),[7] tri-*n*-propylchlorosilane (0.50 ml), chlorobenzene (20 ml), and pyridine (5 ml) was refluxed for 45 min, filtered, and evaporated to dryness on a steam bath. The product was chromatographed on Woelm alumina (activity II) and recrystallized from a methylcyclohexane–toluene solution (3:1). The resultant red-reflecting, green-transmitting crystals (0.19 g) were crushed and vacuum dried at 100°. *Anal.* Calcd for $C_{42}H_{40}N_8OSi_2$: C, 69.20; H, 5.53; Si, 7.71. Found: C, 68.74; H, 5.26, Si, 8.06.

$PcSi(OSi(C_3H_7)_3)_2$.—A mixture of $PcSiCl_2$ (2.1 g),[8] tri-*n*-propylsilanol (4.0 ml), xylene (50 ml), and pyridine (20 ml) was

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(1) This paper is based in part on the Ph.D. thesis of A. R. Kane, University Microfilms No. 70-5101. The work was supported by the National Science Foundation under Grants GP 1702 and GP 8368 and under the RPCT Program, by the National Aeronautics and Space Administration under its fellowship program, and by the Office of Naval Research.

(2) The abbreviation Pc is used for the phthalocyanine ligand, $C_{32}H_{16}N_8$.

(3) T. R. Janson, A. R. Kane, J. F. Sullivan, K. Knox, and M. E. Kenney, *J. Am. Chem. Soc.*, **91**, 5210 (1969).

(4) A. R. Kane, R. G. Yalman, and M. E. Kenney, *Inorg. Chem.*, **7**, 2588 (1968).

(5) L. E. Sutton and M. E. Kenney, *ibid.*, **6**, 1869 (1967).

(6) J. N. Esposito, L. E. Sutton, and M. E. Kenney, *ibid.*, **6**, 1116 (1967).

(7) J. N. Esposito, J. E. Lloyd, and M. E. Kenney, *ibid.*, **5**, 1979 (1966).

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