CONTRIBUTION FROM THE CASE INSTITUTE OF TECHNOLOGY,
CLEVELAND 6, OHIO

Phthalocyaninosilicon Compounds[1]

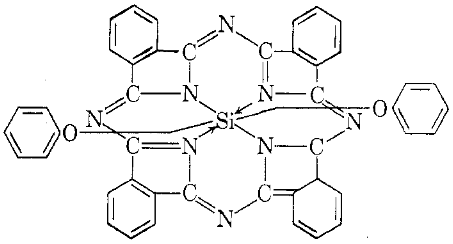
BY RALPH D. JOYNER AND MALCOLM E. KENNEY

Received September 14, 1961

Four compounds are described, $PcSiCl_2$, $PcSi(OH)_2$, $PcSi[OSi(C_6H_5)_3]_2$, and $PcSi[OSi(OCH_2C_6H_5)(C_6H_5)_2]_2$. All these compounds possess Si–N–C links which are stable and the latter two contain both tetracoördinate and hexacoördinate silicon atoms.

Introduction

Recently it has been reported that $PcSi(OC_6H_5)_2$ has been obtained.[2,3] This compound is presumed to have the structure



a structure in which the silicon is octahedrally coördinated. A number of related phthalocyaninogermanium compounds have been isolated and purified.[4,5] All these compounds are chemically and thermally stable. Evidence also has been presented in the report on $PcSi(OC_6H_5)_2$ for the existence of $PcSiCl_2$ and $PcSi(OH)_2$. Further work now has established methods for synthesizing these and two other phthalocyaninosilicon compounds and has shown that these compounds also are stable. The phthalocyaninosilicon compounds as a group are of interest because of the apparent hexacoordination of the silicon and the stability of the Si–N bonds.

Experimental

Dichloro-(phthalocyanino)-silicon ($PcSiCl_2$).—A mixture of 50 ml. (0.44 mole) of $SiCl_4$, 50 g. (0.39 mole) of phthalonitrile, and 75 ml. of quinoline was brought very slowly to reflux with constant stirring. The unreacted $SiCl_4$ which distilled from the reaction was collected and returned to the reaction at a rate such that the temperature of the mixture was maintained at above 200° for 2 hr. This procedure yielded 4.2 g. of an air-stable crystalline material after separation of reaction products.

The crystals were purified by a vacuum sublimation technique similar to that used for $PcGeCl_2$.[4] A 0.5-g. sample, closely covered with platinum gauze (to prevent mechanical transfer of particles of the sample), was heated for 1 hr. at 430–450° in a vacuum sublimator equipped with a collecting finger which was held at a fixed temperature with refluxing mercury. A slightly impure product weighing 250 mg. was obtained. This was resublimed under identical conditions and gave 75 mg. of well formed crystals which were blue-green by transmitted light and red by reflected light. *Anal.* Calcd. for $C_{32}H_{16}N_8SiCl_2$: C, 62.85; H, 2.64; Si, 4.59; Cl, 11.60. Found: C, 63.26; H, 2.86; Si, 4.90; Cl, 11.80.[6]

An alternate synthetic route was developed for $PcSiCl_2$ which utilized hexachlorodisiloxane. A mixture of 50 g. (0.18 mole) of hexachlorodisiloxane, 200 g. of phthalonitrile (1.6 moles), and 400 ml. of quinoline was heated very slowly to reflux with constant stirring. The heating and stirring were continued for 4 hr. Following this the liquid portion of the reaction product was decanted and rejected and the remaining tarry mass was slurried with dimethylformamide. The liquid portion again was decanted and rejected. This separation process was repeated several times with dimethylformamide and then several times with acetone. The resulting solid was extracted with acetic acid for 6 hr. in a Soxhlet extractor and then washed with acetone. The crystalline material remaining on the frit weighed 26 g. Its infrared spectrum was the same as that obtained from the product of the silicon tetrachloride–phthalonitrile reaction.

Comparison of the two synthetic routes indicated that the hexachlorodisiloxane method was better from the standpoint of yield and convenience. Attempted synthesis of $PcSiCl_2$ based on the reactions of methyltrichlorosilane, and phenyltrichlorosilane with phthalonitrile were unsuccessful.

Dihydroxy-(phthalocyanino)-silicon ($PcSi(OH)_2$).—A suspension of 250 mg. of $PcSiCl_2$ was refluxed for 10 hr. in 20 ml. of a mixture consisting of equal volumes of pyridine and

---

[1] This paper is based on a thesis submitted by R. D. Joyner in partial fulfillment of the requirements for the Ph.D. degree. The work was supported by the Research Corporation and by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, and was presented at the 139th National A.C.S. Meeting.

[2] Pc = $C_{32}H_{16}N_8$, the phthalocyanino ligand. The nomenclature used in this paper has been modified from that used in previous papers at the suggestion of Dr. R. M. Adams, Chairman, Committee on Nomenclature, Inorganic Section, American Chemical Society.

[3] R. D. Joyner, J. Cekada, Jr., R. G. Linck, and M. E. Kenney, *J. Inorg. & Nuclear Chem.*, **15**, 387 (1960).

[4] R. D. Joyner and M. E. Kenney, *J. Am. Chem. Soc.*, **82**, 5790 (1960).

[5] R. D. Joyner and M. E. Kenney, *J. Inorg. & Nuclear Chem.*, in press.

[6] Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

TABLE I

PROMINENT INFRARED BANDS (CM.$^{-1}$)[7]

$PcSiCl_2$ (Nujol)	$PcSi(OH)_2$ (Nujol)	$PcSi(OC_6H_5)_2$ (KBr)	$Pc(OSi(C_6H_5)_3)_2$ (Nujol)	$PcSi[OSi(OCH_2C_6H_5)(C_6H_5)_2]_2$ (Nujol)	$PcSi(OCH_2C_6H_5)_2$ (Nujol)
		Common Bands			
735	730	740	738	734	734
763	761	765	765	764	763
916	914	915	914	914	913
1083	1080	1085	1087	1087	1083
1123	1122	1126	1127	1127	1126
		Characteristic Bands			
695	781	701	703	699	698
786	831	885	757	715	783
869	1074		1000	850	800
886	1138		1027	1030	814
1064			1043	1055	1032

concentrated aqueous ammonia. The product was filtered, washed, and dried. *Anal.* Calcd. for $C_{32}H_{18}N_8SiO_2$: C, 66.88; H, 3.16; N, 19.50; Si, 4.89. Found: C, 66.94, 66.76; H, 3.51, 3.18; N, 19.52; Si, 5.07. Another sample of $PcSiCl_2$ treated in the same fashion gave similar results. Found: C, 67.02; H, 3.28; N, 19.79; Si, 5.14.

Sulfuric acid was used in an alternate synthesis of $PcSi(OH)_2$. A sample of $PcSiCl_2$ was treated with a large excess of concentrated H_2SO_4 and the resulting mixture was diluted with enough water to precipitate all the phthalocyanino compound from solution. The suspension obtained was filtered and the solid washed with aqueous ammonia and water. No evidence indicating appreciable loss was observed and the infrared spectrum of the product showed no infrared bands attributable to PcH_2. (The mechanics of this process are similar to those used industrially in acid pasting PcCu.)

Bis-(triphenylsiloxy)-(phthalocyanino)-silicon ($PcSi[OSi(C_6H_5)_3]_2$).—A mixture of 1.0 g. (3.6 mmole) of triphenylsilanol, 0.25 g. (0.43 mmole) of $PcSi(OH)_2$, and 10 drops of pyridine was allowed to react at reflux for 0.5 hr. The excess silanol was removed from the product with boiling xylene and the solid remaining was washed with hot benzene, ethanol, and acetone. A 300-mg. portion of this was heated to 380° in a vacuum sublimator fitted with a collecting finger kept at constant temperature with refluxing 1-chloronaphthalene. A yield of 100 mg. of homogeneous air-stable crystals with typical phthalocyanino color characteristics was obtained in 0.75 hr. *Anal.* Calcd. for: $C_{68}H_{46}N_8Si_3O_2$: C, 74.83; H, 4.25; N, 10.27; Si, 7.72. Found: C, 74.67; H, 4.37; N, 10.07; Si, 7.67.

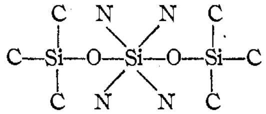
This compound also was prepared by a second method. A mixture of 5 g. (8 mmole) of $PcSiCl_2$ and 100 ml. (0.96 mole) of benzyl alcohol was heated to reflux, held at this temperature for 1 hr., and then filtered and cooled. Brilliant, well formed crystals of what was presumed to be $PcSi(OCH_2C_6H_5)_2$ were formed. These were washed and dried. A 450-mg. (0.60 mmole assuming $PcSi(OCH_2C_6H_5)_2$) portion of the crystals and 250 mg. (0.91 mmole) of triphenylsilanol were placed in 5 ml. of benzyl alcohol. The mixture was heated to reflux, filtered, and allowed to cool. The crystals obtained were recrystallized from benzyl alcohol in which a small amount of triphenylsilanol had been dissolved. The infrared spectrum of these crystals was the same as that obtained from the crystals produced by sublimation. Found: C, 75.15; H, 4.26; N, 10.32; Si, 7.72.

Attempts to prepare $PcSi(OSi(C_6H_5)_3)_2$ and the related $PcSi[OSi(OH)(C_6H_5)_2]_2$ by heating mixtures of benzene, $PcSi(OH)_2$, and either triphenylsilanol or diphenylsilanediol to reflux were unsuccessful. The only phthalocyanino compound recovered from the reaction products was $PcSi(OH)_2$. $PcSi[OSi(OH)(C_6H_5)_2]_2$ was not isolated from a product obtained by heating diphenylsilanediol, $PcSi(OH)_2$, and a few drops of pyridine.

Bis-(benzyloxydiphenylsiloxy)-(phthalocyanino)-silicon $\{PcSi[OSi(OCH_2C_6H_5)(C_6H_5)_2]_2\}$.—A 350-mg. (0.46 mmole) sample of $PcSi(OCH_2C_6H_5)_2$ was mixed with 200 mg. (0.93 mmole) of diphenylsilanediol and 5 ml. of benzyl alcohol. This was refluxed for 2 min., filtered, and cooled. The blue-green crystals obtained as a product were recrystallized from a fresh solution of 100 mg. of diphenylsilanediol in 3 ml. of benzyl alcohol. *Anal.* Calcd. for $C_{70}H_{50}N_8Si_3O_4$: C, 73.01; H, 4.38; Si, 7.32; N, 9.73. Found: C, 73.20; H, 4.54; Si, 7.52; N, 10.53, 10.68, 9.29, 9.62.

Discussion

The bulk of the siloxy groups in the siloxysilicon compounds and the nature of the phthalocyanine ring argue for a *trans*-octahedral arrangement for these groups just as in the case of their siloxygermanium analogs.[5] Accordingly, the backbone of $Pc(OSi(C_6H_5)_3)_2$ may be assumed to be of the type

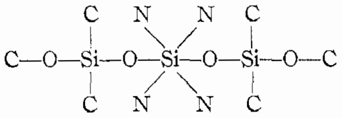


This structure is unusual in that it contains both tetracoördinate and hexacoördinate silicon in the same unit. The backbone of PcSi[OS-

---

(7) Reproductions of these spectra are available in the thesis of R. D. J., University Microfilms No. 61-3317, p. 49.

$(OCH_2C_6H_5)(C_6H_5)_2]_2$



also shows the same structural feature. Steric considerations suggest that other phthalocyaninosilicon compounds also have a *trans* arrangement.

The Si–N bonds in the phthalocyaninosilicon compounds show a marked chemical resistance. For example, the Si–N bonds in $PcSi(OH)_2$ are not broken by concentrated H_2SO_4, refluxing benzyl alcohol, or refluxing aqueous ammonia–pyridine mixtures even though both benzyl alcohol and concentrated H_2SO_4 dissolve $PcSi(OH)_2$ and benzyl alcohol reacts with the OH groups. (It seems probable that concentrated H_2SO_4 also interacts with the OH groups to give a derivative of the OSO_3H type which easily hydrolyzes back to $PcSi(OH)_2$, but this was not investigated.) This inertness of the Si–N bonds probably is associated to some extent with the size of the organic residue. However, it also must be a function of the fact that the four N atoms of the Si–N bonds are held symmetrically around the Si atom by the ring and the fact that demetallation of the ring requires the rupture of all four of these bonds. The resistance of the phthalocyaninosilicon compounds to pyrolytic decomposition is not unexpected in view of the thermal stability of other organosilicon compounds containing Si–N bonds.

Attempts to convert $PcSi(OH)_2$ to a sodium salt were unsuccessful and suggest that the hydrogen atoms of the hydroxy groups are less acidic than in ordinary silanols. Perhaps this is due to reduced d_π–p_π bonding between the silicon and oxygen atoms because of the release of some charge to the silicon atoms by the rings.

The reasons for the ineffectiveness of methyl- and phenyltrichlorsilanes as reactants for the synthesis of phthalocyaninosilicon compounds are not readily apparent. An influencing factor may be the reduced tendency which silicon atoms with alkyl groups attached sometimes have for forming compounds with coördination numbers greater than four.[8]

These compounds show the usual phthalocyanino bands in the 700–1150-cm.$^{-1}$ region. The band near 900 cm.$^{-1}$ can be used to differentiate these compounds from their germanium analogs (which have a similar band at a lower frequency). $PcSi(OH)_2$ shows a relatively sharp absorption at 3535 cm.$^{-1}$ and a strong absorption at 831 cm.$^{-1}$. Both of these can be attributed to the presence of OH groups.

---

[8] C. Eaborn, "Organosilicon Compounds," Academic Press, New York, N. Y., 1960, p. 93.